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Appendix I

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Technology Screening—Not Retained Technologies

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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
CERCLA	<i>Comprehensive Environmental Response, Compensation, and Liability Act of 1980</i>
CNF	Central Neutralization Facility
COPC	contaminant of potential concern
CPS	calcium polysulfide
CSTR	continuous stirred-tank bioreactor
CVOC	chlorinated volatile organic compound
CY	calendar year
DIC	dissolved inorganic carbon
DO	dissolved oxygen
DoD	U.S. Department of Defense
DOE	U.S. Department of Energy
DTSC	Department of Toxic Substances Control (California)
ECI	Electrocoatings, Inc.
Ecology	Washington State Department of Ecology
EOS®	Emulsified Oil Substrate
EPA	U.S. Environmental Protection Agency
ERDF	Environmental Restoration Disposal Facility
ERH	electrical resistance heating
ESD	Explanation of Significant Differences
ESS	ex situ solidification/stabilization

FS	feasibility study
GCW	groundwater circulation well
HRC™	hydrogen release compound
HTTD	high-temperature thermal desorption
INEEL	Idaho National Engineering and Environmental Laboratory
IRZ	in situ reactive zone
ISB	in situ bioremediation
ISCO	in situ oxidation
ISPT	in situ pilot test
ISTD	in situ thermal desorption
ISGR	in situ gaseous reduction
ISRM	in situ redox manipulation
ISV	in situ vitrification
MCL	maximum contaminant level
MRC™	Metals Remediation Compound
MTBE	methyl tert butyl ether
NAPL	non-aqueous phase liquid
NEPA	<i>National Environmental Policy Act</i>
NOM	natural organic material
NPDES	National Pollutant Discharge Elimination System
NPL	National Priorities List
NZVI	nano-scale zero-valent iron
O&M	operation and maintenance
ORNL	Oak Ridge National Laboratory
OU	operable unit
PAH	polynuclear aromatic hydrocarbons
PCB	polychlorinated biphenyl
PCE	tetrachloroethylene
PCP	pentachlorophenol
PG&E	Pacific Gas and Electric Company

PNNL	Pacific Northwest National Laboratory
RAO	remedial action objective
RI/FS	Remedial Investigation/Feasibility Study
RO	reverse osmosis
ROD	Record of Decision
ROI	radius of influence
RPO	Remediation Process Optimization
RUM	Ringold Formation upper mud
SPSH	six-phase soil heating
SPT	Selma Pressure Treating
SRB	sulfate-reducing bioreactors
SRS	Savannah River Site
SVE	soil vapor extraction
SVOC	semivolatile organic compounds
TCE	trichloroethylene
TCH	thermal conductive heating
TOC	total organic carbon
TPH	total petroleum hydrocarbons
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, hexavalent chromium, other metals, and organic compounds (polychlorinated biphenyls [PCBs], polynuclear aromatic hydrocarbons [PAHs], 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, void fill grouting, and soil blending were not retained for treatment of impacted waste sites at 100-K. Since no ex situ treatment options were retained, backfill of treated soil is not applicable. Since disposal to the Environmental Restoration Disposal Facility (ERDF) is considered adequate and reliable for impacted media at 100-K, 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-K, 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, hexavalent chromium, 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.

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-impacted
6 waste (primarily uranium). Portland cement (Type I/II) and blast furnace slag (BFS) 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 resulted from the cement stabilization process (DOE/RL-94-61).

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

18 **11.1.1.3 Evaluation and Screening Rationale**

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

25 **11.1.2 Soil Washing**

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

28 **11.1.2.1 Description**

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

36 A wide range of physical processes can be used for soil washing. These range from simple screening to
37 complex grinding or scrubbing, combined with chemical dissolution. Contaminants are generally more
38 strongly associated with the finer grained soil particles; therefore, it is sometimes possible to separate the
39 coarse fraction and it will be clean. However, if the contaminants are strongly sorbed to the surfaces of
40 the coarse particles, simple separation may not be effective, and more aggressive—and thus expensive—
41 processes 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 (WHC-SD-EN-TI-268).
4 The study evaluated physical separation (wet sieving), physical treatment processes (attrition scrubbing
5 and autogenous surface grinding), and chemical extraction methods to separate radioactively-
6 contaminated soil fractions from uncontaminated soil fractions. Particle size distribution data indicated
7 that the evaluated soil was primarily comprised of poorly graded gravel with approximately 17 percent
8 sand, and minor amounts of cobbles and silt-clay fractions. The effectiveness of soil-washing tests was
9 evaluated based on removal of cesium-137 from the gravel- and sand-size fractions. The study concluded
10 that by using water-based autogenous surface grinding on the gravel media only, approximately
11 55 percent of media contained residual cesium-137, and could be recovered for backfill. By treating both
12 gravel (using autogenous surface grinding) and sand (using two-stage attrition scrubbing with an
13 electrolyte followed by chemical extraction), 55 percent treated gravel fraction and about 11 percent of
14 the treated sand fraction could be recovered for backfill (*100 Area Soil Washing: Bench-Scale Tests on*
15 *116-F-4 Pluto Crib Soil*, [WHC-SD-EN-TI-268]).

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

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

42 **11.1.2.3 Evaluation and Screening Rationale**

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

46 As discussed in the draft BC Crib Focused Feasibility Study (*Focused Feasibility Study for the BC Crib*
47 *and Trenches Area Waste Sites* [DOE/RL-2004-66]), the effectiveness of soil washing is limited for many

1 radionuclides. The majority of contaminants appear to be strongly bound to the surfaces of all particle
2 sizes. As a consequence, more aggressive and costly approaches would be required, which also may not
3 be effective. Given that pilot tests at the Hanford Site have not been extremely effective, soil washing was
4 not retained for further consideration.

5 **11.1.3 Ex Situ Vitrification**

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

8 **11.1.3.1 Description**

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

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

22 **11.1.3.2 Relevant Demonstration Projects**

23 In the early 1990s, DOE developed a Transportable Vitrification System to effectively vitrify applicable
24 mixed-waste sludges and solids across the various DOE complex sites (DOE, 1998). Multiple studies
25 were completed in collaboration with Westinghouse Savannah River Company, Oak Ridge National
26 Laboratory, and Clemson University. A mixed-waste demonstration was completed in 1997 using
27 Savannah River B&C pond sludge, and a mix of B&C pond sludge and Central Neutralization Facility
28 (CNF) sludge. The study indicated the system vitrified 84 m³ (2,966 ft³) of mixed waste into 34 m³
29 (1,200 ft³) of glass waste, resulting in a 60 percent waste volume reduction. Results of the study indicated
30 the need for high capital costs and extensive upfront development. However, it indicated the technology is
31 capable of producing highly durable glass waste forms with long-term integrity, and a significant
32 reduction in waste volume compared to other stabilization techniques.

33 A vitrification plant is currently being constructed to treat tank wastes at the Hanford Site. The Waste
34 Treatment and Immobilization Plant (WTP) will cover 65 ac and will consist of four nuclear facilities:
35 Pretreatment, Low-Activity Waste vitrification, High-Level Waste vitrification, and an Analytical Laboratory.
36 Construction activities began in 2002; it is anticipated the plant will be operational in 2019. A number of
37 tests have been performed to support the process and design associated with this facility. Information
38 regarding the WTP Research and Technology Program is presented in the WTP Project Execution Plan
39 (*Project Execution Plan for the River Protection Project Waste Treatment and Immobilization Plant*
40 [DOE/ORP-2003-01]). However, treatability tests on contaminated soil have not been performed.

41 **11.1.3.3 Evaluation and Screening Rationale**

42 Ex situ vitrification is considered to have low implementability given that high complexity of equipment
43 is required and the safety concerns with implementation, which include maintaining the integrity of the

1 tanks. Similarly, given the relative high cost and potential application of other technologies with high
2 effectiveness and implementability, ex situ vitrification is not considered favorable for implementation for
3 treatment of contaminated soil at the 100 Area.

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

10 As presented in RPP-ENV-34028, estimated costs for implementation of this technology can range from
11 \$500 to \$1,000 per calendar year (CY). These costs include soil excavation, screening to remove debris,
12 installation of the vitrification system and off-gas treatment system, operation and maintenance (O&M),
13 utilities, site management, and sampling support, and onsite disposal of vitrified material and off-gas
14 treatment. For the WTP facility, DOE/ORP-2003-01, *Project Execution Plan for the River Protection*
15 *Project Waste Treatment and Immobilization Plant*, indicated that the total project cost for the WTP is
16 estimated to be \$5.781 billion.

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

19 **11.1.4 Ex Situ Thermal Desorption**

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

21 **11.1.4.1 Description**

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

28 Treatment to low levels of organic contaminants can be achieved with this technology. Based on the
29 operating temperatures, thermal desorption processes can be categorized as either high-temperature
30 thermal desorption (HTTD, 320 to 560°C [608 to 1,040°F]) or low-temperature thermal desorption
31 (90 to 320°C [194 to 608°F]). HTTD targets semivolatile organic compounds (SVOCs), PAHs, PCBs, and
32 pesticides. Volatile organic compounds (VOCs) can also be treated with HTTD, although the process is
33 not as cost effective. Low-temperature thermal desorption targets nonhalogenated VOCs and fuel, and can
34 treat SVOCs but at a reduced effectiveness.

35 **11.1.4.2 Relevant Demonstration Projects**

36 A full-scale demonstration project was completed in 1992 at the Outboard Marine Corporation site in
37 Waukegan, Illinois, for the treatment of PCBs from soil, sediments, and sludges using thermal desorption.
38 The demonstration involved treatment using an anaerobic thermal processor (ATP) licensed by SoilTech
39 ATP Systems, Inc. The study indicates that a total of 224 tons of PCB-contaminated soil was treated, and
40 treatment efficiencies for removal of PCB of approximately 99.9 percent were achieved
41 (EPA 540-MR-92-078).

1 **11.1.4.3 Evaluation and Screening Rationale**

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

9 **11.2 In Situ Treatment—Reagent Approach**

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

13 **11.2.1 In Situ Solidification**

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

16 **11.2.1.1 Description**

17 Solidification alters the physical and/or chemical characteristics of a soil through the addition of binders,
18 including cements and chemical grouts, to immobilize contaminants. The immobilization primarily works
19 by coating and isolation, processes that make the contaminants less prone to leaching or dissolution.
20 Multiple types of grouting/binding materials and emplacement techniques have been developed and
21 demonstrated. Jet grouting and permeation grouting are the two general grout approaches potentially
22 applicable for subsurface contaminant solidification in Hanford Site vadose zone sediments. Jet grouting
23 uses high-energy emplacement of cement or chemical grout materials whereby the sediment is displaced
24 and mixed with the grouting material. Permeation grouting is injection of a liquid grout that fills the pore
25 space of the formation, and then gels to form a solid material. While permeation grouting is a relatively
26 mature technology for many geotechnical applications, there are uncertainties with grout for in situ
27 contaminant stabilization (*Evaluation of Vadose Zone Treatment Technologies to Immobilize Tc-99*
28 [WMP-27397]). The uncertainties include: 1) the effectiveness of delivery depends upon subsurface
29 heterogeneity; and 2) the presence of fines adversely affect grout placement. Generally, grout is emplaced
30 via an array of closely spaced vertical boreholes into the subsurface volume to be stabilized.

31 Two types of grout materials may be used: particulate (cement) grouts and chemical grouts. Cement
32 grouts use Portland cement as the primary component. Portland cement is a mixture of preprocessed
33 mineral solids pulverized, fired, and ground into a fine solid dust. This product is combined with up to
34 5 percent gypsum, and mixed with water and small quantities of additives to form a flowable mixture of
35 solids and water, and composing a suspended solids grout. A chemical grout is a solution comprised of a
36 binder (other than Portland cement) that reacts in place to form a gel or solid after injection into a porous
37 subsurface soil, sediment, or rock volume. Chemical grouts do not contain mineral solids in suspension,
38 and therefore their delivery in the subsurface is not limited by particle filtration. Instead, delivery is a
39 function of grout viscosity and gelling time.

40 **11.2.1.2 Relevant Demonstration Projects**

41 Several DOE sites, including the Hanford Site, Oak Ridge National Laboratory (ORNL), Brookhaven
42 National Laboratory, Idaho National Laboratory, Savannah River Site, and Sandia National Laboratories
43 have evaluated, tested, and/or implemented in situ grouting for shallow waste isolation applications as

1 summarized below. In situ grouting has been evaluated at the Hanford Site for application to waste site
2 isolation (e.g., near surface formation of in situ waste barriers) through a number of efforts in the 1990s
3 [e.g., “Injectable Barriers for Waste Isolation” (Persoff et al., 1995); “Feasibility of Permeation Grouting
4 for Constructing Subsurface Barriers” (SAND94-0786); “Durability of Polymers for Containment
5 Barriers” (Heiser et al., 1994); *Summary Report on Close-Coupled Subsurface Barrier Technology Initial
6 Field Trials to Full-Scale Demonstration* (BNL-52531); and *In Situ Remediation Integrated Program FY
7 1994 Program Summary* (DOE/RL-95-32)]. These documents provide laboratory and field data for jet
8 grouting techniques applied to shallow waste isolation at the Hanford Site and Brookhaven National
9 Laboratory.

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

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

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

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

41 **11.2.1.3 Evaluation and Screening Rationale**

42 In situ solidification using commercially available grouting equipment with cement grouts is considered
43 to have moderate implementability when applied over smaller areas. Such limited areas may extend over
44 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
45 large-scale grouting of soil volumes. The effectiveness of in situ solidification is a function of the

1 distribution of the grout into the formation, the degree of encapsulation of contaminated sediment
2 particles, and the long-term durability of shallow soil encapsulation when exposed to the elements.
3 The effectiveness of grout emplacement depends on the application method. Typical applications would
4 involve 0.6 m (2 ft) diameter grout column with 0.5 m spacing. Using estimated installation costs for in
5 situ solidification using jet grouting at Idaho National Engineering and Environmental Laboratory
6 (INEEL) (Holdren et. al., 2007), unit costs in excess of \$1,500 per yd³ are estimated. Consequently, the
7 relative capital cost is high. Because of the high capital cost, the potential for incomplete contact of grout
8 in the targeted treatment zone, and uncertainty regarding the durability of shallow soil encapsulation
9 when exposed to the elements, in situ solidification was not retained for further evaluation.

10 **11.2.2 In Situ Stabilization/Sequestration**

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

12 **11.2.2.1 Description**

13 The focus of Sr-90 sequestration studies at the Hanford Site has been on apatite sequestration. Apatite
14 minerals sequester elements into their molecular structures via isomorphic substitution, whereby elements
15 of similar physical and chemical characteristics replace calcium, phosphate, or hydroxide in the
16 hexagonal crystal structure (Hughes et al., 1989; Spence and Shi, 2005). Apatite minerals are very stable
17 and practically insoluble in water. The substitution of strontium for calcium in the crystal structure is
18 thermodynamically favorable, and will proceed provided the two elements coexist. The mixed Sr- Ca-
19 apatites have lower solubility than Ca-apatite or strontiapatite.

20 Methods of emplacing apatite in vadose zone soil include injection and infiltration of an aqueous solution
21 containing a Ca-citrate complex and Na-phosphate. Phosphate adsorption is slow (hours) so rapid
22 infiltration can result in deeper phosphate mass at depth. Citrate is needed to keep Ca in solution long
23 enough (days) to inject into the subsurface; a solution containing Ca²⁺ and phosphate only will rapidly
24 form mono- and di-calcium phosphate, but not apatite (Andronescu et al., 2002; Elliot et al. 1973;
25 Papargyris et al., 2002). As Ca-citrate is degraded, the free Ca and phosphate combine to form amorphous
26 apatite. The formation of amorphous apatite occurs within a week and crystalline apatite forms within a
27 few weeks.

28 **11.2.2.2 Relevant Demonstration Projects**

29 A laboratory scale study investigating apatite sequestration of Sr-90 was conducted by the Pacific
30 Northwest National Laboratory (PNNL-18303). The results of the laboratory study indicate that
31 Ca-citrate-phosphate solution can be infiltrated into unsaturated sediments to result in apatite precipitate
32 to provide treatment of Sr-90 contamination. After 1.3 years of contact, 9 to 16 percent Sr-90 had
33 substituted for Ca in apatite. Sr-90 substitution in apatite did not decrease with depth due to the 20 to
34 30 nm apatite crystals conglomerated forming a porous 10 to 50 micron conglomerate precipitate.
35 Microbial redistribution during solution infiltration and a high rate of citrate biodegradation for river
36 water microbes (water used for solution infiltration) resulted in a relatively even spatial distribution of the
37 citrate biodegradation rate and ultimately apatite precipitate.

38 Overall, the laboratory results indicate that the most effective infiltration strategy to precipitate apatite at
39 depth may be to infiltrate a high concentration solution (6 mM Ca, 15 mM citrate, 60 mM phosphate) at a
40 rapid rate (near ponded conditions), followed by rapid, then slow water infiltration (Szecsody et al.,
41 2008). Repeated infiltration events, with sufficient time between events to allow water drainage in the
42 sediment profile, also may be used to build up the mass of apatite precipitate at greater depth. Low-K
43 zones were effectively treated, as the higher residual water content maintained in these zones resulted in
44 higher apatite precipitate concentration. High-K zones did not receive sufficient treatment by infiltration,

1 although an alternative strategy of air/surfactant (foam) was demonstrated effective for targeting
2 high-K zones.

3 ***11.2.2.3 Evaluation and Screening Rationale***

4 Laboratory scale studies have demonstrated that in situ stabilization of Sr-90 in the vadose zone can be
5 achieved through the infiltration of Ca-citrate-phosphate solutions to induce the formation of apatite,
6 which in turn sequesters the Sr-90. However, there is still uncertainty with regard to how uniformly
7 phosphate solutions can be delivered on a field scale in heterogeneous soils, and how that nonuniformity
8 would impact the percentage of Sr-90 that can be sequestered in the vadose zone. Furthermore,
9 sequestration of Sr-90 does not remove the COPC, and therefore does not change the potential risk from
10 human or ecological direct contact with shallow soil. Therefore, in situ stabilization/sequestration was
11 screened out in favor of the other technologies such as shallow excavation.

12 **11.2.3 In Situ Chemical Reduction**

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

14 ***11.2.3.1 Description***

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

23 ***11.2.3.2 Relevant Demonstration Projects***

24 The U.S. Department of Defense (DoD) conducted a field test site to evaluate the effectiveness of the in
25 situ gaseous reduction at a chromate-contaminated waste site located at the White Sands Missile Range
26 (PNNL-12121). The field demonstration involved the injection of a mixture of 200 ppm hydrogen sulfide
27 diluted in air. The gas mixture was drawn through the site soil by a vacuum applied to extraction
28 boreholes located at the site boundary, and residual hydrogen sulfide was removed prior to release of the
29 air back to the atmosphere. The injection test lasted 76 days with no detectable releases of hydrogen
30 sulfide to the site atmosphere. Comparison of Cr(VI) analyses of soil samples taken before and after the
31 test indicated that 70 percent of the Cr(VI) originally present at the site was reduced and thereby
32 immobilized by in situ gaseous reduction. Treatment was generally better in zones of higher permeability
33 sand containing less silt and clay, indicating that geologic heterogeneity is a limitation to treatment
34 effectiveness.

35 ***11.2.3.3 Evaluation and Screening Rationale***

36 The application of toxic hydrogen sulfide gas to the near surface carries significant risk. Transportation
37 and handling of reducing agents also poses more of a health and safety concern during application,
38 compared to biological reduction substrates. Due to more rapid chemical reactions, the application of
39 liquid reducing agents to uniformly contact contaminated vadose zone soil may be more problematic than
40 using biological substrates. Based on these implementability and potential effectiveness issues, in situ
41 chemical reduction was not retained in favor of in situ biological reduction.

1 **11.2.4 In Situ Chemical Oxidation**

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

5 **11.2.4.1 Description**

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

12 **11.2.4.2 Relevant Demonstration Projects**

13 A pilot study was conducted in fall 2006 to evaluate the effectiveness of permanganate injection to treat
14 chlorinated volatile organic compounds (CVOCs) in shallow unsaturated heterogeneous soil
15 (Borchert et al., 2008). The treatment zone was 4.8×5.4 m (16×18 ft) in area and 2.7 m (9 ft) deep.
16 The site geology consisted of silty clay in the upper 1.6 m (5.5 ft) with traces of sand and gravel and an
17 intermittent sandy layer from 0.3 to 0.6 m (1 to 2 ft) below ground surface (bgs), and gravelly sand with
18 some silt and clay from 1.6 to 4.3 m (5.5 to 14 ft) bgs with a discontinuous sandy and silty clay layer from
19 2.4 to 2.7 m (8 to 9 ft) bgs. Groundwater was encountered from 2.4 to 3 m (8 and 10 ft) bgs.
20 The maximum concentrations of trichloroethylene (TCE) and cis-1, 2-DCE were 66,000 and 2,400 $\mu\text{g}/\text{kg}$,
21 respectively. The permanganate soil oxidant demand ranged from about 3 to 17.1 g/kg. Approximately
22 1041 L (275 gal) of 40 percent by weight permanganate (about 3,000 lb [1.5 tons]) were injected at nine
23 locations within the pilot study area. Where oxidant was visually observed, the radius of influence ranged
24 from 2.5 up to 3 m (10 ft). However, several visual borings had limited evidence of permanganate.
25 Performance monitoring indicated that TCE and cis-1,2-DCE concentrations in soil decreased between 44
26 and 93 percent, respectively. However, concentrations in groundwater increased up to tenfold. Results
27 from the pilot study indicated that a majority of oxidant migrated into the shallow groundwater and was
28 consumed by CVOCs and high oxidant demand (up to 20.7 g/kg permanganate). Conclusions state that it
29 is challenging to acquire fine distribution of an oxidant solution in shallow silty clay, even with controlled
30 low pressures and flows and closely spaced injection points. Difficulty was also encountered in creating
31 temporarily saturated zones for aqueous-based ISCO reactions in the unsaturated zone, particularly in
32 permeable portions of the formation. Based on the results of the pilot study, excavation was selected as a
33 more cost-effective remedial alternative for shallow soil.

34 An ozone gas vadose zone sparging system for treating PAHs operated during the summer of 2001 at the
35 Former Fuel Oil Distribution Terminal in Ilion, New York (ITRC, 2005). Adsorbed PAHs were
36 delineated from approximately 0.6 to 2.4 m (2 to 8 ft) bgs, and initial total PAH concentrations exceeded
37 30 mg/kg. The subsurface contained both fill materials and native soil consisting primarily of silty sand.
38 Groundwater was encountered at 2.1 to 2.4 m (7 to 8 ft) bgs. To achieve a target 60-day period for project
39 completion, a nominal 50-lb/day (23 kg/day) ozone-generation system was used to inject both ozone and
40 oxygen. Ten initial sparge points were installed at the site by direct-push methodology. A shallow vapor
41 extraction system was installed to control emissions. The injection system operated over a period of 8
42 weeks. Post-remediation soil sampling results indicated no remaining PAH (primarily
43 benzo[a]anthracene, benzo[a]pyrene, and chrysene) concentrations above method detection limits,
44 achieving the remedial goals of 90 percent concentration reduction in 60 days. Naphthalene was also
45 reduced to below New York State Department of Environmental Conservation Technical and

1 Administrative Guidance Memorandum standards. Average reduction of naphthalene was greater than
2 32 percent in 60 days.

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

19 **11.2.4.3 Evaluation and Screening Rationale**

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

27 **11.2.5 Reductive Dechlorination Using Zero-Valent Metals and Bioremediation**

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

30 **11.2.5.1 Description**

31 Both biological and abiotic methods are potentially applicable for reductive dechlorination of PCBs.
32 During bioremediation, anaerobic bacteria replace chlorine atoms with the electron-donating hydrogen on
33 the PCB molecule. A similar abiotic process occurs with zero-valent metals. Zero-valent metals include
34 iron, palladium, and other combinations (called bi-metals). Bi-metals have been found to be more
35 reactive. Nano-particle-sized bi-metals have also been shown to be superior to micro-sized zero-valent
36 iron (Mikszewski, 2004). The bioremediation process involves mixing an electron donor (such as lactate)
37 with the contaminated soil and maintaining anaerobic conditions for a number of months. A similar
38 process is used with the zero-valent metals.

39 **11.2.5.2 Relevant Demonstration Projects**

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

1 The technology review indicated that NZVI particles are capable of reducing a wide range of
2 environmental pollutants including PCBs. In particular, the properties of NZVI and other nano-scale
3 metals (high surface area to volume ratios, high surface energies, and a large fraction of stepped surface,
4 zero valency) make them extremely chemically reactive. Several laboratory and field-scale
5 demonstrations have been conducted demonstrating the performance of using NZVI for PCB
6 dechlorination. Results of the studies show conflicting results. Where complete dechlorination could be
7 achieved, percent reduction of PCBs ranged from 25 to 84 percent. In the field study where 84 percent
8 reduction was achieved (Gardner, 2004), complete dechlorination was achieved in only 1 day. In another
9 study (Lowry et al., 2004), NZVI was shown to dechlorinate PCBs with congener half-lives ranging from
10 40 days to 77 years, with no biphenyl production noted (indicating incomplete dechlorination).

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

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

29 ***11.2.5.3 Evaluation and Screening Rationale***

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

38 **11.2.6 In Situ Gaseous Reduction with Chemical Reductant or Biological Substrate**

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

41 ***11.2.6.1 Description***

42 ISGR is a vadose zone remediation technology that uses a gaseous reagent (such as hydrogen
43 sulfide/nitrogen gas mixture) to reduce or treat contaminants. It is applicable to redox sensitive
44 contaminants. The objective is to reduce the contaminant chemically (metal or radionuclide) to a less

1 mobile, and sometimes less toxic form, preventing further migration and reducing the risk of
2 contaminating the groundwater. For contaminants such as Cr(VI), uranium, and technetium, the reduced
3 species are significantly less mobile than the oxidized species. With the reduction of iron associated with
4 sediment, the ISGR technology creates a reducing zone within the subsurface that continues to reduce
5 contaminants or other oxidants (for example, oxygen) that migrate into the treatment zone until the
6 reducing capacity becomes depleted (RPP-ENV-34028).

7 **11.2.6.2 Relevant Demonstration Projects**

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

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

23 **11.2.6.3 Evaluation and Screening Rationale**

24 The use of a gas as the reducing agent is advantageous compared to a liquid-based delivery method
25 because the risk of mobilizing contaminants is lower and better diffusion of reagent is expected
26 (RPP-ENV-34028). However, significant uncertainties have been identified regarding the effectiveness of
27 ISGR. Key uncertainties, as identified in WMP-27397, include:

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

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

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

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

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

10 **1.3 In Situ Treatment—Delivery Method**

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

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

18 **1.3.1 Mixing with Conventional Excavation Equipment**

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

21 **1.3.1.1 Description**

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

28 **1.3.1.2 Evaluation and Screening Rationale**

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

36 **1.3.2 Deep Soil Mixing**

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

39 **1.3.2.1 Description**

40 Deep soil mixing uses large-diameter augers or horizontally rotating heads to blend in reactants and
41 homogenize soil. The diameter of the augers can vary from 0.3 to 4 m (0.98 to 13 ft) (Day et al., 1995).

1 Reports indicate depths ranging from 35 to 50 m (114 to 164 ft) can be achieved with this technology
2 (Day et al., 1995; Jasperse et al., 1992).

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

13 ***11.3.2.2 Relevant Demonstration Projects***

14 Deep soil mixing was used to remediate an abandoned transformer repair facility in Miami, Florida
15 (Jasperse et al., 1992). PCB concentrations over the affected area ranged from 200 to 600 ppm, with a
16 maximum concentration of 1,000 ppm. Impacted media was encountered to approximately 15 m (49 ft)
17 bgs. Laboratory bench-scale tests were completed to evaluate potential reagents, and a proprietary
18 pozzolanic additive containing clay absorbents was selected. Full-scale implementation involved use of a
19 four-shaft, deep soil-mixing rig and a reagent mixing plant complete with a four-line pump and control
20 system. Reagents were mixed at a rate of 275 kg/m³ of soil mixed. Results from the study show a
21 decrease in concentrations of PCB after treatment, as well as an increase in unconfined strength and
22 decrease in permeability of the mixed samples over time (Jasperse et al., 1992).

23 ***11.3.2.3 Evaluation and Screening Rationale***

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

34 **11.3.3 Foam Delivery of Reagents**

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

37 ***11.3.3.1 Description***

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

1 ***11.3.3.2 Relevant Demonstration Projects***

2 Foam delivery of amendments is currently in developmental stage; full-scale applications have not been
3 completed. A research plan for foam delivery of amendments to the deep vadose zone was presented by
4 PNNL in 2009 (PNNL-18143). The objective of this study was to develop a foam delivery technology for
5 the distribution of amendments to deep vadose zone sediments for in situ immobilization of metal and
6 radionuclide contaminants.

7 Laboratory batch and column tests have been conducted for foam delivery of calcium polysulfide to
8 immobilize Cr(VI) (Zhong et al., 2008). Batch tests were conducted to study foam properties, and column
9 experiments were performed to study the foam delivery of calcium polysulfide under conditions similar to
10 field vadose zone, and to determine the extent of hexavalent immobilization. Results from the study
11 indicated that a column test calcium polysulfide could be delivered efficiently to unsaturated sediments to
12 immobilize Cr(VI) in situ, and to minimize Cr(VI) mobilization at the reaction front as observed when
13 calcium polysulfide is delivered in a water-based single-phase solution. However, no information is
14 currently available on how far the foam will move out from an injection well in field conditions.

15 ***11.3.3.3 Evaluation and Screening Rationale***

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

22 ***11.3.4 Gaseous Delivery of Reagents (In Situ Gaseous Reduction)***

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

28 ***11.3.5 Horizontal Injection Wells***

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

31 ***11.3.5.1 Description***

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

35 ***11.3.5.2 Relevant Demonstration Projects***

36 An unsuccessful horizontal well technology demonstration was conducted at the Hanford 100-D area
37 from November 2009 through January 2010 (report to be published in 2010). The scope of work consisted
38 of two phases. First, a surface casing was installed at a 16-degree angle from horizontal through the Hanford
39 formation to an estimated depth of 15 m (49 ft) bgs. The second phase was to drill through the Ringold
40 Formation using horizontal directional drilling techniques and drilling mud. Once this drilling was complete,
41 the drill bit would have been knocked off and the well screen installed inside the drill pipe. Installation of
42 surface casing was required to facilitate circulation of drilling mud in the very porous Hanford formation.
43 The casing was advanced with much difficulty to approximately 6 m (20 ft) bgs (85 horizontal linear ft)

1 when downward progress ceased because of inadequate force on the down-hole hammer and difficulty
2 removing cuttings from the inclined casing. Rotary-mud directional drilling through the casing and into
3 the Hanford formation was attempted, but progress was slow and circulation was never established.

4 ***11.3.5.3 Evaluation and Screening Rationale***

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

14 **11.3.6 Jet Grouting**

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

17 ***11.3.6.1 Description***

18 Grout injection addresses subsurface contaminants by high-pressure injection of a grout or binding agent
19 into the subsurface to physically or chemically bind or encapsulate contaminants (DOE/RL-2007-56).
20 Grout injection technologies using multiple types of grouting materials have been applied and are
21 currently undergoing testing for in situ contaminant stabilization at other sites. Similarly, more standard
22 grouting techniques may also potentially be useful for selected applications.

23 ***11.3.6.2 Relevant Demonstration Projects***

24 In situ grouting has been approved by regulating agencies and implemented at several small-scale sites,
25 although in situ grouting has not been applied to large-scale sites with many radiological and chemical
26 hazards (RPP-ENV-34028).

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

34 Grouting of buried mixed waste at DOE's Savannah River Site (SRS) was rejected as a remedial
35 technology (DOE/RL-94-61). Evaluations concluded that grouting would not fill enough voids without
36 creating uncontrolled surface cracking and surface releases of grout contaminated with hazardous and
37 radioactive constituents.

38 ***11.3.6.3 Evaluation and Screening Rationale***

39 Significant uncertainties are associated with the use of grouting for in situ contaminant stabilization,
40 especially for the deep vadose zone (WMP-27397). The principal challenges to implement this
41 technology are application, transport of the grout to the deep vadose zone, and verification of proper

1 placement. Vertical variations in stratigraphy, with some levels having relatively low potential
2 permeability to grout flow, pose significant challenges for the technology (DOE/RL-2007-56).

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

10 **11.4 In Situ Treatment—Other**

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

13 **11.4.1 Desiccation**

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

16 **11.4.1.1 Description**

17 Desiccation involves drying a targeted portion of the vadose zone by injecting dry air and extracting soil
18 moisture at soil gas extraction wells (DOE/RL-2007-56). Because desiccation removes water already in
19 the vadose zone, it reduces the amount of pore fluid available to support downward transport of
20 contaminants in the deep vadose zone, impedes water movement, and augments the impact of surface
21 water infiltration control.

22 The impact of desiccation on the movement of Cr(VI), technetium-99, and uranium is based on physical
23 removal of water from the subsurface. Removing moisture from the contaminated material reduces the
24 driving force for continued vertical migration. Theoretically, desiccation would be effective in
25 immobilizing contaminants to the extent that moisture content is lowered below the point for unsaturated
26 flow to occur. The longevity of the “dry” conditions depends on the soil moisture infiltration rate, the
27 relative humidity of atmospheric air, and the proximity to groundwater. In time, moisture levels recover to
28 pre-extraction concentrations (RPP-ENV-34028). Without surface infiltration control, moisture content
29 would eventually return to a state of equilibrium with surface infiltration rates. Therefore, this technology is
30 considered not to be effective in the long term without concurrent infiltration control. A more detailed
31 evaluation of this technology, including some initial feasibility calculations is presented in WMP-27397.

32 **11.4.1.2 Relevant Demonstration Projects**

33 A very limited desiccation test showing that subsurface airflow can be induced in the Central Plateau
34 vadose zone was performed in conjunction with a leak detection test (CP-18187, 2002).

35 **11.4.1.3 Evaluation and Screening Rationale**

36 Equipment and technology required for implementation of desiccation is well established and common.
37 Soil vapor extraction (SVE) is a well-established technology, and moisture extraction has been safely
38 demonstrated at the Hanford Site (RPP-ENV-34028). However, there is uncertainty with the number of
39 wells, well spacing, and well configuration details required for optimal field/full-scale implementation. In
40 addition, uncertainties are associated with specific aspects of implementation and long-term effectiveness.
41 Desiccation was included in the March 2008 “*Deep Vadose Zone Treatability Test Plan for the Hanford*

1 *Central Plateau Site*” (DOE/RL-2007-56) and is expected to provide information in addressing these
2 uncertainties.

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

6 **11.4.2 In Situ Thermal Desorption**

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

9 **11.4.2.1 Description**

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

19 **11.4.2.2 Relevant Demonstration Projects**

20 Field demonstrations were performed in 1993 and 1994 at the SRS and the Hanford 300 Area to evaluate
21 six-phase soil heating (SPSH), a form of electrical resistive heating, as a vadose remedial technology for
22 tetrachloroethylene (PCE) and TCE (DOE/EM-0272). The demonstration site at the Hanford Site was
23 located in the 300 Area at an uncontaminated, undisturbed site. The objective of the 300 Area
24 demonstration was to refine the design of the six-phase electrodes and other system components, and
25 address scale-up issues in the field. The demonstration site at SRS was located at one of the source areas
26 within the 2.6 km² (1 mi²) VOC groundwater plume. The contaminated target zone was a 3 m (10 ft) thick
27 clay layer at a depth of approximately 12 m (40 ft). TCE and PCE concentrations in sediments ranged
28 from 0 to 181 µg/kg and 0 to 4,529 µg/kg. Six electrodes were placed in the ground in a 9 m (30 ft)
29 diameter area in a hexagonal pattern. An extraction well was placed in the center of the hexagon.
30 Approximately 3.8 to 7.6 L/hr (1 to 2 gal/hr) of water with 500 mg/L sodium chloride were added at each
31 electrode to replenish evaporated water and provide an electrically conductive solution. The soil
32 surrounding each electrode was supplied with water through a drip system. A vacuum system removed
33 contaminant vapors from the subsurface, which were passed through a condenser to remove the steam.
34 The extracted VOCs were treated by electrically heated catalytic oxidation. Key results of the
35 demonstration at SRS indicate 99.7 percent removal of contaminants from within the electrode array.
36 Outside the array, 93 percent of contaminants were removed at a distance of 2.4 m (8 ft) from the array.
37 Clays were heated more rapidly than the adjacent sands because of their higher moisture content (and,
38 thus, electrical conductivity). Completion of a cost-benefit analysis by Los Alamos National Laboratory
39 showed that SPSH could be performed for a cost of \$88 per yd³, assuming that a contaminated site of
40 30 m (100 ft) in diameter and 6 to 36 m (20 to 120 ft) deep could be remediated in 5 years.

41 A full-scale thermal conductive heating treatment system was operated at a confidential chemical
42 manufacturing facility in Portland, Indiana from July to December 1997 (EPA, 2003). The two target
43 treatment areas were 45 × 12 m (150 × 40 ft) to a depth of 5 m (16 ft), and 9 × 6 m (30 × 20 ft) to a depth
44 of 3.4 m (11 ft). Target source areas contained TCE up to 79 mg/kg and PCE up to 3,500 mg/kg. The site

1 geology included fill, a combination of sand, clayey sand and construction debris, to a depth of about
2 2 m (7 ft). Till consisting of moist, damp, silty clay extended to a depth ranging from 5.4 to 5.7 m
3 (18 to 19 ft), with sand seams running through the till. Below the till was a sand and gravel layer
4 extending to a depth of 9 m (30 ft) and consisting of poorly sorted sand. Groundwater was encountered in
5 the sand and gravel layer at depths of 6.7 to 7.6 m (22 to 25 ft). Heater/vacuum wells were installed on a
6 2.2 m (7.5 ft) triangular spacing with approximately one well per 15 m² (161ft²) of surface area treated.
7 Wells were operated at 760 to 871°C (1,400 to 1,600°F) and soil gas was extracted through the wells
8 using a vacuum pump. The surface area between wells was covered by an impermeable silicone rubber
9 sheet to prevent fugitive emissions, and thermally insulated mats were used to minimize surface heat loss.
10 The maximum soil temperature in the treatment area at a depth of 13 ft (3.96 m) ranged from 100 to
11 260°C (212 to 500°F). Off-gases were treated with an 1,800-scfm flameless thermal oxidizer with an
12 operating temperature range of 982 to 1,037°C (1,800 to 1,900°F). Results of confirmatory sampling
13 showed that concentrations of PCE and TCE in both areas were reduced to below the cleanup goals of
14 8 mg/kg for PCE and 25 mg/kg for TCE.

15 **11.4.2.3 Evaluation and Screening Rationale**

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

20 **11.4.3 In Situ Vitrification**

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

23 **11.4.3.1 Description**

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

39 ISV involves passing current through the soil using an array of electrodes. If the soil is too dry,
40 enhancements must be placed to provide an initial flow path for the electrical current. Large areas are treated
41 by fusing together multiple vitrification treatment zones (Dzombak et al., 1997). To accommodate soil
42 densification, clean overburden is placed over the melt zone before the melt is initiated, thereby avoiding
43 subsidence issues while increasing thermal efficiency and radionuclide retention. Excessive water vapor
44 passing through the melt might disrupt or displace the melt; therefore, soil with high moisture content
45 must be treated to remove water prior to in situ vitrification. The process requires 700 to 900 kWh/ton of

1 soil to be treated, including soil water. The overall oxide composition of the soil determines the fusion,
2 melt temperature, and viscosity. In addition, it is essential that the media contain sufficient monovalent
3 alkali earth oxides to provide the electrical conductivity required (RPP-ENV-34028).

4 **11.4.3.2 Relevant Demonstration Projects**

5 Between 1980, when the ISV process was conceived of by PNNL for DOE, and 1997, more than
6 200 tests, demonstrations, and commercial operations of the technology have been conducted
7 (RPP-ENV-34028). A 1997 DOE case study abstract document, *Case Study Abstract: In Situ*
8 *Vitrification*, presented information on a case study conducted at the Hanford Site. Information specific to
9 this case study is limited; however, it does specify that a Toxic Substances Control Act demonstration
10 showed destruction and removal efficiency for PCBs of greater than 99.9999 percent (EPA, 1997).

11 A large-scale ISV test was completed at the 116-B-6A Crib site in 1990 (PNL-8281). The site contained
12 mixed waste (chromium, lead, and cesium-137) at an approximate depth of 6 m (20 ft) bgs.
13 The treatability test consumed 550 MWh of electrical energy, and resulted in a 771 tonne (850 ton) block
14 of vitrified soil. Results from data collection indicated the vitrified block retained over 99.99 percent of
15 chromium and lead, and over 99.98 percent of cesium-137, indicating the favorable resistance of the
16 treated material to leaching. Results also indicated greater treatment depths were in homogeneous soil.
17 The final depth achieved during the treatability test was 4.3 m (14 ft), which is 18 m (60 ft) less than the
18 required treatment depth. The 4.3 m (14 ft) vitrified depth coincided with a cobble layer detected below
19 the crib during the post-treatment core drilling. The rate of melt progression above the cobble layer was
20 satisfactory, indicating the effect of the cobble layer on the achieved treatment depth (PNL-8281).

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

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

1 **11.4.3.3 Evaluation and Screening Rationale**

2 The effective treatment depth of this technology is approximately 7.6 m (25 ft) bgs, and the treatment area
3 is limited by cost (RPP-ENV-34028). Elevated worker safety and exposure concerns could be associated
4 with this process because of volatilization; however, the risk is considered lower than that of excavating
5 highly contaminated and radioactive soil. Working in proximity to high voltage and high temperatures
6 also requires appropriate safety precautions.

7 The cost associated with implementation of ISV, as compared to other technologies is considered high,
8 where electric power is generally the most significant contributor. As presented in Table 9-1 of
9 RPP-ENV-34028, ISV has the highest of all relative technology-specific costs. Given the complex
10 equipment requirements and challenging implementation, as well as the relative high cost, in situ
11 vitrification was not retained for further evaluation.

12 **11.4.4 Phytoremediation**

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

15 **11.4.4.1 Description**

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

21 **11.4.4.2 Relevant Demonstration Projects**

22 A treatability demonstration project is being conducted at the Hanford Site for treatment of Sr-90 in soil
23 and groundwater along the banks of the Columbia River in 100-N using Coyote willows. The Coyote
24 willow is considered the most suitable plant for use along the Columbia River shore. Known for its rapid
25 and robust regrowth abilities, Coyote willow is used extensively along the Columbia and Yakima Rivers
26 for bank stabilization and revegetation purposes. As part of a treatment train of remedial technologies
27 aimed at treating Sr-90 in 100-K, phytoremediation using Coyote willow would be the final
28 polishing step.

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

37 Greenhouse, laboratory (growth chamber), and field studies have shown that Sr-90 is a nutritional analog
38 of calcium, a plant macronutrient. As such, the Coyote willows will actively accumulate Sr-90 in their
39 leaves and stems to concentrations greater than 70 times those present in the soil pore water surrounding
40 their roots. Given the steadily increasing growth rate of the trees at 100-K following yearly harvests of
41 their aboveground tissue, this type of plant can remove significant amounts of contamination from the
42 shoreline area while not disturbing the natural sediment structure. Laboratory studies have also shown
43 that herbivorous insects such as aphids or moth larvae would not be a source of Sr-90 offsite transport

1 from the trees. Further, controlled harvesting schedules and engineered barriers (fencing and netting)
2 would prevent animal intrusion and plant detritus release (PNNL-18294, *100-N Area Strontium-90*
3 *Treatability Demonstration Project: Food Chain Transfer Studies for Phytoremediation Along the 100-N*
4 *Columbia River Riparian Zone*).

5 The phytoremediation demonstration is ongoing at 100-K. Biomass production over the first 3 years
6 followed a typical growth curve. On an mT/ha basis, biomass production amounted to 0.2 mT/ha in 2007,
7 0.87 mT/ha in 2008, and 4.3 mT/ha in 2009. Growth curve extrapolation predicts 13.2 mT/ha during a
8 fourth year and potentially 29.5 mT/ha during a fifth year. The most recent report concludes that the
9 projected biomass yields suggest the trees could prove effective in removing the Sr-90 from the 100-NR-2
10 riparian zone (PNNL-19120, *100-N Area Strontium-90 Treatability Demonstration Project:*
11 *Phytoextraction Along the 100-N Columbia River Riparian Zone—Field Treatability Study*).

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

19 **11.4.4.3 Evaluation and Screening Rationale**

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

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

35 In summary, the technology would only be effective for low concentrations of contaminants in shallow
36 soil over long periods, and many metals and radionuclides would accumulate in the plants rather than
37 being treated, posing risks to ecological receptors. For these reasons, phytoremediation was not retained
38 for further evaluation.

39 **11.5 Containment**

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

1 **11.5.1 Horizontal Subsurface Barriers—Jet Grouting, Soil Freezing, or Wire Saw Barriers**

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

4 **11.5.1.1 Description**

5 Emplaced horizontal barriers are placed beneath existing in situ contaminants. These bottom barriers have
6 features similar to those of vertical barriers in that they minimize movement of contaminants, restrict
7 infiltration of groundwater, and are constructed of similar materials using similar technologies. Horizontal
8 barrier technologies can include (RPP-ENV-34028):

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

19 **11.5.1.2 Relevant Demonstration Projects**

20 Each of these horizontal barrier technologies is in the early development and testing stages
21 (RPP-ENV-34028). Several demonstrations have been performed at near surface depths, but application
22 within the deep vadose could prove to be costly and impractical.

23 **11.5.1.3 Evaluation and Screening Rationale**

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

31 **11.5.2 Dynamic Compaction**

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

34 **11.5.2.1 Description**

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

38 **11.5.2.2 Evaluation and Screening Rationale**

39 The technology is considered to have moderate-to-high effectiveness. It is effective in removing void
40 spaces and compacting surface soil where voids exist around buried waste; however, it is not an effective

1 containment process option for native soil or treatment of hazardous wastes. Implementability is high,
2 given that the technology is simple and widely used. However, because no waste sites containing solid
3 and buried waste are present at the treatment area, this process option was not retained.
4

5 **I2 Additional Information on Technologies Not Retained** 6 **for Groundwater Treatment**

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

9 **I2.1 Ex Situ Treatment**

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

13 **I2.1.1 Ex Situ Chemical Precipitation**

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

16 ***I2.1.1.1 Description***

17 Ex situ chemical precipitation involves the introduction of chemicals to transform dissolved contaminants into
18 insoluble solids, which are removed by sedimentation and filtration. Chemicals used to remove Cr(VI) can
19 include ferrous chloride, ferrous sulfide, zero-valent iron, sulfur dioxide, and various sulfites (SGW-38338,
20 Section 4.2). Ferrous iron is commonly used for industrial wastewaters, such as from metal plating.
21 Carbon-14, which is typically in chemical forms of carbonate and bicarbonate (depending on the pH)
22 (IAEA, 2004), can be removed by raising the pH of the water. Effective post-treatment for solids removal,
23 but conditioning is required. Solids removal typically includes flocculation and/or coagulation, settling,
24 and filtration. Sludge handling, dewatering, and disposal are also required. The volume and/or mass of the
25 sludge generated can be extremely large and would need final disposed at ERDF. Site-specific jar testing
26 would be required to obtain design and operational parameters.

27 ***I2.1.1.2 Relevant Demonstration Projects***

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

38 ***I2.1.1.3 Evaluation and Screening Rationale***

39 This technology is effective for Cr(VI) and could possibly be effective for carbon-14. Additional testing
40 would be required to determine the efficacy of this technology to carbon-14. Site specific testing for all
41 COPCs would be required to determine operational parameters. Vendors and equipment for this

1 technology are readily available; however, this technology is unproven at the Hanford Site and large
2 volumes of sludge are produced.

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

10 **I2.1.2 Electrocoagulation**

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

13 **I2.1.2.1 Description**

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

19 **I2.1.2.2 Relevant Demonstration Projects**

20 A 2007 treatability test evaluated the potential for this technology for 100-D of the Hanford Site
21 (DOE/RL-2008-13, *Treatability Test Report for the Removal of Chromium from Groundwater at*
22 *100 D Area Using Electrocoagulation*). The test objectives were to: (1) determine the operability,
23 robustness, and treatment efficiency of an electrocoagulation system; (2) characterize the volume and
24 composition of the resulting waste; and (3) obtain design data for scaling the process from a 190 L/min
25 (50 gal/min) to a 1,900 L/min (500 gal/min) system.

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

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

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

39 **I2.1.2.3 Evaluation and Screening Rationale**

40 The effectiveness of electrocoagulation for the 100 Area is anticipated to be low or moderate, particularly
41 in light of the challenges encountered in the above-described pilot test. The technology is not widely used
42 for Cr(VI), although it may be applicable to technetium-99; however, the technetium-99 plume is small

1 and, therefore, the benefit would not be significant, and additional challenges related to the reversible
2 potential of technetium-99 reduction may result. Implementability is also considered low or moderate
3 because further development of the process would be required. In addition, the process may render the
4 treated water less suitable for re-injection. Capital costs are moderate or high, and O&M costs are
5 moderate. Part of the high cost is due to the production of significant volumes of sludge that must be
6 managed and disposed of. The costs for electrocoagulation do not appear to be any lower than for the
7 existing ion exchange systems. Because of poor performance and implementability as well as high cost,
8 the technology was not retained for further evaluation.

9 **12.1.3 Wetlands**

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

11 **12.1.3.1 Description**

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

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

20 Wetlands can also be used to treat other COPCs, such as nitrate, petroleum, and TCE. Several removal
21 mechanisms have been identified for treatment of nitrate in water such as decomposition, nitrification/
22 denitrification, settling, volatilization, adsorption, and nutrient uptake (SGW-37783, *Literature Survey for*
23 *Groundwater Treatment Options for Nitrate, Iodine-129, and Uranium, 200-ZP-1 Operable Unit,*
24 *Hanford Site*). Biodegradation is an important mechanism for removal of petroleum hydrocarbons, and
25 uptake by plants is an important mechanism for removal of TCE. Phytoremediation (one component of
26 wetland treatment) has been used to treat Sr-90, but it is not known to treat other radionuclides
27 (SGW-34562, 2008, *Alternative Remediation Technology Study for Groundwater Treatment at 200-PO-1*
28 *Operable Unit at Hanford Site*).

29 **12.1.3.2 Relevant Demonstration Projects**

30 A number of demonstration projects use wetlands to remove nitrates (SGW-37783). For example, a
31 constructed wetland is used to remove nitrate from the municipal drinking water supply in Orange
32 County, California. Up to 1.5 m³/s (33 million gal/day) were treated prior to groundwater recharge.
33 The influent contained 3.1 to 10.9 mg/L of nitrate (as nitrogen). The average nitrate removal was 522 mg
34 (0.018 oz) of nitrate (as nitrogen) per m²/day, and exiting nitrate concentrations sometimes fell to as low
35 as 0.1 mg/L nitrate (as nitrogen), with hydraulic detention times from 0.3 to 9.6 days. Bacterial
36 denitrification was concluded to be the primary nitrate loss mechanism. A review of 19 surface flow
37 wetlands showed that nearly all reduced total nitrogen. A comparison of surface and subsurface flow
38 wetlands showed that subsurface flow wetlands outperformed surface flow wetlands and yielded lower
39 effluent nitrate concentrations (ranging from less than 1 to less than 10 mg/L).

40 **12.1.3.3 Evaluation and Screening Rationale**

41 The land area required for wetlands is likely to be very large for the volume of groundwater that will be
42 produced by the 100 Area pump-and-treat systems, even under favorable (warm) conditions. Even more
43 area would be required for effective treatment in the winter, when plants and micro-organisms in the

1 wetland would be less active. Problems with freezing would be likely, as average minimum temperatures
2 are below freezing more than half of the year (PNNL-6415, *Hanford Site National Environmental Policy*
3 *Act [NEPA] Characterization*). Therefore, the technology is not well suited to the climate at the Hanford
4 Site. The effectiveness of this technology at the site is considered moderate since additional research and
5 testing would be required to verify the effectiveness of this technology for COPCs other than nitrate.
6 Implementability is considered low to moderate. Construction of wetlands at the Hanford Site would
7 require lining to prevent the infiltration of the water as well as provision of organic substrate to support
8 wetland plants. Wetland treatment does not have significant advantages over ion exchange, which is
9 already in place and performing well.

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

14 **I2.1.4 Subgrade Bioreactors**

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

17 **I2.1.4.1 Description**

18 Biological treatment using SGBRs is a potential treatment technology for Cr(VI) and nitrate in
19 groundwater. If implemented on a full-scale, a SGBR may consist of a lined excavation backfilled with a
20 mixture of sand/gravel, a biodegradable substrate such as wood mulch, and possibly zero-valent iron
21 (ZVI). The contaminated groundwater would pass through the basin in which the Cr(VI) and nitrate are
22 chemically and/or biologically reduced to less mobile and/or less toxic compounds (i.e., trivalent
23 chromium and nitrogen gas). A second stage, aeration/filtration basin could be provided to remove any
24 residual organic carbon that may be present and to remove any dissolved by-products of biodegradation
25 (ferrous iron, arsenic, and manganese), as well as suspended solids, prior to the discharge of the treated
26 groundwater back to the aquifer.

27 **I2.1.4.2 Relevant Demonstration Projects**

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

29 The biological processes involved in biological treatment of reducible metals like Cr(VI) are similar to
30 those involved in other bioreactor concepts used in the remediation industry, such as sulfate-reducing
31 bioreactors that are used to treat acid mine drainage. Based on case studies, the effectiveness of
32 bioreactors has been demonstrated at temperatures between 2 and 16°C (“Passive Treatment of Acid Mine
33 Drainage in Bioreactors Using Sulfate-Reducing Bacteria: Critical Review and Research Needs”
34 [Neculita et al., 2007]).

35 Ex-situ bioreactors for nitrate removal have been pilot tested at the Hanford Site in the past (*Development*
36 *of a Biological Treatment System for Hanford Groundwater Remediation: FY 1989 Status Report*
37 [PNL-7290]). A pilot-scale test was conducted in 1989 using simulated Hanford Site groundwater with a
38 continually stirred tank bioreactor (CSTR). The CSTR system was operated continuously for 5 months
39 with a simulated groundwater influent containing 400 mg/L nitrate. Using acetate as the primary carbon
40 source for microbial growth, a nitrate removal efficiency of greater than 99 percent was maintained at an
41 influent flow rate of 6 L/hr (8-hour residence time).

1 **12.1.4.3 Evaluation and Screening Rationale**

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

9 **12.1.5 Bioreactors**

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

12 **12.1.5.1 Description**

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

17 **12.1.5.2 Relevant Demonstration Projects**

18 There are few reported applications of ex situ bioreactors specifically for Cr(VI) (Chen and Gu, 2005).
19 However, bioreactors for nitrate removal have been pilot tested at the Hanford Site in the past
20 (PNNL-6415, *Development of a Biological Treatment System for Hanford Groundwater Remediation*). A
21 pilot-scale test was conducted in 1989 using simulated Hanford Site groundwater with a continuous
22 stirred-tank bioreactor (CSTR). The CSTR system was operated continuously for 5 months with a
23 simulated groundwater influent containing 400 mg/L nitrate. Using acetate as the primary carbon source
24 for microbial growth, a nitrate removal efficiency of greater than 99 percent was maintained at an influent
25 flow rate of 6 L/hr (8-hour residence time).

26 The biological processes involved in biological treatment of Cr(VI) are similar to those involved in other
27 bioreactor concepts used in the remediation industry, such as sulfate-reducing bioreactors (SRB) that are
28 used to treat acid mine drainage. Based on case studies for SRBs, the effectiveness of bioreactors has
29 been demonstrated at temperatures between 2 and 16°C (Neculita et al., 2007). Daily average low
30 temperatures at the Hanford Site are typically below 0°C (32°F) during the winter months, which may
31 necessitate heating/insulating portions of the ex situ bioreactor system to maintain the viability of the
32 microbes.

33 **12.1.5.3 Evaluation and Screening Rationale**

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

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

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

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

4 **I2.1.6 Phytoremediation**

5 Phytoremediation was not retained for treatment of groundwater and soil contaminated with Cr(VI) or
6 other COPCs. Additional information on this process can be found in Section I1.2.2.4.

7 **I2.1.6.1 Description**

8 For groundwater, phytoremediation is limited to the depth to which the plants can extract water. Water cannot
9 be wicked and delivered vertically more than about 6 m (20 ft); thus, the potentiometric surface must be within
10 3 or 6 m (10 or 20 ft) of the bottom of the root mass for this system to be viable (WSRC-TR-2005-00198,
11 *Enhanced Attenuation: Approaches to Increase the Natural Treatment Capacity of a System*). Because of
12 this limitation, unless groundwater was first extracted (by pumping) and then phytoremediated (that is, the
13 plants would be irrigated with the contaminated groundwater), phytoremediation would not be suitable for
14 groundwater remediation at the Hanford Site except immediately adjacent to the river. There are methods
15 of encouraging plant roots to grow deeper, but not to the depths that would be required at most of the
16 100 Area of the Hanford Site. Phytoremediation systems (including by land application) are only
17 operational when the soil is warm and plants are active, so treatment effectiveness would be reduced in
18 the winter. The land requirements for phytoremediation are also relatively large.

19 **I2.1.6.2 Relevant Demonstration Projects**

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

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

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

32 **I2.1.6.3 Evaluation and Screening Rationale**

33 Because of the large depth to groundwater at most of the Hanford Site, phytoremediation would be
34 feasible immediately adjacent to the river only. Therefore, implementability of phytoremediation is considered
35 low or moderate. It is usually implemented over long-time scales, such as years or decades. The sparse
36 vegetation that naturally grows on the Hanford Site suggests that significant efforts and inputs (such as organic
37 matter and water) would be required to establish a vigorous plant community. However, capital costs
38 would still be relatively low. Once the plants are established, O&M costs would also be low because
39 requirements to sustain them are low (food and water). However, metals concentrations and radionuclide
40 activities may accumulate in the plants to the point that they must be disposed of periodically in a secure
41 facility, such as ERDF. Ultimately, the plants would need to be disposed of at ERDF to avoid returning
42 contaminants to the soil from which they were originally extracted (as plants decompose) if

1 phytoremediation is used for contaminants that are not transformed to innocuous forms by the plants or
2 micro-organisms.

3 Phytoremediation is only effective when the plants are active; therefore, the technology would not be
4 effective during the winter. Because of the uncertainty of continued effectiveness throughout the year as
5 well as the very limited ability of the plants to root deep enough to effect groundwater in most areas at the
6 Hanford Site, effectiveness is considered low to moderate. There are also concerns about contaminants
7 entering the food chain as animals eat the vegetation or bees pollinate flowers. In summary, the
8 technology would only be effective for low concentrations of contaminants where groundwater is shallow
9 over long periods, and many metals and radionuclides would accumulate in the plants and not actually be
10 treated, posing risks to ecological receptors. For these reasons, phytoremediation was not retained for
11 further evaluation.

12 **12.1.7 Membrane Separation (Reverse Osmosis)**

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

15 **12.1.7.1 Description**

16 RO is a pressure-driven process that uses semi-permeable membranes to purify water. Contaminated
17 water is passed through the membrane while the contaminants are contained within the membrane.
18 The water that is allowed to pass through the membrane is called the permeate, and typically contains
19 only a small fraction (less than 5 percent) of the ions in the feed solution. The water that does not pass
20 through the membrane (containing the ions that do not pass through the membrane) is called the retentate
21 or brine, concentrate, or reject. It has a high total dissolved solids concentration and would contain most
22 of the COPCs being treated. With appropriately sized membranes and multiple stages of membranes, very
23 low concentrations of ions can be achieved. RO is among the technologies that EPA considers effective
24 for removing total chromium to below 100 µg/L (along with coagulation/filtration, ion exchange, and
25 lime softening) (EPA, 2010, “Basic Information on Chromium in Drinking Water”). In addition to
26 chromium, other COPCs that RO can remove include nitrate, TCE, some VOCs, and some petroleum
27 compounds (Dvorak and Skipton, 2008 *Drinking Water Treatment: Reverse Osmosis*). In
28 New Hampshire, the typical production efficiency of RO for nitrate removal is approximately 25 percent.
29 That is, for every 15 L (4 gal) of untreated water entering the device, only 3.7 L (1 gal) of treated water is
30 produced (WD-WSEB-3-9). This low efficiency is a result of New Hampshire’s cold groundwater
31 temperatures, which are likely similar to groundwater temperatures at the Hanford Site.

32 RO for removal of Sr-90 “shows promise” (Liu and Liptak, 1997), and a later study (EPA and NSF, 2005)
33 showed 97 percent removal (from 960 to 33 µg/L) of strontium by RO. No commercially available
34 treatment option is available to remove tritium from groundwater (WSRC-RP-97-849).

35 Brine production is a significant issue with RO; the need to minimize and manage (for example,
36 evaporate) the brine can lead to significant increases in water treatment costs. RO is commonly used to
37 desalinate seawater, which typically generates much greater volumes of brine than for treating
38 groundwater; however, in this application, the brine can simply be returned to the seawater.
39 Nano-filtration is very similar to RO but uses membranes with large openings (EPA 815-R-06-009,
40 *Membrane Filtration Guidance Manual*). Options for managing brine and other process residuals include
41 discharge to a suitable surface water body, discharge to a sanitary sewer, deep well injection, land
42 application, or treatment with supernatant recycle and solids disposal. The treatment processes can
43 include clarification, sedimentation in lagoons, gravity thickening, centrifuging, belt filter pressing, and
44 evaporation (EPA, 815-R-06-009).

1 **12.1.7.2 Relevant Demonstration Projects**

2 A process was bench tested at the 200 West Area of the Hanford Site that combines three different
3 membrane technologies: RO, coupled transport, and nano-filtration. These technologies were used to
4 purify 72 L (19 gal) of groundwater while extracting and concentrating uranium, technetium, and nitrate
5 into separate solutions (significant Cr(VI) concentrations were not present). This separation allows for the
6 future use of the radionuclides, if needed, and reduces the amount of waste that will need to be disposed
7 of. This process has the potential to concentrate the contaminants into solutions with volumes in a ratio of
8 1 to 10,000 of the feed volume, compared to a volume reduction ration of 10 to 100 for ion exchange and
9 stand-alone RO (WHC-SA-2755-FP, *Testing of a Benchscale Reverse Osmosis/Coupled Transport*
10 *System for Treating Contaminated Groundwater*). The experiment demonstrated the effectiveness of the
11 process as theorized for all ions except for technetium, suggesting that design modifications may be
12 necessary.

13 The Effluent Treatment Facility in the 200 East Area of the Hanford Site treats liquid effluent to remove
14 toxic metals, radionuclides, and ammonia, and to destroy organic compounds. The treatment process
15 constitutes best available technology and includes pH adjustment, filtration, ultraviolet light, and
16 hydrogen peroxide destruction of organic compounds, RO to remove dissolved solids, and ion exchange
17 to remove the last traces of contaminants. The facility began operating in December 1995. The maximum
18 treatment capacity of the facility is 570 L/min (150 gal/min) (PNNL-18427, *Hanford Site Environmental*
19 *Report for Calendar Year 2008*).

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

27 **12.1.7.3 Evaluation and Screening Rationale**

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

36 **12.2 Discharge**

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

39 **12.2.1 Surface Water Discharge under a NPDES Permit**

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

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

1 **I2.2.1.1 Description**

2 Almost any type of treated groundwater may be discharged to surface water under an NPDES permit.
3 This is common practice for municipal and industrial wastewaters, as well as groundwater at many
4 hazardous waste sites. The discharge standards are set based on the flows and water quality in the
5 receiving stream so that the discharge does not have any adverse impacts on the quality of the stream.
6 Routine monitoring is required to verify compliance. This monitoring often includes toxicity testing to
7 evaluate the presence of substance toxic to aquatic organisms. The physical location of the discharge
8 point can also be designed to minimize impacts to the stream (e.g., mid-stream diffusers can be used to
9 distribute the flow).

10 **I2.2.1.2 Relevant Policy**

11 Presidential Proclamation 7319 issued in June 2000 reserved 195,000 acres of land as the Hanford Reach
12 National Monument for the purpose of protecting ecological habitat and natural and cultural resources
13 along the 51-mile-long "Hanford Reach" stretch of the Columbia River (65 FR 37253). The proclamation
14 prohibits new development along the Hanford Reach, including the lower river corridor where an outfall
15 would need to be constructed to discharge treated groundwater to the river under an NPDES permit.

16 **I2.2.1.3 Evaluation and Screening Rationale**

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

23 **I2.3 In Situ Treatment**

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

26 **I2.3.1 In Situ Chemical Reduction**

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

28 **I2.3.1.1 Description**

29 Chemical reducing agents such as calcium polysulfide (CPS) or dithionite are injected into the
30 contaminated groundwater plume to transform Cr(VI) to less mobile and less toxic trivalent chrome),
31 thereby facilitating lower concentrations of chromium in groundwater. Alternative chemical reducing
32 agents include ferrous sulfate and zero valent iron.

33 **I2.3.1.2 Relevant Demonstration Projects**

34 A field treatability test was conducted at 100-K during the summer of 2005 to evaluate the effectiveness
35 of using CPS to reduce Cr(VI) in groundwater [*Treatability Test Report for Calcium Polysulfide in the*
36 *100-K Area* (DOE/RL-2006-17)]. The field test used a "five-spot" configuration, which involved four
37 injection wells drilled orthogonally around an existing monitoring well from which groundwater was
38 withdrawn and mixed with CPS. This solution then was injected in approximately equal amounts to set up
39 a circulation cell in the aquifer. The test was conducted for a period of 45 days. Cr(VI) was eliminated
40 from the treated aquifer, as demonstrated by the lack of this Cr(VI) concentrations in groundwater in the
41 injection wells and extraction well. Measurements of dissolved oxygen (DO) and oxidation/reduction
42 potential showed that the treated aquifer also was strongly reduced by the treatment. Analysis of

1 groundwater chemistry before, during, and after the test shows that manganese, iron, and arsenic were
2 mobilized under the strongly reducing conditions in the aquifer, but all of these remained far below
3 drinking water standards.

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

9 **12.3.1.3 Evaluation and Screening Rationale**

10 Transportation and handling of reducing agents also poses more of a health and safety concern during
11 application, as compared to biological reduction substrates. Because of more rapid chemical reactions, the
12 application of liquid reducing agents to treat large areas of a plume may be more challenging than using
13 biological substrates. Based on these implementability and potential effectiveness issues, in situ chemical
14 reduction was not retained in favor of in situ biological reduction.

15 **12.3.2 Hydrogen or Other Organic Gas Sparging**

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

18 **12.3.2.1 Description**

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

25 **12.3.2.2 Relevant Demonstration Projects**

26 A propane biosparging field demonstration was conducted at the National Environmental Technology
27 Test Site in Port Hueneme, California, from May 2001 to March 2002 (NAVFAC, 2003, Technical
28 Report TR-2230-ENV, *Cost and Performance Report, In-situ Remediation of MTBE Contaminated*
29 *Aquifers using Propane Biosparging*). The COPCs in groundwater included fuel constituents and methyl
30 tert butyl ether (MTBE) up to 6,300 µg/L and tert-butyl alcohol up to 470 µg/L. Unconsolidated
31 sediments at the site were comprised of sands, silts, clays, and small amounts of gravel and fill material.
32 The uppermost water-bearing unit was a shallow, semi-perched, unconfined aquifer (upper silty sand,
33 underlain by fine to coarse grain sand, and a basal clay layer). Depth to groundwater ranged from 1.8 to
34 2.4 m (6 to 8 ft) bgs, and the saturated aquifer thickness was 4.8 to 5.4 m (16 to 18 ft).

35 The field demonstration area (27 × 18 m [90 × 60 ft]) included a test plot consisting of seven propane
36 injection points, a control plot consisting of eight oxygen injection points and seven bacteria injection
37 points. The propane system operated for four 10-minute cycles per day and yielded approximately
38 0.226 kg/day (0.5 lb/day) of propane at the test plot. After several months of operation, the propane flow
39 was decreased from 0.03 m³/hr to between 0.0085 and 0.0113 m³/hr (1 standard ft³/hr to between 0.3 and
40 0.4 standard ft³/hr). The oxygen control system was operated for four 6-minute cycles per day, yielding
41 approximately 2.26 kg/day (5 lb/day) of oxygen in the test and control plots.

42 In the test plot, MTBE concentrations decreased by 62 to 88 percent in shallow wells and by 86 to
43 97 percent in deep wells. In the control plot, MTBE concentrations decreased by 86 to 97 percent in

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

6 ***12.3.2.3 Evaluation and Screening Rationale***

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

13 **12.3.3 Groundwater Circulation Wells**

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

16 ***12.3.3.1 Description***

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

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

26 The zone of influence that can be achieved with groundwater circulation wells are highly sensitive to site
27 lithologic conditions. A viable circulation cell may not develop if vertical anisotropy in lithology (that is,
28 the presence of laterally extensive silty-clay layers) impedes the circulation flow path or if there is not
29 enough anisotropy. Typically, this technology will not be successful when the ratio of horizontal to
30 vertical hydraulic conductivity is greater than 10 (Spargo et al., 1999). A single thin layer of
31 low-permeability material can also prevent development of a recirculation cell. If the anisotropy is too
32 low, the radius of the circulation cell will be very small; this could be the case at the Hanford Site. Other
33 common problems include well clogging resulting from changing redox conditions within the
34 groundwater circulating well (GCW) and down-well equipment (for example, packers) problems.

35 ***12.3.3.2 Relevant Demonstration Projects***

36 A summary and analysis of more than 50 GCW field demonstrations was provided in “Groundwater
37 Circulating Well Technology Assessment” (Spargo et al., 1999). One case study was a GCW
38 demonstration sponsored by the DoD that was originally scheduled to be performed at the Hanford Site,
39 but was relocated to Edwards Air Force Base OU 1, Site 19. This site was selected based on its high
40 hydraulic conductivity (KH = 10 ft/d, KV = 1 ft/d) and the presence of TCE contamination. One GCW
41 was installed to 15 m (50 ft) bgs and operated for 191 days during the demonstration. Results of the
42 demonstration indicate an ROI of approximately 9 m (30 ft), an asymmetrical circulation cell, and

1 groundwater flow short-circuiting near the GCW. Post-operation data showed contaminant rebound in
2 monitoring wells.

3 Of the remaining GCW case studies, few sites demonstrated clear success, and at just as many sites, the
4 technology failed to meet remedial objectives. However, most of the case studies indicated that the data
5 collected were insufficient to demonstrate the efficacy of the GCW technology.

6 ***12.3.3.3 Evaluation and Screening Rationale***

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

13 **12.3.4 Horizontal Wells**

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

16 ***12.3.4.1 Description***

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

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

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

31 ***12.3.4.2 Relevant Demonstration Projects***

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

38 Installation of surface casing was required to facilitate circulation of drilling mud in the porous Hanford
39 formation. The casing was advanced with significant difficulty to approximately 6 m (20 ft) bgs (25 m
40 (85 horizontal linear ft) when downward progress ceased because of inadequate force on the downhole
41 hammer and difficulty removing cuttings from the inclined casing. Rotary-mud directional drilling

1 through the casing and into the Hanford formation was attempted but progress was slow and circulation was
2 never established.

3 ***12.3.4.3 Evaluation and Screening Rationale***

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

6 **12.4 Containment**

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

9 **12.4.1 Containment Wall**

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

12 ***12.4.1.1 Description***

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

20 ***12.4.1.2 Relevant Demonstration Projects***

21 In 1994, the Washington State Department of Ecology (Ecology) and EPA issued an action memorandum
22 to DOE to immediately initiate groundwater remedial actions at 100-N, to include the design,
23 construction, and operation of a pump-and-treat system and the construction of a sheetpile barrier wall at
24 N-Springs. However, 6 months later, Ecology and EPA concurred with DOE that installation of the
25 sheetpile wall could not be achieved in the manner specified, based on results of a construction test in late
26 1994. The two agencies subsequently directed DOE to proceed with the pump-and-treat system (only)
27 (DOE/RL-2004-01, *Annual Summary Report Calendar Year 2000 for the 100-HR-3, 100-KR-4, and*
28 *100-NR-2 Operable Units and Pump-and-Treat Operations*). A grouted-hinge sheetpile barrier in the
29 aquifer near the river's edge had been specified, but attempts to install a sheetpile barrier were
30 unsuccessful (WHC-EP-0878, "Coordination of Groundwater Activities in the 100 N Area").

31 ***12.4.1.3 Evaluation and Screening Rationale***

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

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

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

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

9 Implementability is low, as evidenced by failed attempts to install a sheetpile wall at N-Springs. Capital
10 costs would be high and O&M costs would be low or moderate. As a consequence of installation
11 challenges and high costs, containing walls were not retained for further evaluation.

12 **12.4.2 Reactive Biological Barrier**

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

15 **12.4.2.1 Description**

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

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

33 **12.4.2.2 Relevant Demonstration Projects**

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

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

1 reductive bioimmobilization under different redox conditions at this and other contaminated sites was
2 currently under study as of the publication date.

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

12 Molasses and lactate were injected at a Cr(VI)-contaminated site near Flanders, Belgium, in 2005 to 2006
13 (Vanbroekhoven et al., 2007). Frequent re-injections were important to maintain reduced conditions.
14 Results of this pilot test showed efficient Cr(VI) removal from the groundwater for the lactate injection
15 zone within 200 days, while for the molasses zone-efficient removal was observed only after
16 approximately 400 days. Based on the success of this pilot test, a full-scale process was planned.

17 A recent study evaluated a biological barrier comprised of sand and sawdust that had been treating nitrate
18 for 15 years (Robertson et al., 2008). Sediment cores were retrieved and reaction rates were measured in
19 column tests and compared to rates measured in year 1 using the same reactive mixture. The rates after
20 15 years were within about 50 percent of the year-1 rates. Near the end of the year-15 column test, wood
21 particles were removed from the reactive media, and nitrate removal subsequently declined by about
22 80 percent, indicating that the wood particles were principally responsible for denitrification. The authors
23 concluded from this work that some denitrifying biological barriers can remain maintenance free and be
24 adequately reactive for decades.

25 ***12.4.2.3 Evaluation and Screening Rationale***

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

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

37 **12.4.3 Hydraulic Containment via Injection**

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

40 ***12.4.3.1 Description***

41 Hydraulic containment via injection involves injecting water into a line of closely spaced injection wells
42 or a trench installed close to and parallel to the river. A groundwater mound would be created under the
43 injection points, which would result in an inward gradient and stop the migration of groundwater to the

1 river. This injection would mimic the natural conditions encountered during periods of high river stage.
2 Some extraction of groundwater upgradient of the barrier, with discharge into wells side gradient, would
3 be required to maintain the water balance. Source of water for injection could be from existing permitted
4 Columbia River supply and/or groundwater.

5 ***12.4.3.2 Relevant Demonstration Projects***

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

18 ***12.4.3.3 Evaluation and Screening Rationale***

19 The primary disadvantage of hydraulic containment via injection is that the injection locations will need
20 to be a considerable distance from the river because of logistics issues. As a consequence, the Cr(VI) that
21 is currently downgradient of the injection points would be flushed into the river without control. This
22 flushing should only be temporary, but is likely to be considered dilution by the regulators and, therefore,
23 not allowed. Based on extensive experience with saltwater intrusion barriers, operational complexity
24 associated injection well clogging rehabilitation likely would be encountered. In addition, the current
25 remedies at both 100-K and 100-HR-3 include hydraulic containment using extraction wells. As a result,
26 additional technologies to create barriers to contaminant migration are not needed. For these reasons,
27 hydraulic containment via injection was not retained for further evaluation.
28

29 **13 Bioremediation as a Potential Remedial Action for Cr(VI) in the Groundwater and** 30 **Vadose Zone of the Hanford 100 Area**

31 **13.1 Introduction**

32 Bioremediation has been used successfully to treat groundwater contaminated with a range of inorganic
33 and organic contaminants at a large number of sites throughout the country (e.g., SERDP, 2009; ESTCP,
34 2008). One of the primary advantages of this technology is that it appears that it can be cost-effectively
35 applied to a variety of in situ settings ranging from focused remediation of specific, small-scale target
36 areas to applications that consist of large-scale, plume-wide remediation efforts.

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

1 applicable to the evaluation and implementation of in situ bioremediation of Cr (VI) are summarized in
2 Chapter I5 of this Appendix.

3 **I3.2 Scientific Basis of Bioremediation**

4 The aqueous speciation, and mobility of chromium in groundwater are governed by the chemical
5 (e.g., redox) and physical characteristics of the aquifer system and the composition and abundance of the
6 microbial assemblage that is present. Chromium is stable in solution as the highly mobile anionic Cr(VI)
7 species in oxygen-rich aquifers with a near-neutral pH (like the unconfined aquifer at Hanford) that
8 contain low quantities of natural organic material (NOM). Conversely, Cr(VI) can be reduced to the
9 highly insoluble trivalent form (Cr(III)) if the aquifer conditions are sufficiently reducing to convert
10 Cr(VI) to Cr(III).

11 The imposition of reducing conditions on an oxidizing aquifer by the addition of a carbon source
12 (substrate) that is easily metabolized by the native microbial assemblage forms the foundation of
13 engineered bioremediation applications for Cr(VI) and many other contaminants.
14

15 **14 Overview of Cr(VI) Bioremediation Processes**

16 In situ bioremediation for Cr(VI) in oxygenated groundwater (or vadose zone pore water) typically
17 employs the injection or infiltration of organic carbon compounds (substrates) to stimulate microbial
18 activity and lower the redox state within the subsurface. Once a sufficient amount of substrate is added,
19 the native population of microbes in the subsurface will increase rapidly until the population reaches
20 equilibrium with the increased food supply. If sufficient substrate is supplied, the increased metabolic
21 oxygen demand of the expanded microbial population will exceed the rate that oxygen is being supplied
22 to the system and oxygen levels in the groundwater will approach zero. Once oxygen in the targeted
23 aquifer zone is depleted, microbes able to use other constituents (e.g., nitrate, ferric iron, and sulfate) as
24 electron acceptors for their metabolic reactions will further lower the redox state of the aquifer.
25 Consequently, in situ bioremediation is an effective method for imposing reducing conditions on a
26 targeted zone of an oxidizing, aquifer in order to convert soluble and mobile Cr(VI) to Cr(III). Once
27 Cr(III) is formed, it typically precipitates as low solubility hydroxide phases (e.g., Cr(OH)₃; Eary and
28 Rai, 1987).

29 Numerous aerobic and anaerobic microbes are known to enzymatically catalyze the reduction of Cr(VI) to
30 Cr(III) (either for detoxification or possibly for metabolic purposes (Sharma, 2002; Faybishenko et al.,
31 2008). However, the direct reduction of Cr(VI) to Cr(III) by microbial enzymatic processes is believed to
32 be a slower process than the reduction of Cr(VI) by sulfide and ferrous iron (Wielinga et. al., 2001).
33 These Cr(VI) reducing compounds may be produced rapidly and in great abundance by sulfate and iron
34 reducing bacteria that are common in many aquifers where the organic carbon supply is high enough for
35 the available oxygen to have been depleted. Compared to the ability of ferrous iron or sulfide to reduce
36 Cr(VI) to Cr(III), methane is a poor reductant for Cr(VI) and high levels of methane indicate an
37 inefficient use of substrate during bioremediation activities.

38 **I4.1 Longevity of Treatment and the Potential for Re-oxidation of Cr(III) Phases**

39 If iron- and sulfate-reducing conditions are sustained long enough during active bioremediation activities,
40 substantial amounts of ferrous iron and sulfide-rich phases may be produced as secondary phases within
41 the aquifer matrix. If produced in sufficient abundance, these strongly reducing minerals or phases will
42 maintain reducing conditions in the treatment zone for a substantial period of time after substrate addition

1 has ceased (e.g., 1 to 2 years). This residual reducing capacity will provide an additional treatment
2 capacity that will continue to remediate Cr(VI) from lower permeability layers that may migrate into the
3 higher permeability treated zone after active treatment is completed. This residual treatment capacity will
4 gradually wane as the reduced iron and sulfide phases are progressively re-oxidized by the influx of
5 upgradient-oxygenated groundwater into the treatment zone. The longevity and effectiveness of the
6 residual treatment effect (e.g., ranging from a few months up to a year or more) will, in part, be a function
7 of the groundwater flow rate, and the distribution and total mass of the reduced phases that were produced
8 within the target area during bioremediation. After any future full-scale implementation of this
9 technology, periodic re-application of substrate into the treatment zone could be used to regenerate and
10 extend the longevity of the reductive capacity stored in the aquifer matrix.

11 Despite the demonstrated effectiveness of Cr(VI) bioremediation, concerns are sometimes raised about
12 the stability and permanence of Cr(III) compounds after bioremediation activities are completed and
13 oxidizing conditions are gradually re-established in the aquifer. In general, Cr(III) is highly resistant to
14 re-oxidation under environmental conditions, and DO and manganese oxides are the only commonly
15 occurring inorganic oxidants that could conceivably oxidize Cr(III) to Cr(VI) in most waste materials and
16 soils (Eary and Rai, 1987). The remainder of this section summarizes the information obtained concerning
17 the potential re-oxidation of Cr(III) compounds by DO or manganese (IV) oxides after bioremediation is
18 completed in 100-D.

19 **14.1.1 Dissolved Oxygen**

20 The stability of Cr(III) compounds under oxygenated groundwater conditions is fundamental to the
21 successful long-term remediation of Cr(VI) using in situ bioremediation. Based on thermodynamic
22 considerations alone, Cr(III) compounds are predicted to be unstable under oxygenated groundwater
23 conditions; however, as a result of kinetic and other barriers to this reaction, the oxidation of Cr(III)
24 compounds by DO is essentially non-existent under environmental conditions (Rai et al., 1989; Eary and
25 Rai, 1987). Consequently, Cr(III) compounds precipitated during bioremediation will not be reoxidized to
26 Cr(VI) by DO, even after fully oxygenated conditions are re-established in the aquifer.

27 **14.1.2 Manganese (IV) Oxides**

28 Reductive dissolution of natural Mn(IV) oxides and the subsequent re-precipitation of the dissolved
29 manganese as more poorly structured and reactive Mn(IV) oxides is a common process in aquifers
30 undergoing bioremediation. Reactive Mn(IV) oxides (e.g., birnessite and pyrolusite) have been
31 demonstrated to oxidize aqueous species of Cr(III) in laboratory tests and in some relatively unusual
32 natural environments (e.g., Tokunaga et al., 2007; James and Bartlett, 1983; Eary and Rai, 1987; and
33 Kim et al., 2002). At least one of these field studies indicated that oxidation of solid phase Cr(III) by
34 manganese oxides can occur at rates high enough to exceed the groundwater standard for total chromium.
35 These findings, however, were limited to field settings with extremely chromium- and manganese-oxide
36 rich sediments (e.g., 60,000 mg/kg Cr(III), as the ultramafic-mineral chromite). The geochemical
37 conditions and mineralogy of these sites are significantly different than those of the Hanford Site and the
38 evidence of Cr(III) oxidation by Mn(IV) under such extreme conditions is not relevant to the proposed
39 test area.

40 Laboratory testing has demonstrated the rate of Cr(III) oxidation by Mn(IV) compounds is much lower if
41 the Cr(III) is present as a solid phase. Laboratory testing of mixed chromite and manganese oxide
42 suspensions over a range of pH values (Oze et al., 2007) confirmed that chromite was subject to oxidative
43 dissolution in the presence of high-concentration manganese oxides. However, the rates of chromite

1 oxidative dissolution by manganese oxides decreased steadily as the solution pH was increased from 3 to
2 5 to approximately 6.8. Oxidative dissolution had essentially ceased near a pH of 8 (approximately the pH
3 of Hanford Site groundwater). Even under the extreme conditions of this laboratory study, the fastest
4 oxidation rates observed for solid phase Cr(III) were much slower than the rates typically observed for
5 dissolved Cr(III) species (Oze et al., 2007). Although the oxidation of Cr(III) in ultramafic minerals does
6 occur at noteworthy rates under the very unusual geologic settings described above, there is substantial
7 evidence that re-oxidation of solid phase Cr(III) by Mn(IV) oxides is not realistic under the groundwater
8 and aquifer matrix conditions during and after in situ bioremediation. The factors and processes gleaned
9 from relevant publications that are expected to prevent or greatly minimize post-treatment re-oxidation of
10 Cr(III) by Mn(IV) oxides include the following:

- 11 • Mn(IV) oxides are most effective as an oxidizer when dissolved Cr(III) is sorbed directly onto the
12 reactive manganese oxide surface. At neutral or slightly basic pH conditions that will eventually be
13 re-established after bioremediation, the concentrations of dissolved Cr(III) available for re-oxidation
14 will be minimized by the extremely low solubility of the Cr(III) and mixed Fe(II), and Cr(III) phases
15 that will be formed in groundwater during bioremediation (Oze et al., 2007, Tokunaga et al., 2007).
- 16 • In those relatively rare cases where a Cr(III) phase may be in direct contact with a freshly precipitated
17 manganese oxide surface, the extent of oxidation-reduction reaction between the two phases will
18 eventually be minimized by the development of a less-reactive, mixed-valence layer between the
19 two phases.
- 20 • The catalytic and oxidative capacity of freshly precipitated manganese oxides generally decreases
21 over time as the reactive surfaces are neutralized by the sorption of other metal ions or coated by
22 natural organic matter (NOM) or other common solid phases (e.g., iron hydroxides/oxides).
- 23 • Recent studies (e.g., Wu and Deng, 2006) indicate that the oxidation of Cr(III) by Mn(IV) oxide is
24 countered by the presence of reductive agents such as Fe(II) and sulfide compounds also present in
25 the aquifer. These reducing compounds will be abundant in the targeted section of the aquifer and
26 should inhibit or reverse any potential re-oxidation of Cr(III) within the treated area.

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

29 **14.2 Fate and Transport of Some Potential Chemical Byproducts of Bioremediation**

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

32 **14.2.1 Iron and Manganese, and Arsenic**

33 Ferric (Fe III) hydroxides and manganese (Mn IV) oxide phases in the matrix of bioremediated aquifers
34 commonly undergo reductive dissolution and the iron and manganese are mobilized as Fe(II) and Mn(II)
35 aqueous species at concentrations substantially higher than background levels. Although some microbes
36 are capable of using manganese oxides as an electron acceptor with the consequent production of Mn(II),
37 the main mechanism expected to drive the reduction of manganese oxides is reaction with dissolved
38 Fe(II) and sulfide produced during the microbially mediated reduction of Fe(III) compounds and
39 dissolved sulfate (Morse et al., 1987; Streckopytov and Larsen, 2001; Poulton et al., 2004; Li et al., 2006).

40 Local variations in the concentration of dissolved iron and manganese would be expected, since the
41 processes controlling reductive dissolution are highly dependent on local mineralogy, and the pH and

1 alkalinity of the system. Transport of dissolved Fe(II) and Mn(II) for a substantial distance out of the
2 treatment area is unlikely since they would be subject to rapid re-oxidation, re-precipitation, or sorption,
3 once transported away from the highly reducing conditions within the target zone. Any Fe(II) and Mn(II)
4 remaining in solution within the target area after bioremediation activities are terminated, will either be
5 transported downgradient of the target area, oxidized, and precipitated as oxidized insoluble phases, or
6 precipitated in place as reducing or mixed valent phases (e.g., FeS and Green Rust), or eventually as
7 oxide and hydroxide phases after bioremediation activities are complete and more oxidizing conditions
8 are gradually re-established.

9 As with iron and manganese, the fate and transport characteristics of arsenic are dominated by the redox
10 and pH characteristics of the aquifer. Arsenic (As) can exist in four oxidation states (-3, 0, +3, +5) but is
11 typically present in oxidizing groundwater with a pH between 6 and 8 as one of two anionic As (V) or
12 "arsenate" species. At a pH less than 7.0, H_2AsO_4^- predominates while at a pH greater than 7.0, the
13 HAsO_4^{2-} complex is dominant (Scott, 1991). As (V) species have a relatively high sorption affinity for
14 iron oxides/hydroxides under near neutral pH conditions. Naturally occurring iron hydroxides oxides in
15 aquifer materials commonly contain substantial amount of arsenic that have been accumulated (sorbed)
16 over time from the ambient pore water or groundwater. Under anoxic groundwater conditions (at the same
17 pH range as above), arsenic is stable in the trivalent state and predominantly exists as the more mobile
18 neutral arsenite species (H_3AsO_3) (Scott, 1991). Previous 100 Area investigations (e.g., PNNL-18784)
19 demonstrate that arsenic is present in the matrix of the 100 Area unconfined aquifer. Consequently,
20 reductive dissolution of the iron hydroxide/oxide phases during in situ bioremediation, may lead to the
21 solubilization of elevated levels of arsenic as the relatively mobile neutral trivalent species (H_3AsO_3).

22 Under moderately acidic (e.g., pH 5.5) sulfate reducing conditions, As(III) may sorb to or co-precipitate
23 with metal sulfide phases (e.g., iron sulfides). Generally, however, under the higher pH and mildly
24 alkaline conditions and conditions that should predominate during bioremediation of Cr(VI) in the
25 100 Area, the neutral and relatively mobile As(III) specie H_3AsO_3 will likely predominate in solution.

26 The relatively high mobility of Arsenic III species solubilized during bioremediation should be largely
27 limited to the aquifer zone where Fe(II) and Mn(II) are stable in solution. Manganese oxides play a major
28 role in accelerating the oxidation of As(III) to As(V) in aqueous solutions and Fe(III) hydroxides have a
29 high affinity for As(V) (Scott, 1991). Consequently, if As(III) migrates out of the strongly reducing
30 bioremediation zone, it will also be subject to oxidation and sorption by previously existing or freshly
31 re-precipitated manganese oxides and iron hydroxides in the aquifer.

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

37 **14.2.1.1 Barium**

38 Although barium is strongly sorbed by clays, manganese oxides, and ferric hydroxides; the very low
39 barium concentrations in aquifers containing sulfate commonly reflects the precipitation of the extremely
40 insoluble sulfate mineral barite (BaSO_4). Barite is commonly the solubility-limiting phase even in
41 aquifers containing dissolved sulfate concentrations that are substantially lower than those typical of the
42 100 Area unconfined aquifer (e.g., 50 to 100 mg/L). Nevertheless, it is possible that the development of
43 locally intense reducing conditions within a targeted area of the unconfined aquifer during bioremediation
44 could lead to the near total conversion of groundwater sulfate to sulfide in that area. The reductive
45 dissolution of iron hydroxides, manganese oxides, and high levels of sulfate reduction, would likely result

1 in the increased solubility of barium. Although this process can result in an increase in the barium
2 concentrations of the highly reducing section of the aquifer, this effect would be transient and any
3 elevated barium concentrations that develop should rapidly decrease back to near background levels (due
4 to Ba sorption and re-precipitation of Barite) once the groundwater migrates out of the intensely reducing
5 zone and mixes with groundwater that retains background levels of sulfate.

6 **14.2.1.2 Volatile Fatty Acids and Methane**

7 If the substrate supply to a system exceeds the availability of electron acceptors such as oxygen, nitrate,
8 sulfate, and Fe(III), microbial fermentation of the substrate may become the dominant metabolic process,
9 resulting in the development of very low groundwater redox conditions. Fermentation is a balanced
10 reduction-oxidation reaction where the same organic molecule (e.g., the substrate) serves as both an
11 electron acceptor and donor. These microbially mediated energy-producing reactions result in the
12 conversion of the original substrate (e.g., lactate) into simpler organic compound (e.g., methane and
13 volatile fatty acids [VFA] such as propionate). Compared to the relatively rapid rates of Cr(VI) reduction
14 obtained by direct and indirect Cr(VI) reduction processes that are driven by iron and sulfate reducing
15 bacteria, fermentation reactions are less efficient processes for reducing Cr(VI). Therefore, high
16 concentrations of methane and VFA in groundwater during bioremediation can be indicative of excessive
17 (wasteful) substrate use. The fate and transport of these organic byproducts can be managed by limiting
18 the amount of substrate to the minimum amount needed to obtain the necessary rate and extent of Cr(VI)
19 remediation. Elevated levels of methane and VFA in the groundwater downgradient of the target area
20 should be rapidly reduced by a combination of aerobic and anaerobic microbial degradation.
21

22 **15 Evaluation of Potential Substrates for In Situ Bioremediation in the 100 Area**

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

28 Parsons Corp (2004) and Air Force Center for Engineering and the Environment (AFCEE) (2010),
29 evaluated many of the organic substrates that can be used to support bioremediation of groundwater such
30 as low-molecular-weight fatty acids (e.g., lactate, butyrate, and acetate), alcohols (e.g., methanol and
31 ethanol) cheese whey (lactose), sugar syrups (e.g., molasses or corn syrup), vegetable oils, a commercial
32 product marketed as HRC, and solid substrates such as mulch and compost. Of these, lactate, molasses,
33 HRC, and vegetable oils are most commonly added for enhanced anaerobic bioremediation. Effective
34 substrates that are used less frequently include ethanol, methanol, butyrate, high-fructose corn syrup, and
35 cheese whey.

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

- 1 • **Miscible Liquids.** Miscible substrates applied as a dissolved or “aqueous-phase” solutions offer the
 2 greatest potential for uniform distribution throughout the aquifer matrix relative to substrates applied
 3 as a viscous fluid or solid phase. Molasses and lactate are the most common substrates applied in an
 4 aqueous phase. Miscible substrates travel with advective groundwater flow and are typically applied
 5 in a continuous or periodic (pulsed) mode to maintain a specified reactive treatment zone.
- 6 • **Viscous Fluids.** Slow-release, viscous fluid substrates include HRC and neat vegetable oils. These
 7 substrates are intended to be long-lasting, where a single or limited number of injections are sufficient
 8 for site remediation. They are intended to be relatively immobile in the subsurface and rely on
 9 advection and dispersion of soluble compounds (e.g., lactic acid for HRC or metabolic acids
 10 generated by degradation of vegetable oil) for effective delivery throughout the aquifer matrix.
- 11 • **Low Viscosity Emulsions.** Vegetable oil emulsions have been developed in an effort to improve the
 12 distribution of substrate in the subsurface while still providing a long-lasting source of organic
 13 carbon. Micro-emulsions consisting of 5 to 10 percent vegetable oil in water by volume are relatively
 14 low-viscosity mixtures (e.g., nondairy creamers like Coffee Mate^{®1}) compared to the viscous fluids
 15 described above. The use of micro-emulsions is the result of lessons learned in early vegetable oil
 16 field trials in which high-injection backpressures, ROI, and reductions in hydraulic conductivity were
 17 observed using coarse viscous emulsions or neat vegetable oil.
- 18 • **Solid Substrates.** Solid phase substrates include mulch and compost. Mulch is generally obtained
 19 from shredding and chipping of tree and shrub trimmings, and is primarily composed of cellulose and
 20 lignin. Often “green” plant material or compost is incorporated to provide a source of nitrogen for
 21 microbial growth and as a source of more readily degraded organic carbon. Degradation of the
 22 substrate by microbial processes in the subsurface provides a number of breakdown products,
 23 including metabolic and humic acids, which act as secondary fermentable substrates. Solid substrates
 24 are typically placed in trenches or in excavations as backfill in a one-time event using conventional
 25 construction techniques.

Table I-1. Substrates Used for Enhanced Anaerobic Bioremediation

Substrate	Typical Delivery Techniques	Form of Application	Frequency of Injection
Soluble Substrates			
Lactate and Butyrate	Injection wells or circulation systems	Acids or salts diluted in water	Continuously or monthly
Methanol and Ethanol	Injection wells or circulation systems	Diluted in water	Continuously or monthly
Sodium Benzoate	Injection wells or circulation systems	Dissolved in water	Continuously or monthly
Molasses, High Fructose Corn Syrup	Injection wells	Dissolved in water	Continuously or monthly
Whey	Injection wells, direct injection, or circulation systems	Dissolved in water or slurry	Continuously, monthly, or annually

¹ 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
Viscous Fluid Substrates			
HRC [®] Products	Direct injection or borehole backfill	Straight injection	Every 1 to 3 years, potential one-time application
Vegetable Oils	Direct injection or injection wells	Straight oil injection with water push, or high oil: water content (>20% oil) emulsions	One-time application
Low-Viscosity Fluid Substrates			
Vegetable Oil Emulsions	Direct injection or injection wells	Low oil content (<10%) micro-emulsions suspended in water	Every 2 to 3 years, potential one-time application
Solid Substrates			
Mulch and Compost	Trenching or excavation	Trenching, excavation, or surface amendments	One-time application

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

® HRC = Hydrogen Release Compound

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 site
4 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 (e.g., DO, nitrate, or sulfate), aquifer
6 matrix characteristics (e.g., lithology, stratification, or fracture flow versus porous flow), aquifer
7 hydrology (e.g., transmissivity or flow velocity), nature and extent of the plume (e.g., small concentrated
8 or large diffuse plumes). In addition, the following criteria should be included as part of any evaluation
9 conducted to select the preferred substrate(s) for implementation during bioremediation of the Cr(VI)
10 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 similar aquifer
13 conditions similar to the 100 Area unconfined aquifer? Include an evaluation of previous
14 bioremediation 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?

- 1 • **Treatment Efficacy and Longevity.** How effective is the substrate in reducing Cr(VI)? How long
2 will the substrate last in the aquifer? How many electrons per unit of substrate are available to support
3 reduction of Cr(VI)?
- 4 • **Cost.** In some cases, very large volumes of substrate may be required to support in situ
5 bioremediation. What is the approximate “cost per electron donated” for the substrate? In some cases,
6 this may be a difficult metric to quantify, and other relative measures of cost may be required.
- 7 • **Delivery, Mixing, and Implementation.** What are the factors influencing the preparation and use of
8 the substrate at the test location? What factors will drive full-scale implementation?
- 9 • **Intellectual Property Encumbrances.** The rapid growth in the use of in situ bioremediation has lead
10 to the development of a vibrant market with a number of proprietary blends. The substrate selected
11 should not be encumbered with intellectual property constraints that prevent or hinder its use.
- 12 • **Worker and Environmental Safety.** Some substrates have physical or chemical characteristics that
13 prevent their use in large quantities, or are complicated by permitting constraints.

14 **15.1 Substrate Selection for In Situ Bioremediation of the 100 Area Unconfined** 15 **Aquifer**

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

20 **15.1.1 Initial Screening**

21 Because of the generally transmissive nature of the unconfined aquifer (and the vadose zone) in the
22 100 Area, the high mobility of Cr(VI), the large sizes of the plumes, and the relative proximity of the
23 ecologically sensitive Columbia River, highly soluble, relatively mobile, and fast degrading substrates are
24 preferred over longer-lasting but relatively immobile substrates Table I-2). This screening criterion
25 eliminated emulsified vegetable oil, and Chitin from further consideration for use as substrates for Cr(VI
26 remediation in the 100 Area. However, these relatively immobile substrates could be used to supplement
27 the more soluble substrates to provide longer lasting reducing conditions directly around an injection
28 well. This reducing area around the injection well will then continue to treat the re-injected water that will
29 contain some Cr(VI).

30 **15.1.2 Secondary Screening**

31 The remaining candidates presented in Table I-2 (methanol, ethanol, acetate sodium lactate, molasses, and
32 whey) are all highly mobile and rapidly metabolized by microbes in groundwater systems such as the
33 unconfined aquifer. Methanol and ethanol are flammable and were screened out based on health and
34 safety issues. Acetate was screened out because it is weakly acidic and represents a potential handling
35 risk. In addition, acetate has may reduce the pH of groundwater in the targeted area to below the optimum
36 range for microbial growth. Even moderately more acidic condition in the target area could increase the
37 solubility of some metals sorbed onto the aquifer matrix. Molasses has been used frequently for the
38 bioremediation of Cr(VI) and other contaminants but is known to have a tendency to promote biofouling.
39 For this reason, molasses was eliminated from consideration.

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

Substrate	Handling and Safety	Treatment Efficacy	Materials Properties	Longevity	Byproduct Production	Delivery and Mixing Consideration	Full-Scale Infrastructure Requirements	Lifecycle Costs	Permitting	Comments
Methanol	Flammable product; requires special handling.	Effective, half-life of Cr(VI) is days.	Miscible, low viscosity and density are desirable for in situ mixing.	Several months	Microbial degradation produces CO ₂ . Methane and hydrogen sulfide can be produced.	Among the best reductants for delivery and mixing.	Flammable storage required, otherwise injection requires mixer and pump.	Low due to 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 donor for recirculation systems. Issues with transportation and handling of a flammable liquid.
Ethanol	Flammable product; requires special handling.	Effective, half-life of Cr(VI) is days.	Miscible, low viscosity and density are desirable for in situ mixing.	Several months	Microbial degradation produces CO ₂ . Methane and hydrogen sulfide can be produced.	Among the best reductants for delivery and mixing.	Flammable storage required; otherwise, injection requires mixer and pump.	Low due to cost of ethanol and infrastructure needed to implement approach.	Food Grade	Completely miscible in water making it one of the most suitable reductants for recirculation systems. Issues with transportation and handling of a flammable liquid.
Acetate	Weak acid; requires some special handling.	Effective, half-life of Cr(VI) is days.	Miscible, low viscosity and density are desirable for in situ mixing, low pH is a concern at some sites.	Several months	Microbial degradation produces CO ₂ . Methane and hydrogen sulfide can be produced.	Among the best reductants for delivery and mixing.	Injection requires mixer, pump, and piping.	Low due to cost of acetate and infrastructure needed to implement.	Food Grade	Very soluble reductant, making it a good reductant for recirculation systems. Issues with transportation and handling related to properties.
Lactate	No known safety or handling issues.	Effective, half-life of Cr(VI) is days.	Very soluble, low viscosity are desirable for in situ mixing, slightly denser than water.	Several months	Microbial degradation produces CO ₂ . Methane and hydrogen sulfide can be produced.	Good reductant for delivery and mixing.	Injection requires mixer, pump and piping.	Low due to cost of lactate and infrastructure needed to implement in field.	Food or Pharmaceutical I Grade	One of the most commonly used soluble reductants, density greater than water; therefore, must be injected in dilute concentrations.
Molasses	No known safety or handling issues.	Effective, half-life of Cr(VI) is days.	Good solubility, very high viscosity making it difficult to inject and mix in aquifer.	Several months	Microbial degradation produces CO ₂ . Methane and hydrogen sulfide can be produced since sulfate compounds are present in molasses.	Can be a challenge to deliver and mix in aquifer due to relatively high viscosity.	Injection requires mixer, pump and piping.	Low due to cost of molasses and infrastructure needed to implement. Patent licensing fee required.	Food Grade	Broad spectrum reductant containing simple and complex sugars. Viscosity is a problem along with the potential to biofoul injection wells and well packs. Potential intellectual property encumbrances. Tested at the Hanford Site.
Emulsified Vegetable Oil	No known safety or handling issues.	Effective, half-life of Cr(VI) is several days.	Emulsion is like a soluble product, good viscosity and pH.	Several months to years	Microbial degradation produces CO ₂ . Methane and hydrogen sulfide can be produced.	Similar to lactate.	Injection requires mixer, pump and piping.	Low to Moderate due to cost of oil and number of wells need to implement approach.	Food Grade	Complex unsaturated alkanes that degrade to release electrons for chromium reduction over a very long period. Tested at the Hanford Site.
Metals Remediation Compound (by REGENESIS, makers of HRC®)	No known safety or handling issues.	Effective, half-life of Cr(VI) is days.	Very high viscosity, slightly soluble sulfur and polylactate compound.	Several months to years	Microbial degradation produces CO ₂ . Methane and hydrogen sulfide can be produced.	High viscosity makes this a challenge to inject and mix. Usually requires heating and special delivery infrastructure.	Vendor conducts injection.	Low to Moderate due to cost of MRC and number of wells needed to implement approach.	Lactate ester and sulfide compound	Proprietary slow release polylactate ester and sulfide compound. Viscosity like that of molasses in cold temperature. Potential intellectual property encumbrances. A similar HRC® product has been tested at the Hanford Site . Potential intellectual property encumbrances.

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
Whey	No known safety issues; whey solutions must be refrigerated.	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 ₂ . Methane and hydrogen sulfide can be produced.	Good reductant for delivery and mixing.	Injection requires mixer, pump and piping.	Low due to cost of whey and infrastructure needed to implement in field.	Food Grade	Reductant containing lactose and complex sugars. Cheese whey is longer-lived, with a low degradation rate. Must be injected in dilute concentrations.
Chitin	No known safety or handling issues.	Effective, half life of Cr(VI) is days.	Solid 3 mm flakes. High viscosity mix with guar gum. Very low density.	Several months to years	Microbial degradation produces CO ₂ . Methane and hydrogen sulfide can be produced.	Can be a challenge to deliver and mix in aquifer. Fracturing has been used to increase mixing.	Injection requires mixer, pump and piping.	Low to Moderate due to 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.

® HRC = Hydrogen Release Compound

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

5 **15.1.3 Final Screening**

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

12 Whey is a milk by-product of cheese making that consists primarily of water and about 4 to 5 percent
13 lactose, (a disaccharide with 12 carbon atoms per molecule) and minor amounts of protein, fat, and ash. If
14 used in the original liquid form, whey must be kept refrigerated prior to use. Liquid whey is easily diluted
15 with water and can be readily injected into aquifers. Whey can also be obtained in a dried powder form
16 (commonly in 50 lb [23 kg] bags) that consist of approximately 70 to 75 percent lactose, 10 to 13 percent
17 protein, and 7 to 13 percent ash (Mora et. al., 2008). Whey powder is readily soluble and can be mixed
18 with water onsite to the preferred concentration, immediately prior to use.

19 Because of the greater complexity of the organic constituents in whey, it has a longer biodegradation
20 half-life than lactate. The somewhat slower biodegradation rate of whey should allow for the remediation
21 of larger areas within Cr(VI) plumes than will lactate under similar operating conditions. While whey has
22 not been used as a bioremediation substrate nearly as frequently as lactate, it has been used at a few
23 Cr(VI) sites, such as the Pacific Gas and Electric Hinkley Compressor Station (Cal/EPA, 2010), and for
24 the in situ remediation (reductive dechlorination)of chlorinated solvents such as TCE (Mora et. al., 2008).
25 Disadvantages of both dried and liquid whey, relative to lactate, include: (1) long-term or large-scale in
26 situ treatment will require onsite refrigerated storage of liquid whey or frequent handling of large
27 quantities of dried whey, and (2) the relatively high concentration of the disaccharide lactose in whey may
28 result in high acid production rates during fermentation reactions, potentially lowering the pH within the
29 target area (Mora, 2008). As long as excessively high concentrations of whey are not injected or
30 infiltrated into the aquifer, however, the moderately elevated alkalinity (e.g., 100 to 120 mg/L as CaCO₃)
31 that typifies most areas of the unconfined aquifer in the 100 Area, should be sufficient to largely offset the
32 reduction of pH as the result of elevated levels of organic acids generated during the in situ fermentation
33 of whey.

34 Although whey would likely perform well as a bioremediation substrate in the unconfined aquifer of the
35 100 Area, lactate is more readily available, easier to store and transport, and has fewer potential unwanted
36 side effects. Consequently, lactate is generally preferred as the substrate of choice for in situ
37 bioremediation of Cr(VI) in the unconfined aquifer.
38

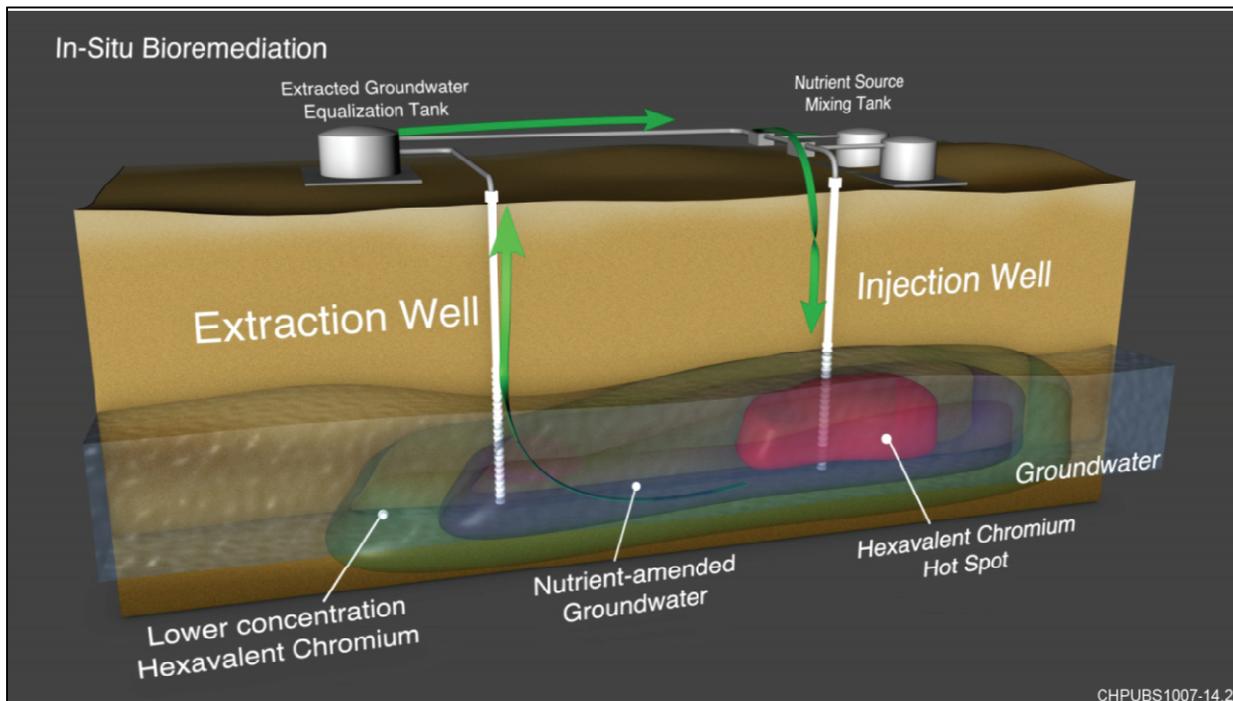
39 **16 In Situ Groundwater Remediation by Bio-Injection**

40 **16.1 Conceptual Design**

41 The general aquifer characteristics of the 100 Area unconfined aquifer, including high transmissivity and
42 moderately alkalinity, are consistent with the deployment of bioremediation as a remedial action for
43 Cr(VI) groundwater contamination. More specifically, a small-scale recirculating bioinjection system

1 (Figure I-1) may be used to remediate selected groundwater hot spots where high concentrations of
2 Cr(VI) are present, or the system could be expanded and used to establish large zones of treatment within
3 a plume. Bio-injection could also be used as a means of treating the Cr(VI) in the extracted water rather
4 than sending the water to the ion-exchange treatment plant. In this way, it combines the extraction removal
5 process of a pump-and-treat system with the in situ bioremediation process. In either approach, this
6 technology could be applied in 100 Area Cr(VI) plumes where traditional pump-and-treat systems are
7 active or where pump-and-treat systems are not deployed.

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



15
16 **Figure I-1. Cross Section of a Recirculating In Situ Bioremediation System**

17 **16.1.1 Implementation Factors**

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

- 23 • **Method of Delivery.** Vertical injection wells screened in the aquifer are typically used to deliver
24 carbon compounds into groundwater. Other approaches include surface infiltration trenches,
25 horizontal wells, and direct-push technology. Vertical wells are recommended because they can be
26 reliably installed, accept high volumes of liquid, and are easily maintained.

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

35 **16.2 Previous Studies and Applications of Bio-injection and Similar Technologies to** 36 **Cr(VI) Remediation in Groundwater**

37 In situ bioremediation has been used to successfully treat Cr(VI)-contaminated groundwater at locations
38 both on and off the Hanford Site. In addition, it has been used at many sites to remediate a range of
39 other contaminants including metals, sulfate, nitrate, and chlorinated solvents. These applications
40 provide information that can be used to guide the implementation of in situ bioremediation for Cr(VI)
41 Several cases where in situ bioremediation has been successfully used to treat Cr(VI) are summarized
42 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 of the ISRM barrier previously installed in 100-D. Substrates selected for the treatability test included a soluble (miscible) substrate (molasses) and an immiscible slow-release substrate (emulsified vegetable oil in the form of a commercially available product called EOS[®]-598²). This treatability study is reported in 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 unit E. Depth to the water table ranges from less than 1 m near the river to approximately 25 m (82 ft) farther inland. The base of the unconfined aquifer is a fine-grained silty sand to clay overbank interval, designated the RUM 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 I-2). The test cells were located such that existing Well 199-D5-40 could be used as a background monitoring location for both test cells. Field test operations were conducted by injecting the substrate using process water from 100-D pressurized water supply as the carrier solution. The substrate solutions were fed into the manifold system using a chemical metering pump.

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

EOS Injection. The substrate injection was conducted over a period of 17 hours using process water injected at approximately 40 gpm amended with approximately 60 g/L emulsion (EOS-598 product) and

² EOS[®]-598—Emulsified Oil Substrate, manufactured by EOS Remediation, LLC, 1101 Nowell Road, Raleigh, North Carolina.

1 100 mg/L sodium bromide. Emulsion amendment was not continuous during this time but occurred in
2 seven discrete pulses, with a total emulsion injection time of 10.5 hours. Injection pressure was variable
3 throughout the injection, ranging from 3 to 17 psi. Approximately 5,560 L (1,470 gal) of EOS were
4 injected, with a total injection volume of about 157,700 L (41,700 gal). At the end of the substrate
5 injection, 30,600 L (8,100 gal) process water was injected for approximately 3 hours to clear the injection
6 system of substrate.



7
8 **Figure I-2. Molasses Injected at 100-D Area Biostimulation Treatability Test Site to Nourish Bacteria**

9 **16.3.3 Results**

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

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

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

28 **16.3.4 Lessons Learned**

29 Aquifer permeability reduction within the molasses injection test cell was moderate and likely due to
30 growth of bacteria. Hydraulic slug testing was conducted 60 and 420 days after substrate injection showed
31 minimal impact from injection of the molasses substrate in the short term. Over the longer term,

1 permeability was reduced by factors ranging from 0.55 to 0.02, likely due to biomass growth.
2 The biomass concentration would be expected to slowly decline over time and lead to restored
3 permeability.

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

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

14 **16.4 Hanford 100-H Lawrence Berkeley National Laboratory Hydrogen Release** 15 **Compound Treatability Study**

16 Since 2004, biostimulation tests have been performed at 100-H by personnel at Lawrence Berkeley
17 National Laboratory (Faybishenko et al., 2008). In these tests, a commercial polylactate called Hydrogen
18 Release Compound (HRC)³ was injected into the aquifer to stimulate microbial activity and transform
19 Cr(VI) to Cr(III). Results from the tests show Cr(VI) concentrations in the treated area decreased to below
20 drinking water standards and remained at that level for nearly 3 years. The principle difference between
21 this test and the test described in the previous section is the use of polylactate. This is a liquid that is
22 difficult to inject any distance from a well because of its high viscosity; therefore, this substance is limited
23 in its ability to treat large areas of an aquifer. Over several months, polylactate slowly disperses into the
24 aquifer, at which point it acts as a more mobile substrate.

25 **16.4.1 Site Conditions**

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

33 **16.4.2 Technical Approach**

34 The well layout for the treatability study included an injection well (699-96-45), a pumping/monitoring
35 well (699-96-44) located approximately 5.3 m (17.5 ft) downgradient of the injection well, a
36 monitoring well (699-96-41) located midway between 699-96-44 and 699-96-45, a monitoring well
37 (699-96-42) located approximately 4.6 m (15 ft) cross gradient from 699-96-44, and an existing
38 upgradient background monitoring well (699-96-43). Newly installed wells were drilled to a depth of
39 18 m (60 ft) bgs.

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

1 On August 3, 2004, 18.2 kg (40 lbs) of HRC were injected into 699-96-45, through a straddle packer that
2 isolated the injection interval to 13 to 14 m (43 to 46 ft). To trace the post-HRC injection carbon
3 production generated by metabolic processes, 10 g (.35 oz.) of ¹³C-labeled lactate were mixed with the
4 HRC. Before the injection, the HRC was pre-heated to about 35 degrees Celsius (°C) and diluted with
5 4 gal (15 L) of distilled water. The injection hose was initially filled with 2.5 gal (9.5 L) of water (as a
6 primer). A total of 4.5 gal (17 L) of water was injected as a chaser after the HRC injection. Following the
7 HRC injection, potassium bromide (KBr) was also injected into the same injection interval. Groundwater
8 was pumped from downgradient Well 699-96-44 to create a direct water flow path between wells.
9 Pumping continued for 25 days.

10 **16.4.3 Results**

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

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

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

24 **Biogeochemical Response.** The maximum biomass in both the pumping and injection wells was reached
25 15 to 20 days following injection. The maximum average biomass increased approximately 50-fold in
26 699-96-44, and approximately 38-fold in 699-96-45. The lower biomass in water samples from the
27 injection well may have resulted from filtering of bacteria attached to colloids during groundwater
28 sampling and analysis.

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

34 The HRC injection generated reducing conditions, which is evident from the drop in the DO
35 concentration from 8.2 to 0.35 mg/L and redox potential from 240 to 130 mV in downgradient monitoring
36 Well 699-96-44. Although DO in 699-96-45 increased to 5.5 mg/L after the conclusion of pumping, it
37 then gradually decreased over the next year. Over the next 3 years after pumping ceased, DO in 699-96-4
38 ranging from 6 to 7 mg/L, compared with 8 to 9 mg/L in upgradient Monitoring Well 699-96-43. At the
39 same time, pH dropped from 8.9 to 6.5-7.0 and stabilized at this level. Through monitoring conducted in
40 June 2007, redox potential and DO in the injection and downgradient monitoring wells had not returned
41 to the background levels. The slow recovery of background redox conditions could have been caused by
42 the presence of some HRC breakdown products (lactic and acetic acid) between the injection and
43 downgradient monitoring wells. Post-HRC injection decaying biomass may have also served as a
44 carbon source.

1 An increase in the ^{13}C of dissolved inorganic carbon (DIC) from -12 percent (prior-HRC injection) to
2 greater than 50 percent (which is higher than that in the injected HRC) was likely caused by the creation
3 of CO_2 as a byproduct of microbial metabolism. It should be noted that the release rate of ^{13}C -labeled
4 lactate that was added to the HRC could be higher than that of polylactate, which is the main component
5 of HRC. The carbon isotope ratios of the DIC decreased after pumping was stopped, but remained above
6 background for the 3-year period of observations through June 2007.

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

12 **16.4.4 Lessons Learned**

13 Hydraulic and chemical transport processes in the Hanford formation were likely affected by
14 biogeochemical processes after the HRC injection. A post-HRC injection (July 2005 and April 2006)
15 increase in the tracer travel time could likely be explained by the decrease in the hydraulic conductivity
16 due to partial blocking of flow pathways within heterogeneous media by biofilms and CO_2 gas.

17 **16.5 Other Relevant Hanford Site Studies**

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

20 **16.5.1 Fortifying the 100-D Area In Situ Redox Manipulation Barrier with Iron**

21 The ISRM barrier was implemented to passively treat Cr(VI) contamination in the 100-D southern plume
22 and prevent the discharge of elevated levels of Cr(VI) to the Columbia River (EPA et al., 1999). At the
23 time the ISRM barrier was implemented, the magnitude and extent of high Cr(VI) concentrations in the
24 100-D hot spot upgradient of the barrier were not understood. When performance-monitoring data
25 indicated that Cr(VI) was breaking through the ISRM treatment zone, scientists proposed that fortifying
26 the barrier with additional reduced iron would increase the long-term effectiveness of the barrier.
27 Consequently, a treatability study was conducted to evaluate whether augmentation of the ISRM barrier
28 with nano-scale zero-valent iron (ZVI) would be an effective approach to augmenting the performance
29 and longevity of this passive treatment system.

30 In 2006, DOE began a test to determine whether injections of tiny iron particles (only 70 nanometers
31 [3 millionths of an inch] in diameter) could fortify the weaker portions of the ISRM barrier. The small
32 size of the particles would allow them to flow into the aquifer, thus treating the water more effectively
33 given the very large surface area of the material (30 m^2/g [150,000 ft^2/lb]). Higher surface area means that
34 more of the iron would be available to react with and remediate the groundwater.

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

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

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

10 **16.5.2 100-K Area Calcium Polysulfide Injection Treatability Test**

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

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

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

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

35

1 post-treatment aquifer tests showed that chemical injection did not degrade the permeability of the
2 aquifer.

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

8 **16.6 Pacific Gas and Electric Company Hinkley Compressor Station, San Bernardino** 9 **County, California**

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

19 **16.6.1 Site Conditions**

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

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

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

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

39 **16.6.2 Technical Approach**

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

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

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

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

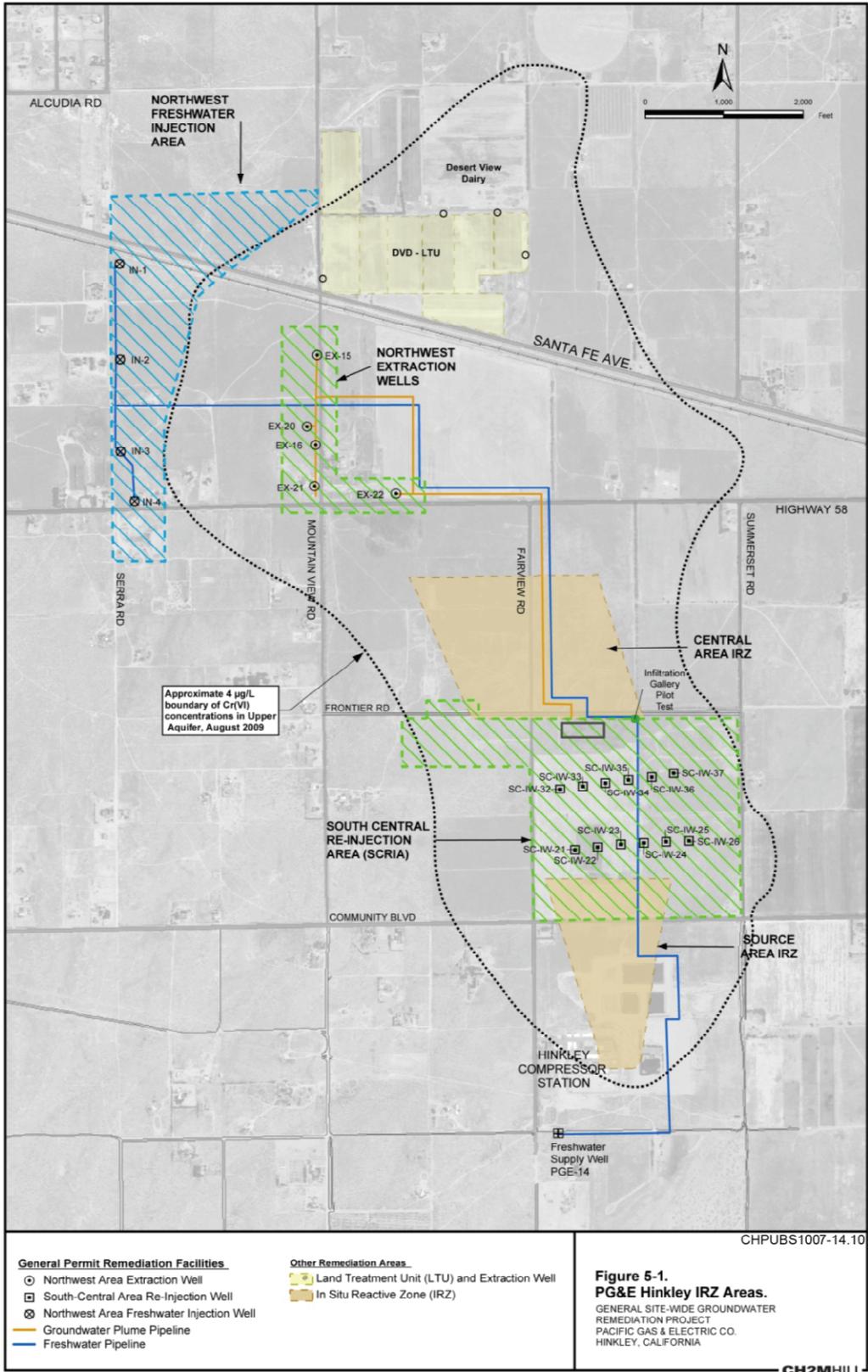
20 **16.6.3 Results**

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

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

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

33



Source: CH2M HILL, 2010.

Figure I-4. PG&E Hinkley IRZ Areas

1
 2
 3

1 **16.6.4 Lessons Learned**

2 At the Source Area IRZ, 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 interval). 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 IRZ and treatment of Cr(VI) will continue with ongoing changes in injection rate and locations as
9 well as ethanol reagent concentrations to optimize TOC distribution and Cr(VI) treatment, and to
10 minimize the migration of secondary byproducts.

11 Operations of the Central Area IRZ 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; and second, wells once used for injection showed limited extraction capacity,
16 thereby limiting the effectiveness of reversing injection and extraction wells. To reduce the frequency of
17 well fouling and enhance carbon distribution efficiency, operation of the Central Area IRZ system was
18 modified from the original dipole configuration to the current 10 injection/two extraction well
19 configuration 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 IRZ 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 (located approximately 12 m [40 ft] downgradient of the injection wells). The ethanol dosage was
25 decreased in upgradient injection locations. The effect of the decreased dosing was observed at the three
26 sentry wells, as manganese concentrations stabilized or decreased. The system continues to be operated at
27 reduced 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 located in San Bernardino County, approximately 24 km
30 (15 mi) southeast of Needles, California. PG&E is addressing the presence of Cr(VI) in groundwater
31 under the oversight of the California Environmental Protection Agency, Department of Toxic Substances
32 Control (DTSC). The Cr(VI) source was chromium salt historically used as a corrosion inhibitor in the
33 station's cooling towers. In 1996, PG&E and DTSC entered into a Corrective Action Consent Agreement
34 to 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: an Upland reductive zone in situ pilot test (ISPT) to
36 evaluate how well recirculation wells can distribute reductant (ethanol) throughout the aquifer to achieve
37 treatment across a transect of the plume, and a Floodplain ISPT to evaluate the efficacy of using lactate to
38 enhance the existing reducing environment in the floodplain adjacent to the Colorado River.

39 **16.7.1 Case Study References**

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

41 California Department of Toxic Substances Control (DTSC) Project Website. Available at:

42 <http://dtsc-topock.com/>.

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

17 **16.7.2 Site Conditions**

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

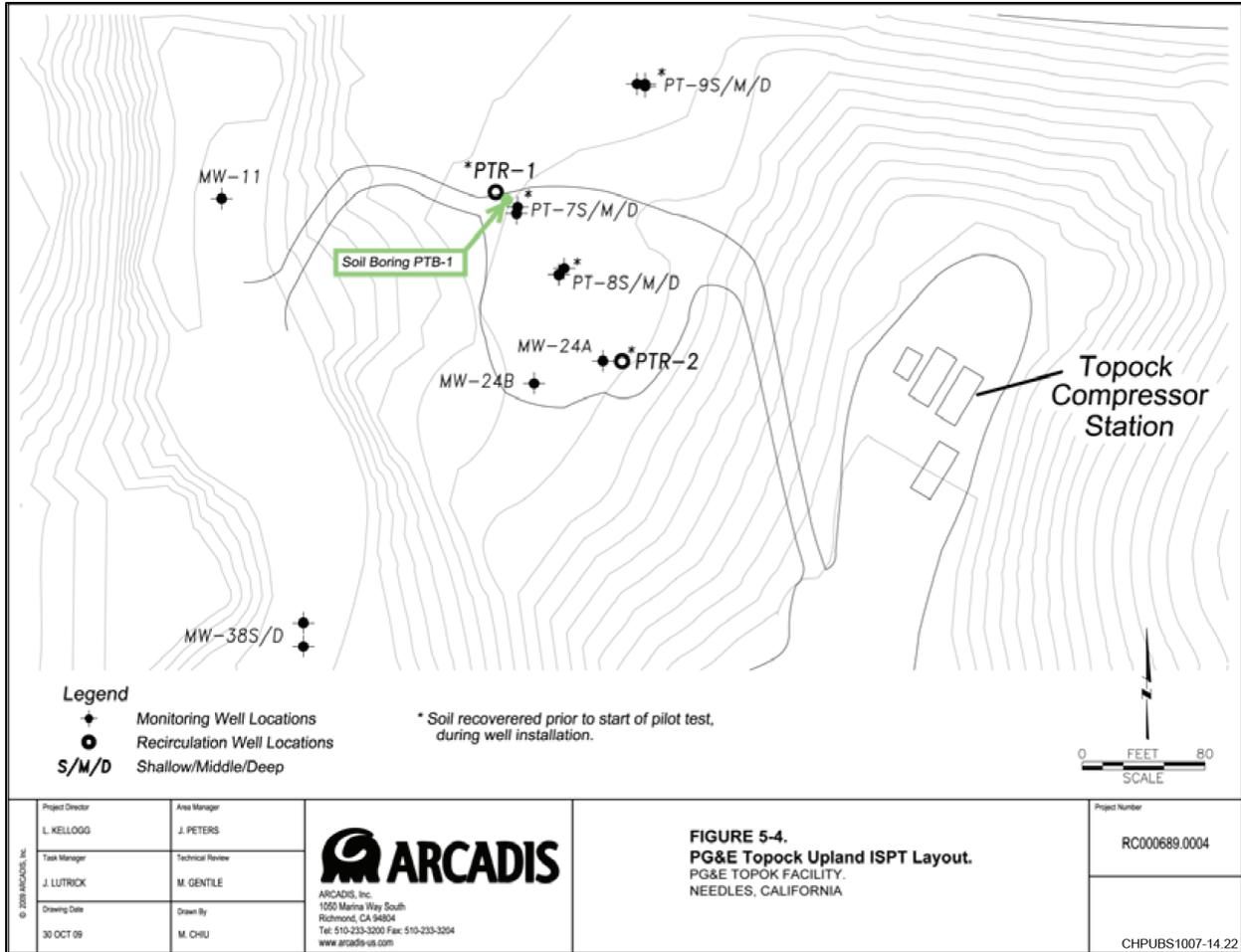
23 In the Upland area, the depth to groundwater is approximately 115 ft bgs. The subsurface shallow aquifer
24 zone consists of alluvial deposits 45 to 61 m (150 to 200 ft) thick, and approximately 309 m (1000 ft) of
25 the unit is saturated. Hydraulic gradients across the Upland area are between 0.0001 to 0.001 ft/ft. In the
26 Floodplain area, the depth to groundwater is approximately 4.5 m (15 ft) bgs, but can fluctuate
27 dramatically as a result of interactions between groundwater and the Colorado River. The measured
28 saturated thickness of the alluvial aquifer ranges from 23.5 to 29 m (77 to 95 ft). Natural groundwater
29 gradients in the alluvial aquifer are relatively flat, on the order of 0.0001 to 0.001 ft/ft. Current estimates
30 of groundwater seepage velocity in the vicinity of the pilot test area under the influence of nearby
31 groundwater extraction range from about 0.1 to 1 ft per day.

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

35 **16.7.3 Technical Approach**

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

37 **Upland ISPT.** The Upland ISPT well configuration is shown on Figure I-5. The Upland ISPT consisted of
38 the recirculation of the reagent mixture between two dual-screen recirculation wells (PTR-1 and PTR-2)
39 screened between approximately 36 to 49 m (120 and 160 ft) bgs (upper screens) and 52 to 64 m (170 and
40 210 ft) bgs (lower screens).



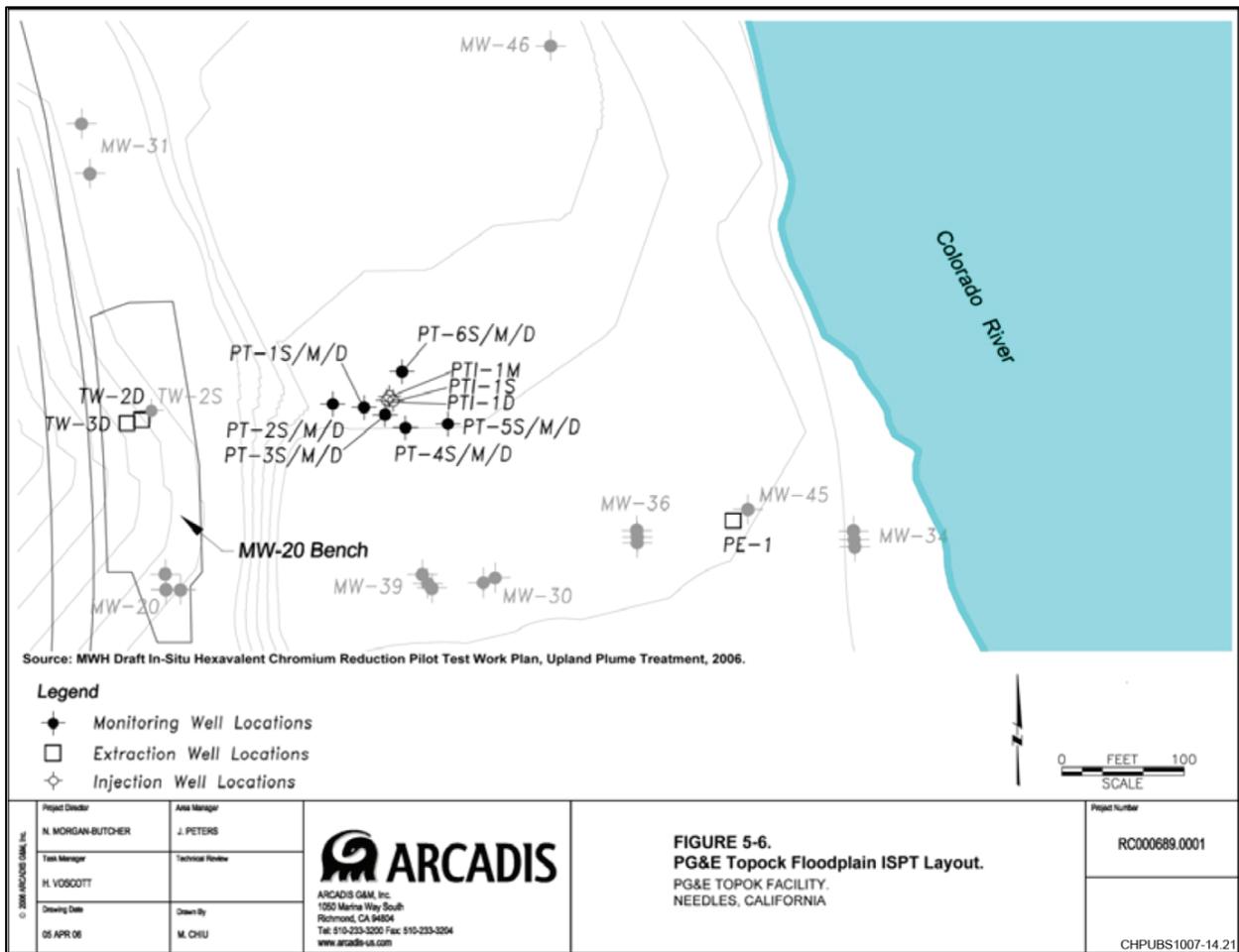
Source: PG&E, 2009a.

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

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

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

1 **Floodplain ISPT.** The Floodplain ISPT well configuration is shown on Figure I-6. The Floodplain ISPT
 2 test area was located within the zone of influence of existing groundwater Extraction Well TW-2
 3 (located 61 m [200 ft] to the west). The induced gradient generated by pumping groundwater from TW-2
 4 allowed the test to monitor the potential radius of impact of the reagents, their persistence, and their
 5 effectiveness at reducing Cr(VI) under active circulation conditions. A three-well injection cluster with
 6 separate 3 m (10 ft) screens (PTI-1S, PTI-1M, and PTI-1D) was installed to allow for controlled injection
 7 into both the shallow fluvial deposits and deeper alluvial fan deposits of the aquifer in this area. The depth
 8 of the three injection wells ranged from approximately 21 to 36 m (70 to 120 ft). The lactate solution and
 9 chase water were allowed to gravity feed. The planned concentration of lactate in the initial injection was
 10 23 kg (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
 12 6, 2006; August 11, 2006; September 7, 2006; November 1, 2006; May 7 and 8, 2007; and July 17
 13 and 18, 2007. Approximately 1,160 kg (2,557 lbs) of 60 percent sodium lactate diluted with water to
 14 270,000 L (72,000 gal) were injected over the course of the six events.



15 Source: PG&E, 2009b.

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

18

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 nondetect 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 nondetect levels (less than
10 0.1 mg/kg). Selective extraction results indicate that chromium present in the soil was redistributed to a
11 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 Cr(III) formed by the reduction of Cr(VI) was removed from groundwater to less
19 than 1 µg/L, likely by precipitation and filtration by the aquifer. The extent of Cr(VI) reduction was
20 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
38 the aquifer and the extent of Cr(VI) reduction during the periods between injections was increased.
39 The increased longevity of Cr(VI) reduction suggests that more residual reducing capacity was
40 generated by:

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

1 3. Forming of a reduced Fe solid phase, other than FeS (for example, magnetite [Fe₃O₄], an iron
2 mineral that contains reduced iron [Fe(II)]) can be created in the IRZ

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

5 **16.7.5 Lessons Learned**

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

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

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

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

32 **16.8 Abandoned Manufacturing Facility, Emeryville, California**

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

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

16.8.1 Case Study References

California State Water Resources Control Board, 2008, Project Fact Sheet. Available at:

http://geotracker.waterboards.ca.gov/profile_report.asp?global_id=SL20254872.

California Department of Toxic Substances Control (DTSC), 2006, In-Situ Bioremediation of Chlorinated Hydrocarbons, An Assessment of Projects in California, Office of Pollution Prevention and Technology Development, February. Available at:

http://www.dtsc.ca.gov/TechnologyDevelopment/upload/Final_ISB_Report4.pdf.

U.S. Environmental Protection Agency (EPA), 2000, Cost and Performance Report, Anaerobic In-Situ Reactive Zone at an Abandoned Manufacturing Facility, Emeryville, California, Office of Solid Waste and Emergency Response, Technology Innovation Office, March. Available at:

<http://www.costperformance.org/pdf/EmeryvilleBio.PDF>.

16.8.2 Site Conditions

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

16.8.3 Technical Approach

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

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

16.8.4 Results

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

16.9 Avco Lycoming Site, Williamsport, Pennsylvania

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

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

7 **16.9.1 Case Study References**

8 U.S. Environmental Protection Agency (EPA) Project Website. Available at:
9 <http://www.epa.gov/reg3hwmd/npl/PAD003053709.htm>.

10 U.S. Environmental Protection Agency (EPA) CLU-in Website. Available at:
11 <http://www.clu-in.org/products/newsletters/tnandt/view.cfm?issue=0703.cfm>.

12 EPA/625/R-00/005, 2000, In Situ Treatment of soil and Groundwater Contaminated with Chromium,
13 Technical Resource Guide, U.S. Environmental Protection Agency, October. Available at:
14 www.clu-in.org/download/remed/epa625r00005.pdf.

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

18 **16.9.2 Site Conditions**

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

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

24 **16.9.3 Technical Approach**

25 A full-scale remediation system was installed in January 1997 to develop and maintain an anaerobic
26 environment capable of reducing and precipitating Cr(VI) over a 1,100 m² (12,000 ft²) treatment area.
27 The system utilized 20 injection wells and 16 existing municipal wells to establish reactive zones.
28 Thirty-eight L (10 gal) of solution per well were injected twice a day. The mixing ratio for molasses
29 varied from 1:200 to 1:20. A programmable logic controller monitored and controlled the feed rate and
30 frequency of the molasses feed and solution feed pumps, as well as the timing of the solenoid valve
31 network that controlled the metered flow to the injection wells.

32 **16.9.4 Results**

33 The injection of the molasses-based substrate was successful in creating an anaerobic groundwater
34 environment and resulted in the chromium plume shrinking to approximately one-fourth its original area
35 in less than 2 years. The concentration of Cr(VI) was reduced from 1,950 to 10 µg/L in the southern
36 portion of the treatment area. The peak chromium concentrations are isolated to one area at slightly above
37 500 µg/L.

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

1 meet the cleanup goals for Cr(VI) and total dissolved chromium. In the remaining wells, Cr(VI)
2 concentrations decreased 75 to 99 percent from pre-treatment levels. No evidence of secondary metal
3 byproduct migration has been found in any of the system's eight downgradient monitoring wells, where
4 cleanup goals continue to be met.

5 **16.10 Odessa Chromium I Superfund Site Odessa, Ector County, Texas**

6 The Odessa Chromium I Superfund Site is a 80,000 m² (20 ac) portion of an aquifer located near 44th
7 Street and Brazos Avenue in the City of Odessa, in Ector County, Texas. Two potential chromium release
8 sources to groundwater were identified: a former chrome-plating facility that operated between 1972 and
9 1977, and another currently operating metal-plating facility.

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

16 An experimental ferrous sulfate in situ treatment pilot study was conducted in December 1998 and
17 January 1999. The pilot study demonstrated accelerated achievement of the remediation goals; however,
18 the use of ferrous sulfate eventually led to plugging of injection wells and reduced injection capacity.
19 MRC^{TM3} was evaluated as an alternate injection reagent, and eventually selected for full-scale injection.
20 MRC consists of an organosulfur compound esterified to a carbon backbone, which releases both lactate
21 as a carbon source for bioremediation, and an organosulfur compound that acts as a direct chemical
22 reductant for Cr(VI).

23 **16.10.1 Case Study References**

24 Regenes Case Study for Chromium Immobilization. Available at:
25 <http://regenes.com/regenes-resource-center/case-studies/cs-detail.aspx?ID=97>.

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

29 **16.10.2 Site Conditions**

30 The surficial soil at the site is predominately a fine sandy loam to sandy clay that ranges in depth from
31 20 to 61 cm (8 to 24 in.). Pleistocene windblown sand, clay deposits, and alluvium deposits underlie the
32 surficial soil. Beneath the Pleistocene is 7.6 to 11m (25 to 35 ft) of caliche deposits, which can be
33 relatively impermeable in local areas. Underlying the caliche are scattered erosional remnants of the
34 Ogallala Formation composed of gravels, sands, silts, and clays. This formation does not generally extend
35 to depths below 23 m (75 ft) in the area. The Trinity Formation, the main fresh water producing aquifer in
36 the area, underlies the Ogallala interval. The thickness of this formation ranges from 17 to 21m (55 to
37 70 ft) and is composed of sands and sandstones with minor amounts of siltstone, clay, and gravel.
38 Beneath the Trinity Formation is the Chinle Formation of the Dockum Group, which consists of up to
39 183m (600 ft) of clays and shales that prevent downward migration of contaminants.

³ MRC—Metals Remediation Compound is manufactured by Regenes-Advanced Technologies for Contaminated Site Remediation, 1011 Calle Sombra, San Clemente, California.

1 Total unfiltered chromium concentrations at the site source area have historically fluctuated between
2 1,000 and 12,000 µg/L.

3 **16.10.3 Technical Approach**

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

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

11 **16.10.4 Results**

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

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

22 **16.10.5 Lessons Learned**

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

27 **16.11 Selma Pressure Treating Superfund Site, Selma, California**

28 The Selma Pressure Treating (SPT) Site is a former wood-treating facility located approximately 15 mi
29 (24 km) south of the City of Fresno, in Selma, California. Wood-treatment operations began at the site in
30 1936 and, in 1965; a new pressure-treating facility began operating at the site. The pressure treating
31 process consisted of impregnating wood in pressurized vessels with chromium-containing chemical
32 preservatives. Releases of pressure-treating chemicals to the subsurface resulted in chromium impacts
33 to groundwater.

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

1 **16.11.1 Case Study References**

2 California Department of Toxic Substances Control (DTSC) Contract. Available at:

3 http://www.envirostor.dtsc.ca.gov/public/final_documents2.asp?global_id=10240051&doc_id=6023728.

5 U.S. Environmental Protection Agency Project Website. Available at:

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

8 U.S. Environmental Protection Agency (EPA), 2006, *Five-Year Review Report, Second Five-Year Review Report, Selma Pressure Treating Superfund Site, Selma, California*, September. Available at:

9 <http://yosemite.epa.gov/R9/SFUND/R9SFDOW.NSF/3dc283e6c5d6056f88257426007417a2/51473f5f82d22982882575fd00805137!OpenDocument>.

12 **16.11.2 Site Conditions**

13 The aquifer underlying the SPT site is unconfined and consists of discontinuous fine-grained lenses and
14 cemented zones that act as localized barriers to groundwater flow and contaminant transport.

15 The water-bearing unit is divided into a shallow zone from 6 to 15 m (20 to 50 ft) bgs, an intermediate
16 zone from 14 to 23 m (45 to 75 ft) bgs, and a deep zone from 23 to 36 m (75 to 120 ft) bgs.

17 Baseline Cr(VI) concentrations have been detected in site groundwater at concentrations in excess
18 80,000 µg/L. In 1997, the Cr(VI) plume extended approximately 900 m (3,000 ft) downgradient from the
19 primary site.

20 **16.11.3 Technical Approach**

21 In 2005, an ISB pilot test (Phase 1) was conducted within the relatively shallow chromium contamination
22 source area. The pilot test used direct-push/direct-injection methods, and targeted an approximately 7.6 m
23 (25 ft) thick treatment zone in a 40,000 ft² (portion of the hot spot. Subsequent injections in Phases 1a and
24 2 focused on areas adjacent to the hot spot and downgradient of the hotspot, respectively. The direct-push
25 injection grid was based on an assumed 4.5 m (15 ft) ROI. In most cases, there was no overlap of the
26 4.5 m (15 ft) ROI circles. Solutions of less than 5 percent molasses were injected at about 90 to 180 psi to
27 approximate a 4,000 mg/L molasses target concentration. This concentration of substrate was an overdose
28 amount with a 5 times safety factor.

29 As the treatment continued on a full-scale capacity downgradient where the plume increased in depth, it
30 was determined that direct-push delivery was unreliable at depths below 18 to 21 m (60 to 70 ft) due to
31 refusal of the direct-push equipment. Therefore, Phase 2B ISB, which began operations mid-2006,
32 utilized a recirculation system to deliver organic substrates into the deeper aquifer at 21 to 36 m
33 (70 to 120 ft) bgs. The recirculation system distributed substrate throughout the treatment area by
34 extracting groundwater from radially arranged extraction wells (five wells) and injection of water into
35 centrally located injection wells (11 wells). The extraction wells were placed upgradient, between, and
36 downgradient of the injection wells. Sodium lactate, which was determined to have greater longevity at
37 the site compared to molasses, was later used during Phase 2B to enhance reduction of residual Cr(VI)
38 bound up in zones of lower hydraulic conductivity.

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

1 converted to injection wells. Ongoing injections at the site will consist of the substrate-amended flow
2 from the four original pump-and-treat wells (approximately 200 gpm [750 L]).

3 **16.11.4 Results**

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

9 **16.11.5 Lessons Learned**

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

18 **16.12 Schwerin Concaves, Inc., Walla Walla, Washington**

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

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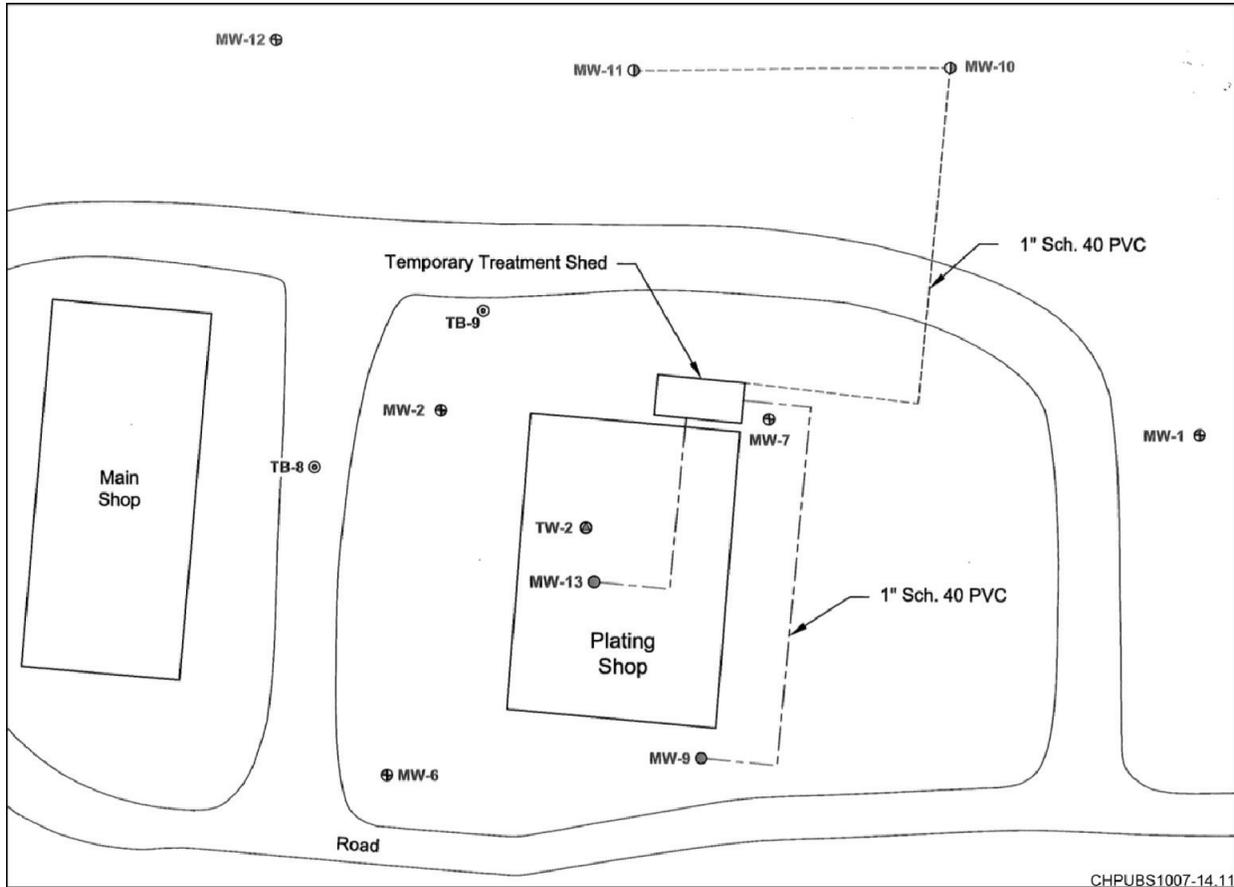
35 **16.12.2 Site Conditions**

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

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

3 **16.12.3 Technical Approach**

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



10
11 Source: Hart Crowser, 2007.

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

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

18 **16.12.4 Results**

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

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

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

16 **16.12.5 Lessons Learned**

17 Lessons learned from evaluating this case study include the importance of carefully selecting an in situ
18 bioremediation system design that is suitable for the project location. In the case of the Schwerin
19 Concaves Site, aquifer sediments were not conducive to establishment of a large-scale recirculation
20 system, though slug injection of substrate did work well. The injection operations mode also plays a large
21 factor in the rate at which biofouling may impact injection well performance. Using pulsed-injection
22 operating modes, or continuous-injection at a lower concentration, may serve to limit the degree of
23 fouling at the injection well.
24

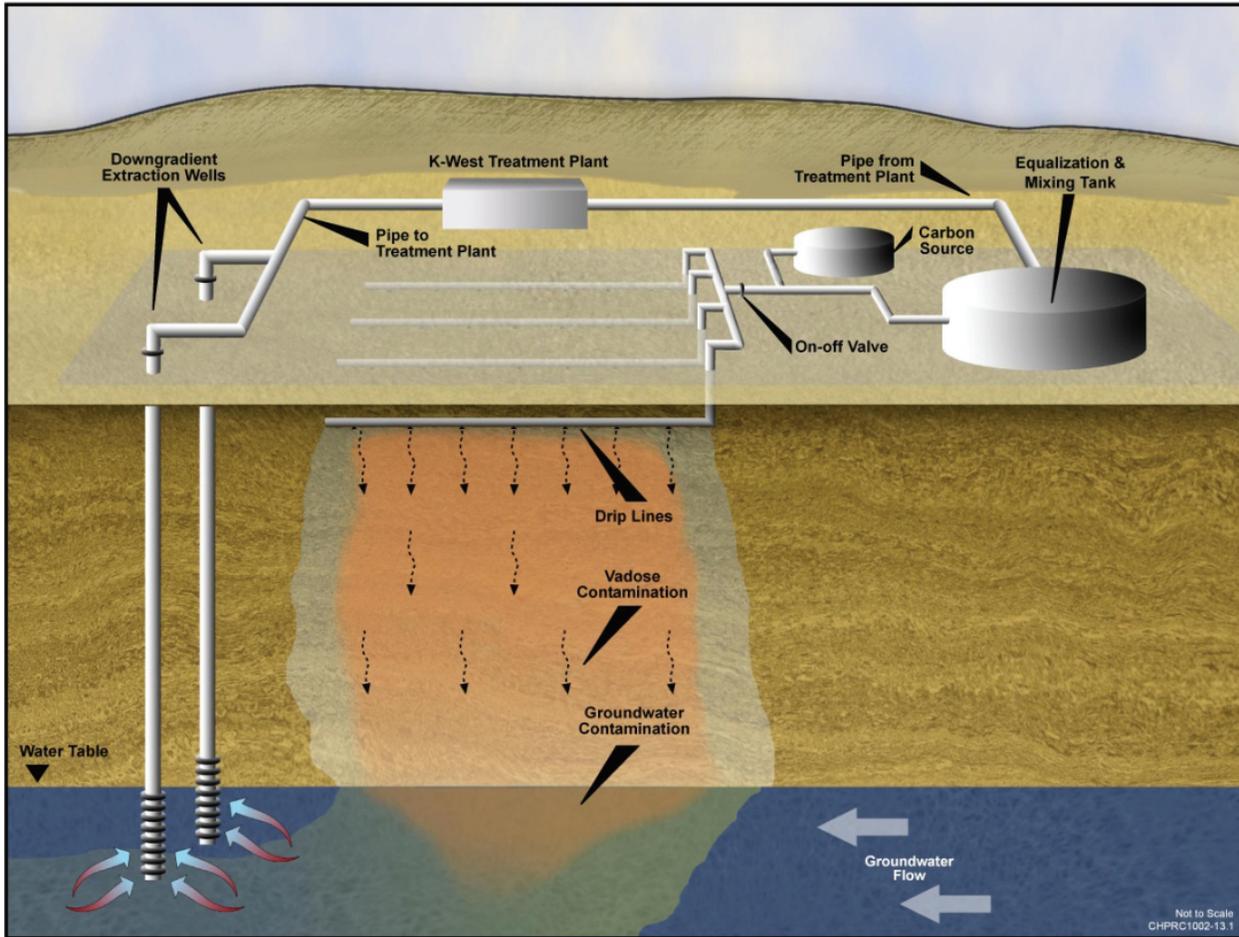
25 **17 Vadose Zone Treatment by Bioinfiltration**

26 As mentioned above, numerous studies have demonstrated that the sufficient addition of simple organic
27 carbon compounds (e.g., lactate) will stimulate the rapid growth of the native microbial assemblage in an
28 aquifer, ultimately resulting in the development of localized reducing conditions. This approach has been
29 successfully used numerous times to bioremediate Cr(VI) by converting it to less toxic trivalent
30 chromium (Cr(III)) (see Chapter I-5). Once formed, Cr(III) will typically sorb to mineral substrates or
31 precipitate as an insoluble solid phase such as Cr(OH)₃ and is therefore effectively immobile in an aquifer
32 (Hansel et al., 2003).

33 Similar microbial and related geochemical processes are known to occur in the vadose zone as well as in
34 the saturated aquifer soils. Laboratory studies have demonstrated the processes, showing that adding
35 water and organic nutrients to columns packed with vadose zone materials contaminated with Cr(VI)
36 cause the effective conversion of Cr(VI) to Cr(III) (Tokunaga et al., 2003, "In-situ reduction of Cr(VI) in
37 heavily contaminated soils through organic carbon amendment," and Oliver, 2001, *Microbial Reduction*
38 *of Hexavalent Chromium Under Vadose Zone Conditions*). Consequently, in situ bioremediation of the
39 vadose zone by the controlled infiltration of carbon-amended water been identified as a technology with
40 the potential to rapidly and effectively reduce Cr(VI) to Cr(III) in those areas in the 100 Area Reactor
41 sites where the deep vadose zone (e.g., greater than 6 m [20 ft] bgs) that are contaminated with Cr(VI).
42 Hereafter, the proposed method of vadose zone bioremediation is referred to as bioinfiltration.

1 **17.1.1 Conceptual design**

2 Figure I-8 presents the conceptual design of a bioinfiltration system. The bioinfiltration system could be
3 implemented in a closed loop system, much as described above for bio-injection. The extracted water
4 would be piped to a surge tank prior to being amended with a concentrated lactate/water solution that is
5 metered in from a separate mixing tank (Figure I-8). The amended solution is then piped to a drip
6 infiltration system for controlled distribution into the vadose zone.



7

8

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

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

17.2 Bioinfiltration Remediation Processes and Approach

Once treatment starts, the infiltration of sufficiently carbon-amended water into the vadose zone will lead to rapid microbial growth in the affected area. There will, however, be a lag period of several days or more between start-up of infiltration and the expansion of, and compositional changes in, the microbial assemblage sufficient to induce strongly reducing (e.g., sulfate reducing) conditions. Consequently, if the initial volume of amended solution and the infiltration rates are too high, a nonreducing wetted front could migrate downward through the vadose zone well ahead of a much more slowly advancing reducing front. Such a rapidly advancing wetted front could solubilize and transport a substantial fraction of the Cr(VI) in the vadose zone affected prior to the arrival of the reduction front. Saturated flow leaching tests performed on Hanford Site soils containing Cr(VI) suggested that as much as 95 percent of the Cr(VI) in the test soils was leached from the column during the first pore volume (PNNL-17674, *Geochemical Characterization of Chromate Contamination in the 100 Area Vadose Zone at the Hanford Site*). 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 Cr(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 100-D (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 bioinfiltration are expected to be rapidly oxidized and attenuated once exposed to the oxygenated groundwater in the aquifer.

The primary operational factors that will be varied during operation of the system will be the concentration of carbon in the solution applied and the rate of application. Generally, the higher the carbon concentration in the solution, the farther the reducing conditions will penetrate into the vadose zone for a given volume of solution. Different flow rates will result in different infiltration properties. For example, at very high application rates, flow will occur largely through coarser-grained materials, potentially bypassing 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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