DOE/RL-2019-28
Revision 0

200-DV-1 OPERABLE UNIT LABORATORY TREATABILITY STUDY TEST PLAN

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

P.O. Box 550
Richland, Washington 99352

Approved for Public Release;
Further Dissemination Unlimited

DOE/RL-2019-28
Revision 0

200-DV-1 OPERABLE UNIT LABORATORY TREATABILITY STUDY TEST PLAN

Date Published
August 2019

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

U.S. DEPARTMENT OF ENERGY | Richland Operations Office
P.O. Box 550
Richland, Washington 99352

APPROVED
By Janis D. Aardal at 6:46 am, Aug 21, 2019

Release Approval | Date

Approved for Public Release;
Further Dissemination Unlimited

TRADEMARK DISCLAIMER

Reference herein to any specific commercial product, process, or service by tradename, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

This report has been reproduced from the best available copy.

Printed in the United States of America

Contents

1 Project Description 1-1

2 Laboratory Approach for Treatability Testing 2-1

3 Gas-Phase Combined Bioreduction and Chemical Sequestration 3-1

3.1 Technical Basis 3-1

3.2 Laboratory Test Objectives 3-2

3.3 Laboratory Experimental Design and Procedures 3-4

4 Gas-Phase Bioremediation 4-1

4.1 Technical Basis 4-1

4.2 Laboratory Test Objectives 4-2

4.3 Laboratory Experimental Design and Procedures 4-2

5 Gas-Phase Chemical Sequestration 5-1

5.1 Technical Basis 5-1

5.2 Laboratory Test Objectives 5-2

5.3 Laboratory Experimental Design and Procedures 5-3

6 Particulate-Phase Chemical Sequestration 6-1

6.1 Technical Basis 6-1

6.2 Laboratory Test Objectives 6-2

6.3 Laboratory Experimental Design and Procedures 6-3

7 Particulate-Phase Combined Chemical Reduction and Sequestration 7-1

7.1 Technical Basis 7-1

7.2 Laboratory Test Objectives 7-2

7.3 Laboratory Experimental Design and Procedures 7-4

8 Liquid-Phase Chemical Sequestration 8-1

8.1 Technical Basis 8-1

8.2 Laboratory Test Objectives 8-2

8.3 Laboratory Experimental Design and Procedures 8-4

9 Liquid-Phase Combined Chemical Reduction and Sequestration 9-1

9.1 Technical Basis 9-1

9.2 Laboratory Test Objectives 9-2

9.3 Laboratory Experimental Design and Procedures 9-4

10 Liquid-Phase Combined Bioreduction and Chemical Sequestration 10-1

10.1 Technical Basis 10-1

10.2 Laboratory Test Objectives 10-2

10.3 Laboratory Experimental Design and Procedures 10-3

11 Data Analysis and Interpretation 11-1

12 Data Management 12-1

13 Data Quality 13-1

14 Waste Management 14-1

15 Schedule 15-1

16 Reporting 16-1

17 Management and Staffing 17-1

18 Budget 18-1

19 References 19-1

Tables

Table 1-1. Recommended Laboratory Studies by the TTER 1-1

Table 2-1. Summary of Biogeochemical Analysis Methods 2-2

Table 3-1. Primary Parameters Targeted by the Gas-Phase Combined Bioreduction and Chemical Sequestration Technology 3-3

Table 4-1. Primary Parameters Targeted by the Gas-Phase Bioremediation Technology 4-2

Table 5-1. Primary Parameters Targeted by the Gas-Phase Chemical Sequestration Technology 5-2

Table 6-1. Primary Parameters Targeted by the Particulate-Phase Chemical Sequestration Technology 6-2

Table 6-2. Experimental Treatments for Objective #1 of the Laboratory Testing of the Particulate-Phase Chemical Sequestration Technology 6-2

Table 7-1. Primary Parameters Targeted by the Particulate-Phase Combined Chemical Reduction and Sequestration Technology 7-2

Table 7-2. Experimental Treatments for Objective #1 of the Laboratory Testing of the Particulate-Phase Chemical Reduction and Sequestration Technology 7-3

Table 8-1. Primary Parameters Targeted by the Liquid-Phase Chemical Sequestration Technology 8-3

Table 8-2. Experimental Treatments for Objective #1 of the Laboratory Testing of the Liquid-Phase Chemical Sequestration Technology 8-3

Table 8-3. Experimental Treatments for Objectives #2 and #3 of the Laboratory Testing of the Liquid-Phase Chemical Sequestration Technology 8-4

Table 9-1. Primary Parameters Targeted by the Liquid-Phase Combined Chemical Reduction and Sequestration Technology 9-3

Table 9-2. Experimental Treatments for Objective #1 of the Laboratory Testing of the Liquid-Phase Chemical Reduction and Sequestration Technology 9-3

Table 10-1. Primary Parameters Targeted by the Liquid-Phase Combined Bioreduction and Chemical Sequestration Technology 10-2

Table 10-2. Experimental Treatments for Objective #1 of the Laboratory Testing of the Liquid-Phase Bioreduction and Sequestration Technology 10-3
Table 15-1. Implementation Schedule for the 200-DV-1 OU Laboratory Treatability Test Plan 15-2
Table 18-1. Overall Estimated Cost of 200-DV-1 OU Laboratory Treatability Test 18-1

This page intentionally left blank.

Terms

COI	contaminant of interest
CPS	calcium polysulfide
DOE-RL	U.S. Department of Energy, Richland Operations Office
ESTCP	Environmental Security Technology Certification Program
FS	feasibility study
GEDIT	gaseous electron donor injection technology
NQA	Nuclear Quality Assurance
NQAP	Nuclear Quality Assurance Program
OU	operable unit
PRB	permeable reactive barrier
PRZ	periodically rewetted zone
redox	reduction-oxidation
SMI	sulfur-modified iron
TTER	treatability test evaluation report
ZVI	zerovalent iron

This page intentionally left blank.

1 Project Description

In accordance with DOE/RL-2011-102, *Remedial Investigation/Feasibility Study and RCRA Facility Investigation/Corrective Measures Study Work Plan for the 200-DV-1 Operable Unit*, following characterization of the 200-DV-1 Operable Unit (OU) waste sites, deep vadose zone technologies will be evaluated to identify potential technologies that could enhance future remediation and determine whether to conduct a treatability test to support remedy selection. Therefore, a comprehensive evaluation of currently available deep vadose zone technologies for 200-DV-1 OU was recently conducted to identify and assess data needed to support remedial technology screening and alternative evaluation for the Hanford Site Central Plateau. The results of this evaluation were reported in DOE/RL-2017-58, Draft A, *Technology Evaluation and Treatability Studies Assessment for the Hanford Central Plateau Deep Vadose Zone* (hereinafter referred to as the treatability test evaluation report [TTER]).

The evaluation considered the potential need for laboratory, modeling, and field studies to provide necessary information for future feasibility studies (FSs) for the 200-DV-1 OU and other source OUs in the Hanford Site Central Plateau. This document provides a test plan for laboratory-scale treatability testing of the deep vadose zone remediation technologies selected during this evaluation. Table 1-1 summarizes the recommended laboratory studies identified in the TTER (DOE/RL-2017-58).

Table 1-1. Recommended Laboratory Studies by the TTER

Technology Process Option	COI to Study	Examples of Potentially Applicable 200-DV-1 Waste Sites	Examples of Other Potentially Applicable Waste Sites
Technologies for Unsaturated Zone Applications			
Gas-phase combined bioreduction and chemical sequestration	**Tc-99**	BY Cribs [a]	BC Cribs and Trenches [b]
Gas-phase bioremediation	**Nitrate**	Unknown [b]	Unknown [b]
	CN	BY Cribs [a]	Unknown [b]
	Cr(VI)	Unknown [b]	216-S-10, [b] 216-S-8, [b] 216-T-4a [b]
Gas-phase chemical sequestration	**I-129**	Unknown [b]	216-A-10, [b] 216-A-5, [b] 216-S-7 [b]
Technologies for the 200-DV-1 Perched Water and Use as a Horizontal Permeable Reactive Barrier at the Water Table			
Particulate-phase chemical sequestration	**U and Tc-99**	Perched water, [a] below perched water, [a] and below BY Cribs [a]	216-U-1&2, [a] S-SX Tank Farm, [a] C Tank Farm, [a] BC Cribs and Trenches [b]
	Cr(VI)	Unknown [b]	216-S-10, [b] 216-S-8, [b] 216-T-4a [b]
	I-129	Unknown [b]	216-A-10, [b] 216-A-5, [b] 216-S-7 [b]
Particulate-phase combined chemical reduction and sequestration	**U and Tc-99**	Perched water, [a] below perched water, [a] and below BY Cribs [a]	216-U-1&2, [a] S-SX Tank Farm, [a] C Tank Farm, [a] BC Cribs and Trenches [b]
Liquid-phase chemical sequestration	**U and Tc-99**	Perched water, [a] below perched water, [a] and below BY Cribs [a]	216-U-1&2, [a] S-SX Tank Farm, [a] C Tank Farm, [a] BC Cribs and Trenches [b]
	Cr(VI)	Unknown [b]	216-S-10, [b] 216-S-8, [b] 216-T-4a [b]
	I-129	Unknown [b]	216-A-10, [b] 216-A-5, [b] 216-S-7 [b]

Table 1-1. Recommended Laboratory Studies by the TTER

Technology Process Option	COI to Study	Examples of Potentially Applicable 200-DV-1 Waste Sites	Examples of Other Potentially Applicable Waste Sites
Liquid-phase combined chemical reduction and sequestration	**U and Tc-99**	Perched water, [a] below perched water, [a] and below BY Cribs [a]	216-U-1&2, [a] S-SX Tank Farm, [a] C Tank Farm, [a] BC Cribs and Trenches [b]
Liquid-phase combined bioreduction and chemical sequestration	**U, Tc-99, nitrate**	Perched water, [a] below perched water, [a] and below BY Cribs [a]	216-U-1&2, [a] S-SX Tank Farm, [a] C Tank Farm, [a] BC Cribs and Trenches [b]
	CN	BY Cribs [a]	Unknown [b]

Reference: DOE/RL-2017-58, Draft A, *Technology Evaluation and Treatability Studies Assessment for the Hanford Central Plateau Deep Vadose Zone* (referred to as the treatability test evaluation report [TTER]).

Notes: Laboratory quantification of effectiveness is needed for use in combination with existing field-scale information from other sites to evaluate these technologies in a feasibility study.

The COIs shown in bold are primary known contaminant targets. Other COIs are potential co-contaminants to evaluate with primary COIs.

a. These are likely continuing sources of contaminants to groundwater.

b. The remedial investigation evaluation will determine the waste sites that impact groundwater.

COI = contaminant of interest

Three general types of treatment technologies were selected for the laboratory studies to address the identified data gaps: gas phase, particulate phase, and liquid phase. While the gas-phase technologies were selected for unsaturated system applications, both the particulate- and liquid-phase technologies were identified for perched water remediation and/or water table applications as permeable reactive barriers (PRBs). The application for injecting a PRB at the water table interface with the vadose zone (the same technologies selected for perched water remediation) is for locations where contaminants in the vadose zone are at or near the water table.

The technologies selected for the laboratory treatability study were considered as not readily implementable for field conditions due to identified data gaps. Therefore, the laboratory study described in this document is designed to address these data gaps. Technologies that demonstrate a minimum level of effectiveness in the laboratory treatability study may need to be followed by a phased remedy implementation or field treatability test, as appropriate.

Chapter 2 provides a general description of the laboratory study approach, followed by chapters for each of the selected technologies, which describe the technical basis for the laboratory study and provide a detailed experimental design that will be used during the study.

2 Laboratory Approach for Treatability Testing

Technologies selected for the treatability testing rely on biological and/or chemical reductive treatment to degrade or change the chemical properties of the contaminant, chemical treatment for sequestration of the contaminant in mineral phases, or a combination of reduction and sequestration treatment. All of these approaches render the contaminant less mobile in the subsurface. The designs of the studies described in this document aim at determining the effectiveness and scale-up potential for these in situ processes by addressing the identified data gaps to enable their consideration in an FS in accordance with the TTER (DOE/RL-2017-58).

The testing approach was developed to provide multiple incremental decision points throughout the study to assess potential technology performance under site-specific conditions and to determine whether the technology is promising enough to continue with the laboratory testing. Each assessment stage will be conducted by the project team, including Pacific Northwest National Laboratory staff and Hanford Site contractor staff, who will periodically interface with the U.S. Department of Energy, Richland Operations Office (DOE-RL). The main components of the approach for treatability testing include the following:

- An initial assessment of overall technology effectiveness conducted in ideal conditions (as a proof-of-principal step) to determine whether the technology is promising. This determination is recommended to be based on an overall minimum success rate of 35% of contaminant transformation to immobile, temporarily immobile, or nontoxic end products.
- A detailed evaluation of process-specific rates and extent of reduction, degradation, and/or sequestration with an assessment of potential contaminant remobilization to determine if a minimum of 35% nonreversible sequestration/transformation is achieved.
- A quantification of immobilized end product stability (i.e., longevity) for the primary contaminants and co-contaminants (if applicable) to determine if a minimum of 50% stable mobility reduction is achieved.

Laboratory experiments for the different technologies are designed similarly to allow cross-comparison of the technology performance and to support the final evaluation of laboratory treatability testing results.

Overall, potential co-contaminants identified in this study are to be evaluated primarily for their interference on remediation of the contaminants of interest (COIs). Potential treatment of some co-contaminants for specific technologies will also be evaluated during the experiments.

Previous field treatability efforts highlighted the importance of laboratory testing with site-specific geochemical conditions prior to performing a direct field investigation. For instance, technology limitations were identified during the baseline laboratory testing and analysis (using the sediment samples obtained from the 216-U-8 field test site) for uranium reactive gas sequestration technology treatability study (PNNL-27773, *Deep Vadose Zone Treatability Test of Uranium Reactive Gas Sequestration for the Hanford Central Plateau: Final Report*). These previous efforts demonstrated that certain contaminant phases are known to be affected by disposal characteristics, the presence of co-contaminant interferences, or sediment/co-contaminant properties that may lead to deviations from the expected behavior of tested technologies. The laboratory treatability tests outlined in this document are designed to minimize these challenges (as much as possible) by using site-specific, field-contaminated sediment samples and relying heavily on the 200-DV-1 OU characterization results conducted in accordance with DOE/RL-2011-104-ADD1, *Characterization Sampling and Analysis Plan for the 200-DV-1 Operable Unit Addendum 1: Attenuation Process Characterization*. These characterization results have been published in several Pacific Northwest National Laboratory reports (PNNL-26266, *Geochemical,*

Microbial, and Physical Characterization of 200-DV-1 Operable Unit B-Complex Cores from Boreholes C9552, C9487, and C9488 on the Hanford Site Central Plateau; PNNL-26208, *Contaminant Attenuation and Transport Characterization of 200-DV-1 Operable Unit Sediment Samples*; and PNNL-27524, *Contaminant Attenuation and Transport Characterization of 200-DV-1 Operable Unit Sediment Samples from Boreholes C9497, C9498, C9603, C9488, and C9513*). These publications describe the biogeochemical characteristics of contaminants, geochemical nature of the sediments and pore water, and contaminant attenuation characteristics.

For the laboratory testing of each technology described in this document, necessary initial sediment characterization and contaminant evaluation will be conducted, as needed. It is important to note that the intention of the laboratory testing is not to optimize the delivery of the reactive agents for a field application, but rather to evaluate their effectiveness under site-specific conditions. Furthermore, because of the long timeframes needed for some mineral-phase precipitation processes associated with several of the tested technologies, aging of the experimental setups and potential methods of acceleration (e.g., elevated temperature) will be considered. This will be important, in particular, for adding contaminants such as uranium or technetium-99 into the sediments (where field contaminated sediments are not available). A standard procedure will be developed for adding these contaminants to appropriate sediment samples to ensure consistency with the field conditions. A series of control experiments (with no treatment) will be used for each testing activity to ensure a scientifically defensible evaluation of the technology performance and effectiveness. All experiments will be conducted in triplicate, unless stated otherwise.

Sacrificial replicate systems will be used in some of the tests to determine process rates from monitoring parameters over time. The number of sacrificial replicates will depend on the expected rate of the process (i.e., longer processes may require more replicate samples); however, a minimum of four samples representing initial, final, and two intermediary conditions will be used for rate determinations. Furthermore, sufficient incubation time will be selected for each sequestration treatment to allow precipitated phases to mineralize, if that is part of the treatment process.

Table 2-1 summarizes the methods that will be used for the biogeochemical analyses described in this document during the study.

Table 2-1. Summary of Biogeochemical Analysis Methods

Contaminants or Co-Contaminants of Interest	Analytical Measurement/Approach	Analytical Method References
U	ICP/MS, KPA	ASTM D5198 [a] Brina and Miller, 1992
Tc-99	ICP/MS, LSC	ASTM D5198
Cr, Cr(VI)	ICP/MS	ASTM D5198
NO_3	IC	EPA 9056A [b]
I-129	GC/MS; IC – ICP/MS	Zhang et al., 2010
CN (aqueous)	Spectrophotometry	EPA 9014 [c]
C-14	LSC	OP-DVZ-AFRI-001 [d]
Sr-90 [e]	LSC	Analyzed per Pacific Northwest National Laboratory method [d]

Table 2-1. Summary of Biogeochemical Analysis Methods

Contaminants or Co-Contaminants of Interest	Analytical Measurement/Approach	Analytical Method References
Microbial biomass quantification	CFU, total cellular protein, and QPCR	Peterson, 1979 LeBrón et al., 2009 Goldman and Green, 2015

Note: The references cited in this table are listed in Chapter 19.

a. ASTM D5198-17, *Standard Practice for Nitric Acid Digestion of Solid Waste*.

b. EPA Method 9056A, "Determination of Inorganic Anions by Ion Chromatography" (SW-846, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, Third Edition; Final Update V*, as amended).

c. EPA Method 9014, "Titrimetric and Manual Spectrophotometric Determinative Methods for Cyanide" (SW-846).

d. Liquid scintillation spectrometry.

e. If a contaminant is added to meet an experimental need, nonradioactive isotopes may be used if their chemical behavior is expected to be the same. In this case, alternative analysis methods for those isotopes would be identified in specific test instructions.

CFU = colony-forming units
GC/MS = gas chromatography/mass spectrometry
IC = ion chromatography
ICP/MS = inductively coupled plasma/mass spectrometry
KPA = kinetic phosphorescence
LSC = liquid scintillation counting
PNNL = Pacific Northwest National Laboratory
QPCR = quantitative polymerase chain reaction

This page intentionally left blank.

3 Gas-Phase Combined Bioreduction and Chemical Sequestration

Bioreduction combined with chemical sequestration is a potential two-step remediation approach for vadose zone treatment of contaminants. As a first step, biologically mediated reducing conditions would be generated by injecting a gas-phase amendment to promote reduction of reduction-oxidation (redox)-sensitive contaminants (e.g., technetium-99), resulting in removal of those contaminants from the aqueous phase into the solid phase. This would be followed by adding a chemical sequestering agent to allow sequestration of the reduced contaminants to limit their reoxidation back into the aqueous phase.

Laboratory treatability testing of the gas-phase combined bioreduction and chemical sequestration technology is selected for technetium-99 remediation (because of its high mobility under oxidizing conditions as pertechnetate oxyanion [technetium(VII)O_4^-]), primarily for the BY Cribs. The technology could also be applicable to BC Cribs and Trenches (200-BC-1 OU) (Table 3-1) (DOE/RL-2017-58). The effects of potential co-contaminants on technetium-99 treatability will be evaluated for uranium, iodine-129, nitrate, cyanide, and hexavalent chromium (Cr(VI)). For uranium and Cr(VI), it is anticipated that this technology may also be an effective treatment because these co-contaminants may use some of the reducing and/or sequestering capacities provided by the amendments. Nitrate and cyanide may also be biodegraded in a reducing environment. Iodine-129 as aqueous, and adsorbed iodide or iodate will likely show a slight increase in mobility as iodate would be reduced to the more mobile iodide species. However, considerable iodate is also incorporated into calcite and iron oxides, which may counter this effect. Iodine-129 mobility as a co-contaminant during this treatment will need to be monitored during laboratory testing.

The recommended laboratory treatability study is intended to quantify the effectiveness of combined biodegradation and chemical sequestration through gas-phase amendments for Hanford Site-specific, scale-up parameters that can be used in conjunction with the field-scale information in an Environmental Security Technology Certification Program (ESTCP) demonstration of gas-phase bioremediation (DOD, 2010, *In Situ Bioremediation of Perchlorate and Nitrate in Vadose Zone Soil using Gaseous Electron Donor Injection Technology (GEDIT)*) and the uranium reactive gas sequestration project (PNNL-27773; DOE/RL-2010-87, *Field Test Plan for the Uranium Sequestration Pilot Test*) to support future FS evaluations of this technology. An additional factor for determining effectiveness is the ability to deliver gaseous substrates to the targeted zones in the subsurface for technology deployment in the field. These were considered for determining the objectives for the testing of this technology (Section 3.2).

3.1 Technical Basis

The use of gas-phase amendments such as hydrogen and hydrocarbons for vadose zone bioremediation has been successfully demonstrated for perchlorate and nitrate biodegradation as part of the ESTCP program (DOE, 2010). This approach is also described in a U.S. Patent[1] (gaseous electron donor injection technology [GEDIT)]. Based on the ESTCP demonstration results, technetium-99 may be bioreduced using this method, as demonstrated with various ferrous iron minerals at the laboratory scale (Plymale et al., 2011, “Competitive Reduction of Pertechnetate ((TcO4-)-Tc-99) by Dissimilatory Metal Reducing Bacteria and Biogenic Fe(II)”; Fredrickson et al., 2004, “Reduction of TcO4- by sediment-associated biogenic Fe(II)”). Once technetium-99 is bioreduced and precipitated, then it may be amenable to long-term sequestration (e.g., coating with an aluminosilicate, phosphate, or carbonate) to reduce its mobility. This approach has been demonstrated in the laboratory using combined hydrogen

[1] Evans, P.J., “Process for In Situ Bioremediation of Subsurface Contaminants,” U.S. Patent 7,282,149, filed June 6, 2006, and issued October 16, 2007.

sulfide (reductant) and ammonia (sequestration) treatment (Szecsody et al., 2015, “Remediation of technetium in the vadose zone using reactive gasses NH3 and H2S”).

A scoping test of gas-phase bioreduction in Hanford Site sediments using a series of gaseous and volatile liquid substrates was previously conducted (PNNL-28055, *Evaluation of Central Plateau Remediation Alternatives: Interim Status Report*). The results indicated that the Hanford Site’s deep vadose zone likely has adequate conditions (e.g., nutrients and baseline microbial communities) to support in situ microbial remediation processes. For this scoping test, the substrate utilization was achieved at two different volumetric water contents (4% and 8%) for nearly all of the substrates tested. However, butyrate, pentane, hydrogen, and butyl acetate showed the highest levels of substrate utilization starting from as early as 5 days after treatment. Microbial responses were generally faster and more consistent at 8% volumetric water content compared to 4%. The results indicate the importance of substrate selection and the importance of aqueous thin films and pore-scale water connectivity for rapid response to gaseous substrates. Nutrient amendments (with high humidity to avoid desiccation) will need to be carefully considered for sustained activity and to increase the treatment zone of influence in deep vadose zone sediments.

Similarly, the use of carbon dioxide for in situ sequestration of contaminants was also tested through a series of batch experiments (PNNL-28055). Initial testing for contaminant sequestration using carbon dioxide was conducted for uranium and iodine. While 25% to 60% of aqueous iodine was removed from solution, the technology was ineffective for uranium and actually resulted in increased uranium solubility in Ringold Formation and Cold Creek unit sediments for the short duration of the experiments. In the previous study of uranium sequestration using carbon dioxide gas, uranium mobility increase was also observed over 1 to 2 months, followed by a mobility decrease in the 3- to 12-month timeframe (PNNL-18879, *Remediation of Uranium in the Hanford Vadose Zone Using Gas-Transported Reactants: Laboratory-Scale Experiments*). PNNL-28055 noted the sequestration approach as a promising two-step, reduction-sequestration process for technetium-99. The mechanism is hypothesized to be temporary immobilization by bioreduction of pertechnetate to technetium(IV)O_2, then coating by calcite (from the carbon dioxide gas) for creating a stable immobile form.

Delivery of carbon dioxide gas into vadose zone for uranium sequestration at the Hanford Site has previously been investigated at the laboratory scale as part of the investigation to decrease uranium mobility by in situ geochemical manipulation at low water content (PNNL-18879). A decrease in uranium mobility was observed for gas-phase amendments such as ammonia, hydrogen sulfide, phosphate, and carbon dioxide over the 12-month timeframe. The ammonia and carbon dioxide gas showed the greatest overall performance and ability to implement at field scale for uranium.

3.2 Laboratory Test Objectives

Table 3-1 presents the primary parameters targeted by the gas-phase combined bioreduction and chemical sequestration technology for technetium-99.

Table 3-1. Primary Parameters Targeted by the Gas-Phase Combined Bioreduction and Chemical Sequestration Technology

Primary COIs	**Tc-99**
Primary Treatment Zones/ Applicable 200-DV-1 Waste Sites	BY Cribs (unsaturated zone)
Secondary Treatment Zones/ Applicable 200-DV-1 Waste Sites	BC Cribs and Trenches (unsaturated zone)
Potential Co-Contaminants	U, I-129, NO_3^-, CN, and Cr(VI)
Potential Bioreducing Amendments	Pentane and butyrate
Potential Sequestration Amendments*	CO_2

Note: The COI shown in bold is a primary known contaminant target. Other COIs are potential co-contaminants to evaluate with primary COIs.

*Ammonia sequestration related data needs are addressed in PNNL-27773, *Deep Vadose Zone Treatability Test of Uranium Reactive Gas Sequestration for the Hanford Central Plateau: Final Report*. No additional testing was recommended in DOE/RL-2017-58, Draft A, *Technology Evaluation and Treatability Studies Assessment For The Hanford Central Plateau Deep Vadose Zone*. However, if CO_2 sequestration does not perform sufficiently to meet the success criteria, testing of ammonia sequestration following bioreduction will be included.

COI = contaminant of interest

- **Objective #1**: (Proof-of-Principle) Quantify the immobilized technetium-99 fraction and mass and order-of-magnitude immobilization rate through a combined treatment of gas-phase bioreduction and chemical sequestration in sediments spiked with technetium-99[2] (without co-contaminants), and investigate any potential remobilization.

- **Objective #2:** (Proof-of-Principle) Quantify the immobilized technetium-99 fraction and mass and order-of-magnitude immobilization rate through a combined treatment of gas-phase bioreduction and chemical sequestration in the presence of co-contaminants uranium, iodine-129, nitrate, cyanide, carbon-14, and Cr(VI), and investigate any potential remobilization of technetium-99 or other contaminants throughout the process.

Project team assessment: If Objectives #1 and #2 determine that the technology is promising (i.e., if over 35% of the contaminant is transformed to the endpoint expected), the following tasks will be executed:

- **Objective #3:** Determine the rate of technetium-99 reduction for top-performing gaseous substrates in unsaturated, field-contaminated sediments from BY Cribs and evaluate the influence of co-contaminants.

- **Objective #4:** Determine the rate and extent of technetium-99 incorporation into precipitates for top-performing reduction and sequestering agents to immobilize technetium-99 in field-contaminated BY Crib sediments and determine the influence of comingled contaminants.

[2] Addition of technetium-99 to a sediment results in mainly aqueous and adsorbed technetium-99, whereas field-contaminated sediments have technetium-99 mass in additional solid phases due to the decades of contact time. In these preliminary experiments, sediments spiked with technetium-99 will be used, and follow-on experiments will use technetium-99 field-contaminated sediments. Nitrate contamination appears to not form precipitates with decades of contact time with sediments; therefore, nitrate will be added to sediments in these preliminary experiments.

Project team assessment: If a minimum of 35% non-reoxidizable sequestration of technetium-99 is observed, the following task will be executed:

- **Objective #5:** Quantify the stability (i.e., longevity) of the immobilized technetium-99, and co-contaminant species, and determine the rate of reoxidation and mobilization.

Project team assessment: If technetium-99 mobility is reduced by 50% in 100 pore volumes for Objective #5, the following tasks will be executed:

- **Objective #6:** Quantify the transport properties of the selected gaseous substrates in the BY Cribs sediments at various degrees of water saturation.
- **Objective #7:** Quantify the transport properties of the sequestering agent in the BY Cribs sediments at various degrees of water saturation.

3.3 Laboratory Experimental Design and Procedures

The purpose of Objectives #1 and #2 is to provide a proof-of-principle for this technology and generally assess its overall effectiveness for the selected contaminants at site-specific conditions. If this step provides a desired success rate (as evaluated and decided by the project team), the subsequent objectives listed in Section 3.2 will be executed to provide specific information to aid in a potential field application and design process.

To address Objectives #1 and #2, a set of batch experiments will be used to determine the overall effectiveness of the technology in saturated conditions to avoid any limitations from an unsaturated system. These batch systems will include two principal treatments: (1) BY Crib sediments with technetium-99 contamination (added at representative concentrations) only, and (2) BY Crib sediments with technetium-99 contamination and potential co-contaminants (all added at representative concentrations). Nitrate will be tested separately because it is an electron acceptor and will have an effect on the bioreduction process; however, the remainder of the co-contaminants will be tested simultaneously.

A volume of gas-phase amendments (Table 3-1) will be introduced sequentially (first the bioreducing agent, then the sequestering agent) into the headspace of the batch containers through diffusion from a gas source (e.g., using a metallized bag that is impermeable to most gases). The system (i.e., the metallized bag size and gas-phase concentration) will be designed to provide sufficient amendments over time to the aqueous phase to drive reduction and sequestration reactions via partitioning of the amendments between the aqueous and gas phases. This will require calculating an appropriate mass loading to maximize the reductive and sequestration capacities in the sediments. Gas-phase amendments will be mixed with nitrogen gas to ensure anoxic conditions. A preliminary assessment of a “clean” system (i.e., pore water with BY Crib sediments containing only the background microbial population without any contaminants) may also be needed to determine the timeframe for necessary microbial growth using the selected substrates. This preliminary assessment (precursor to the experiments addressing the objectives) will help determine the optimal water-to-sediment ratio for the experimental systems to achieve appropriate contaminant exposure and bacterial growth.

For Objectives #1 and #2, the amendments will be applied sequentially to avoid any interference of the sequestering agent on the microbiological system required to develop the reduced conditions because the sequestering agent is expected to manipulate the system pH. Following the bioreduction and sequestration phases, the batch systems will be exposed to oxidizing conditions to measure the remobilization potential.

A number of sacrificial replicates of the batch systems (all in triplicate) will be used to quantify changes in primary contaminant and co-contaminant concentration in aqueous phase. Microbial biomass will be analyzed from aqueous and sediment sub-samples to correlate the observed technetium-99 reduction (removal from the aqueous phase) to increase in biomass in the reductive system. Solid-phase characterization of immobilized technetium-99 will be evaluated by sequential extractions. Total organic and inorganic carbon will also be monitored.

To address Objective #3, the top performing gaseous substrate will be selected from the previous experiments. This anoxic gas amendment will be introduced to a set of unsaturated soil columns operated in batch mode (stop flow) or vials by diffusion using a similar system (as previously described). Unsaturated columns will be set up at two different moisture content levels (4% and 8%) to achieve conditions that are similar to the field conditions in the vadose zone. For these experiments, field-contaminated sediments are preferred, and sediment and contaminant characterization is needed to determine whether the technetium-99 concentrations in these sediments are comparable to typical conditions observed in the BY Cribs. In the case where field contaminated sediments are not available (or technetium-99 concentrations are not sufficient), BY Crib sediments will be spiked with technetium-99. The selected co-contaminants will be added to these sediments at site-specific concentrations.

Sufficient sacrificial replicates of the column systems (in triplicate) will be used to address Objectives #3, #4, and #5 (if needed) and to allow for monitoring of the aqueous-phase technetium-99 concentrations and sediment-phase analyses at different time intervals. Reduction rate and extent will be quantified based on the incremental observations of technetium-99 removal from the aqueous phase. It is assumed that the sediment reduction capacity will be achieved when the aqueous concentration of technetium-99 stabilizes.

Following reduction, remaining replicate columns will be exposed to the sequestrating agent (carbon dioxide) to assess the rate and extent of technetium-99 sequestration to address Objective #4. Sediment associated technetium-99 will be characterized by performing sequential extractions using deoxygenated water (to quantify soluble technetium-99), oxygenated water (to quantify the rapidly oxidizable/reversible immobilization), and an acid (to quantify the technetium-99 fraction not readily dissolved).

If a desired amount of sequestration is achieved during these column experiments, the remaining unsaturated columns will be used to address Objective #5 to determine the stability of the immobilized technetium-99. This effort will involve surface-phase analyses (using spectroscopic techniques) and a liquid-phase leaching experiment where oxygenated groundwater will be applied to these columns. After the oxygen breakthrough, potential technetium-99 release will be monitored for 100 pore volumes of water flowing through these columns. Note that the site specificity of groundwater formulation will be an important factor in these leaching tests.

Finally, if a 50% reduction is observed in technetium-99 mobility during the leaching experiments, the transport properties of the selected gaseous substrate and sequestering agents will be quantified to address Objectives #6 and #7. This will involve using a column apparatus to calculate and verify partitioning of the gas amendment for bioreduction into the pore water and for partitioning and precipitation of the sequestering agent in pore water.

This page intentionally left blank.

4 Gas-Phase Bioremediation

Gas-phase bioremediation in the vadose zone involves degradation of contaminants through in situ biostimulation of microbial processes by injecting reactive gases (Höhener and Ponsin, 2014, "In situ vadose zone bioremediation"). The treatability testing of this technology is selected for nitrate in the unsaturated zones because it is a potential source to groundwater. Nitrate is one of contaminants of concern identified for the 200-ZP-1 and 200-UP-1 OUs. Table 4-1 presents the selected primary parameters targeted for this technology as identified in DOE/RL-2017-58. The relevant co-contaminants to evaluate with nitrate are cyanide and Cr(VI). Known specific applicability of this treatment is for cyanide in the BY Cribs.

Laboratory treatability testing of this technology will focus on generating Hanford Site-specific information needed to determine the most appropriate gas-phase amendments and technology effectiveness using Hanford Site sediments and native microbial populations, pore water chemistry, and moisture content.

4.1 Technical Basis

As described in Chapter 3, the use of gas-phase carbon amendments has been successfully demonstrated for degradation of perchlorate and nitrate in the vadose zone as part of the ESTCP program (DOD, 2010). The approach is also described in a U.S. Patent for GEDIT. Based on the ESTCP demonstration results and preliminary laboratory testing (PNNL-28055), gas-phase bioremediation may be an effective treatment to reduce the mass of nitrate and cyanide and to immobilize chromate.

Evans and Trute, 2006, "In situ bioremediation of nitrate and perchlorate in vadose zone soil for groundwater protection using gaseous electron donor injection technology," stimulated the biodegradation of nitrate and perchlorate using an aqueous electron donor injection technology. Laboratory microcosm studies demonstrated that hydrogen and ethanol promoted nitrate and perchlorate reduction in vadose zone soil. The moisture content was an important factor during these experiments, and the transport properties of electron donors showed wide variation. Ethyl acetate and butyraldehyde were transported through column studies more rapidly than butyl acetate and ethanol. As much as 100% of the nitrate was reduced in laboratory columns treated with ethyl acetate.

For Hanford Site-specific application, a scoping test of gas-phase bioreduction was conducted using a series of gaseous and volatile liquid substrates (PNNL-28055). The results indicated that the Hanford Site's deep vadose zone likely has adequate conditions (e.g., nutrients and baseline microbial communities) to support in situ microbial remediation. For this scoping test, microbiological reduction of Hanford Site sediments was achieved at two different volumetric water contents (4% and 8%) for nearly all substrates tested. Butyrate, pentane, ethane, hydrogen, and butyl acetate generated rapid microbial response and achieved reduced sediment conditions within 5 days following treatment. Microbial responses were generally faster and more consistent at 8% volumetric water content compared to 4%. The results indicate the importance of substrate selection and aqueous thin films and of pore-scale water connectivity to elicit a rapid microbiological response to gaseous substrates. Nutrient amendments (with high humidity to avoid desiccation) will need to be carefully considered for sustained activity and to increase the treatment zone of influence in deep vadose zone sediments.

4.2 Laboratory Test Objectives

Table 4-1 presents the primary parameters targeted by the gas-phase bioremediation technology.

Table 4-1. Primary Parameters Targeted by the Gas-Phase Bioremediation Technology

Primary COIs	**NO_3^-**
Primary Treatment Zones/ Applicable 200-DV-1 Waste Sites	Unknown
Secondary Treatment Zones/ Applicable 200-DV-1 Waste Sites	Unknown
Potential Co-Contaminants	Cr(VI) (S and T Cribs), CN (BY Cribs)
Potential Bioremediation Amendments	Pentane and butyrate

Note: The COI shown in bold is a primary known contaminant targets. Other COIs are potential co-contaminants to evaluate with primary COIs.

COI = contaminant of interest

- **Objective #1 (proof-of-principle):** Determine the percent mass of nitrate that is reductively transformed to nitrogen gas following the delivery of gaseous substrates with saturated sediments from the BY Cribs.
- **Objective #2 (proof-of-principle):** Determine the percent mass of nitrate that is reductively transformed in the presence of potential co-contaminants (i.e., Cr(VI) and cyanide) following the delivery of gaseous substrates with saturated sediments from the BY Cribs.

Project team assessment: If Objectives #1 and #2 determine that the technology is promising (i.e., if over 35% of the nitrate is transformed to nitrogen gas), the following task will be executed using the most effective bioremediation amendment determined:

- **Objective #3:** Determine the rate and extent of nitrate transformation (at different initial contaminant concentrations) in the unsaturated BY Crib sediments for the selected gaseous substrates (at varying substrate concentrations and degrees of water saturation) with and without co-contaminants, and quantify the unit mass of gaseous substrate required for nitrate transformation.

Project team assessment: If a minimum of 50% nitrate transformation to nitrogen gas is observed above, the following task will be executed. If this information is available from the gas-phase combined bioreduction and chemical sequestration testing in Chapter 3 (Objective #6), this task will not be executed.

- **Objective #4:** Quantify the transport properties of the selected gaseous substrate in the BY Cribs sediments at various degrees of water saturation.

4.3 Laboratory Experimental Design and Procedures

The purpose of Objective #1 is to provide a proof-of-principle for this technology and generally assess its overall effectiveness for the selected contaminants at site-specific conditions. If this step provides a desired success rate (as evaluated and decided by the project team), the subsequent objectives listed in Section 4.2 will be executed to provide specific information to aid in a potential field application and design process.

To address Objectives #1 and #2, a set of microcosm systems will be used under ideal saturated conditions to avoid any limitations from an unsaturated system to determine the overall effectiveness of the technology. These microcosm systems will include two principal treatments: (1) BY Crib sediments with nitrate contamination (added at representative concentrations) only, and (2) BY Crib sediments with nitrate contamination and potential co-contaminants (all added at representative concentrations).

A volume of gas-phase amendments (Table 4-1) will be introduced into the headspace of the batch containers through diffusion from a gas source (e.g., using a metallized bag as a source of gas amendment). The system (i.e., the metallized bag size and gas-phase concentration) will be designed to provide sufficient amendments over time to the aqueous phase to drive degradation reactions via partitioning of the amendments between the aqueous and gas phases. This will require calculating appropriate mass loading to maximize the reductive capacity in the sediments. Gas-phase amendment will be mixed with nitrogen gas to ensure anoxic conditions for bioreduction. A preliminary assessment of a "clean" system (i.e., pore water with BY Crib sediments containing only the background microbial population without any contaminants) may also be needed to refine the timeframe for necessary microbial growth using the selected substrates. This preliminary assessment (precursor to the experiments addressing the objectives) will help determine the optimal water-to-sediment ratio for the experimental systems to achieve appropriate contaminant exposure and bacterial growth.

A number of sacrificial replicates of the batch systems (all in triplicate) will be used to monitor concentration changes over time for the primary contaminant and co-contaminants in the aqueous phase throughout the experiment to monitor contaminant removal from the solution phase. Nitrate and cyanide will be lost from the system because they are degraded, and Cr(VI) will be reduced to stable Cr(VI). Microbial biomass will be quantified to correlate the observed changes in nitrate concentrations to the increase in biomass in the microcosm system. Potential intermediate products such as nitrite and ammonia will also be monitored.

To address Objective #3, the top-performing substrate will be selected from the previous experiments. A range of concentrations (based on the initial experiments) of anoxic gas amendment will be introduced to a set of partially saturated batch systems with two different moisture levels (4% and 8%). Varying concentrations of nitrate and co-contaminants will be added to the system with the BY Cribs sediments to evaluate the effects of contaminant concentration on the microbial performance. Sufficient replicates of the batch systems will be used to evaluate the rate and extent of nitrate transformation over time, co-contaminant degradation, the accumulation of reaction products, and changes in microbial biomass. If a desired amount of nitrate degradation is achieved during the batch experiments, the remaining systems will be used to address Objective #4 to evaluate the transport properties of the gaseous substrate. This will involve using a column apparatus for calculating and verifying the partitioning of the gas amendment into pore water.

This page intentionally left blank.

5 Gas-Phase Chemical Sequestration

Gas-phase sequestration can be used in the vadose zone to produce fewer mobile precipitates of some inorganic contaminants and is considered as a potential remediation approach for the Central Plateau.

Laboratory treatability testing of the gas-phase chemical sequestration technology is selected for potential iodine-129 remediation in the A and S Crib source areas with the evaluation of the effects of potential co-contaminants uranium, strontium-90, technetium-99, and Cr(VI); however, the need for vadose zone treatment at these locations has not yet been established. Therefore, this treatability test is of lower priority and may not be conducted pending the outcome of additional Central Plateau risk-based investigations.

5.1 Technical Basis

Gas-phase chemical sequestration can render certain inorganic contaminants less mobile through sequestration as a result of sediment dissolution/precipitation reactions driven by reactive gases. An evaluation of several reactive gas injections into the subsurface has been conducted for reducing uranium mobility in the vadose zone at the Hanford Site (Szescody et al., 2010). This work involved injecting gaseous hydrogen sulfide, sulfur dioxide, carbon dioxide, ammonia, and two organo-phosphate gases (triethyl phosphate and dimethyl methyl phosphonate), in addition to other reactants, delivered as a mist, foam, or liquid into low-water-content sediments into one-dimensional columns packed with uranium-contaminated sediments. Advection of reactive gases was found to be the easiest to implement into low-water-content sediments in the laboratory-scale experiments. Overall, the ammonia and carbon dioxide gas showed the most effective geochemical performance and ability to implement at field scale. Ammonia injection as a reactive gas for uranium sequestration has also been investigated for a field-scale treatability study (PNNL-27773).

Recent laboratory evaluations have shown that iodate (an important chemical species of iodine-129 and iodine-127) can be co-precipitated with carbonates (PNNL-24709, *Conceptual Model of Iodine Behavior in the Subsurface at the Hanford Site*). Iodine association with carbonate precipitates has also been observed in recent vadose zone characterization studies (PNNL-26208; PNNL-26266), although those chemical extractions could also indicate iodine associated with iron oxides. Thus, there is technical basis to suggest that creating conditions for carbonate precipitation may provide in situ treatment for iodine-129 contamination. Gas-phase carbon dioxide injection could induce carbonate precipitation, resulting in iodate co-precipitation and reducing iodine-129 mobility. The technology may also reduce the mobility of uranium, Cr(VI), and strontium-90 (Mucci and Morse, 1983, “The Incorporation of Mg2+ and Sr2+ into Calcite Overgrowths - Influences of Growth-Rate and Solution Composition”; Szescody et al., 2010).

5.2 Laboratory Test Objectives

Table 5-1 presents the primary parameters targeted by the gas-phase chemical sequestration technology.

Table 5-1. Primary Parameters Targeted by the Gas-Phase Chemical Sequestration Technology

Primary COIs	**I-129**
Primary Treatment Zones/ Applicable 200-DV-1 Waste Sites	216-S-9
Secondary Treatment Zones/ Applicable 200-DV-1 Waste Sites	216-A-10, 216-A-5, 216-S-7
Potential Co-Contaminants	U, Sr-90, Tc-99, and Cr(VI)
Potential Sequestration Treatments*	CO_2

Note: The COI shown in bold is a primary known contaminant targets. Other COIs are potential co-contaminants to evaluate with primary COIs.

*Ammonia injection related data needs are addressed in PNNL-27773, *Deep Vadose Zone Treatability Test of Uranium Reactive Gas Sequestration for the Hanford Central Plateau: Final Repor*t. No additional testing was recommended in DOE/RL-2017-58, Draft A, *Technology Evaluation and Treatability Studies Assessment For The Hanford Central Plateau Deep Vadose Zone*.

COI = contaminant of interest

- **Objective #1: (proof-of-principle):** Quantify the fraction and mass of iodine sequestered, and order-of-magnitude sequestration rate through a gas-phase treatment for iodine-129-contaminated sediments[3] (representative of the A and S Cribs) with no co-contaminants and investigate any potential remobilization.
- **Objective #2: (proof-of-principle):** Quantify the fraction and mass of iodine sequestered, and order-of-magnitude sequestration rate through a gas-phase treatment for iodine-129-contaminated sediments (representative of the A and S Cribs) in the presence of co-contaminants uranium, strontium-90, technetium-99, and Cr(VI) (including the rate of co-contaminant loss from the aqueous phase); and investigate potential remobilization of iodine-129 and other co-contaminants throughout the process.

Project team assessment: If Objectives #1 and #2 determine that the technology is promising (i.e., if over 35% of the contaminant is sequestered to the endpoint expected), the following task will be executed:

- **Objective #3:** Quantify the iodine-129 (or iodine-127) sequestration at varying degrees of water saturation and in the presence of co-contaminants.

Project team assessment: If <35% non-reoxidizable sequestration of iodine-129 is observed or the information is available from the combined bioreduction and chemical sequestration technology testing, as described in Chapter 3, the following task will not be executed:

- **Objective #4:** Quantify the stability of the immobilized contaminants and co-contaminant species, as well as the potential remobilization rates.

[3] Iodine-127-contaminated sediment will be used as a surrogate to iodine-129 due to higher concentrations present.

Project team assessment: If <50% mobility reduction is observed or the information is available from the combined bioreduction and chemical sequestration technology testing, as described in Chapter 3, the following task will not be executed:

- **Objective #5:** Quantify the transport of carbon dioxide gas into sediments (i.e., retardation and gas-to-liquid partitioning rate) at varying low water saturation levels (2% to 8%) and determine gas saturation with distance from the injection point (via modeling only).

5.3 Laboratory Experimental Design and Procedures

The purpose of Objective #1 is to provide a proof-of-principle for this technology and generally assess its overall effectiveness for the selected contaminants at site-specific conditions. If this step provides a desired success rate (as evaluated and decided by the project team), the subsequent objectives listed in Section 5.2 will be executed to provide specific information to aid in a potential field application and design process.

To address Objectives #1 and #2, a set of batch systems will be used in saturated conditions to avoid any limitations from an unsaturated system to determine the overall effectiveness of the technology. The batch systems will include two principal treatments: (1) sediments representative of conditions at the A and S Cribs[4] with iodine-129/iodine-127 contamination only, and (2) with iodine-129/iodine-127 contamination and potential co-contaminants (all added at representative concentrations).

A volume of gas-phase amendment (Table 5-1) will be introduced into the headspace of the batch containers through diffusion from a gas source (e.g., using a metallized bag as a source of gaseous amendment). The system (i.e., the metallized bag size and gas-phase concentration) will be designed to provide sufficient amendments over time to the aqueous phase to drive sequestration reactions via partitioning of the amendments between the aqueous and gas phases. This will require calculating an appropriate mass loading to maximize the sequestration capacity in the sediments.

A number of sacrificial replicates of the batch systems (all in triplicate) will be used to monitor iodine-129/iodine-127 speciation and aqueous concentration changes over time, as well as the concentrations of co-contaminants in the aqueous phase throughout the experiment. In addition to monitoring aqueous iodine-129/iodine-127 concentrations for reduction, sequestration, and reoxidation stages of the experiments, solid-phase iodine-129/iodine-127 species and concentrations will also be evaluated via appropriate extraction techniques.

To address Objective #3, a set of unsaturated soil columns operated in batch mode (stop flow) will be used. Unsaturated columns will be set up at two different moisture content levels (4% and 8%) to achieve conditions that are similar to the field conditions in the vadose zone. For these experiments, field contaminated sediments are preferred, and a sediment and contaminant characterization is needed. The selected co-contaminants will be added to these sediments at relevant concentrations.

Sufficient sacrificial replicates of the column systems (in triplicate) will be used to address Objectives #3, #4, and #5 (if needed) and to allow for monitoring of the aqueous-phase iodine-129/iodine-127 concentrations and sediment-phase analyses at different time intervals. Sequential extractions will be applied for analyzing the sediment-associated iodine-129/iodine-127 by using water and an acid.

[4] Surrogate sediments may need to be used.

If a desired amount of sequestration is achieved during these column experiments, the remaining unsaturated columns will be used to address Objective #4 to determine the stability of the immobilized iodine-129/iodine-127. This effort will involve surface-phase analyses and a liquid-phase leaching experiment where groundwater with a tracer will be applied to these columns. After tracer breakthrough, potential iodine-129/iodine-127 release will be monitored for 100 pore volumes of water flowing through these columns. Note that groundwater formulation will be an important factor in these leaching tests.

If a 50% reduction is observed in iodine-129/iodine-127 mobility during the leaching experiments, the transport properties of the selected gaseous sequestering agent will be quantified to address Objective #5. This will involve using a column apparatus for calculating and verifying the partitioning and precipitation of the sequestering agent in pore water.

6 Particulate-Phase Chemical Sequestration

Deployment of nano- or micron-sized reactive particles into subsurface for sequestering mobile contaminants is considered in this treatability study for technetium-99 and uranium remediation in perched water aquifer and also for a water table PRB application. For effective treatment, the emplaced reactive particles need to support specific reactions, result in stable contaminant forms, and be effectively distributed in situ via a limited number of injection locations. The treatability study will also investigate the effects of potential co-contaminants of iodine-129, Cr(VI), and nitrate in the BY Cribs water table PRB conditions, and only nitrate in the perched water conditions at concentrations that are relevant to these zones.

6.1 Technical Basis

The use of apatite, a calcium-phosphate mineral ($Ca_{10}(PO_4)_6(OH)_2$), for radioactive waste cleanup (whether a PRB or a waste form) is the focus of a growing body of research. Apatite minerals sequester elements into their molecular structures via isomorphic substitution, whereby elements of similar physical and chemical characteristics replace calcium, phosphate, or hydroxide in the hexagonal structure (Hughes et al., 1989, "Structural Variations in Natural F, OH, and Cl Apatites"; Spence and Shi, 2005, *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes*).[5] Apatite removes radionuclides from solution by surface sorption, ion exchange, and surface precipitation and by providing phosphate to precipitate low-solubility minerals (Rigali et al., 2016, "Radionuclide removal by apatite"). Stannous apatite-based waste forms, PRBs, and separation processes have shown the potential for technetium-99 management (Asmussen et al., 2016, "The function of Sn(II)-apatite as a Tc immobilizing agent"; LAB-RPT-12-00001, *Laboratory Report on the Reduction and Stabilization (Immobilization) of Pertechnetate to Technetium Dioxide Using Tin(II) Apatite*; SAND2003-3360, *Anionic Sorbents for Arsenic and Technetium Species*; Billinghurst et al., 1981, "Investigation of the interaction of hydroxyapatite with technetium in association with stannous pyrophosphate"; PNNL-23667, *Evaluation of Technetium Getters to Improve the Performance of Cast Stone*; RPP-53855, *Reduction and Stabilization [Immobilization] of Pertechnetate to an Immobile Reduced Technetium Species Using Tin(II) Apatite*). Uranium sequestration can occur by apatite addition due to the creation of autunite, coating of apatite on uranium surface phases, and uranium adsorption to apatite (Wellman et al., 2005, "Synthesis and characterization of sodium meta-autunite, Na[UO2PO4]·3H2O"; Wellman et al., 2006, "Comparative Analysis of Soluble Phosphate Amendments for the Remediation of Heavy Metal Contaminants: Effect on Sediment Hydraulic Conductivity"), so the use of Sn(II)-coated apatite will likely also sequester uranium. The co-contaminant chromate would be reduced by the Sn(II) and precipitate as chromium hydroxide, and nitrate may also be reduced. Therefore, presence of co-contaminants chromate and nitrate would decrease the Sn-apatite reactivity for pertechnetate. Iodine-129 (as primarily iodate) would likely be reduced, increasing its mobility to a small extent.

A treatability study was conducted to evaluate the ability of jet injection technology to deliver different apatite materials or apatite-forming chemical solutions into the vadose zone to install a PRB in the 100-N Area (SGW-47062, *Treatability Test Report for Field-Scale Apatite Jet Injection Demonstration for the 100-NR-2 Operable Unit*). Water was used for delivering for pre-formed apatite-only tests. Jet injection was observed to be a viable method for emplacing phosphate and pre-formed apatite in the vadose zone. While injection of phosphate-only treatment resulted in a greater fraction of strontium-90

[5] Because of the extensive substitution into the general apatite structure, more than 350 apatite minerals have been identified (Moëlo et al., 2000, "La lulzacite, Sr2Fe2+(Fe2+,Mg)2Al4(PO4)4(OH)10, un nouveau phosphate de strontium (Saint-Aubin-des-Châteaux, Loire-Atlantique, France)").

incorporated into phosphate precipitates, it was noted that, over time, zones that received solid-phase apatite were expected to also incorporate additional strontium-90 mass into the apatite.

The existing data show best potential effectiveness for technetium-99 and uranium removal by injecting reactive particulate matter with apatite sequestration.

6.2 Laboratory Test Objectives

Table 6-1 presents the primary parameters targeted by the particulate-phase chemical sequestration technology.

Table 6-1. Primary Parameters Targeted by the Particulate-Phase Chemical Sequestration Technology

Primary COIs	**U, Tc-99**
Primary Treatment Zones/ Applicable 200-DV-1 Waste Sites	Perched water, below BY Cribs water table permeable reactive barrier
Secondary Treatment Zones/ Applicable 200-DV-1 Waste Sites	216-U-1&2, S-SX Tank Farm, C Tank Farm, BC Cribs and Trenches
Potential Co-Contaminants	Cr(VI) (S and T Cribs), I-129 (A Cribs), NO_3^-
Potential Sequestration Treatments	Stannous apatite particle injection

Note: The COIs shown in bold are primary known contaminant targets. Other COIs are potential co-contaminants to evaluate with primary COIs.

COI = contaminant of interest

- **Objective #1 (proof-of-principle):** Quantify the decrease in contaminant (technetium-99 and uranium) mass and order-of-magnitude sequestration rate for the treatment combinations summarized in Table 6-2.

Table 6-2. Experimental Treatments for Objective #1 of the Laboratory Testing of the Particulate-Phase Chemical Sequestration Technology

Treatment Zone/ Sediment-Pore Water	Co-Contaminants Added	Technology Treatments Tested
BY Cribs pore water (no sediment)	—	Stannous apatite [a]
BY Cribs sediment/pore water	—	Stannous apatite [a]
BY Cribs sediment/delivery fluid [b]	—	Stannous apatite [a]
BY Cribs sediment/pore water	Cr(VI), I-129, NO_3^-	Stannous apatite [a]
Perched water pore water (no sediment)	NO_3^- (added as $NaNO_3$)	Stannous apatite [a]
Perched water sediment/delivery fluid [b]	NO_3^- (added as $NaNO_3$)	Stannous apatite [a]

a. Stannous apatite will be synthesized based on LAB-RPT-12-00001, *Laboratory Report on the Reduction and Stabilization (Immobilization) of Pertechnetate to Technetium Dioxide Using Tin(II) Apatite.*

b. A typical delivery fluid (e.g., associated with hydraulic fracturing) will be selected for this testing.

Project team assessment: If Objective #1 determines that the technology is promising (i.e., if over 35% of the contaminant is transformed to the endpoint expected), the following task(s) will be executed:

- **Objective #2:** Determine the sequestration rates for primary contaminants and evaluate co-contaminant effects for (1) perched water application and (2) BY Crib application.
- **Objective #3:** Quantify the longevity of the immobilized contaminants and co-contaminant species, and the potential remobilization rates for (1) perched water application and (2) BY Crib application.

6.3 Laboratory Experimental Design and Procedures

The purpose of Objective #1 is to provide a proof-of-principle for this technology and generally assess its overall effectiveness for the selected contaminants at site-specific conditions. If this step provides a desired success rate (as evaluated and decided by the project team), the subsequent objectives listed in Section 6.2 will be executed to provide specific information to aid in a potential field application and design process.

To address Objective #1, a set of batch systems will be used in saturated conditions (at a sediment-to-water ratio of about 2:1) to determine the overall effectiveness of this technology. A total of seven different combinations of treatment systems will be tested with the batch settings, as shown in Table 6-2. In these experiments, a set of no sediment treatments will be used to evaluate the pure sequestration capability of the injected particles. These samples will be considered for additional surface-phase analyses to identify the location of uranium and technetium-99 in relationship to the particles (if possible) to confirm that the desired mechanisms are occurring for immobilization.

All of the treatments will be executed in triplicate, with sufficient replicates for intermediate incubation time analyses (a minimum of four). The headspace for the batch settings will contain nitrogen gas. In addition to the selected treatment combinations and a default no-treatment sediment control (used in all the experimental approaches described in this document), a microbial control (a sterilized sediment system) will also be used in this setting to allow for evaluation of any effects of natural background microbial population on treatment effectiveness. Note that the two types of environmental settings tested herein (BY Cribs and perched water) will also support this evaluation with the differences between their native background microbial environment.

Stannous apatite particles will be synthesized (based on LAB-RPT-12-00001) and introduced into the batch containers. The appropriate loading of these amendments will be determined based on the surface area calculations to achieve the desired treatment capacity in the system (comparable to liquid-phase loading discussed in Chapters 8 through 10).

With sufficient replicates, the rate and extent of sequestration will be determined by monitoring the aqueous-phase concentrations of uranium and technetium-99, and also the co-contaminants (where they were applied). Solid-phase analysis will also be conducted through appropriate sequential extraction techniques. For technetium-99 surface association of Hanford Site groundwater, oxic Hanford Site groundwater and strong acid will be used to determine the mobile, desorbed, and immobilized fractions. Uranium sequential extractions will be designed to evaluate the contaminant transformation by using Hanford Site groundwater (for aqueous uranium); oxic Hanford Site groundwater (readily desorbed, ion exchange, and uranium); acetic acid (slow dissolution from most carbonates); and strong acid (dissolution of all immobile phases). Co-contaminants will be analyzed in both aqueous and surface phases (sequential extraction liquid-phase samples).

To address Objective #2(1) for representative rate determination for perched water application, a long column setting will be used in a stop-flow fashion for a volumetric treatment (i.e., essentially a no-flow batch experiment but at a high sediment-to-water ratio of the aquifer). Short columns will also be packed at the same time and run in parallel for use in column leaching experiments to address Objective #3(1). These experiments will be conducted in duplicate.

The long columns for sequestration rate determination will allow for a high sediment-to-water ratio that would more closely resemble field conditions. All reactants (contaminants, co-contaminants, and the phosphate amendment) will be mixed and packed into the columns initially. At specific times ranging from hours to hundreds of hours, a small volume of groundwater (e.g., one-tenth of a pore volume) will be injected into the inlet, resulting in an effluent sample to be pushed from the end of the column; this effluent will be monitored for contaminant mobility change. Each effluent sample will represent an incrementally longer residence time for the amendment in the column. Necessary residence and sampling times for the sequestration reaction experiments will be determined based on the batch experiments conducted for Objective #1. The same aqueous and sediment analyses used in the batch experiments (described previously) will also be used with these column settings. Sequential extractions will be conducted to evaluate contaminant distribution in different solid phases and to calculate the mass balance, as well as any mass leaving the columns. These extractions will be applied at various increments along the column to determine the effect of residence time on the sequestration extent.

To address Objective #3(1), another set of experiments will be used with small columns. All reactants (contaminants, co-contaminants, and the stannous apatite amendment) will be mixed and packed into the columns initially. After the same full incubation time as for the long columns, groundwater will be injected at a slow flow rate for at least 100 pore volumes (approximating natural groundwater conditions) to evaluate the leaching characteristics of the treated sediments. The same aqueous and sediment analyses previously described will also be used with these column settings. The leaching tests with the injection of oxic Hanford Site groundwater will allow for evaluation of the stability of the sequestered contaminants.

To address Objective #2(2) for BY Crib water table PRB application, short columns will be packed with uncontaminated sediment, which will then be injected with 5 to 10 pore volumes of the amendment solution (particulate amendment and carrier fluid), approximating a field-scale injection downgradient of contaminants. Groundwater contaminated with technetium-99 and uranium (with or without co-contaminants) will be injected into these columns in flow conditions relevant to the BY Cribs. The columns will be run until near full breakthrough to determine the estimated capacity and contaminant sequestration rates. Bromide will also be run through the columns as a tracer to track the regular breakthrough behavior. Once the near full breakthrough is achieved, these columns will be evaluated for any leaching with the injection of oxic Hanford Site groundwater to address Objective #3(2). For leaching experiments, an appropriate number of pore volume flow will be calculated and applied based on a typical groundwater/water table application in the BY Cribs subsurface conditions.

7 Particulate-Phase Combined Chemical Reduction and Sequestration

Deployment by injection of nanoparticles or micron-sized particles may be effective for directly treating targeted hot spots or for creating a horizontal PRB for saturated zone applications (although not for unsaturated zone applications). Particulates such as sulfur-modified iron (SMI) have been developed as reactive materials that can be used in situ to produce stable, reduced-phase precipitates of some inorganic contaminants. Sequestration reactions following contaminant reduction can achieve a long-lasting reduction in contaminant mobility. However, the emplaced reactive particles need to support suitable reactions, result in stable contaminant forms, and be effectively distributed in situ via a limited number of injection locations.

This recommended treatability study for particulate-phase combined chemical reduction and sequestration is intended to determine the effectiveness of the technology for uranium and technetium-99 treatment in perched water and/or for a water table PRB application beneath the BY Cribs.
The treatability study will consider perched aquifer and water table water chemistry, contaminant concentrations, and co-contaminant interactions.

7.1 Technical Basis

In situ manipulation of redox conditions has been tested and implemented in bench-scale experimental settings and at the Hanford Site field conditions for reducing contaminant species via particulate-phase amendments. Reducing amendments such as zerovalent iron (ZVI) and SMI are demonstrated to effectively reduce uranium and technetium-99 (PNNL-28054, *Evaluation of Perched Water Post-Extraction Remedy Technologies: Interim Status Report*). Recent bench-scale testing (PNNL-28054) showed complete reduction of uranium and technetium-99 by applying high-concentration ZVI and SMI (at 1.0%). However, reduction alone is not a viable long-term remediation strategy, especially for technetium-99, as the contaminants can be reoxidized. In these bench-scale testing efforts, apatite was also applied as the sequestration agent following SMI and ZVI. The results demonstrated stable immobilized form of contaminants with almost no reoxidation effects.

Uranium treatment in water-saturated sediments using phosphate has been shown to be effective in Hanford Site 300 Area sediments (PNNL-21733, *Use of Polyphosphate to Decrease Uranium Leaching in Hanford 300 Area Smear Zone Sediment*; Wellman et al., 2006; Wellman et al., 2008, "Sequestration and retention of uranium(VI) in the presence of hydroxylapatite under dynamic geochemical conditions"; PNNL-17818, *300 Area Treatability Test: Laboratory Development of Polyphosphate Remediation Technology for In situ Treatment of Uranium Contamination in the Vadose Zone and Capillary Fringe*; Wellman et al., 2005; Wellman et al., 2007, "Dissolution kinetics of synthetic and natural meta-autunite minerals, X 3− n (n) + [(UO 2)(PO 4)] 2 xH 2 O, under acidic conditions"); Hanford Site 200 East Area sediments (Shi et al., 2009, "Inhibition Effect of Secondary Phosphate Mineral Precipitation on Uranium Release from Contaminated Sediments"); sediments in Rifle, Colorado (PNNL-25303, *Use of a Ca-Citrate-Phosphate Solution to Form Hydroxyapatite for Uranium Stabilization of Old Rifle Sediments: Laboratory Proof of Principle Studies*; Pan et al., 2016, "Phosphate-Induced Immobilization of Uranium in Hanford Sediments"); and at other sites (Lammers et al., 2017, "Groundwater uranium stabilization by a metastable hydroxyapatite"). The mechanisms that decrease uranium mobility with phosphate addition are precipitation of a uranium-phosphate mineral (autunite), increased uranium sorption to calcium-phosphate precipitates (apatite), and apatite coating on existing uranium surface phases. Similarly, uranium treatment using ammonia gas injection in the vadose zone sediments has been shown to be effective for reducing the mobility of water leachable uranium by both the formation of uranium silicates and coating of aluminosilicates on top of existing uranium surface phases (Szecsody et al., 2012, "Geochemical and Geophysical Changes during Ammonia Gas Treatment of

Vadose Zone Sediments for Uranium Remediation"; PNNL-18879). Alkaline treatment with ammonia gas in the vadose zone has been extended into water-saturated systems using both NH_4OH and NaOH (Emerson et al., 2017, "Effects of ammonium on uranium partitioning and kaolinite mineral dissolution"; Emerson et al., 2018, "Potential for U sequestration with select minerals and sediments via base treatment").

An apatite PRB was designed and implemented successfully using an injection of calcium-citrate/ sodium-phosphate to reduce the strontium-90 flux from the groundwater along the 100-N Area shoreline to the Columbia River along a 701 m (2,300 ft) wide zone (DOE/RL-2016-68, *Calendar Year 2016 Annual Summary Report for the 100-HR-3 and 100-KR-4 Pump and Treat Operations, and 100-NR-2 Groundwater Remediation*). The same calcium-citrate/sodium-phosphate injection solution was used for a single well demonstration for uranium contamination at the Rifle, Colorado site and has reduced uranium mobility for over a year (PNNL-25303). A different phosphate solution (sodium-phosphate and sodium-tripolyphosphate) was successfully implemented in the Hanford Site 300 Area periodically rewetted zone (PRZ) to decrease uranium mobility through a series of 60 injection wells and infiltration system covering 1.4 ha (3.5 ac) of uranium-contaminated sediments (PNNL-21733).

The existing data show best potential effectiveness with SMI reduction and phosphate sequestration.

7.2 Laboratory Test Objectives

Table 7-1 presents the primary parameters targeted by the particulate-phase combined chemical reduction and sequestration technology.

Table 7-1. Primary Parameters Targeted by the Particulate-Phase Combined Chemical Reduction and Sequestration Technology

Primary COIs	**U, Tc-99**
Primary Treatment Zones/ Applicable 200-DV-1 Waste Sites	Perched water, below BY Cribs water table permeable reactive barrier
Secondary Treatment Zones/ Applicable 200-DV-1 Waste Sites	216-U-1&2, S-SX Tank Farm, C Tank Farm, BC Cribs and Trenches
Potential Co-Contaminants	NO_3^-, Cr(VI) (S and T Cribs), I-129 (A Cribs)
Potential Reductant Treatments	ZVI, SMI [a]
Potential Sequestration Treatments	Best performing phosphate amendment from Chapter 8 (in liquid form mixed with the carrier fluid) [b]

Note: The COIs shown in bold are primary known contaminant targets. Other COIs are potential co-contaminants to evaluate with primary COIs.

a. By itself, SMI is expected to perform better with technetium-99; however, the technical basis is not sufficient for selecting ZVI or SMI for an application with a phosphate amendment. Objective #1 will be performed with both ZVI and SMI, and then the best performing amendment will be used for the remainder of the testing.

b. The carrier fluid may need to be designed differently for perched water and permeable reactive barrier application in order to obtain the correct residence time for phosphate precipitation. Controlling pH will be important for optimum phosphate precipitation.

COI = contaminant of interest SMI = sulfur-modified iron ZVI = zerovalent iron

- **Objective #1 (proof-of-principle):** Quantify the decrease in contaminant (technetium-99 and uranium) mass and order-of-magnitude sequestration rate for the treatment combinations summarized in Table 7-2.

Table 7-2. Experimental Treatments for Objective #1 of the Laboratory Testing of the Particulate-Phase Chemical Reduction and Sequestration Technology

Treatment Zone/ Sediment-Pore Water	Co-Contaminants Added	Technology Treatments Tested
BY Crib pore water (no sediment)	—	SMI added to the best performing phosphate amendment (Chapter 8)
BY Cribs sediment/pore water	—	SMI added to the best performing phosphate amendment (Chapter 8)
BY Cribs sediment delivery fluid*	—	SMI added to the best performing phosphate amendment (Chapter 8)
BY Cribs sediment/pore water	Cr(VI), I-129, NO_3^-	SMI added to the best performing phosphate amendment (Chapter 8)
Perched water pore water (no sediment)	NO_3^- (added as $NaNO_3$)	SMI added to the best performing phosphate amendment (Chapter 8)
Perched water sediment/ delivery fluid*	NO_3^- (added as $NaNO_3$)	SMI added to the best performing phosphate amendment (Chapter 8)
BY Crib pore water (no sediment)	—	ZVI added to the best performing phosphate amendment (Chapter 8)
BY Cribs sediment/pore water	—	ZVI added to the best performing phosphate amendment (Chapter 8)
BY Cribs sediment/ delivery fluid*	—	ZVI added to the best performing phosphate amendment (Chapter 8)
BY Cribs sediment/pore water	Cr(VI), I-129, NO_3^-	ZVI added to the best performing phosphate amendment (Chapter 8)
Perched water pore water (no sediment)	NO_3^- (added as $NaNO_3$)	ZVI added to the best performing phosphate amendment (Chapter 8)
Perched water sediment/ delivery fluid*	NO_3^- (added as $NaNO_3$)	ZVI added to the best performing phosphate amendment (Chapter 8)

*A typical delivery fluid (e.g., associated with hydraulic fracturing) will be selected for this testing.

SMI = sulfur-modified iron

ZVI = zerovalent iron

Project team assessment: If Objective #1 determines that the technology is promising (i.e., if over 35% of the contaminant is transformed to the endpoint expected), the following tasks will be executed with the best performing amendment:

- **Objective #2:** Determine the immobilization (via reduction and sequestration) rates for primary contaminants and evaluate co-contaminant effects for (1) perched water application and (2) BY Crib application.
- **Objective #3:** Quantify the longevity of the immobilized contaminants and co-contaminant species, and the potential remobilization rates for (1) perched water application and (2) BY Crib application.

7.3 Laboratory Experimental Design and Procedures

The purpose of Objective #1 is to provide a proof-of-principle for this technology and generally assess its overall effectiveness for the selected contaminants at site-specific conditions. If this step provides a desired success rate (as evaluated and decided by the project team), the subsequent objectives listed in Section 7.2 will be executed to provide specific information to aid in a potential field application and design process.

To address Objective #1, a set of batch systems will be used in saturated conditions (at a sediment-to-water ratio of about 2:1) to determine the overall effectiveness of this technology. All of the treatment combinations shown in Table 7-2 will be tested with these batch settings. In these experiments, a set of no sediment treatments will be used to evaluate the pure sequestration capability of the injected particles/phosphate amendment. These samples will be considered for additional surface-phase analyses to identify the location of uranium and technetium-99 in relationship to the particles (if possible) and to confirm that the desired mechanisms are taking place for immobilization.

All of the treatments will be executed in triplicate, with sufficient replicates for intermediate incubation time analyses (minimum of four). The headspace for the batch settings will contain nitrogen gas. In addition to the selected treatment combinations and a default no-treatment sediment control (used in all the experimental approaches described in this document), a microbial control (a sterilized sediment system) will also be used in this setting to allow for evaluation of any effects of natural background microbial population on the treatment effectiveness. Note that the two types of environmental settings tested herein (BY Cribs and perched water) will also support this evaluation with the differences between their native background microbial environment.

SMI and ZVI particles will be added separately to the selected liquid-phase phosphate amendment (selected based on the results of the testing from Chapter 8) in combinations with a selected carrier fluid. The appropriate loading of these amendments will be determined based on the surface area calculations to achieve the desired treatment capacity in the system (comparable to liquid-phase loading, as discussed in Chapters 8 through 10).

With sufficient replicates, the rate and extent of immobilization via reduction and sequestration will be determined by monitoring the aqueous-phase concentrations of uranium and technetium-99 and also the co-contaminants (where they were applied). Solid-phase analysis will also be conducted through appropriate sequential extraction techniques. For technetium-99 surface association, Hanford Site groundwater, oxic Hanford Site groundwater, and strong acid will be used for determining the mobile, desorbed, and immobilized fractions. Uranium sequential extractions will be designed to evaluate the contaminant transformation by using Hanford Site groundwater (for aqueous uranium), oxic Hanford Site groundwater (readily desorbed, ion exchange, and uranium), acetic acid (slow dissolution from most carbonates), and strong acid (dissolution of all immobile phases). Co-contaminants will be analyzed in both aqueous and surface phases (sequential extraction liquid-phase samples).

To address Objective #2(1) for representative rate determination for perched water application, a long column setting will be used in a stop-flow fashion for a volumetric treatment (i.e., essentially a no-flow batch experiment but at a high sediment-to-water ratio of the aquifer). Short columns will also be packed at the same time and run in parallel for use in column leaching experiments to address Objective #3(1). These experiments will be conducted in duplicate.

The long columns for immobilization (via reduction and sequestration) rate determination will allow for a high sediment-to-water ratio that would more closely remember field conditions. All reactants (contaminants, co-contaminants, the best performing particulate amendment, SMI or ZVI, and the

phosphate amendment) will be mixed and packed into the columns initially. At specific times ranging from hours to hundreds of hours, a small volume of groundwater (e.g., one-tenth of a pore volume) will be injected into the inlet, resulting in an effluent sample to be pushed from the end of the column; this effluent will be monitored for contaminant mobility change. Each effluent sample will represent an incrementally longer residence time for the amendments in the column. Necessary residence and sampling times for the sequestration reactions will be determined based on the batch experiments conducted for Objective #1. The same aqueous and sediment analyses used for the batch experiments (described previously) will also be used with these column settings. Sequential extractions will be conducted to evaluate contaminant distribution in different solid phases and to calculate the mass balance, as well as any mass leaving the columns. The extractions will be applied at various increments along the column to determine the effect of residence time on the sequestration extent.

To address Objective #3(1), another set of experiments will be used with small columns. All reactants (contaminants, co-contaminants, best performing particulate, and the phosphate amendments) will be mixed and packed into the columns initially. After the same full incubation time used for the long columns, groundwater will be injected at a slow flow rate for at least 100 pore volumes (approximating natural groundwater conditions) to evaluate the leaching characteristics of the treated sediments. The same aqueous and sediment analyses described previously will also be used with these column settings. These leaching tests with the injection of oxic Hanford Site groundwater will allow for evaluation of the stability of the immobilized contaminants.

To address Objective #2(2) for BY Crib water table PRB application, short columns will be packed with uncontaminated sediment, which will then be injected with 5 to 10 pore volumes of the amendment solution (best performing particulate and phosphate amendments, and a carrier fluid), approximating a field-scale injection downgradient of contaminants. Groundwater contaminated with technetium-99 and uranium (with or without co-contaminants) will then be injected into the columns under flow conditions relevant to the BY Cribs. The columns will be run until near full breakthrough to determine the estimated capacity and contaminant sequestration rates. Bromide will also be run through the columns as a tracer to track the regular breakthrough behavior. Once near full breakthrough is achieved, the columns will be evaluated for any leaching with the injection of oxic Hanford Site groundwater to address Objective #3(2). For leaching experiments, an appropriate number of pore volume of flow will be calculated and applied based on a typical groundwater/water table application in the BY Cribs subsurface conditions.

This page intentionally left blank.

8 Liquid-Phase Chemical Sequestration

Chemical sequestration can be used in the vadose zone by injecting liquid-phase amendments into high-water-content zones to produce fewer mobile precipitates of some inorganic contaminants. This technology is considered as a potential remediation approach for the 200-DV-1 OU perched water zone (or below perched water) and/or the water table PRB.

The laboratory testing of this technology is selected primarily for a potential uranium and technetium-99 treatment in Central Plateau areas such as perched water, below perched water, and/or under the BY Cribs in the unconfined aquifer (i.e., at the water table) with the evaluation of the potential effects of co-contaminants such as Cr(VI) in the S and T Cribs, iodine-129 in the A Cribs, strontium-90, and carbon-14. Although not specifically identified in DOE/RL-2017-58, nitrate will also be considered only for its potential interference (not treatability in the BY Cribs conditions). Nitrate is also important for perched water experiments because it provides the high ionic-strength nature of the pore water in this zone; therefore, it will be added to those experiments as sodium nitrate.

To apply these methods to the Central Plateau, information is needed regarding whether candidate sequestration approaches will work to reduce contaminant mobility for the contaminant concentration and geochemical conditions of the targeted applications in the perched water and as a water table PRB. In addition, delivery of liquid-phase sequestration chemicals needs to be evaluated for the perched water (low hydraulic driving forces available) or the water table PRB (where large lateral areas may need to be treated). However, this objective can be met by reviewing previous field applications of this technology at the Hanford Site or will need to be a part of a field-testing effort. Therefore, the laboratory experiments outlined herein do not include this objective.

8.1 Technical Basis

Chemical sequestration using liquid-phase amendments to facilitate sequestration of uranium or strontium-90 has been successfully demonstrated and applied at the Hanford Site with polyphosphate and calcium-citrate/sodium-phosphate amendments (SGW-59614, *300-FF-5 Operable Unit Enhanced Attenuation Stage A Delivery Performance Report*; DOE/RL-2016-68). Bench-scale experiments showed over 90% sequestration of uranium within 7 days of application of apatite, with very minimal reoxidation (PNNL-28054). However, technetium-99 is not expected to be sequestered by apatite alone without first applying a reductant (Billinghurst et al., 1981; PNNL-28054). Only about 20% removal of pertechnetate from the solution was observed with direct apatite application during recent bench-scale testing (PNNL-28054).

Enhanced uranium attenuation is being implemented in the 300 Area Industrial Complex by applying polyphosphate solutions to the vadose zone (using drip infiltration system), to the PRZ (using subsurface injection), and to the top of the aquifer (using deeper subsurface injection) (SGW-59614). Delivering high phosphate concentrations via subsurface injection was successful, however, the infiltration method was found to be uneven. Adding polyphosphate solutions induced some initial uranium mobilization followed by reprecipitation. The chemical interactions resulted in conditions favorable for formation of amorphous calcium-phosphate phases that result in uranium sequestration. Polyphosphate injections appeared to not have altered the hydraulic conductivity of the aquifer.

Uranium treatment in water-saturated sediments using phosphate has been shown to be effective in Hanford Site 300 Area sediments (PNNL-21733; Wellman et al., 2006; Wellman et al., 2008; PNNL-17818; Wellman et al., 2005; Wellman et al., 2007); Hanford Site 200 East sediments (Shi et al., 2009); sediments in Rifle, Colorado (PNNL-25303; Pan et al., 2016); and at other sites (Lammers et al., 2017). The mechanisms that decrease uranium mobility with phosphate addition are precipitation of a uranium-phosphate mineral (autunite), increased uranium sorption to calcium-phosphate precipitates (apatite), and apatite coating on existing uranium surface phases. Similarly, uranium treatment using ammonia gas injection in vadose zone sediments has been effective in some sediments for reducing the mobility of water leachable uranium by both the formation of uranium silicates and coating of aluminosilicates on top of existing uranium surface phases (Szecsody et al., 2012; PNNL-18879). Alkaline treatment with ammonia gas in the vadose zone has been extended into water-saturated systems using both NH_4OH and NaOH (Emerson et al., 2017, 2018).

An apatite PRB was designed and implemented successfully using an injection of calcium-citrate/ sodium-phosphate to reduce strontium-90 flux from groundwater along the 100-N Area shoreline to the Columbia River along a 701 m (2,300 ft) wide zone (DOE/RL-2016-68). The same calcium-citrate/ sodium-phosphate injection solution was used for a single well demonstration for uranium contamination at the Rifle, Colorado site and has reduced uranium mobility for over the period of a year (PNNL-25303). A different phosphate solution (sodium-phosphate and sodium-tripolyphosphate) was successfully implemented in the Hanford Site 300 Area PRZ to decrease uranium mobility through a series of 60 injection wells and infiltration system covering 1.4 ha (3.5 ac) of uranium-contaminated sediments (PNNL-21733).

In addition, 14-C-carbonate is reported to substitute into the apatite structure (Heslop et al., 2005, "A comparative study of the metastable equilibrium solubility behavior of high-crystallinity and low-crystallinity carbonated apatites using pH and solution strontium as independent variables"). In contrast, previous studies have shown that iodate and iodide are not incorporated into apatite, except in systems with extremely high phosphate/iodine loading (PNNL-28064, *Evaluation of Remediation Technologies for Iodine-129: FY18 Bench Scale Results*). For in situ sequestration of iodine, co-precipitation with calcium-carbonate was investigated, focusing on iodate uptake as a function of calcite precipitation rate, the impact of solution chemistry on iodate uptake by calcite, and the impact of surface area on iodate uptake. None of the approaches were effective at removing more than 70% iodate from solution. Precipitation of initially amorphous calcium-phosphate was also tested and showed inconsistent removal of a small amount of iodate from solution via sorption onto or incorporation into apatite. Nitrate is unlikely to substitute into the apatite structure or to be coated by apatite precipitates because there are few (if any) nitrate-containing precipitates.

Overall, the existing data for the liquid-phase chemical sequestration technology show best potential effectiveness with apatite sequestration.

8.2 Laboratory Test Objectives

Table 8-1 presents the primary parameters targeted by the liquid-phase chemical sequestration technology.

Table 8-1. Primary Parameters Targeted by the Liquid-Phase Chemical Sequestration Technology

Primary COIs	**U, Tc-99**
Primary Treatment Zones/ Applicable 200-DV-1 Waste Sites	Perched water, below BY Cribs water table permeable reactive barrier
Secondary Treatment Zones/ Applicable 200-DV-1 Waste Sites	216-U-1&2, S-SX Tank Farm, C Tank Farm, BC Cribs and Trenches
Potential Co-Contaminants	Cr(VI) (S and T Cribs), I-129 (A Cribs), Sr-90, C-14, NO_3 [a]
Potential Sequestration Treatments	Apatite (calcium (Ca)-citrate/sodium (Na)phosphate solution) [b]; Na-phosphate/polyphosphate solution

Note: The COIs shown in bold are primary known contaminant targets. Other COIs are potential co-contaminants to evaluate with primary COIs.

a. Nitrate is included only to provide the high ionic strength nature of the perched water and allow a representative condition of the BY Cribs. However, it is not expected to be treated with this technology.

b. Calcium-citrate-phosphate formulation (SGW-47614, *Field Test Instruction 100-NR-2 Operable Unit Design Optimization Study for Sequestration of SR-90 Saturated Zone Apatite Permeable Reactive Barrier Extension*) is a solution consisting of 3.6 mM calcium, 9 mM citrate, and 40 mM phosphate; other chemical formulations may be used as long as the resulting concentrations are consistent.

COI = contaminant of interest

- **Objective # 1 (proof-of-principle):** Quantify the decrease in contaminant (uranium and technetium-99) mass and order-of-magnitude sequestration rate for the treatment amendments summarized in Table 8-2.[6]

Table 8-2. Experimental Treatments for Objective #1 of the Laboratory Testing of the Liquid-Phase Chemical Sequestration Technology

Treatment Zone/ Sediment-Pore Water	Co-Contaminants Added	Technology Treatments Tested
BY Cribs sediment/pore water	—	Cal-citrate/naphosphate
BY Cribs sediment/pore water	—	Na-phosphate/polyphosphate
BY Cribs sediment/pore water	Cr(VI), I-129, Sr-90, C-14, NO_3^-	Cal-citrate/naphosphate
BY Cribs sediment/pore water	Cr(VI), I-129, Sr-90, C-14, NO_3^-	Na-phosphate/polyphosphate
Perched water sediment pore water	NO_3^- (added as $NaNO_3$)	Cal-citrate/naphosphate
Perched water sediment/ pore water	NO_3^- (added as $NaNO_3$)	Na-phosphate/polyphosphate

[6] Co-contaminants Cr(VI), iodine-129 (as iodate), strontium-90, and carbon-14 are likely to incorporate into apatite (or surface phases be coated by apatite) in varying degrees and may influence uranium or technetium-99 incorporation or coating. Although nitrate is unlikely to be incorporated into or be coated by apatite, the influence of the high ionic strength sodium nitrate solution would cause some uranium and technetium (as pertechnetate) desorption, which may influence uranium and technetium-99 incorporation into or coating by phosphate precipitates.

Project team assessment: If Objective #1 determines that the technology is promising (i.e., if over 35% of the contaminant is transformed to the endpoint expected), the following task(s) will be executed with the best performing treatment amendment.

- **Objective #2:** Determine the sequestration rates for primary contaminants and evaluate co-contaminant effects for the best performing amendment determined in Objective #1 for (1) perched water application and (2) BY Crib application (Table 8-3).
- **Objective #3: Quantify** the longevity of the immobilized contaminants and co-contaminant species, and also the potential remobilization rates for (1) perched water application and (2) BY Crib application (Table 8-3).

Table 8-3. Experimental Treatments for Objectives #2 and #3 of the Laboratory Testing of the Liquid-Phase Chemical Sequestration Technology

Treatment Zone/ Sediment-Pore Water	Co-Contaminants Added	Technology Treatments Tested
BY Crib sediment/ pore water	—	Best performing amendment from Objective #1
BY Crib sediment/ pore water	Cr(VI), I-129, Sr-90, C-14, NO_3^-	
Perched water sediment/ pore water	NO_3^- (added as $NaNO_3$)	

8.3 Laboratory Experimental Design and Procedures

The purpose of Objective #1 is to provide a proof-of-principle for this technology and generally assess its overall effectiveness for the selected contaminants at site-specific conditions. If this step provides a desired success rate (as evaluated and decided by the project team), the subsequent objectives listed in Section 8.2 will be executed to provide specific information to aid a potential field application and design process.

To address Objective #1, a set of batch systems will be used in saturated conditions (at a sediment-to-water ratio of about 2:1) to determine the overall effectiveness of this technology. A total of six different combinations of treatment systems will be tested with these batch settings, as shown in Table 8-2. All of the treatments will be executed in triplicate, with sufficient replicates for intermediate incubation time analyses (a minimum of four). The headspace for the batch settings will contain nitrogen gas. In addition to the selected treatment combinations and a default no-treatment control (used in all of the experimental approaches described in this document), a microbial control (a sterilized system) will also be used in this setting to allow for evaluating any effects of natural background microbial population on the treatment effectiveness. Note that the two types of environmental settings tested herein (BY Cribs and perched water) will also support this evaluation with the differences between their native background microbial environment.

Two types of liquid-phase amendments will be introduced into these batch containers. The appropriate loading of the amendments will be calculated to achieve the desired treatment loading in the system.

With the number of replicates, the rate and extent of sequestration will be determined by monitoring the aqueous-phase concentrations of uranium and technetium-99, as well as the co-contaminants (where they were applied). Sediment-phase analysis will also be conducted through appropriate sequential extraction

techniques. For technetium-99, surface association Hanford Site groundwater, oxic Hanford Site groundwater, and strong acid will be used for determining the mobile, desorbed, and immobilized fractions. Uranium sequential extractions will be designed to evaluate the contaminant transformation by using Hanford Site groundwater (for aqueous uranium); oxic Hanford Site groundwater (readily desorbed, ion exchange, and uranium); acetic acid (slow dissolution from most carbonates); and strong acid (dissolution of all immobile phases). Co-contaminants will be analyzed in both aqueous and surface phases (sequential extraction liquid samples). The best performing amendment will be selected for the remainder of the experiments, as described in the following discussion.

To address Objective #2(1) for representative sequestration rate determination for perched water application, a long column setting will be used in a stop-flow fashion for a volumetric treatment (i.e., essentially a no-flow batch experiment but at a high sediment-to-water ratio of the aquifer). Short columns will also be packed at the same time and run in parallel for use in column leaching experiments to address Objective #3(1). Table 8-3 summarizes the combinations of experimental setups that will be tested with these columns. These experiments will be conducted in duplicate.

The long-columns for sequestration rate determination will allow for high a sediment-to-water ratio that would more closely resemble field conditions. All reactants (contaminants, co-contaminants, and the phosphate amendment) will be mixed and packed into the columns initially. At specific times ranging from hours to hundreds of hours, a small volume of groundwater (e.g., one-tenth of a pore volume) will be injected into the inlet, resulting in an effluent sample to be pushed from the end of the column; this effluent will be monitored for contaminant mobility change. Each effluent sample will represent an incrementally longer residence time for the amendment in the column. Necessary residence and sampling times for the sequestration reaction experiments will be determined based on the batch experiments conducted for Objective #1. The same aqueous and sediment analyses used in the batch experiments (described previously) will also be used with these column settings. Sequential extractions will be conducted to evaluate contaminant distribution in different solid phases and to calculate the mass balance, as well as any mass leaving the columns. The extractions will be applied at various increments along the column to determine the effect of residence time on the sequestration extent.

To address Objective #3(1), another set of experiments will be used with small columns. All reactants (contaminants, co-contaminants, and phosphate amendment) will be mixed and packed into the columns initially. After the same full incubation time as for the long columns, groundwater will be injected at a slow flow rate for at least 100 pore volumes (approximating natural groundwater conditions) to evaluate the leaching characteristics of the treated sediments. The same aqueous and sediment analyses as previously described will also be used with these column settings. The leaching tests with the injection of oxic Hanford Site groundwater will allow an evaluation of the stability of the sequestered contaminants.

To address Objective #2(2) for BY Crib water table PRB application, short columns will be packed with uncontaminated sediment, which will then be injected with 5 to 10 pore volumes of the phosphate amendment solution, approximating a field-scale injection downgradient of the contaminants. Groundwater contaminated with technetium-99 and uranium (with or without co-contaminants) will be injected into these columns in flow conditions relevant to the BY Cribs. These columns will be run until near full breakthrough to determine the estimated capacity and contaminant sequestration rates. Bromide will also be run through the columns as a tracer to track the regular breakthrough behavior. Once near full breakthrough is achieved, the columns will be evaluated for any leaching with the injection of oxic Hanford Site groundwater to address Objective #3(2). For leaching experiments, an appropriate number of pore flow volume will be calculated and applied based on a typical groundwater/water table application in the BY Cribs subsurface conditions.

This page intentionally left blank.

9 Liquid-Phase Combined Chemical Reduction and Sequestration

In situ manipulation of geochemical conditions for reducing and precipitating redox-sensitive contaminants, followed by sequestration of precipitates in stable minerals forms, by adding chemicals to the subsurface may be an effective remediation approach for the 200-DV-1 OU perched water zone (or below perched water) and/or as water table PRB (PNNL-18114, *Remediation of Deep Vadose Zone Radionuclide and Metal Contamination: Status and Issues*; DOE/RL-2017-58).

Laboratory testing of this technology is selected primarily for potential uranium and technetium-99 treatment in Central Plateau areas such as perched water, below perched water, and/or BY Cribs water table with the evaluation of the potential effects of co-contaminants such as Cr(VI) in the S and T Cribs, iodine-129 in the A Cribs, strontium-90, and carbon-14. Nitrate will also be considered as a co-contaminant in the perched water zone, but it will be considered only for its potential interference, not treatability, in the BY Cribs conditions.

To apply these methods to the Central Plateau, information is needed regarding whether candidate reduction and sequestration approaches are effective in reducing contaminant mobility for the contaminant concentration and geochemical conditions for the targeted applications in the perched water and as a water table PRB. In addition, delivery of liquid-phase sequestration chemicals needs to be evaluated for the perched water (low hydraulic driving forces available) or the water table PRB (where large lateral areas may need to be treated). However, this objective can be met by reviewing previous field applications of this technology at the Hanford Site or will need to be a part of a field-testing effort. Therefore, the laboratory experiments outlined herein do not include this objective.

9.1 Technical Basis

In situ manipulation of redox conditions has been tested and implemented in bench-scale experimental settings at the Hanford Site field conditions for reducing contaminant species. Reducing amendments such as sodium dithionite, sulfide salts and minerals, and ferrous iron have been the primary chemicals tested for this purpose (PNNL-18114; DOE/RL-2017-58). Sodium dithionate and ferrous iron have been shown as an effective reductant for Cr(VI), particularly in saturated systems and with some effects on other contaminants (PNNL-18114; PNNL-13349, *100-D Area In situ Redox Treatability Test for Chromate-Contaminated Groundwater*; Ludwig et al., 2007, "In Situ Chemical Reduction of Cr(VI) in Groundwater Using a Combination of Ferrous and Sodium Dithionite: A Field Investigation"; DOE/RL-2008-10, *In situ Redox Manipulation (ISRM) Annual Report Fiscal Year 2007*). Calcium polysulfide (CPS) is demonstrated to also reduce Cr(VI), as well as uranium and technetium-99 (PNNL-28054; PNNL-18114; DOE/RL-2006-17, *Treatability Test Report for Calcium Polysulfide in the 100-K Area*; SGW-38255, *Chromium Treatment Technology Information Exchange for Remediation of Chromium in Groundwater at the Department of Energy Hanford Site*). Recent bench-scale testing (PNNL-28054) showed complete reduction of uranium and technetium-99 by applying high-concentration CPS (5%). However, reduction alone is not a viable long-term remediation strategy for technetium-99, as it is readily oxidized. CPS was also found to be ineffective for nitrate. These bench-scale experiments showed that the combined application of CPS and apatite in these experiments resulted in almost complete immobilization of uranium and technetium-99 with no reoxidation.

Chemical sequestration using liquid-phase amendments to facilitate sequestration of uranium or strontium-90 has been successfully demonstrated and applied at the Hanford Site with polyphosphate and Ca-citrate/Na-phosphate amendments (SGW-59614; DOE/RL-2016-68). Enhanced uranium attenuation is being implemented in the 300 Area Industrial Complex by applying polyphosphate solutions to the vadose zone (using drip infiltration system), to the PRZ (using subsurface injection), and to the top of the

aquifer (using deeper subsurface injection; SGW-59614). Delivering high phosphate concentrations via subsurface injection was successful, however, the infiltration method was found to be uneven. Addition of polyphosphate solutions induced some initial uranium mobilization followed by reprecipitation. The chemical interactions resulted in conditions favorable for formation of the amorphous calcium-phosphate phases that result in uranium sequestration. Polyphosphate injections appeared to not have altered the hydraulic conductivity of the aquifer.

Uranium treatment in water-saturated sediments using phosphate has been shown to be effective in Hanford 300 Area sediments (PNNL-21733; Wellman et al., 2006; Wellman et al., 2008; PNNL-17818; Wellman et al., 2005; Wellman et al., 2007), Hanford 200 East sediments (Shi et al., 2009), sediments in Rifle, Colorado (PNNL-25303; Pan et al., 2016), and at other sites (Lammers et al., 2017). The mechanisms that decrease uranium mobility with phosphate addition are precipitation of a uranium-phosphate mineral (autunite), increased uranium sorption to calcium-phosphate precipitates (apatite), and apatite coating on existing uranium surface phases. Similarly, uranium treatment using ammonia gas injection in vadose zone sediments has been shown as effective for reducing the mobility of water leachable uranium by both the formation of uranium silicates and coating of aluminosilicates on top of existing uranium surface phases (Szecsody et al., 2012; Szescody et al., 2010). Alkaline treatment with ammonia gas in the vadose zone has been extended into water-saturated systems using both NH_4OH and NaOH (Emerson et al., 2017, 2018).

An apatite PRB was designed and implemented successfully using an injection of Ca-citrate/ Na-phosphate to reduce strontium-90 flux from groundwater along the 100-N Area shoreline to the Columbia River along a 701 m (2,300 ft) wide zone (DOE/RL-201668). The same Ca-citrate/ Na-phosphate injection solution was used for a single well demonstration for uranium contamination at the Rifle, Colorado site and has reduced uranium mobility for over the period of one year (PNNL-25303). A different phosphate solution (Na-phosphate and Na-tripolyphosphate) was successfully implemented in the Hanford 300 Area PRZ to decrease uranium mobility through a series of 60 injection wells and infiltration system covering 1.4 ha (3.5 ac) of uranium-contaminated sediments (PNNL-21733).

The existing data show best potential effectiveness with CPS reduction and apatite sequestration.

9.2 Laboratory Test Objectives

Table 9-1 presents the primary parameters targeted by the liquid-phase combined chemical reduction and sequestration technology.

Table 9-1. Primary Parameters Targeted by the Liquid-Phase Combined Chemical Reduction and Sequestration Technology

Primary COIs	**U, Tc-99**
Primary Treatment Zones/ Applicable 200-DV-1 Waste Sites	Perched water, below BY Cribs water table permeable reactive barrier
Secondary Treatment Zones/ Applicable 200-DV-1 Waste Sites	216-U-1&2, S-SX Tank Farm, C Tank Farm, BC Cribs and Trenches
Potential Co-Contaminants	Cr(VI)(S and T Cribs), I-129 (A Cribs), NO_3^-
Potential Reductant Treatments	CPS
Potential Sequestration Treatments	Phosphate*

Note: The COIs shown in bold are primary known contaminant targets. Other COIs are potential co-contaminants to evaluate with primary COIs.

*Best performing phosphate amendment from the testing of the liquid-phase chemical sequestration technology (Chapter 8).

COI = contaminant of interest

CPS = calcium polysulfide

- **Objective # 1 (proof-of-principle):** Quantify the decrease in contaminant (technetium-99 and uranium) mass and order-of-magnitude sequestration rate for the treatment combinations summarized in Table 9-2.

Table 9-2. Experimental Treatments for Objective #1 of the Laboratory Testing of the Liquid-Phase Chemical Reduction and Sequestration Technology

Treatment Zone/ Sediment-Pore Water	Co-Contaminant(s) Added	Technology Treatments Tested
BY Cribs sediment/pore water	Cr(VI), I-129, Sr-90, C-14, NO_3^-	CPS and phosphate*
BY Cribs sediment/pore water	—	CPS and phosphate*
Perched water sediment/pore water	NO_3^- (added as $NaNO_3$)	CPS and phosphate*

*Best performing phosphate amendment from the testing of the liquid-phase chemical sequestration technology (Chapter 8).

CPS = calcium polysulfide

Project team assessment: If Objective #1 determines that the technology is promising (i.e., if over 35% of the contaminant is transformed to the endpoint expected), the following task(s) will be executed.

- **Objective #2:** Determine the reduction rates for primary contaminants and evaluate co-contaminant effects for (1) perched water application and (2) BY Cribs application.
- **Objective #3:** Determine the rate and extent of technetium-99 and uranium sequestration and evaluate co-contaminant effects for (1) perched water application and (2) BY Cribs application.

Project team assessment: If a minimum of 35% non-reoxidizable sequestration of contaminants is observed, the following task will be executed:

- **Objective #4:** Quantify the longevity of the immobilized contaminants and co-contaminant species, and the potential reoxidation rates.

9.3 Laboratory Experimental Design and Procedures

The purpose of Objective #1 is to provide a proof-of-principle for this technology and generally assess its overall effectiveness for the selected contaminants at site-specific conditions. If this step provides a desired success rate (as evaluated and decided by the project team), the subsequent objectives listed in Section 9.2 will be executed to provide specific information to aid in a potential field application and design process.

To address Objective #1, a set of batch systems will be used in saturated conditions (at a sediment-to-water ratio of about 2:1) to determine the overall effectiveness of this technology. A total of three different combinations of treatment systems will be tested with these batch settings, as shown in Table 9-2. All of the treatments will be executed in triplicate, with sufficient replicates for intermediate analyses. The headspace for the batch settings will contain nitrogen gas.

The appropriate loading of the reducing and sequestering amendments will be calculated to the desired treatment loading in the system. While the concentration for the perched water experiments will be estimated based on the amount needed for reducing technetium-99 and uranium contamination, the amount of reducing agent needed for a PRB application in the BY Cribs will include some additional amount to provide a lasting reducing effect.

As a first step, the CPS amendment will be added to the batch reactors for reducing technetium-99 and uranium. Once the maximum amount of reduction is achieved (i.e., technetium-99 and uranium are removed from the solution), the phosphate amendment will be added for the sequestration step. With sufficient replicates, the overall rate and extent of reduction and sequestration will be determined by monitoring the aqueous-phase concentrations of uranium and technetium-99, and also the co-contaminants (where they were applied). Sediment-phase analysis will also be conducted through appropriate sequential extraction techniques. For technetium-99 surface association Hanford Site groundwater, oxic Hanford Site groundwater and strong acid will be used to determining the mobile, desorbed, and immobilized fractions. Uranium sequential extractions will be designed to evaluate contaminant transformation by using Hanford Site groundwater (for aqueous uranium); oxic Hanford Site groundwater (readily desorbed, ion exchange, and uranium); acetic acid (slow dissolution from most carbonates); and strong acid (dissolution of all immobile phases). Co-contaminants will be analyzed in both aqueous and surface phases (sequential extraction liquid-phase samples).

To address Objectives #2(1) and #3(1) for representative rate determination for perched water application, a long column setting will be used in a stop-flow fashion for a volumetric treatment (i.e., essentially a no-flow batch experiment but at a high sediment-to-water ratio of the aquifer). A set of short columns will also be packed at the same time and run in parallel for use in leaching experiments to address Objective #4 (if needed). Table 9-2 summarizes the combinations of experimental setups that will be tested with these columns. The experiments will be conducted in duplicate.

The long-columns for sequestration rate determination will allow for a high sediment-to-water ratio that would more closely resemble field conditions. For perched water conditions, the reducing amendment will be mixed and packed into the columns initially with the contaminants and co-contaminants. Sufficient small replicates will be used to monitor the reduction process by analyzing aqueous-phase concentrations, as well as conducting sequential extractions on the sediments. Once it is determined that the maximum reduction is achieved, the sequestration amendment will then be injected into the column at specific times ranging from hours to hundreds of hours, with a small volume of groundwater (e.g., one-tenth of a pore volume). The effluent will be monitored for contaminant mobility change. Each effluent sample will represent an incrementally longer residence time for the amendment in the column. Necessary residence and sampling times for the sequestration reaction experiments will be determined based on the batch experiments conducted for Objective #1. The same aqueous and sediment analyses used in the batch experiments (described previously) will also be used with these column settings. Sequential extractions will be conducted to evaluate contaminant distribution in different solid phases and to calculate the mass balance, as well as any mass leaving the columns. The extractions will be applied at various increments along the column to determine the effect of residence time on the sequestration extent. To address Objective #4, the short columns that ran parallel to the long-columns will be used for leaching tests with the injection of oxic Hanford groundwater to evaluate the stability of the sequestered contaminants. For leaching experiments, at least 100 pore volumes of flow will be applied. The same aqueous and sediment analyses described previously will also be used with these column settings.

To address Objectives #2(2) and #3(2) for BY Crib water table PRB application, short columns will be packed with uncontaminated sediment and CPS amendment initially. After incubation, phosphate will be amended and incubated to allow for precipitation to occur prior to injecting the groundwater with technetium-99 and uranium contamination (with and without co-contaminants). These columns will be run until near full breakthrough to determine the estimated capacity and sequestration rates. Bromide will also be run through the columns as a tracer to track the regular breakthrough behavior. Once near full breakthrough is achieved, the columns will be evaluated for any leaching with the injection of oxic Hanford Site groundwater to address Objective #3(2). For leaching experiments, an appropriate number of pore volume of flow will be calculated and applied based on a typical groundwater/water table application in the BY Cribs subsurface conditions.

This page intentionally left blank.

10 Liquid-Phase Combined Bioreduction and Chemical Sequestration

In situ manipulation of biogeochemical conditions for reducing and precipitating redox-sensitive contaminants, followed by sequestration of precipitates in stable minerals forms, by adding chemicals to the subsurface may be an effective remediation approach for the 200-DV-1 OU perched water zone (or below perched water) and/or as water table PRB (PNNL-18114; DOE/RL-2017-58).

Laboratory testing of this technology is selected primarily for a potential uranium, technetium-99, and nitrate treatment in Central Plateau areas such as perched water, below perched water, and/or BY Cribs water table with the evaluation of the potential effects of co-contaminants such as Cr(VI) in the S and T Cribs, iodine-129 in the A Cribs, and cyanide in the BY Cribs.

To apply these methods to the Central Plateau, information is needed regarding whether candidate bioreduction/sequestration approaches will work for the contaminant concentration and geochemical conditions of the targeted applications in the perched water and as a water table PRB. In addition, delivery of liquid-phase sequestration chemicals needs to be evaluated for the perched water (low hydraulic driving forces available) or the water table PRB (where large lateral areas may need to be treated). However, this objective can be met by reviewing previous field applications of this technology at the Hanford Site or will need to be a part of a field-testing effort. Therefore, the laboratory experiments outlined herein do not include this objective.

10.1 Technical Basis

Direct chemical sequestration has been applied for uranium and strontium-90 and may be appropriate for iodine-129, Cr(VI), and carbon-14 (PNNL-28064; PNNL-28054; Heslop et al., 2005; Billinghurst et al., 1981; SGW-59614). However, technetium-99 treatment may require an initial reduction step prior to sequestration. If technetium-99 can be reduced microbiologically, then it may be amenable to long-term sequestration to reduce contaminant mobility, as has been demonstrated in the laboratory with combined hydrogen sulfide (reductant) and ammonia (sequestration) treatment (Szecsody et al., 2015).

Technetium-99 can be directly bioreduced by iron-reducing bacteria (Plymale et al., 2011) or sulfate-reducing bacteria (Renshaw et al., 2005, “Reductive precipitation of the nuclear fuel cycle contaminant Tc(VII) by Geobacter sulfurreducens”). In addition, technetium-99 can be abiotically reduced by ferrous iron phases that were produced microbiologically, which has been demonstrated at field scale (Istok et al., 2004, “In Situ Bioreduction of Technetium and Uranium in a Nitrate-Contaminated Aquifer”). Reduction alone is not a viable long-term remediation strategy for technetium-99 because it is readily reoxidized; therefore, long-term sequestration requires reduction then sequestration. This has been demonstrated in the laboratory with combined hydrogen sulfide (reductant) and ammonia (sequestration) treatment (Szecsody et al., 2015), in which aluminosilicate coatings (from the ammonia treatment) on reduced/precipitated technetium dioxide was used as the mechanism to decrease technetium-99 mobility over the long term. Similarly, in a recent bench-scale testing, PNNL-28054 showed complete reduction of uranium and technetium-99 by applying high-concentration CPS and apatite, with no reoxidation. A different reduction/sequestration strategy has also been investigated for technetium-99 that produces a stannous apatite product (RPP-53855).

In addition, bioreduction may be suitable to treat nitrate, Cr(VI), and potentially cyanide. Evans and Trute, 2006, stimulated nitrate and perchlorate biodegradation by aqueous electron donor injection technology. Laboratory microcosm studies demonstrated that hydrogen and ethanol promoted nitrate and perchlorate reduction in vadose zone soil. The moisture content was an important factor during these experiments, and the transport properties of electron donors showed wide variation. Ethyl acetate and

butyraldehyde were transported through column studies more rapidly than butyl acetate and ethanol. Nitrate removal in the column studies (up to 100%) was best stimulated by ethyl acetate.

Emulsified vegetable oil has been demonstrated as an effective biostimulation substrate for of hexavalent uranium reduction at field-scale (Tang et al., 2013, "U(VI) Bioreduction with Emulsified Vegetable Oil as the Electron Donor – Model Application to a Field Test"; Gihring et al., 2011, "A Limited Microbial Consortium Is Responsible for Extended Bioreduction of Uranium in a Contaminated Aquifer"). Ethanol has also been used successfully to stimulate hexavalent uranium, technetium-99, and nitrate reduction (Wu et al., 2006, "Pilot-Scale in Situ Bioremediation of Uranium in a Highly Contaminated Aquifer. 1. Conditioning of a Treatment Zone"; Istok et al., 2004). Acetate has also been used or uranium reduction at the Rifle, Colorado site (Williams et al., 2011, "Acetate availability and its influence on sustainable bioremediation of uranium-contaminated groundwater").

For Hanford Site-specific applications, bench-scale testing of gas-phase bioreduction was conducted using a series of gaseous and volatile liquid substrates (PNNL-28055). The results indicated that the Hanford Site's deep vadose zone likely has adequate conditions (e.g., nutrients and baseline microbial communities) to support in situ microbial remediation processes. For this bench-scale testing, the substrate was used at two different volumetric water contents (4% and 8%) for nearly all of the substrates tested. However, butyrate, pentane, hydrogen, and butyl acetate showed the highest levels of substrate use beginning from as early as 5 days after treatment. Microbial responses were generally faster and more consistent at 8% volumetric water content compared to 4%. The results indicate the importance of substrate selection and the importance of aqueous thin films and pore-scale water connectivity for rapid response to gaseous substrates. Nutrient amendments may need to be carefully considered for sustained activity and to increase the treatment zone of influence in deep vadose zone sediments.

The existing data show that potential effectiveness may be achieved with either a slow-release or short-duration bioreduction substrate (because each has potential delivery advantageous and challenges), as well as apatite sequestration.

10.2 Laboratory Test Objectives

Table 10-1 presents the primary parameters targeted by the liquid-phase combined bioreduction and chemical sequestration technology.

Table 10-1. Primary Parameters Targeted by the Liquid-Phase Combined Bioreduction and Chemical Sequestration Technology

Primary COIs	**U, Tc-99, NO_3^-**
Primary Treatment Zones/ Applicable 200-DV-1 Waste Sites	Perched water, below BY Cribs water table permeable reactive barrier
Secondary Treatment Zones/ Applicable 200-DV-1 Waste Sites	216-U-1&2, S-SX Tank Farm, C Tank Farm, BC Cribs and Trenches
Potential Co-Contaminants	Cr(VI) (S and T Cribs), I-129 (A Cribs), CN (BY Cribs)
Potential Reductant Treatments	Long-duration substrate (e.g., vegetable oil or a slow-release compound), short-duration substrate (e.g., an organic acid or sugar)
Potential Sequestration Treatments	Phosphate*

Note: The COIs shown in bold are primary known contaminant targets. Other COIs are potential co-contaminants to evaluate with primary COIs.

*Best performing phosphate amendment from the testing of the liquid-phase chemical sequestration technology (Chapter 8).

COI = contaminant of interest

- **Objective # 1 (proof-of-principle):** Quantify the fraction of immobilized contaminants (uranium, technetium-99, and nitrate) and mass, as well as the order-of-magnitude immobilization rate (combined reduction and sequestration), through a combined treatment of liquid-phase bioreduction and chemical sequestration for the treatment combinations as summarized in Table 10-2.

Table 10-2. Experimental Treatments for Objective #1 of the Laboratory Testing of the Liquid-Phase Bioreduction and Sequestration Technology

Treatment Zone/Sediment-Pore Water	Co-Contaminants Added	Technology Treatments Tested	Loading Considerations
BY Cribs sediment/ pore water	Cr(VI), I-129, CN	Bioreductant (select three types) and phosphate*	Full reduction of all redox-sensitive contaminants
BY Cribs sediment/ pore water	—	Bioreductant (select three types) and phosphate*	Full reduction of all redox-sensitive contaminants
Perched water sediment/ pore water	—	Bioreductant (select three types) and phosphate*	Full reduction of all redox-sensitive contaminants
Perched water sediment/ pore water	—	Bioreductant (select three types) and phosphate*	Partial reduction of NO_3^-

*Best performing phosphate amendment from the testing of the liquid-phase chemical sequestration technology (Chapter 8).

Project team assessment: If Objective #1 determines that the technology is promising (i.e., if over 35% of the contaminant is transformed to the endpoint expected), the following task(s) will be executed.

- **Objective #2:** Determine the immobilization (or removal) rates for varying initial contaminant and amendment concentrations for (1) perched water application and (2) BY Cribs application.

Project team assessment: If a minimum of 35% non-reoxidizable sequestration or removal of contaminants is observed, the following task will be executed:

- **Objective #3:** Quantify the longevity of the immobilized contaminants and co-contaminant species, as well as the potential remobilization rates, for (1) perched water application and (2) BY Cribs application.

10.3 Laboratory Experimental Design and Procedures

The purpose of Objective #1 is to provide a proof-of-principle for this technology and generally assess its overall effectiveness for the selected contaminants at site-specific conditions. If this step provides a desired success rate (as evaluated and decided by the project team), the subsequent objectives listed in Section 10.2 will be executed to provide specific information to aid a potential field application and design process.

To address Objective #1, a set of batch systems will be used in saturated conditions (at a sediment-to-water ratio of about 2:1) to determine the overall effectiveness of this technology. A total of 12 different combinations of treatment systems will be tested with these batch settings (Table 10-2), including three types of reducing substrates and four combinations of applied zone, co-contaminant conditions, and loading considerations. All of the treatments will be executed in triplicate, with enough replicates for intermediate analyses. The headspace for the batch settings will contain nitrogen gas to sustain anoxic conditions. The reducing and sequestering amendments will be applied sequentially to avoid any interference of the sequestering agent on the microbiological system required to develop the

reductive capacity. Following the bioreduction and sequestration phases, the batch systems will be exposed to oxidizing conditions to measure the remobilization potential.

The appropriate loading of reducing and sequestering amendments will be calculated to the desired treatment loading in the system. While the concentration for the perched water experiments will be estimated based on the amount needed for full or partial reduction, the amount of reducing agent needed for a PRB application in the BY Cribs will include some additional amount to provide a lasting reducing effect.

A number of sacrificial replicates of the batch systems (all in triplicate) will be used to monitor concentration changes over time for the primary contaminants and the co-contaminants in the aqueous phase throughout the experiment to monitor the removal and precipitation/immobilization of contaminants from the solution phase and quantify potential remobilization. Biomass will also be quantified to correlate the observed technetium-99, uranium, and nitrate reduction (removal from the aqueous phase) to increase in biomass in the reductive system. Sediment-phase analysis will also be conducted through appropriate sequential extraction techniques. For technetium-99 surface association, Hanford Site groundwater, oxic Hanford Site groundwater, and strong acid will be used for determining the mobile, desorbed, and immobilized fractions. Uranium sequential extractions will be designed to evaluate the contaminant transformation by using Hanford Site groundwater (for aqueous uranium); oxic Hanford Site groundwater (readily desorbed, ion exchange, and uranium); acetic acid (slow dissolution from most carbonates); and strong acid (dissolution of all immobile phases). Co-contaminants will be analyzed in both aqueous and surface phases, and total organic and inorganic carbon will also be monitored (sequential extraction liquid-phase samples).

To address Objective #2(1) for representative rate determination for perched water application, a long column setting will be used in a stop-flow fashion for a volumetric treatment (i.e., essentially a no-flow batch experiment but at a high sediment-to-water ratio of the aquifer). A set of short columns will also be packed at the same time and run in parallel for use in leaching experiments to address Objective #3(1) (if needed). Table 10-2 summarizes the combinations of experimental setups that will be tested with these columns. These experiments will be conducted in duplicate.

For perched water conditions, the bioreducing amendment will be mixed and packed into the columns initially with the contaminants and co-contaminants. Sufficient small replicates will be used to monitor the reduction process by analyzing aqueous-phase concentrations, as well as conducting sequential extractions on the sediments. Once it is determined that the maximum reduction is achieved, the sequestration amendment will then be injected into the column at specific times ranging from hours to hundreds of hours, with a small volume of groundwater (e.g., one-tenth of a pore volume). The effluent will be monitored for contaminant mobility change. Each effluent sample will represent an incrementally longer residence time for the amendment in the column.

Necessary residence and sampling times for the sequestration reaction experiments will be determined based on the batch experiments conducted for Objective #1. The same aqueous and sediment analyses used in the batch experiments (described previously) will also be used with these column settings. Sequential extractions will be conducted to evaluate contaminant distribution in different solid phases and to calculate the mass balance, as well as any mass leaving the columns. The extractions will be applied at various increments along the column to determine the effect of residence time on the sequestration extent.

To address Objective #3(1), the short columns that ran parallel to these will be used for leaching tests with the injection of oxic Hanford Site groundwater to evaluate the stability of the sequestered contaminants. For leaching experiments, at least 100 pore volumes of flow will be applied. The same aqueous and sediment analyses described previously will also be used with these column settings.

To address Objectives #2(2) and #3(2) for BY Crib water table PRB application, short columns will be packed with uncontaminated sediment and bioreducing amendment initially. After incubation, phosphate will be amended and incubated to allow for precipitation to occur prior to injecting the groundwater with technetium-99 and uranium contamination (with and without co-contaminants). These columns will be run until near full breakthrough to determine the estimated capacity and sequestration rates. Bromide will also be run through the columns as a tracer to track the regular breakthrough behavior. Once near full breakthrough is achieved, the columns will be evaluated for any leaching with the injection of oxic Hanford Site groundwater to address Objective #3(2). For leaching experiments, an appropriate of pore flow volume will be calculated and applied based on a typical groundwater/water table application in the BY Cribs subsurface conditions.

This page intentionally left blank.

11 Data Analysis and Interpretation

This chapter describes the procedures that will be used to analyze and interpret data from the laboratory treatability tests described in this document, including criteria that will be used for evaluating the technology effectiveness.

Overall, data generated during the treatability experiments will be summarized in tabular and/or graphical form. The exact presentation of the data will depend on the experimental design and parameters, as well as the biogeochemical processes being evaluated. However, these analyses, at a minimum, will include plots of concentration versus time, such as changes in aqueous concentrations of contaminants as a function of time indicating removal from or release into the aqueous phase (depending on the processes/mechanisms being tested). Other examples of time-dependent analyses will include plots of biomass versus time, leaching concentration over time, or leaching mass over cumulative pore volume. In general, data that are analyzed with respect to time will provide a process-rate estimation.

Additional types of data may include fractions of contaminants in various different solid phases (i.e., resulting from concentrations of contaminants in sequential extraction solutions), other surface-phase data identifying contaminants and other elements and their location on sediment grains, or mass-balance types of analyses based on observations of total mass leaching from column experiments. Additional calculations will also be presented to support the analysis and interpretation. Some of these calculations will include determination of amendment loading and/or capacity.

Laboratory data interpretation will be based on the test objectives identified for each technology and experimental procedure (as described in Chapters 3 through 10). The interpretation will target data assessment in relation to potential field application for remediation as input to future FSs.

This page intentionally left blank.

12 Data Management

Data resulting from implementing this test plan will be managed and stored in accordance with the data quality procedures described in Chapter 13 to ensure that analytical data are appropriately reviewed, managed, and stored. An archive of the data, plans, and reports associated with this testing will be created and maintained consistent with Hanford Site record storage requirements.

A project-specific database will be developed and maintained to collect, organize, store, verify/validate, and manage analytical laboratory data. Electronic files will be managed in accordance with the data quality procedures described in Chapter 13.

This page intentionally left blank.

13 Data Quality

The implementation of this test plan will be governed by a Nuclear Quality Assurance Program (NQAP). The NQAP will implement the requirements of the DOE O 414.1D, *Quality Assurance*; and 10 CFR 830, "Nuclear Safety Management," Subpart A, "Quality Assurance Requirements." The NQAP will use ASME NQA-1-2012, *Quality Assurance Requirements for Nuclear Facility Applications*, as its consensus standard and ASME NQA-1-2012, Subpart 4.2.1, "Guidance on Graded Application of Nuclear Quality Assurance (NQA) Standard for Research and Development," as the basis for its graded approach to quality.

The following two quality grading levels are defined for an NQAP:

- **Basic research:** The required degree of formality and level of work control is limited. However, sufficient documentation is retained to allow the research to be performed again without recourse to the original researcher(s). The documentation is also reviewed by a technically competent individual other than the originator.
- **Not basic research:** The level of work control is greater than basic research. Approved plans and procedures govern the research, software is qualified, calculations are documented and reviewed, externally sourced data is evaluated, and measuring instrumentation is calibrated. Sufficient documentation is retained to allow the research to be performed again without recourse to the original researcher(s). The documentation is also reviewed by a technically competent individual other than the originator.

The work supporting the implementation of this laboratory treatability study will be performed in accordance with the "not basic research" grading-level controls.

This page intentionally left blank.

14 Waste Management

Waste generated by laboratory treatability testing will be managed in an environmentally sound manner in accordance with approved waste control and disposal procedures for the laboratory. The types and quantities of waste that will be generated will be identified early in the process, based on knowledge of the treatment technology and the experimental design, to ensure proper disposal and planning of activities.

This page intentionally left blank.

15 Schedule

An overall 3-year schedule is planned for implementing this test plan for the 200-DV-1 OU laboratory treatability test, as shown in Table 15-1. While the actual laboratory activities for each technology test are estimated to take a total of 2 years, the schedule accounts for developing detailed test instructions required to meet the quality procedures described in Chapter 13 and to provide time for the initial determination of the best performing phosphate amendment (as described in Chapter 8) prior to starting some of the other testing activities.

The selected phosphate amendment from addressing Objective #1 for the liquid-phase chemical sequestration technology will be used for testing other liquid-phase technologies (described in Chapters 8 through 10) and the particulate-phase chemical reduction and sequestration technology; therefore, the initiation dates for those tasks will not begin until the completion of Objective #1 testing for the liquid-phase chemical sequestration technology.

The overall schedule for the effort may be reduced depending on the outcome of tiered testing approaches for the technologies. Reporting efforts for documenting the results of the study are also highlighted in the schedule.

Table 15-1. Implementation Schedule for the 200-DV-1 OU Laboratory Treatability Test Plan

Project Tasks	FY 2020				FY 2021				FY 2022			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Test instructions to meet quality program requirements												
Gas-phase combined bioreduction/chemical sequestration												
Gas-phase bioremediation												
Gas-phase chemical sequestration												
Particulate-phase chemical sequestration												
Particulate-phase combined chemical reduction and sequestration												
Liquid-phase chemical sequestration												
Liquid-phase combined chemical reduction and sequestration												
Liquid-phase combined bioreduction and chemical sequestration												
Reporting												

FY = fiscal year
Q1 = first quarter
Q2 = second quarter
Q3 = third quarter
Q4 = fourth quarter

16 Reporting

The results of the 200-DV-1 OU laboratory treatability test conducted in accordance with this plan will be presented and documented in two interim reports at the end of fiscal years 2020 and 2021, with a final treatability test report at the end of fiscal year 2022, as shown in the schedule in Table 15-1. The final report will be prepared in accordance with the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* guidance for treatability studies (EPA/540/R-92/071a, *Guidance for Conducting Treatability Studies under CERCLA: Final*).

A separate data usability assessment report will also be prepared to evaluate whether the type, quality, and quantity of data that were collected or generated met the intent of the data quality objectives prepared for this laboratory treatability test.

This page intentionally left blank.

17 Management and Staffing

DOE-RL is responsible for completing the 200-DV-1 OU laboratory treatability test. The test will be managed by the Hanford Site contractor. Staffing will include personnel from the Hanford Site contractor and subcontractors as specified by the project manager. The project manager will ensure that the personnel selected are qualified to perform all activities in accordance with the requirements specified in this test plan. Specific staffing plans are provided in work planning documents or subcontracts prepared on a task-specific basis.

This page intentionally left blank.

18 Budget

This laboratory treatability test will be conducted by the Hanford Site contractor, as directed by DOE-RL. A cost estimate for the work required to complete this treatability test is presented in Table 18-1. Overall cost of the project is approximately $4.1 million over a 3-year period.

Table 18-1. Overall Estimated Cost of 200-DV-1 OU Laboratory Treatability Test

Project Tasks	Cost
Perform laboratory technology testing	$3,815,000
Reporting	$350,000
Project total	**$4,165,000**

This page intentionally left blank.

19 References

10 CFR 830, "Nuclear Safety Management," Subpart A, "Quality Assurance Requirements," *Code of Federal Regulations*. Available at: http://www.gpo.gov/fdsys/pkg/CFR-2010-title10-vol4/xml/CFR-2010-title10-vol4-part830-subpartA.xml.

ASME NQA-1-2012, 2013, *Quality Assurance Requirements for Nuclear Facility Applications*, American National Standards Institute/American Society of Mechanical Engineers, New York, New York.

Asmussen, R. Matthew., James J. Neeway, Amanda R. Lawter, Tatiana G. Levitskaia, Wayne W. Lukens, and Nikkola P. Qafoku, 2016, "The function of Sn(II)-apatite as a Tc immobilizing agent," *Journal of Nuclear Materials* 480:393-402.

ASTM D5198-17, 2017, *Standard Practice for Nitric Acid Digestion of Solid Waste*, ASTM International, West Conshohocken, Pennsylvania.

Billinghurst, Mervyn W., Diane Jette, and Elizabeth Somers, 1981, "Investigation of the interaction of hydroxyapatite with technetium in association with stannous pyrophosphate," *The International Journal of Applied Radiation and Isotopes* 32(8):559-566.

Brina, Rossella and Allan G. Miller, 1992, "Direct Detection of Trace Levels of Uranium by Laser-Induced Kinetic Phosphorimetry," *Analytical Chemistry* 64:413-1418.

Comprehensive Environmental Response, Compensation, and Liability Act of 1980, Pub. L. 107-377, as amended, 42 USC 9601, et seq., December 31, 2002. Available at: https://www.csu.edu/cerc/researchreports/documents/CERCLASummary1980.pdf.

DOD, 2010, *In Situ Bioremediation of Perchlorate and Nitrate in Vadose Zone Soil using Gaseous Electron Donor Injection Technology (GEDIT)*, ESTCP Cost Performance Report (ER-0511), Environmental Security Technology Certification Program, U.S. Department of Defense, Washington, D.C.

DOE O 414.1D, Chg 1 (Admin Chg), 2013, *Quality Assurance*, U.S. Department of Energy, Washington, D.C. Available at: https://www.directives.doe.gov/directives-documents/400-series/0414.1-BOrder-d-admchg1.

DOE/RL-2006-17, 2006, *Treatability Test Report for Calcium Polysulfide in the 100-K Area*, Rev. 0. U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: https://pdw.hanford.gov/document/DA02107064.

DOE/RL-2008-10, 2008, *In situ Redox Manipulation (ISRM) Annual Report Fiscal Year 2007*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: https://pdw.hanford.gov/document/0809110636.

DOE/RL-2010-87, 2015, *Field Test Plan for the Uranium Sequestration Pilot Test*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: https://pdw.hanford.gov/document/008164H.

DOE/RL-2011-102, *Remedial Investigation/Feasibility Study and RCRA Facility Investigation/Corrective Measures Study Work Plan for the 200-DV-1 Operable Unit*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: https://pdw.hanford.gov/document/0075538H.

DOE/RL-2011-104-ADD1, 2017, *Characterization Sampling and Analysis Plan for the 200-DV-1 Operable Unit Addendum 1: Attenuation Process Characterization*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: https://pdw.hanford.gov/document/0071507H.

DOE/RL-2016-68, 2017, *Calendar Year 2016 Annual Summary Report for the 100-HR-3 and 100-KR-4 Pump and Treat Operations, and 100-NR-2 Groundwater Remediation*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: https://pdw.hanford.gov/document/0067961H.

DOE/RL-2017-58, 2019, *Technology Evaluation and Treatability Studies Assessment for the Hanford Central Plateau Deep Vadose Zone*, Draft A, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: https://pdw.hanford.gov/document/AR-01097.

Emerson, Hilary P., Silvina Di Pietro, Yelena Katsenovich, and Jim Szecsody, 2017, "Effects of ammonium on uranium partitioning and kaolinite mineral dissolution," *Journal of Environmental Radioactivity* 167:150-159.

Emerson, Hilary P., Silvina Di Pietro, Yelena Katsenovich, and Jim Szecsody, 2018, "Potential for U sequestration with select minerals and sediments via base treatment," *Journal of Environmental Management* 223:108-114.

EPA/540/R-92/071a, 1992, *Guidance for Conducting Treatability Studies under CERCLA: Final*, OSWER Directive No. 9380.3-10, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C. Available at: https://pdw.hanford.gov/document/D196100932.

Evans, Patrick J. and Mary M. Trute, 2006, "In situ bioremediation of nitrate and perchlorate in vadose zone soil for groundwater protection using gaseous electron donor injection technology," *Water Environment Research* 78(13):2436-2446.

Fredrickson, James K., John M. Zachara, David W. Kennedy, Ravi K. Kukkadapu, James P. McKinley, Steve M. Heald, Chongxuan X. Liu, and Andrew E. Plymale, 2004, "Reduction of TcO4- by sediment-associated biogenic Fe(II)," *Geochimica Et Cosmochimica Acta* 68 (15):3171-3187.

Gihring, Thomas M., Gengxin Zhang, Craig C. Brandt, Scott C. Brooks, James H. Campbell, Susan Carroll, Craig S. Criddle, Stefan J. Green, Phil Jardine, Joel E. Kostka, Kenneth Lowe, Tonia L. Mehlhorn, Will Overholt, David B. Watson, Zamin Yang, Wei-Min Wu, and Christopher W. Schadt, 2011, "A Limited Microbial Consortium Is Responsible for Extended Bioreduction of Uranium in a Contaminated Aquifer," 77(17):5955-5965.

Goldman, Emanuel and Lorrence H. Green, 2015, *Practical Handbook of Microbiology*, CRC Press Taylor & Francis Group, Boca Raton, Florida.

Heslop, D.D., Y. Bi, A.A. Baig, M. Otsuka, and W.I. Higuchi, 2005, "A comparative study of the metastable equilibrium solubility behavior of high-crystallinity and low-crystallinity carbonated apatites using pH and solution strontium as independent variables," *Journal of Colloid and Interface Science* 289(1):14-25.

Höhener, Patrick and Viloaine Ponsin, 2014, "In situ vadose zone bioremediation," *Current Opinion in Biotechnology* 27:1-7.

Hughes, J., M. Cameron, and K. Crowley, 1989, "Structural Variations in Natural F, OH, and Cl Apatites," *American Mineralogist* 74:870-876.

Istok, J.D., J.M. Senko, L.R. Krumholz, D. Watson, M.A. Bogle, A. Peacock, Y.J. Chang, and D.C. White, 2004, "In Situ Bioreduction of Technetium and Uranium in a Nitrate-Contaminated Aquifer," *Environmental Science & Technology* 38(2):468-475. Available at: https://doi.org/10.1021/es034639p.

LAB-RPT-12-00001, 2012, *Laboratory Report on the Reduction and Stabilization (Immobilization) of Pertechnetate to Technetium Dioxide Using Tin(II) Apatite*, Rev. 0, Washington River Protection Solutions, Richland, Washington. Available at: https://digital.library.unt.edu/ark:/67531/metadc839092/m1/1/.

Lammers, Laura N., Hope Rasmussen, David Adilman, Jamie L. deLemos, Peter Zeeb, Douglas G. Larson, and Andrew N. Quicksall, 2017, "Groundwater uranium stabilization by a metastable hydroxyapatite," *Applied Geochemistry* 84:105-113.

LeBrón, C., C. Acheson, P. Dennis, X. Druar, J. Wilkinson, E. Ney, D. Major, E. Petrovskis, N. Barros, C. Yeager, F. Loeffler, K. Ritalahti, J. Hatt, E. Edwards, M. Duhamel, and W. Chan, 2009, *Standardized Procedures for Use of Nucleic Acid-Based Tools*, SERDP, U.S. Environmental Protection Agency, Arlington, Virginia.

Ludwig, R.D., S. Chunming, T.R. Lee, R.T. Wilkin, S.D. Acree, R.R. Ross, and A. Keeley, 2007, "In Situ Chemical Reduction of Cr(VI) in Groundwater Using a Combination of Ferrous and Sodium Dithionite: A Field Investigation," *Environmental Science & Technology* 41(15):5299–5305.

Moëlo, Y., B. Lasnier, P. Palvadeau, P. Léone, and F. Fontan, 2000, "La lulzacite, Sr2Fe2+(Fe2+,Mg)2Al4(PO4)4(OH)10, un nouveau phosphate de strontium (Saint-Aubin-des-Châteaux, Loire-Atlantique, France)," Comptes Rendus de l'Académie des Sciences – Series IIA - *Earth and Planetary Science* 330:317–324.

Mucci, A. and J.W. Morse, 1983, "The Incorporation of Mg2+ and Sr2+ into Calcite Overgrowths - Influences of Growth-Rate and Solution Composition," *Geochimica Et Cosmochimica Acta* 47(2):217-233.

Pan, Zezhen, Daniel E. Giammar, Vrajesh Mehta, Lyndsay D. Troyer, Jeffrey G. Catalano, and Zheming Wang, 2016, "Phosphate-Induced Immobilization of Uranium in Hanford Sediments," *Environmental Science & Technology* 50(24):13486-13494.

Peterson, G.L., 1979, "Review of the folin phenol protein quantitation method of Lowry, Rosebrough, Farr, and Randall," *Analytical Biochemistry* 100:201-220.

Plymale, Andrew E., James K. Fredrickson, John M. Zachara, Alice C. Dohnalkova, Steve M. Heald, Dean A. Moore, David W. Kennedy, Matthew J. Marshall, Chongmin M. Wang, Charles T. Resch, and Ponnsamy Nachimuthu, 2011, "Competitive Reduction of Pertechnetate ((TcO4-)-Tc-99) by Dissimilatory Metal Reducing Bacteria and Biogenic Fe(II)," *Environmental Science & Technology* 45(3):951-957.

PNNL-13349, 2000, *100-D Area In situ Redox Treatability Test for Chromate-Contaminated Groundwater*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www.pnl.gov/main/publications/external/technical_reports/PNNL-13349.pdf.

PNNL-17818, 2008, *300 Area Treatability Test: Laboratory Development of Polyphosphate Remediation Technology for In situ Treatment of Uranium Contamination in the Vadose Zone and Capillary Fringe*, Pacific Northwest National Laboratory, Richland, Washington. Available at: https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-17818.pdf.

PNNL-18114, 2008, *Remediation of Deep Vadose Zone Radionuclide and Metal Contamination: Status and Issues*, Pacific Northwest National Laboratory, Richland, Washington. Available at: https://pdw.hanford.gov/arpir/pdf.cfm?accession=0086028.

PNNL-18879, 2010, *Remediation of Uranium in the Hanford Vadose Zone Using Gas-Transported Reactants: Laboratory-Scale Experiments*, Pacific Northwest National Laboratory, Richland, Washington. Available at: https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-18879.pdf.

PNNL-21733, 2012, *Use of Polyphosphate to Decrease Uranium Leaching in Hanford 300 Area Smear Zone Sediment*, Pacific Northwest National Laboratory, Richland, Washington. Available at: https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-21733.pdf.

PNNL-23667, 2015, *Evaluation of Technetium Getters to Improve the Performance of Cast Stone*, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington. Available at: https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-23667Rev1.pdf.

PNNL-24709, 2017, *Conceptual Model of Iodine Behavior in the Subsurface at the Hanford Site*, Rev. 2, Pacific Northwest National Laboratory, Richland, Washington. Available at: https://dx.doi.org/10.2172/1419157.

PNNL-25303, 2016, *Use of a Ca-Citrate-Phosphate Solution to Form Hydroxyapatite for Uranium Stabilization of Old Rifle Sediments: Laboratory Proof of Principle Studies*, Pacific Northwest National Laboratory, Richland, Washington. Available at: https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-25303.pdf.

PNNL-26208, 2017, *Contaminant Attenuation and Transport Characterization of 200-DV-1 Operable Unit Sediment Samples*, Pacific Northwest National Laboratory, Richland, Washington. Available at: https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-26208.pdf.

PNNL-26266, 2017, *Geochemical, Microbial, and Physical Characterization of 200-DV-1 Operable Unit B-Complex Cores from Boreholes C9552, C9487, and C9488 on the Hanford Site Central Plateau*, Pacific Northwest National Laboratory, Richland, Washington. Available at: https://pdw.hanford.gov/arpir/pdf.cfm?accession=0069249H.

PNNL-27524, 2018, *Contaminant Attenuation and Transport Characterization of 200-DV-1 Operable Unit Sediment Samples from Boreholes C9497, C9498, C9603, C9488, and C9513*, Pacific Northwest National Laboratory, Richland, Washington. Available at: https://dx.doi.org/10.2172/1468977.

PNNL-27773, 2018, *Deep Vadose Zone Treatability Test of Uranium Reactive Gas Sequestration for the Hanford Central Plateau: Final Report*, Pacific Northwest National Laboratory, Richland, Washington. Available at: https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-27773.pdf.

PNNL-28054, 2018, *Evaluation of Perched Water Post-Extraction Remedy Technologies: Interim Status Report*, Pacific Northwest National Laboratory, Richland, Washington. Available at: https://dx.doi.org/10.2172/1485489.

PNNL-28055, 2018, *Evaluation of Central Plateau Remediation Alternatives: Interim Status Report*, Pacific Northwest National Laboratory, Richland, Washington. Available at: https://www.osti.gov/servlets/purl/1489412.

PNNL-28064, 2018, *Evaluation of Remediation Technologies for Iodine-129: FY18 Bench Scale Results*, Pacific Northwest National Laboratory, Richland, Washington. Available at: https://dx.doi.org/10.2172/1488864.

Renshaw, J., J.R. Lloyd, F.R. Livens, L. May, M.V. Coppi, D.R. Lovley, and S. Glasauer, 2005, "Reductive precipitation of the nuclear fuel cycle contaminant Tc(VII) by Geobacter sulfurreducens," *European Symposium on Environmental Biotechnology, ESEB 2004*, 251-254, A.A. Balkema, Netherlands.

Rigali, Mark J., Patrick V. Brady, and Robert C. Moore, 2016, "Radionuclide removal by apatite," *American Mineralogist* 101(12):2611-2619.

RPP-53855, 2012, *Reduction and Stabilization (Immobilization) of Pertechnetate to an Immobile Reduced Technetium Species Using Tin(II) Apatite*, Washington River Protection Solutions, Richland, Washington. Available at: https://www.osti.gov/servlets/purl/1055730.

SAND2003-3360, 2003, *Anionic Sorbents for Arsenic and Technetium Species*, Sandia National Laboratories, Albuquerque, New Mexico. Available at: https://prod-ng.sandia.gov/techlib-noauth/access-control.cgi/2003/033360.pdf.

SGW-38255, 2008, *Chromium Treatment Technology Information Exchange for Remediation of Chromium in Groundwater at the Department of Energy Hanford Site*, Rev. 0, Fluor, Richland, Washington. Available at: https://pdw.hanford.gov/document/0911161138.

SGW-47062, 2010, *Treatability Test Report for Field-Scale Apatite Jet Injection Demonstration for the 100-NR-2 Operable Unit*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington. Available at: https://pdw.hanford.gov/document/1009020871.

SGW-47614, 2010, *Field Test Instruction 100-NR-2 Operable Unit Design Optimization Study for Sequestration of SR-90 Saturated Zone Apatite Permeable Reactive Barrier Extension*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington. Available at: https://pdw.hanford.gov/document/0079738H.

SGW-59614, 2016, *300-FF-5 Operable Unit Enhanced Attenuation Stage A Delivery Performance Report*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington. Available at: https://pdw.hanford.gov/document/0072777H.

Shi, Z., C. Liu, J.M. Zachara, Z. Wang, and B. Deng, 2009, "Inhibition Effect of Secondary Phosphate Mineral Precipitation on Uranium Release from Contaminated Sediments," *Environmental Science & Technology* 43(21):8344-8349.

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

SW-846, 2015, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, Third Edition; Final Update V*, as amended, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C. Available at: https://www.epa.gov/hw-sw846.

Szecsody, J.E., M.J. Truex, L. Zhong, T.C. Johnson, N.P. Qafoku, M.D. Williams, J.W. Greenwood, E.L. Wallin, D. Bargar, and D.K. Faurie, 2012, "Geochemical and Geophysical Changes during Ammonia Gas Treatment of Vadose Zone Sediments for Uranium Remediation," *Vadose Zone Journal* 11(4).

Szecsody, J.E., L. Zhong, M. J. Truex, and J. McKinley, 2015, "Remediation of technetium in the vadose zone using reactive gasses NH3 and H2S," *Vadose Zone Journal* 14(7):1-12.

Tang, G., D.B. Watson, W.-M. Wu, C.W. Schadt, J.C. Parker, and S.C. Brooks, 2013, "U(VI) Bioreduction with Emulsified Vegetable Oil as the Electron Donor – Model Application to a Field Test," *Environmental Science & Technology* 47(7).

Wellman, D.M., J.G. Catalano, J.P. Icenhower, and A.P. Gamerdinger, 2005, "Synthesis and characterization of sodium meta-autunite, Na[UO2PO4]·3H2O," *Radiochimica Acta* 93(7).

Wellman, D.M., J.N. Glovack, K.E. Parker, E.L. Richards, and E. Pierce, 2008, "Sequestration and retention of uranium(VI) in the presence of hydroxylapatite under dynamic geochemical conditions," *Environmental Chemistry* 5:40-50.

Wellman, D.M., J.P. Icenhower, and A.T. Owen, 2006, "Comparative Analysis of Soluble Phosphate Amendments for the Remediation of Heavy Metal Contaminants: Effect on Sediment Hydraulic Conductivity," *Environmental Chemistry* 3:219-224.

Wellman, D.M., K.M. Gunderson, J.P. Icenhower, and S.W. Forrester, 2007, "Dissolution kinetics of synthetic and natural meta-autunite minerals, X 3− n (n) + [(UO 2)(PO 4)] 2 xH 2 O, under acidic conditions," *Geochemistry, Geophysics, Geosystems* 8(11). Available at: https://doi.org/10.1029/2007gc001695.

Williams, K.H., P.E. Long, J.A. Davis, M.J. Wilkins, A.L. N'Guessan, C.I. Steefel, L. Yang, D. Newcomer, F.A. Spane, L.J. Kerkhof, L. McGuinness, R. Dayvault, and D.R. Lovley, 2011, "Acetate availability and its influence on sustainable bioremediation of uranium-contaminated groundwater," *Geomicrobiology Journal* 28:519-539.

Wu, W.-M., J. Carley, M. Fienen, T. Mehlhorn, K. Lowe, J. Nyman, J. Luo, M.E. Gentile, R. Rajan, D. Wagner, R.F. Hickey, B. Gu, D. Watson, O.A. Cirpka, P.K. Kitanidis, P.M. Jardine, and C.S. Criddle, 2006, "Pilot-Scale in Situ Bioremediation of Uranium in a Highly Contaminated Aquifer. 1. Conditioning of a Treatment Zone," *Environmental Science & Technology* 40(12):3978-3985.

Zhang, S., K.A. Schwehr, Y.-F. Ho, C. Xu, K.A. Roberts, D.I. Kaplan, R. Brinkmeyer, C.M. Yeager, and P.H. Santschi, 2010, "A Novel Approach for the Simultaneous Determination of Iodide, Iodate, and Organo-Iodide for ^{127}I and ^{129}I in Environmental Samples Using Gas Chromatography-Mass Spectrometry," *Environmental Science and Technology* 44:9042-9048.