Long-Term Evaluation of Remedial Technology Performance in the Laboratory

Multi-year Experimental Test Plan

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Summary

An understanding of the long-term effectiveness of remediation technologies is central to sustainable environmental cleanup. Long-term experiments are valuable for reducing uncertainty and predicting remediation outcomes at scales required for regulatory compliance. However, these types of tests can be costly and challenging to interpret. Therefore, contaminated sites often rely on short-term laboratory experiments that may not account for the potentially significant effects of gradual, time--dependent processes governing contaminant retention, release, and species transformation. For example, short-term lab experiments (from months to a year) conducted with sediments from the unsaturated and saturated zones at the Hanford Site play an important role in initial evaluations of remediation technologies but cannot capture the full extent of time-dependent reactions, leaving uncertainties in field-scale deployment. Here, long-term testing will be conducted on select technologies based on their performance in short-term testing.

The overall objective is to directly address the challenges described above by generating and analyzing data on long-term (2–10 years) efficacy of selected remediation technologies, integrating this understanding into models, and providing critical input for remediation planning, monitoring, and 5-year review cycles for field-implemented remedies.

Specific objectives include:

1. Evaluating long-term efficiency of promising remedies under site-specific conditions.

2. Generating robust parameters for modeling, reducing uncertainty in predictive simulations.

3. Advancing integrated monitoring by combining geochemical and geophysical observations.

4. Informing field-scale implementation by incrementally advancing technologies, identifying failure mechanisms early, and prioritizing robust, cost-effective remedies.

Through systematic evaluation of technologies in laboratory-scale column experiments, integrated monitoring, and modeling support, this project is designed to bolster confidence in the long-term robustness of selected technologies. The ultimate outcome is the identification and deployment of more reliable, cost-effective remedies that safeguard human health and the environment while reducing the uncertainties that have historically hindered cleanup progress at Hanford Site. An experimental approach was developed and initiated for long-term testing potentially up to 10 years. The table below summarizes the experimental approach developed for testing select technologies and presented in this multi-year experimental test plan.

Table S.1. Summary of experimental matrix targeted for long-term columns.

Amendment[a]	Scenario	Intermediate[b]	Aging Time (years)	Total Columns
Sn-PO$_4$; SMI + Poly-PO$_4$; CPS + PolyPO$_4$; BSN[2]	Permeable Reactive Barrier	Flush & Oxidize	1,3,5,10	6[c]
		Flush	1,3,5,10	6[c]
	Direct Treatment	Oxidize	1,3,5,10	6
		None	3,10	4
No Treatment Control	Permeable Reactive Barrier	Flush	3,10	6[c]
		Flush & Oxidize	3	2
	Direct treatment	None	3,10	4
		Oxidize	3,10	4

(a) Amendments were chosen based on performance in the 200-DV-1 Operable Unit treatability studies and include particulate-phase tin-substituted apatite (Sn-PO$_4$), particulate-phase sulfur modified iron with subsequent treatment with liquid-phase polyphosphate (SMI+Poly-PO$_4$), liquid-phase calcium polysulfide with subsequent treatment with polyphosphate (CPS+Poly-PO$_4$), and particulate-phase bismuth subnitrate (BSN).

(b) Flushing will be conducted approximately 6 months after treatment with injection of approximately 3 pore volumes of synthetic groundwater. Select samples will be further oxidized at 6 months to consider the impacts of long-term exposure to oxygen, though this will not be necessary for amendments that do not generate reducing conditions (i.e., BSN). Oxidation will be conducted via injection of oxygenated synthetic groundwater solutions, which may include nitrate to consume remaining reduction capacity.

(c) The two columns for 10 years of aging will be packed into specific columns with current electrodes on the end caps, potential electrodes on the column body, and oxygen spots for periodic analysis via electrical geophysics (spectral induced polarization) and dissolved oxygen.

Acknowledgments

Acronyms and Abbreviations

BSN	bismuth subnitrate
CPS	calcium polysulfide
COI	contaminant of interest
OU	operable unit
Poly-PO$_4$	polyphosphate
PRB	permeable reactive barrier
ROD/IROD	Record of Decision / Interim Record of Decision
SMI	sulfur modified iron
Sn-PO$_4$	tin-substituted apatite

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1.0   Introduction

Long-term performance is a challenging aspect of remediation technology development and implementation that can be difficult to adequately evaluate due to time, budget, and/or space constraints. While many laboratory-scale efforts have focused on testing and selecting remediation technologies for contaminated subsurface environments, significant uncertainties exist about long-term performance at field-scale due to limitations on collecting data over longer periods. Laboratory sequential extractions and leaching over short periods (< 3 months) are often used to estimate contaminant remobilization potential after remediation. However, short-term testing does not capture slower sequestration mechanisms that may significantly impact contaminant fate, leading to potential challenges extrapolating to longer periods. Processes like geochemical aging and irreversible sorption (Tinnacher et al. 2011; Emerson et al. 2019) as well as diffusion may decrease contaminant mobility, while geochemically and microbiologically driven reoxidation (Szecsody et al. 2018), mineral dissolution, and desorption reactions may increase mobility. Previous batch experiments with different leaching conditions or extractions and multiple isotopes reacted for variable periods have demonstrated changes in sequestration over time (Emerson et al. 2019; Clark et al. 2011; Missana et al. 2004).

To reduce uncertainty from short-term studies, this task is focused on improving our understanding of the long-term performance (2 to 10 years) of optimal technologies identified as part of the treatability studies conducted under the Deep Vadose Zone program (Emerson et al. 2025). Under this program, deep vadose zone technologies have been evaluated for their potential to enhance future remediation of the 200-DV-1 Operable Unit (OU) and other source OUs located in the Hanford Site's Central Plateau, including 200-UP-1, 200-BP-5, and perched water, based on DOE/RL-2011-102 (DOE/RL 2011) and DOE/RL-2019-28 (DOE/RL 2019), and evaluated in DOE/RL-2017-58 (DOE/RL 2017). This task will expand understanding of the best-performing amendments in longer term studies at the laboratory scale with field-relevant solid-to-liquid ratios.

1.1   The Need for Long-Term Evaluations

Previously published work has demonstrated the impact of aging processes with positive and negative effects on contaminant mobility depending on the contaminant and conditions, primarily in the absence of remedial amendments. However, in many cases, the reversibility of adsorption for contaminants (e.g., U) decreased over time (Missana et al. 2004; Clark et al. 2011; Clark et al. 2015; Jung et al. 2019). Limited research has demonstrated that these long-term effects are relevant under Hanford Site conditions.

For example, at the Hanford Site, aging of NH_3-treated sediments after 4 months, 1 year, and 3 years, and aging of Poly-PO_4-treated sediments after 1 week to 9 months showed, in both cases, less U leaching over time (Szecsody et al. 2012a; Szecsody et al. 2012b; Smith and Szecsody 2011). In another study of U sequestration in vadose zone sediments using NH_3 gas, after 4 months of treatment of sediment from the Hanford 300 Area, 93% less U leached compared to untreated sediment (Szecsody et al. 2012a), but after 3 years, 83% less U leached (Zhong et al. 2015), although it is unclear if these results are significantly different as they are from separate experiments that may have been conducted under slightly different conditions.

Alternatively, some data has shown that contaminant mobility may increase over time. The 100D In Situ Redox Manipulation (ISRM) (reduced) permeable barrier was predicted to last 10-20 years based on laboratory studies. While most of the barrier (50-80%) worked well, Cr breakthrough was observed within 3 years in some portions of the barrier due to (a) water table fluctuation oxidizing the top portion of the barrier, and (b) physical heterogeneities, because high-permeability zones were oxidized more quickly, decreasing barrier efficiency (Oostrom et al. 2007; Szecsody et al. 2005). In another example,

short-term batch experiments conducted with U-8 field sediments and NH_3 treatment indicated success, but longer-term (4-month) column leaching indicated poor performance. In this case, acidic co-contaminants decreased carbonate, which is needed for the NH_3 treatment of uranium (U). A combination of a higher-than-expected impact of co-contaminants and long-term effects stopped the field-scale pilot test (Truex et al. 2018). All these examples point to the need for conducting and generating data from long-term experiments.

In addition to the limitations of short-term studies, numerous other factors underscore the importance of long-term evaluation:

- *Reducing uncertainties introduced by uncontrolled variables:* Time-dependent changes, site heterogeneities, and co-contaminant effects can increase uncertainty over time.

- *Regulatory alignment:* Medium- and long-term assessments align with the 5-year review cycle of Records of Decision / Interim Records of Decision (ROD/IROD) at the Hanford Site, directly informing regulatory compliance and adaptive management.

There is a need for systematic long-term studies for the most promising remediation technologies identified in the treatability studies for the 200-DV-1 OU at the Hanford Site. Results from these experiments will enable selection of the most efficient remediation technologies for long-term sequestration because technologies will be compared with consistent testing (i.e., similar amendment loadings, conditions, and reaction times) over longer periods than previous testing could accommodate due to budget constraints associated with the larger number of technologies.

1.2   Objectives

The overall objective of this effort is to extend our understanding of the long-term fate (up to 10 years) of contaminants following remediation under conditions relevant to the 200-DV-1 OU, although these data could also represent similar sites within the Central Plateau. The following specific actions will fulfill this objective:

1. Evaluating long-term efficiency of promising remedies under site-specific conditions.

2. Generating robust parameters for modeling, reducing uncertainty in predictive simulations.

3. Advancing integrated monitoring by combining geochemical and geophysical observations.

4. Informing field-scale implementation by incrementally advancing technologies, identifying failure mechanisms early, and prioritizing robust, cost-effective remedies.

To address these objectives, a series of controlled laboratory-scale column experiments will be conducted to evaluate the performance and durability of promising remediation technologies, previously studied and identified in the 200-DV-1 treatability study reports, over multiple time intervals (1, 3, 5, 8, and 10 years). At variable time points, leaching tests will be conducted to measure the effectiveness of remediation amendments at sequestering contaminants. If available in the future, pilot-scale testing via lysimeters or field locations will be considered. We will determine how effectively these technologies sequester contaminants over extended periods, identifying gradual changes in contaminant mobility due to time--dependent mechanisms of contaminant degradation and/or transformation under representative environmental conditions.

Then, key geochemical, physical, and hydraulic parameters will be derived from the long-term laboratory tests to describe contaminant mobilization and immobilization processes. These parameters will be used to build and calibrate numerical models to simulate contaminant fate. Subsequently, the validated models will extend projections beyond the experimental periods, enabling quantitative estimates of contaminant mobilization potential and associated risks over longer periods (e.g., several decades). The knowledge gained from these tests will be used to update the technical basis for the most promising technologies, incrementally moving them closer to field-scale implementation by closing knowledge gaps with respect to the long-term performance of these amendments. In addition, the outputs will support decision-making regarding the long-term effectiveness and sustainability of the tested remediation technologies.

2.0 Experimental Design and Modeling

This section provides details on the experimental design, analysis, and modeling approaches to be conducted for this task.

The experimental approach includes 1-D columns to be prepared in Year 1 with plans to be sacrificed over time (i.e., at 0, 1, 3, 5, 10 years). Some baseline (time zero) conditions have been established based on previous experiments conducted for the 200-DV-1 OU treatability studies (Emerson et al. 2025) with additional select experiments to be conducted as part of this study.

Based on performance in previous testing, four technologies were chosen for additional testing in long--term column experiments as described in Section 2.1. Depending on client needs, additional technologies could be included in the future. Laboratory experiments for the different technologies are designed similarly to allow for cross-comparison of technology performance and to support final evaluation of treatability results.

2.1 Technologies

The following subsections describe the four technologies selected for experiments from the 200-DV-1 treatability study technologies. These options encompass saturated zone technologies across the different types of inorganic reduction processes, including both particulate-phase and liquid-phase technologies, that performed well under different conditions in the 200-DV-1 treatability studies. At this time, bioreducing technologies (e.g., molasses with Poly-PO$_4$) will not be considered. However, additional technologies could be added in the future as development progresses. Selected technologies include Sn(II)-substituted apatite (Sn-PO$_4$) (Section 2.1.1), sulfur modified iron (SMI) and polyphosphate (SMI and Poly-PO$_4$) (Section 2.1.2), calcium polysulfide (CPS) and Poly-PO$_4$ (Section 2.1.3), and bismuth subnitrate (BSN) (Section 2.1.4).

2.1.1 Sn-PO$_4$ for particulate phase chemical sequestration

Conceptually, Tc(VII) and U(VI) may be reduced in the presence of Sn-PO$_4$ then slowly coated by apatite or incorporated into apatite as P and Ca dissolve and re-precipitate from the surface. Solid phase characterization from 200-DV-1 OU treatability studies showed that, although Tc was reduced from +7 to the +4 oxidation state, U was primarily present in the +6 oxidation state. However, testing has shown potential for sequestration of technetium (Tc-99) from low-activity waste simulants and for getters in cementitious waste forms (Asmussen et al. 2016; Asmussen et al. 2018; Duncan 2012) and for Tc and U for 200-DV-1 OU subsurface remediation (Emerson et al. 2025).

2.1.2 SMI and Poly-PO$_4$ for particulate phase chemical reduction and sequestration

Once emplaced, SMI temporarily reductively precipitates contaminants like Tc and U and transforms others like nitrate to gaseous end products. This treatment is followed by injection of Poly-PO$_4$ to precipitate apatite that may either incorporate or coat precipitated contaminants in apatite. Poly-PO$_4$ is expected to allow apatite to incorporate U(VI)O$_2$ and precipitate on top of (i.e., coat) Tc(IV) and U(IV) species. Notably, the 200-DV-1 treatability studies were the first time both technologies were used together. SMI and Poly-PO$_4$ performed well for both Tc-99 and U under 200-DV-1 OU conditions for direct treatment. However, reaction times (i.e., flow rates or size of injection area) and/or amendment mass may need to be adjusted to make this technology effective as a permeable reactive barrier (PRB). Poly-PO$_4$ has been demonstrated previously by itself in the field along the river corridor at the Hanford

Site for U (CHPRC 2016; CHPRC 2020; Szecsody et al. 2020), and other sites have implemented similar approaches for Sr and U sequestration (Lammers et al. 2017; Fuller et al. 2003; Szecsody et al. 2016).

2.1.3 Calcium polysulfide and Poly-PO$_4$ for liquid phase chemical reduction and sequestration

CPS may temporarily reductively precipitate contaminants like Tc and U and transform others like nitrate to gaseous end products when injected into the subsurface. Chemical reduction using CPS has been demonstrated previously for Cr (Zhang et al. 2020; Chrysochoou et al. 2010), with some testing for Tc-99 and U with CPS followed by a second apatite chemical sequestration step at the laboratory-scale, including preliminary testing with Hanford Site sediments (Gartman et al. 2021; Dresel et al. 2008). This treatment is followed by injection of Poly-PO$_4$ to precipitate apatite that may either incorporate or coat precipitated contaminants in apatite. Poly-PO$_4$ is expected to allow apatite to incorporate U(VI)O$_2$ and precipitate on top of (i.e., coat) Tc(IV) and U(IV) species. Notably, the 200-DV-1 treatability studies were the first time both technologies were used together. CPS and Poly-PO$_4$ performed well for both Tc-99 and U under 200-DV-1 OU conditions for development of a PRB, though they were less successful for source treatment in perched water.

2.1.4 Bismuth subnitrate for particulate phase chemical sequestration

Bi-based materials can form a variety of layered and cluster structures that can accommodate a wide variety of cations and anions (Levitskaia et al. 2022; Perumal et al. 2022). Bi-based materials have been shown to remove contaminants including U as uranyl carbonate complexes (e.g., $UO_2(CO_3)_3^{4-}$), Tc-99 as TcO_4^-, hexavalent chromium (Cr) as chromate (CrO_4^{2-}), and iodine (I) as iodate (IO_3^-) from a variety of geochemical environments (Lawter et al. 2021; Moore et al. 2020; Pearce et al. 2020). Laboratory research using solid phase BSN has shown potential for U and Tc-99 recovery and sequestration from solution in a variety of geochemical environments (Lawter et al. 2021), but BSN has not been implemented in a field site for remediation. 200-DV-1 treatability study results show significant sequestration of U, although Tc-99 sequestration was not observed.

2.2 Experimental Details

The following subtasks will be conducted depending on timing and funding levels. Subtask 1 (sediment and column preparation) will be conducted first and will include the steps for preparing sediments for column experiments. Subtask 2 (1-D periodic column characterization) will occur periodically prior to sacrificial characterization to monitor changes via non-destructive methods. Subtasks 3 and 4 (column leaching experiments and post-experimental sediment characterization, respectively) will occur after 1, 3, 5, and 10 years to evaluate geochemical changes with aging. Subtask 5 (model development and approaches) may begin any time after the first columns are leached. Table 1 describes the general approach and lists the types of column experiments to be conducted for each amendment.

Table 1. Experimental matrix targeted for each amendment.

Scenario[a]	Treatment	Flushing[b]	Oxidation[c]	When to Leach
PRB	Yes	Yes	Yes	1,3,5,10 years
	Yes	Yes	No	3,10 years
	No, Control	Yes	No	3,10 years
Direct Treatment	Yes	No	Yes	1,3,5,10 years
	Yes	No	No	3,10 years
	No, Control	No	Yes	3,10 years

(a) The PRB scenario would target emplacement near the groundwater table for sequestration of contaminants over time, while the direct treatment scenario would target emplacement directly into the perched water zone.

(b) Flushing will be conducted approximately 6 months after treatment with injection of approximately 3 pore volumes of synthetic groundwater.

(c) Select samples will be further oxidized at 6 months to consider the impacts of long-term exposure to oxygen. Oxidation will be conducted via injection of oxygenated synthetic groundwater solutions, which may include nitrate to consume remaining reduction capacity.

2.2.1   Sediment and column preparation (Subtask 1)

Sediments will be prepared with Tc-99 and U and treated with amendments based on Table 2 and Table 3 for amendment and contaminant concentrations, respectively. Sediments will be subsequently homogenized and packed into columns for additional testing as described in Subtasks 2-4. These steps will be conducted in the first year for the four amendments outlined in Section 2.2; however, future experiments may be conducted with different contaminants or additional amendments depending on Hanford Site remediation decisions.

2.2.1.1   Materials

To reduce the potential interactions with co-contaminants, the experiments will primarily use uncontaminated sediments. The synthetic or test sediment will be prepared from Hanford formation sediments collected from a gravel pit in Pasco, WA, that is operated by the Central Pre-Mix Concrete Company. Sediments that have been previously sieved to < 2 mm will be used for experiments. Sediments will then be contaminated with the contaminants of interest (COIs), including the primary COIs (Tc-99 and U) and the secondary COIs (I, Cr, Sr, and NO_3) for either PRB or direct treatment as described in Table 3. For the direct treatment scenario, select experiments will be conducted with a composite sediment. The composite sediment was homogenized from cores within the Cold Creek Unit gravel formations from previous 200-DV-1 characterization campaigns for the D0112 borehole to represent the perched water zones (CPCCo 2022; Emerson et al. 2023).

Synthetic COI concentrations for PRB conditions were based on previously measured concentrations from the Hanford Environmental Information System (HEIS) database, including data until December 2021, for the BY Tank Farm, located in the 200 West Area of the Hanford Site Central Plateau. COI concentrations are based on 35-70 measurements for each COI in sediments for PRB conditions. If iodine is added as I-127, concentrations will be greater based on previous literature measuring background, natural iodine in Hanford Site groundwater. For direct treatment conditions, COI concentrations are based on perched water extraction well data included in the Hypatia module of SOCRATES from 2019 through 2021, which includes 43-88 measurements depending on the COI.

Table 2. Targeted amendments and concentrations

Amendment	Description	Addition per Gram of Sediment
Sn-PO$_4$	Particles	1.5 wt%
SMI	Particles	0.25 wt%
Poly-PO$_4$	350 mmol/L solution	0.06 mL/g (90 mmol PO$_4$/L in pore water)
CPS	29 wt% solution	0.02 mL/g (25 g CPS/L in pore water)
BSN	Particles	3 wt%

Table 3. Targeted COI concentrations based on BY Tank Farms.

Contaminant		To Be Added as
Groundwater/water table conditions (µg/L)		
Tc-99	100	NH$_4$TcO$_4$
U	1000	UO$_2$(NO$_3$)$_2$
I-127	150	NaIO$_3$
Cr	17,500	Na$_2$CrO$_4$
Sr	25,000	Sr(NO$_3$)$_2$
NO$_3$[a]	50,000	NaNO$_3$
Perched water conditions (µg/g)		
Tc-99	0.2	NH$_4$TcO$_4$
U	100	UO$_2$(NO$_3$)$_2$
NO$_3$	1600	NaNO$_3$
(a) 15,000 µg/L of NO$_3$ to be added based on NO$_3$ added from other contaminants		

2.2.1.2 Column packing procedure

For these experiments, the moist sediment will react with contaminants and amendments as described in Table 4. For the PRB scenario, contaminants will be added as part of a contaminant loading phase conducted after initial treatment, while contaminants will be added prior to treatment for the perched water source treatment scenario. Depending on results from the 200-DV-1 OU treatability studies, some scenarios may be removed from the matrix.

Table 4. Experimental matrix for all columns to be prepared for each amendment and scenario.

Amendment	Scenario	Intermediate [a][b]	Contaminants	Aging Time (years)[c]	Post Packing Actions[d]	Total Columns
Sn-PO$_4$	PRB	Flush & Oxidize	No	1,3,5,10	Load & Leach	6[e]
		Flush	No	1,3,5,10	Load & Leach	6[e]
	Direct Treatment	Oxidize	Yes	1,3,5,10	Leach	6
		None	Yes	3,10	Leach	4
SMI + Poly-PO$_4$	PRB	Flush & Oxidize	No	1,3,5,10	Load & Leach	6[e]
		Flush	No	1,3,5,10	Load & Leach	6[e]
	Direct Treatment	Oxidize	Yes	1,3,5,10	Leach	6
		None	Yes	3,10	Leach	4
CPS + PolyPO$_4$	PRB	Flush & Oxidize	No	1,3,5,10	Load & Leach	6[e]
		Flush	No	1,3,5,10	Load & Leach	6[e]
	Direct Treatment	Oxidize	Yes	1,3,5,10	Leach	6
		None	Yes	3,10	Leach	4
BSN	PRB	Flush	No	1,3,5,10	Load & Leach	6[e]
	Direct Treatment	None	Yes	1,3,5,10	Leach	6
Control	PRB	Flush	No	3,10	Load & Leach	4[e]
	PRB	Flush & Oxidize	No	3	Load & Leach	2
	Direct Treatment	None	Yes	3,10	Leach	4
	Direct Treatment	Oxidize	Yes	3,10	Leach	4

(a) Flushing will be conducted approximately 6 months after treatment with injection of approximately 3 pore volumes of synthetic groundwater.

(b) Select samples will be further oxidized at 6 months to consider the impacts of long-term exposure to oxygen. Oxidation will be conducted via injection of oxygenated synthetic groundwater solutions, which may include nitrate to consume remaining reduction capacity.

(c) At 3 and 10 years, column experiments will be conducted in duplicate, while leaching at 1 and 5 years will be conducted on a single column.

(d) The loading step will be conducted immediately after packing sediments into columns, while the leaching step will be conducted after the specified aging period.

(e) The two columns for 10 years of aging will be packed into specific columns with current electrodes on the end caps, potential electrodes on the column body, and oxygen spots for periodic analysis.

2.2.2   1-D periodic column characterization (Subtask 2)

While sediments are aging in columns, periodic non-destructive analysis may be conducted. This may include visual analysis via photography (e.g., for tracking redox fronts), X-ray computed microtomography (e.g., for tracking porosity and moisture content), optical methods for geochemical monitoring (e.g., for dissolved oxygen via PreSens spots), magnetic susceptibility (e.g., for monitoring magnetic mineral content), and electrical geophysics (e.g., for monitoring solid and aqueous phase conductivity and polarization properties). Analysis will be targeted at the frequency identified in Table 5, although additional data may be collected during the first 3 months, when amendments may be altered most significantly.

By reducing the number of technologies being studied (based on 200-DV-1 Treatability studies) and considering differing types of tests to quantify mobility over time, budgeting and space constraints are addressed in the experimental plan. However, time will still be a challenge, though results will be continuously evaluated over time to consider when testing has reached an adequate point to evaluate long-term mobility of contaminants for each technology.

Geophysical monitoring via spectral induced polarization has been identified as a promising technology to understand both delivery as well as changes in long-term reactivity of an amendment over time (Emerson et al. 2021). However, there are no data available to support long-term field monitoring potential. Therefore, select experiments will include electrodes for spectral induced polarization monitoring over time.

Table 5. Targeted frequency of data collection for long-term column experiments

Technique	Data Collection Frequency
Photography	Quarterly
Dissolved oxygen	Monthly
Magnetic susceptibility	Quarterly
Spectral induced polarization	Monthly
X-ray computed microtomography	Biannually

2.2.3   Column leaching experiments (Subtask 3)

In 1-D, saturated columns, synthetic contaminated sediment prepared and packed into columns in Task 1 will undergo additional experiments to characterize the change in contaminant mobility at 1, 3, 5, and 10 years. For the PRB scenario, a loading phase will be conducted to inject contaminants and load them into the solid phase. However, this step will not be necessary for the direct treatment scenario as contaminants will be added in Task 1. Details are included in Sections 2.2.3.1 and 2.2.3.2 for two different options to measure leachability of contaminants from column sediments: Option A – leaching from saturated column experiments with flow, and Option B – sequential extractions from an aliquot of sediments from columns. The option selected will depend on annual funding, with Option A being preferred as it allows for measurement of leaching rates.

2.2.3.1   Option A – Leaching of contaminants from columns

A column leach experiment may be conducted to simulate the leaching behavior of contaminants under controlled, saturated conditions. These types of experiments will help to determine the mass and rate of contaminant leaching. During column leaching experiments, stop flow events will be conducted to further measure release rates of contaminants with variable reaction times with pore water. Stop flow events will range in duration from 10 to 1,000 hours with no flow, providing time for contaminants present in one or more surface phases on the sediment surface to partition into pore water (i.e., from diffusion from intraparticle pore space or time-dependent dissolution of precipitate phases or slow desorption). Figure 1 shows a schematic of a column leaching experiment.
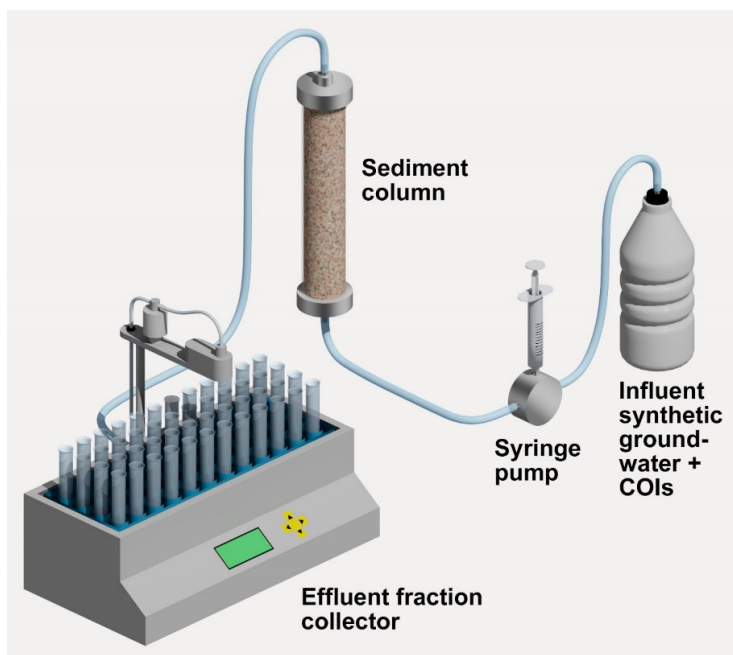
Figure 1. Conceptual diagram of experimental setup for saturated column testing.

2.2.3.2   Option B – Sequential Extractions

Depending on available resources, extractions may be used to measure contaminant mobility in lieu of or to complement column leaching for the time points in Table 1 and Table 4. Extractions may include carbonate extractions, 8 M HNO_3 extractions only, or sequential extractions as described in this section.

Sequential extractions are conducted by adding different solutions that target specific types of phases (e.g., adsorbed/exchanged contaminants or contaminants associated with iron minerals). With each successive chemical addition, the chemical extractions become more aggressive, targeting less mobile or harder-to-solubilize phases. Sequential extractions are operationally defined and may not be representative of the targeted fraction; however, they provide a qualitative understanding of changes in contaminant mobility. They have been used to characterize a wide variety of metals present in sediments in multiple surface phases (Beckett 1989; Chao and Zhou 1983; Gleyzes et al. 2002; Hall et al. 1996; Larner et al. 2006; Mossop and Davidson 2003). Extractions would target contaminants in different forms in sediments including (a) aqueous, (b) adsorbed, (c) readily oxidized, adsorbed, (d) precipitated in carbonates, and (e) precipitated into hard-to-extract phases (i.e., oxides, silicates, alumino-silicates). In addition, alkaline carbonate extractions have been shown previously to represent the labile fraction of uranium (Kohler et al. 2004; Zachara et al. 2007).

2.2.4   Post-experimental sediment characterization (Subtask 4)

Sediments remaining from column experiments may be further characterized via destructive analysis to understand contaminant transformations and longevity of sequestration. Activities may include characterization of element distributions and correlations (e.g., scanning electron microscopy with energy dispersive X-ray and/or X-ray fluorescence spectroscopy), contaminant oxidation states (e.g., X-ray photoelectron spectroscopy and/or X-ray absorption near-edge spectroscopy), and/or contaminant coordination chemistry (e.g., extended X-ray absorption spectroscopy).

2.2.5   Model development and approaches (Subtask 5)

A 1-D, distributed rate contaminant transport model will be used in this effort. Similar models have recently been developed using STOMP and applied to similar types of column experiments (He et al. 2024). These types of models allow for estimation of release rates and partitioning coefficients, which can be used in larger scale fate and transport models.

Computational simulations will be performed to model the lab/field-scale experiments. Capable numerical tools will also be developed for specific applications (e.g., ongoing effort to simulate injection of solid amendments into subsurface; gas phase remedy solution). In addition, different types of monitoring data will be incorporated into numerical models (e.g., hydrogeology, geophysical, geochemical, and/or microbiology), inverse modeling will be applied to estimate effective parameters (e.g., reaction rates), feasibility studies will be conducted on the effectiveness of the potential amendments using 3-D conceptual models, future performance of remedy solutions will be evaluated, and finally the solution delivery strategy will be optimized.

Issues related to scale-dependent behavior will be addressed based on past experience when an additional numerical model (dual domains) was needed to accurately predict U(VI) desorption in large columns (Liu et al. 2008). In addition, there is a gap in the ability to directly use knowledge and data obtained from lab-scale experiments into field-scale reactive transport models. Upscaling is needed to bridge the gap, which is not trivial due to non-linearity caused by spatial heterogeneities. Potential approaches will use volume averaging and machine-learning-based neural network.

3.0   Looking Ahead

Input from workshop-style meetings discussing the challenges and pitfalls of remedy implementation at field scale was combined with the recommendations from the 200-DV-1 treatability studies and used to develop an approach for long-term testing. The experimental approach laid out in this report will be initiated to measure long-term (up to 10 years) sequestration of contaminants. A series of controlled laboratory-scale column experiments will be conducted to evaluate the performance and durability of promising remediation technologies, previously studied and identified in the 200-DV-1 treatability study reports, over multiple time intervals (1, 3, 5, 8, and 10 years). Through systematic evaluation, integrated monitoring, and modeling support, the project is designed to reduce uncertainty in the long-term durability and performance of the selected technologies.

The ultimate outcome is the identification and deployment of reliable, cost-effective remedies that safeguard human health and the environment while reducing the uncertainties that have historically hindered cleanup progress at the Hanford Site. The anticipated impact of this task includes providing long-term datasets (2–10 years) on remediation performance of different technologies – bridging a critical knowledge gap, reducing uncertainty in long-term performance, and directly supporting site decision making for the Central Plateau of the Hanford Site.

4.0 Quality Assurance

This work was performed in accordance with the Pacific Northwest National Laboratory (PNNL) Nuclear Quality Assurance Program (NQAP). The NQAP complies with the United States Department of Energy Order 414.1D, *Quality Assurance*. The NQAP uses NQA-1-2012, *Quality Assurance Requirements for Nuclear Facility Application* as its consensus standard and NQA-1-2012 Subpart 4.2.1 as the basis for its graded approach to quality.

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Pacific Northwest
National Laboratory

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99354

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