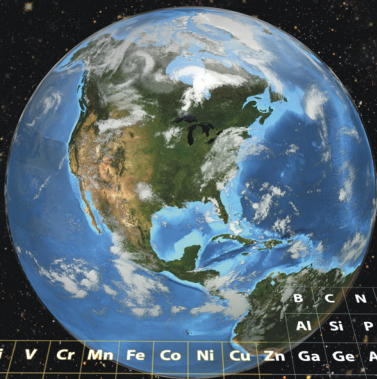


Environmental Sciences Laboratory

Applied Studies and Technology Persistent Secondary Contaminant Sources Final Project Report

March 2023



U.S. DEPARTMENT OF
ENERGY

Legacy
Management

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Abbreviations

AS&T	Applied Studies and Technology
DOE	U.S. Department of Energy
K_d	equilibrium sorption distribution constant
lb	pounds
LM	Office of Legacy Management
mg/L	milligrams per liter
NRZ	naturally reduced zone
PeSCS	persistent secondary contaminant sources
SEM	scanning electron microscope
XRD	X-ray diffraction

Executive Summary

Persistent secondary contaminant sources (PeSCS) are residual solid-phase contaminants that are not the original uranium mill tailings. At several U.S. Department of Energy Office of Legacy Management (LM) sites, the occurrence of PeSCS that were not previously identified, delays natural flushing or remedial time frames and results in the need for updated conceptual site models. The main objective of this project is to better understand how the occurrence and influence of PeSCS affect groundwater quality. Specific objectives are to:

- Gain a better understanding of where and why secondary contaminant sources occur.
- Develop estimates of secondary contaminant mass, form, and release rates through data acquisition and modeling.
- Build a set of modeling techniques that can help predict these release rates at multiple LM sites at multiple scales.
- Use these release rate estimates to evaluate various compliance strategies.

PeSCS typically occur due to reactions below former tailings impoundments or below current tailings disposal cells. The depth and extent of these PeSCS, which can occur in the unsaturated or saturated zones, depends on the volume of former tailings fluids and the underlying geology. In the center of the contaminant plumes, sorption-desorption of the contaminants to aquifer solids can occur, but these secondary sources are not discussed in this report, as they were typically considered in prior conceptual models. Near groundwater discharge zones downgradient from the original tailings impoundments, PeSCS can form in the unsaturated zone or vadose zone due to evapotranspiration of water within the underlying contaminant plume. Downgradient PeSCS can also occur in organic-rich sediments that often exists along riverbanks, which occur at or below the typical water table.

The Plume Persistence Project preceded the PeSCS Project with a focus on initial PeSCS identification as a contaminant source for ongoing groundwater plumes. Solid-phase characterization using fission-track radiography and column testing methods as part of the Plume Persistence Project formed a basis for further refinement and use of those methods for the PeSCS Project.

The PeSCS Project developed a toolbox of methods to determine PeSCS release rates using solid-phase characterization, single-well push-pull tracer tests, cross-hole tracer testing, and unsaturated zone infiltration. These were first developed at the Grand Junction, Colorado, Site and publicly available publications describe all of the methods and results. Similar testing (except for cross-hole testing) has been completed at the Riverton, Wyoming, Processing Site. For the Riverton site, one journal article is available along with a data release report. Additional analyses and future publications are being completed by scientists at the University of Wisconsin-Milwaukee under a National Science Foundation grant.

Results to date from the Grand Junction site indicate that hydraulic and PeSCS control parameters are generally similar at multiple scales (microscope, single well, and cross hole), as the scale of homogeneity was not exceeded (i.e., the scale does not incorporate added heterogeneity). This scale appears to have been exceeded for one cross-hole tracer test at the Grand Junction site. With this scale exceedance, hydraulic parameters were not influenced, but

uranium sorption parameters were lower, possibly due to faster flow pathways with higher permeability and lower uranium sorption. Faster contaminant transport than expected at larger scales is an important consideration if sitewide modeling uses column data or single-well tracer testing for PeSCS mobility parameters in the saturated zone.

Use of the PeSCS toolbox at other LM sites cannot be exactly prescriptive and will require input from subject matter experts. The individual or combined use of solid-phase characterization, column testing, or field tracer testing should keep the site management objectives in mind. However, the following observations are provided:

- Fission-track radiography coupled with scanning electron microscope data can provide information on how PeSCS (especially uranium) may be associated with the mineralogy, but cannot quantify PeSCS mobility.
- Column testing helps to quantify PeSCS mobility and provides easy testing with various influent solutions. Column testing is especially useful for unsaturated zone sediments, where field geochemical conditions (oxidizing) are more easily maintained in the laboratory.
- For saturated zone material, especially under reducing conditions (anoxic), maintaining those conditions in the laboratory are more difficult. Thus, field tracer testing in existing or easily installed monitoring wells (shallow unconsolidated aquifers) might be a more reasonable approach for maintaining in situ geochemistry (e.g., pH and redox conditions).
- Uranium transport modeling at the Monticello, Utah, Processing Site provides an example of where column testing provides necessary PeSCS release rates that can be used to determine several remedial scenarios.

Typically, reactive transport modeling is not done until after site data are collected. However, similar modeling can be integrated early into the data collection process to evaluate data worth. This approach can streamline data collection by identifying the most valuable data before modeling is started.

This report provides a toolbox to apply at LM sites to avoid having an incorrect conceptual site model that does not include PeSCS. With some iterations back and forth, LM sites will typically need to identify PeSCS, determine their influence on groundwater quality, and develop an appropriate reactive transport model. This model can then be used to simulate natural flushing and other possible remedial scenarios to make appropriate site management decisions.

1.0 Project Objectives and Questions

Persistent secondary contaminant sources (PeSCS) are defined as any residual contaminants on the solid phase that are not the primary contaminant source, in this case, uranium mill tailings. PeSCS form on solid phase material below or downgradient from former tailings impoundments, disposal cells, or disposal ponds when contaminated fluids have or continue to interact with materials in the subsurface. Any U.S. Department of Energy (DOE) Office of Legacy Management (LM) site that had leakage of contaminated fluids into the subsurface likely has some PeSCS. Documented PeSCS at LM sites are summarized in a DOE literature review (DOE 2020b). If PeSCS occur at a site and are not adequately identified, predictions of contaminant release based on existing conceptual site models and numerical models will be incorrect (Dam et al. 2015; DOE 2022a). Thus, determination of PeSCS location, release rates, and making future predictions of ongoing groundwater contamination are necessary for LM site management, regardless of the current site groundwater compliance strategy.

The main objective of this project is to better understand how the occurrence and influence of PeSCS affect groundwater quality. Specific objectives are to:

- Gain a better understanding of where and why secondary contaminant sources occur.
- Develop estimates of secondary contaminant mass, form, and release rates through data acquisition and modeling.
- Use these release rate estimates to evaluate various compliance strategies (active treatment, natural flushing, alternate concentration limits, etc.).
- Build a set of modeling techniques that can help predict these release rates at multiple LM sites at multiple scales.

The main questions to answer with this project are:

1. How and where do contaminants (focusing on uranium) reside in the unsaturated and aquifer solids?
2. What are the contaminant amounts and release rates?
3. What are the contaminant release mechanisms?
4. How do the processes related to these three questions influence groundwater quality and plume behavior?

The above objectives and questions were the basis of the original PeSCS project proposal. In addition, PeSCS release rates have been evaluated at multiple scales (microscopic versus laboratory versus field scales). Since the prior Applied Studies and Technology (AS&T) Plume Persistence Project (DOE 2018) and site work from the Riverton, Wyoming, Processing Site (DOE 2016; DOE 2022a) had already addressed PeSCS occurrence and amounts, the current PeSCS-project work was able to focus on release rates at various scales.

For future site management, the occurrences of PeSCS, the influence of PeSCS on groundwater quality, and the subsequent maintenance of water quality meeting site compliance standards are related issues (Figure 1). Predictions of PeSCS affecting future site groundwater quality will require the use of site-scale reactive transport models. Reactive transport models can simultaneously simulate hydrogeologic conditions along with geochemical conditions (such as

mineral dissolution-precipitation, metal desorption-sorption, cation exchange, and kinetic release rates). These models can evaluate various remedial strategies, but first need adequate input parameters. These input parameters are provided through the approaches discussed in this report to determine PeSCS release rates and mechanisms.

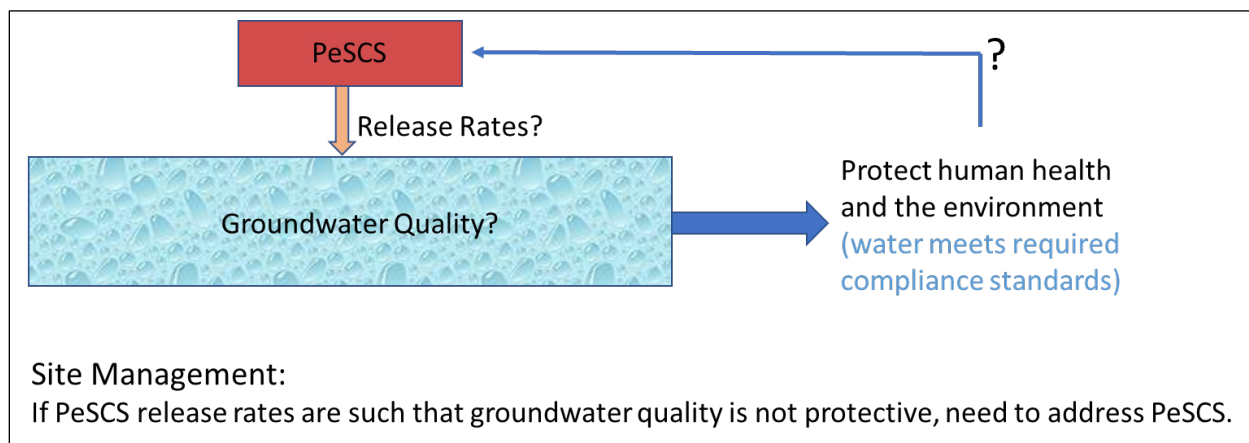


Figure 1. Diagram of PeSCS Influences

2.0 Report Organization

This report provides a summary of the PeSCS Project with the following sections:

- Section 3.0, “Conceptual PeSCS Locations”
- Section 4.0, “Plume Persistence Project”
- Section 5.0, “PeSCS-Project Approach with Testing at Grand Junction and Riverton Sites”
- Section 6.0, “Application of PeSCS-Project Approaches to Other LM Sites”
- Section 7.0, “Conclusion”

Section 3.0 provides an overview of where PeSCS can occur. This section uses information and experience from multiple LM sites, the PeSCS Project, and Plume Persistence Project. Along with Section 4.0, which summarizes the Plume Persistence Project, these two sections discuss answers to the objectives and questions on “How and where PeSCS reside in the subsurface?” and “What are the PeSCS amounts?” Section 3.0 is a conceptual summary of the potential occurrence of PeSCS at any LM site, and Section 4.0 is specifically related to the Grand Junction site.

The remaining sections (Sections 5.0 and 6.0) provide details on the overall approaches to determining PeSCS release rates for use in conceptual site models, scaling efforts of laboratory testing, field testing, and site-level scale, and future reactive transport models. Discussions in these sections are meant as a summary guide for readers considering such approaches, and technical details are provided via references to publications.

3.0 Conceptual PeSCS Locations

This section reviews conceptual PeSCS locations using typical site cross sections (Section 3.1) patterned after two sites, one with an existing disposal cell (Tuba City, Arizona, Disposal Site, <https://www.energy.gov/lm/tuba-city-arizona-disposal-site>) and one where tailings have been removed (Riverton site, <https://www.energy.gov/lm/riverton-wyoming-processing-site>). Conceptual PeSCS locations are discussed for these sites in terms of PeSCS underneath the current or former tailings (Section 3.2), within the main contaminant plume without any major geochemical changes (Section 3.3), and further downgradient when hydrogeologic or geochemical changes occur (Section 3.4). Individual sites may have different and various conceptual components of these example sites. However, these two sites provide good examples of (1) a site where tailings were left in place (Tuba City site) compared to a site where tailings have been removed (Riverton site) and (2) a site located near a river on alluvial floodplain sediments (Riverton site) compared to a site with a deeper water table that occurs within underlying bedrock (Tuba City site).

3.1 Conceptual Cross Sections

PeSCS form below tailings impoundments due to geochemical changes that occur between the tailings fluids and the underlying geologic material. The majority of the PeSCS mass formed when the tailings impoundment was active and had significant leakage of tailings fluids underneath the impoundment. The creation of a disposal cell on top of the former tailings (Figure 2) decreases infiltration of ongoing recharge after the tailings fluids have drained. When the tailings are removed (Figure 3), residual PeSCS that are immediately below the former tailings area, receive a greater amount of recharge, typically via infiltration of precipitation. These two scenarios (construction of disposal cell and removal of tailings) create hydrologic differences that can influence PeSCS release rates through time, but the original PeSCS formation is the same (infiltration of tailings-derived fluids). Both scenarios typically have contaminant plumes created by the uranium mill tailings and both can have ongoing contaminant plumes (Figure 2 and Figure 3) that are due to the occurrence of PeSCS. However, when the tailings are left in place and covered by a disposal cell (Figure 2), any ongoing groundwater contamination could be due to (1) ongoing residual drainage originating from the tailings, (2) recharge infiltrating through the disposal cell, or (3) PeSCS.

Leakage of tailings fluids below a new disposal cell that is not built over former tailings creates a similar conceptual scenario for reactions (discussed in Section 3.2), if tailings fluids leak into the underlying geology. A few examples of LM sites with this scenario include the Durango, Colorado, Disposal Site (<https://www.energy.gov/lm/durango-colorado-disposal-and-processing-sites>), the Gunnison, Colorado, Disposal Site (<https://www.energy.gov/lm/gunnison-colorado-disposal-and-processing-sites>), the Rifle, Colorado, Disposal Site (<https://www.energy.gov/lm/rifle-colorado-disposal-site-and-processing-sites>), and the Grand Junction, Colorado, Disposal Site (<https://www.energy.gov/lm/grand-junction-colorado-disposal-and-processing-sites>). However, the amount of fluids going into the subpile materials would be much less, because there would not have been any active tailings impoundment that would have been open to the atmosphere. No new conceptual figure is provided for this scenario, which would be similar to Figure 2 without a developed contaminant plume.

Necessary site conceptual information that could vary between sites includes underlying geology, depth to the water table, contaminated aquifer depth and thickness, site hydrogeology, and site geochemistry. Typical settings and the potential influences that favor the formation of PeSCS are discussed in the following sections (Sections 3.2 through 3.4).

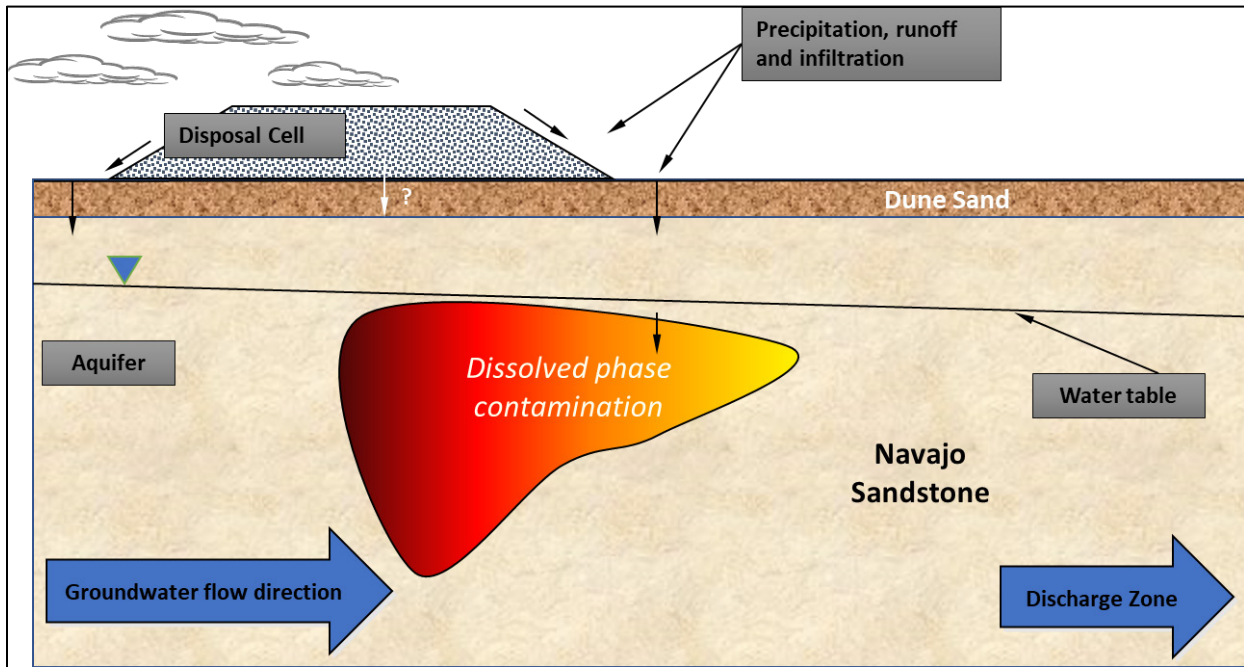


Figure 2. Tuba City Site Conceptual Cross Section

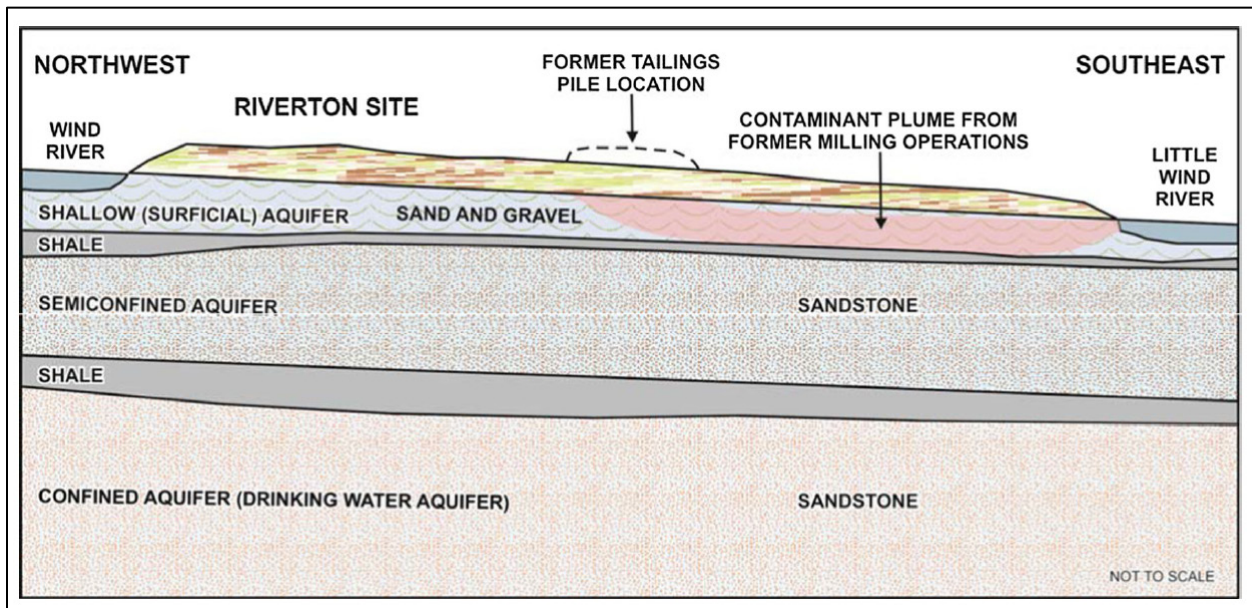
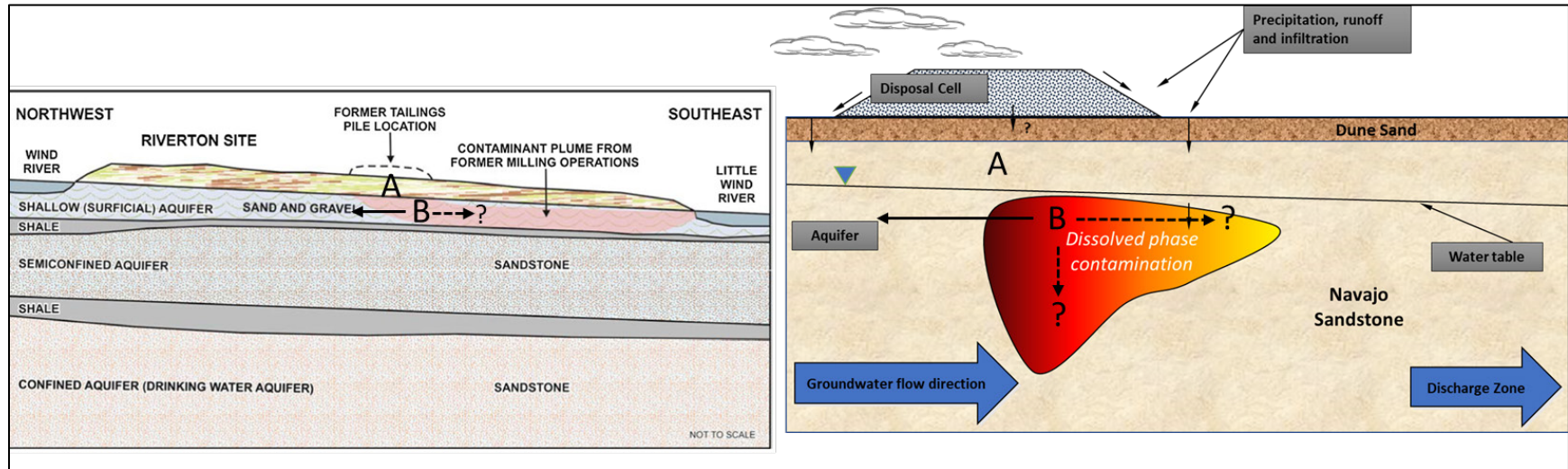


Figure 3. Riverton Site Conceptual Cross Section

3.2 Underneath Tailings

Most LM sites have uranium mill tailings that produce acidic drainage due to the presence of sulfides that were present in the original ore material and residual processing fluids used during ore beneficiation. These sulfides react with oxygen to produce tailings fluids that have a low pH with high concentrations of iron, aluminum, sulfate, and other trace metals that depend on the ore mineralogy that was processed. Typical reactions that occur below the tailings are (1) buffering of the low-pH tailings fluids by carbonate dissolution, (2) precipitation of iron and aluminum oxyhydroxides as the pH increases, and (3) precipitation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) due to the increased calcium concentrations from calcite dissolution in contact with the high sulfate, low-pH tailings fluids. Uranium and other contaminants can be associated with the products of points 2 and 3 to form PeSCS.

The size of the reaction zone (defined as the subsurface horizontal and vertical extent of tailings seepage interaction with the native sediments or bedrock) underneath tailings is highly dependent upon the amount of mill tailings fluids leaking from the tailings impoundment and the amount of carbonate minerals in the underlying geology. Coupled with the depth to the water table and the underlying geology, these reactions may occur only in the unsaturated zone (Figure 4, zone A) or can extend with depth and distance in the saturated zone (Figure 4, zone B). A key reaction is the precipitation of iron oxyhydroxides, which can form sorption surfaces for uranium and other metals. The distance of the iron oxyhydroxide precipitation zone will depend on the buffering reactions (final resulting pH) and the oxidation-reduction potential of groundwater, as ferrous iron (Fe^{2+}) can remain in solution (thus not forming iron oxyhydroxides) under anoxic, more reducing conditions at near neutral pH values (USGS 1962). Precipitation of uranium-forming minerals and other contaminant-bearing minerals is also a possibility. Minerals containing uranium, molybdenum, manganese, or vanadium are typically the ones of concern at LM sites.



Note: A = PeSCS in the unsaturated zone, B = PeSCS in the saturated zone.

Figure 4. Area of PeSCS Below Tailings Impoundments

In the reaction zone underneath tailings impoundments, contaminant plumes form when geochemical attenuation capacities are exceeded (sorption capacity or mineral precipitation). When the source of tailings-derived fluids is reduced or removed, the contaminant plume persists due to desorption or dissolution of the residual contaminants residing on the solid phase materials (i.e., PeSCS). Because of this, the start of the contaminant plume corresponds with upgradient groundwater being influenced by PeSCS. However, within the contaminant plume, once equilibrium between the solid phase and water phase is reached throughout the contaminant plume, it is difficult to identify the extent of the reaction zone PeSCS. Thus, direct solid-phase sampling is generally required to identify the amount and extent of PeSCS distribution, while laboratory microscopy observation helps to determine the exact form of PeSCS within the reaction zone (discussed in Section 5.1). In certain settings with shallow water tables and high evapotranspiration rates, the original PeSCS formed by reactions under the tailings may undergo weathering and subsequently be redeposited without much downgradient movement (PeSCS type E discussed in Section 3.4). This process is similar to evaporite-type deposits.

3.3 Central Contaminant Plume

Conceptual models that do not include PeSCS have typically focused only on initial plume retardation factors during development and the reverse (desorption and mineral dissolution) with plume shrinkage during natural flushing. This central contaminant plume is outside of the reaction zone underneath tailings or disposal cells with contaminant groundwater geochemistry being controlled by the natural system. Thus, the typical reaction is contaminant sorption or desorption on the existing sediments or bedrock. Retardation and natural flushing are calculated using the contaminant distribution between the solid- and water-phases using an equilibrium sorption distribution constant (K_d). The center of the contaminant plume (Figure 5, zone C) has not been a focus of the PeSCS Project, because this area generally exists even without the occurrence of PeSCS. To be clear, contaminants can occur on the solid phase in this central contaminant plume area that need to be accounted for as ongoing sources, but have generally been explained already. Typical LM conceptual site models have already accounted for the hydrogeology and geochemistry of the main contaminant plume, often in the site observational work plans (i.e., DOE 1998a for the Riverton site).

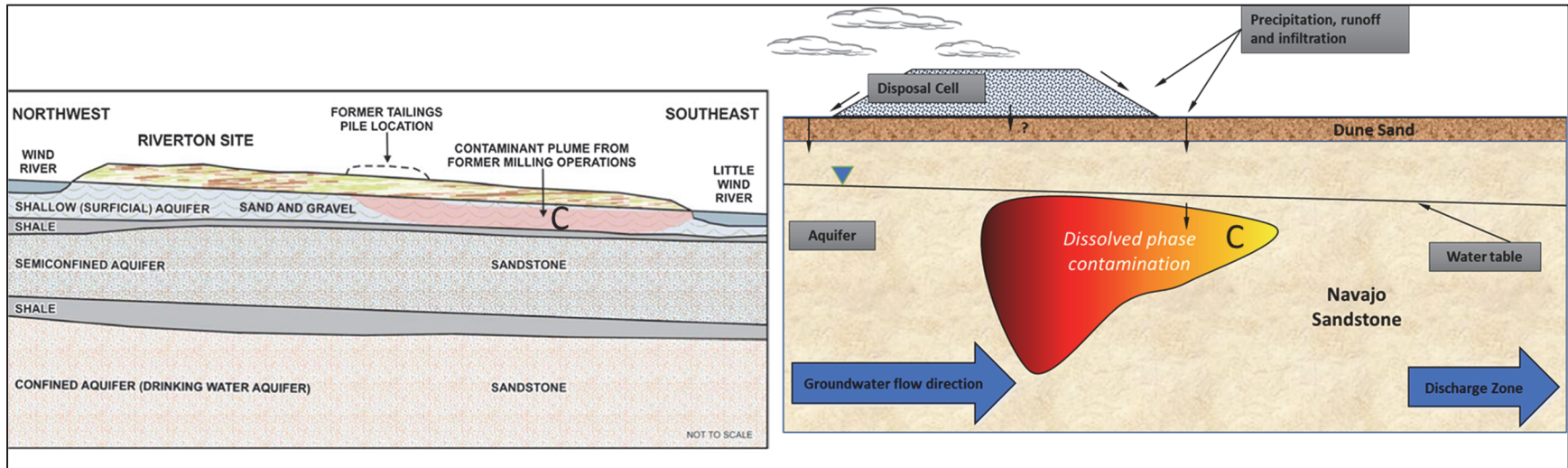
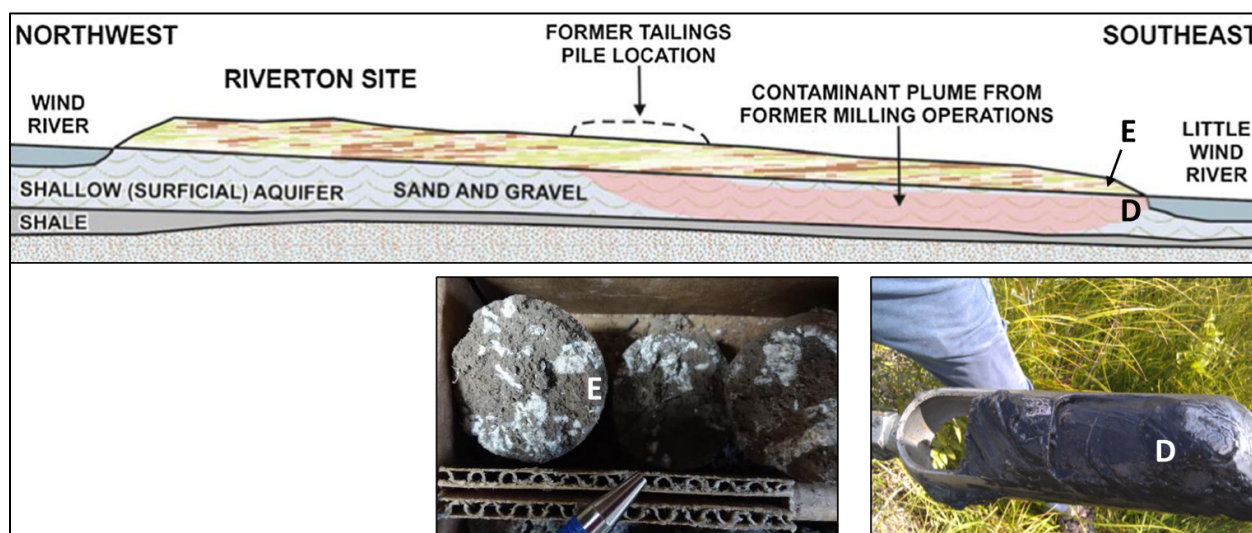


Figure 5. Conceptual Contaminant Plume

3.4 Downgradient Plume

The downgradient plume area is defined as any location outside of the reaction zone or the central contaminant plume, where the hydrogeologic or geochemical conditions change. Typically, this is at a groundwater discharge location, as shown in Figure 6 for the Riverton site conceptual cross section. The Tuba City site example does have a groundwater discharge location (Moenkopi Wash) that could have similar hydrogeologic and geochemical changes, but the current contaminant plume does not extent that far (DOE 2020d). Rock-water interactions in the downgradient plume area are generally related to mineral precipitation-dissolution and contaminant sorption-desorption. These reactions can occur due to a variety of changes in hydrogeologic conditions. However, for LM sites, these are typically areas with high evapotranspiration potential that are subject to flooding (Figure 6, E) or have changes in redox conditions (typically more reducing) due to high organic carbon content in riverbank sediments (Figure 6, D). Type D can also include finer-grained materials, like clays, which create a greater sorption capacity and diffusion of contaminants into lower groundwater flow zones (issue with back diffusion later). These changes result in PeSCS that are a significant distance from the original tailings impoundment. Thus, these secondary solid-phase contaminant sources are not always identified in the original site characterization as the focus was on primary source zones and the central contaminant plume. Once discovered, the PeSCS associated with the groundwater discharge area can significantly change the overall conceptual site model (Dam et al. 2015).



Note: Evaporites (E) and organic-rich material (D) with elevated contaminant concentrations.

Figure 6. Downgradient PeSCS with Conceptual Locations.

PeSCS emplaced in the unsaturated zone (Figure 6, E) occurs when high evapotranspiration rates of the contaminated groundwater leave behind the dissolved constituents. This mechanism has been documented at multiple LM sites (DOE 2020b) and is a focus of the PeSCS Project. The issue with evaporite-type PeSCS is their very soluble nature, with release back into the groundwater after recharge events, such as either large precipitation or flooding events. These PeSCS were the reason for collecting additional solid-phase data and changing the conceptual site model at the Riverton site, after groundwater uranium concentrations increased dramatically

after a large flooding event in 2010 (Dam et al. 2015). Release of contaminants from additional flooding events after 2010 have confirmed this mechanism (DOE 2019; DOE 2022a).

Because contaminant plumes often discharge along river systems where organic-rich sediments can be present at the riverbank or in the case of the Riverton site, in oxbow lake sediments, precipitation or sorption of metals in those sediments is also an important process (Figure 6, D). This mechanism has been a focus of multiple research papers at several LM sites (Janot et al., 2016; Noël et al. 2017a; Noël et al. 2017b; Noël et al. 2019) including the Riverton site (Bone et al. 2017; Perzan et al. 2021). Much of this work was done by scientists from the SLAC National Accelerator Laboratory who refer to these organic-rich sediments as naturally reduced zones (NRZs). Currently NRZs at LM sites may be a mechanism that transfers contaminants from the water phase to the solid phase (PeSCS are being created). However, long-term release of contaminants from these PeSCS (Figure 6, D) under existing or changing geochemical conditions is a possibility. Changing hydrogeologic conditions (e.g., flooding, water table changes, or nearby pumping) can in turn change the geochemical conditions (e.g., the introduction of oxygen). These changes can enhance mineral dissolution or desorption reactions and mobilize contaminants into the groundwater system.

4.0 Plume Persistence Project

The AS&T Plume Persistence Project (DOE 2018) preceded the PeSCS Project and provides solid-phase data from the Grand Junction site. The Plume Persistence Project was the first AS&T project with a specific goal of determining why LM sites often had ongoing contaminant concentrations exceeding predictions. This led to the sampling of solid-phase material in an area near and below former tailings at the Grand Junction site to determine whether PeSCS were present (DOE 2018). Similar questions were posed in the Plume Persistence Project as in the PeSCS Project, which are:

- How and where does uranium reside on the aquifer solids (i.e., uranium form and distribution)?
- What are the uranium amounts and release rates from naturally aged aquifer solids?
- What are the uranium release mechanisms?
- How do the effects of questions 1–3 influence groundwater remediation strategies?

The Plume Persistence Project answered the study questions above using:

1. Sequential chemical extractions to determine uranium concentrations with depth and potential mobility.
2. Fission-track radiography with thin-section petrography (how and where does uranium reside on the microscopic scale).
3. X-ray diffraction (XRD) (uranium association with mineralogy),
4. Column testing (uranium release rates).
5. Reactive transport modeling of the column tests (uranium release mechanisms and influence on groundwater remediation strategies).

With the data designed to answer these five study questions, selective extractions had a limited usefulness in quantifying release rates, while XRD could not identify any uranium minerals. XRD could identify quantities of major minerals like calcite and gypsum. Thus, points 2, 4, and 5 were the most useful approaches to address the study questions, which formed the initial foundation of the PeSCS Project procedures discussed in Section 5.0. The final recommendation from the Plume Persistence Project was to “use tracer tests with companion column tests to determine contaminant release rates and mobility, which may include testing various influent fluids.” (DOE 2018). While the PeSCS Project did continue to examine points 2, 4, and 5, a main objective of the project was to follow the recommendation from the Plume Persistence Project by testing field-scale groundwater tracer tests at the Grand Junction and Riverton sites; thus, addressing the study questions from both projects at multiple scales.

5.0 PeSCS-Project Approach with Testing at Grand Junction and Riverton Sites

This section describes the details of PeSCS-Project procedures tested specifically at the Grand Junction and Riverton sites. For readers interested in the general application of these procedures to other LM sites, Section 6.0 is more applicable.

The PeSCS Project addressed the project objectives and study questions (Section 1.0) using solid-phase analyses, column testing, and field tracer testing at the Grand Junction and Riverton sites (Sections 5.1, 5.2, and 5.3, respectively). The details of these tests with lessons learned on the strengths and limitations of the different methods are discussed below. Section 6.0 discusses how the approaches used at these two sites can be and have been applied to other LM sites.

The PeSCS-Project selected the Grand Junction site for continued analyses because of the prior work done under the Plume Persistence Project. The Riverton site was selected because of extensive solid-phase sampling for PeSCS (DOE 2016) along with column testing (DOE 2022a) after the flooding events mentioned in Section 3.4. In addition, tailings were removed at both sites, allowing for easier access to the contaminated aquifers that are underneath the former tailings areas. Analyses focused on PeSCS underneath former tailings (Figure 4) and downgradient in evaporite-rich material and organic-rich zones (Figure 6).

PeSCS-project related publications for the Grand Junction site are as follows:

- “Using Fission-Track Radiography Coupled with Scanning Electron Microscopy for Efficient Identification of Solid-Phase Uranium Mineralogy at a Former Uranium Pilot Mill (Grand Junction, Colorado)” (Johnson et al. 2021)
- “Column-Test Data Analyses and Geochemical Modeling to Determine Uranium Reactive Transport Parameters at a Former Uranium Mill Site (Grand Junction, Colorado)” (Johnson et al. 2022)
- “Field Experiments of Surface Water to Groundwater Recharge to Characterize the Mobility of Uranium and Vanadium at a Former Mill Tailing Site” (Paradis et al. 2020)

- “Single-Well Push-Pull Tracer Test Analyses to Determine Aquifer Reactive Transport Parameters at a Former Uranium Mill Sites (Grand Junction, Colorado)” (Johnson et al. 2023)
- “Cross-Hole and Vadose-Zone-Injection Tracer Test Analyses to Determine Aquifer Reactive Transport Parameters at a Former Uranium Mill Site (Grand Junction, Colorado)” (Johnson et al. forthcoming)

PeSCS-project related publications for the Riverton site are as follows:

- “Combining Fission-Track Radiography and Scanning Electron Microscopy to Elucidate Uranium Mobility Controls” (Sultana et al. forthcoming)
- “Elucidating Mobilization Mechanisms of Uranium During Recharge of River Water to Contaminated Groundwater” (Paradis et al. 2022)
- *Applied Studies and Technology Persistent Secondary Contaminant Sources Data Release from Field Tracer Testing Studies at the Riverton, Wyoming, Processing Site* (DOE 2023a)

Riverton site-related publications that discuss PeSCS related issues, which were not directly PeSCS-project funded, are as follows:

- *2015 Advanced Site Investigation and Monitoring Report, Riverton, Wyoming, Processing Site* (DOE 2016)
- *Three Years of Multilevel Monitoring Data at the Riverton, Wyoming, Processing Site That Show Contaminant Increases After River Flooding Events and a Large Recharge Event* (DOE 2019)
- *Riverton, Wyoming, Processing Site: 2020 Geochemical Conditions Assessment* (DOE 2022a)

Publications for the Grand Junction site are complete, but collaboration with the University of Wisconsin-Milwaukee for reactive transport modeling of the Riverton site field tracer data is still ongoing. All Riverton site data for use in ongoing analyses has been released through the publications listed above.

5.1 Solid-Phase Analyses

Solid-phase analyses are a necessary first step in identifying PeSCS. Coring and total digestion of solid-phase samples was completed at both sites (Riverton site [DOE 2016] and Grand Junction site [DOE 2018]), which confirmed the conceptual model of PeSCS below the former tailings (Figure 4) and downgradient in evaporite-type deposits and areas with organic-rich sediments (Figure 6). Two types of analyses were used to determine the mineralogy of the PeSCS: (1) sequential extraction, and (2) fission-track radiography coupled with scanning electron microscope (SEM) analyses.

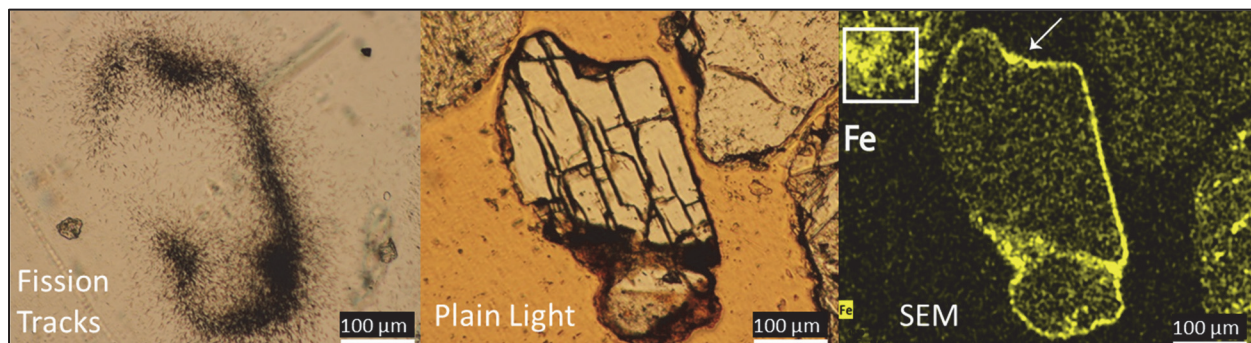
Sequential extractions at the Grand Junction site confirmed that milder leachate fluids, like 5% nitric acid or a carbonate leach, remove less uranium from the solid phase than a full digestion using strong acids (DOE 2018). Sequential extractions allow for a quantification of potentially mobile (5% nitric acid leach) versus immobile amounts of contaminants (total digestion minus 5% nitric acid leach or other similar techniques to determine mobile PeSCS

amounts). However, using one consistent method across a site (i.e. 5% nitric acid leach) is adequate for initially identifying PeSCS locations with depth (Riverton site [DOE 2016] and Grand Junction site [DOE 2018]). Sequential extraction data provide indirect information on how PeSCS are associated with the solid phase (i.e., sorbed to mineral surfaces or precipitated as a mineral) based on the amount of contaminant released with progressively stronger extraction fluid. Relating that release to any exact mineralogy and geochemical mechanism (i.e., sorption or mineral dissolution) can sometimes be challenging based on the combination of mineralogy and available extraction fluids. However, some sequential extraction techniques are designed to identify the amount of a certain mineral, like iron oxyhydroxides (Borggaard 1976), that can in turn control metal sorption.

To evaluate the exact mobility controls on PeSCS, more detailed mineralogy may be necessary, depending on site objectives. Fission-track radiography can specifically identify uranium using microscopic analyses of thin sections after the sample is irradiated and produces radioactive decay of the U-235 isotope (procedural details can be found in the study by Johnson et al. 2021). Fission-track radiography was used to identify grains with elevated uranium concentrations. These were correlated with elemental distributions and mineralogy using a SEM, which confirmed the association of uranium with iron and aluminum oxyhydroxide minerals in materials underlying the former tailings (Johnson et al. 2021; Sultana et al. forthcoming). An example of uranium associated with iron is provided in Figure 7. The precipitation of iron and aluminum oxyhydroxides are consistent with the conceptual model of subpile pH-buffering of the tailings fluid created conditions where iron and aluminum are less soluble in solution. To the authors' knowledge, uranium associated with aluminum precipitation has not been reported in the literature. This microscopic data confirms the uranium association with iron and aluminum oxyhydroxides but it is unclear whether uranium is incorporated into the mineral structure, sorbed to the mineral surfaces, or both. Such incorporation could reduce the uranium mobility, thus, the need for empirical data through column or field testing.

Johnson et al. (2021) and Sultana et al. (forthcoming) both show microscopic evidence for uranium being associated with high carbon content. Similar to the uranium association with iron and aluminum, the geochemical nature of this association is difficult to determine. However, there is no evidence of uranium mineral precipitation, and the uranium is distributed through the high carbon areas (Johnson et al. 2021; Sultana et al. forthcoming). Thus, uranium sorption to the carbon appears likely, similar to the conclusions of Bone et al. 2017.

Excess uranium on solid-phase material was correlated with greater gypsum concentrations identified by XRD analyses and column testing (DOE 2018; Johnson et al. 2021; DOE 2022a) as conceptually hypothesized (Section 3.2). The areas with gypsum often correlated with a greater presence of iron and aluminum precipitates, again matching the conceptual model. However, uranium was not directly identified in microscopic analyses as being associated with gypsum (Johnson et al. 2021; Sultana et al. forthcoming), albeit the addition of uranium release during gypsum dissolution in column studies did improve geochemical modeling results (Johnson et al. 2022). Thus, the coprecipitation of uranium with gypsum is a possibility, but may vary depending on site conditions. Solid-phase analyses provide useful information on PeSCS spatial occurrence, likely geochemical reactions, and potential PeSCS mobility based on observed mineralogy, but actual PeSCS mobility is difficult to quantify without additional work (i.e., column testing and field studies).



Note: Small black lines in the fission-track image are created by uranium and yellow areas in the SEM image are created by iron.

Abbreviation: µm = micrometers

Figure 7. Uranium Associated with Iron-Rich Coatings (after Sultana et al. forthcoming)

5.2 Column Testing

Column testing (Figure 8) is an empirical method to determine potential PeSCS release rates. The Plume Persistence Project measured several columns for uranium effluent only (DOE 2018). This method quantifies uranium release concentrations and generally confirms that more uranium on the solid phase typically leads to a greater uranium release to the water phase. Geochemical modeling is required to determine the geochemical controls on PeSCS release rates. Thus, one column for the Plume Persistence Project (Figure 9) analyzed all influent and effluent constituents to provide data for geochemical modeling. This modeling used various combination of likely mechanisms to determine which ones were controlling the uranium release rates (DOE 2018). The modeling results indicated uranium sorption as a key process with some control on uranium concentrations attributed to cation exchange. Release of sulfate is controlled by the dissolution of gypsum and could be specifically modeled, allowing for the quantification of the amount of soluble gypsum (DOE 2018).

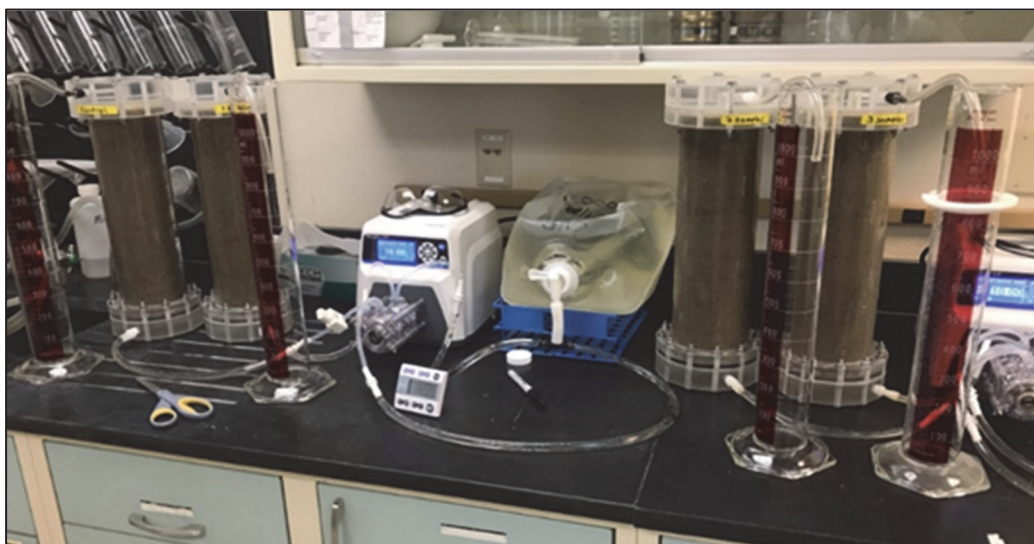
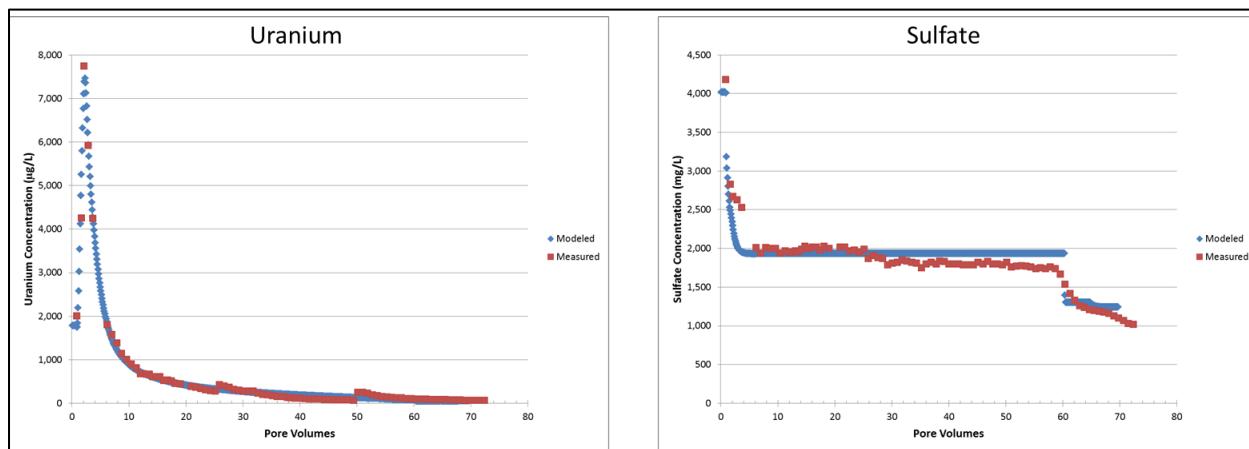


Figure 8. Photo of Column Testing



Abbreviations: µg/L = micrograms per liter, mg/L = milligrams per liter

Figure 9. Example of Measured Column Effluent Uranium and Sulfate Concentration Compared to Modeled (Grand Junction Site from DOE [2018])

Building upon the refined approach in the Plume Persistence Project by measuring all constituents in solution, the PeSCS Project did additional column testing on Grand Junction site sediments (Johnson et al. 2022). This work targeted three PeSCS zones (the unsaturated zone below former tailings, an organic-rich zone, and a gypsum-rich zone) and used different influent waters to simulate different waters that would potentially interact with the solid phase (i.e. precipitation, river water, and background groundwater). This approach allowed for the derivation of uranium sorption parameters for each zone. Similar to the Plume Persistence Project results, uranium release rates are mainly controlled by uranium sorption/desorption with overall geochemical controls provided by the addition of cation exchange and calcite solubility. Again, sulfate is controlled by gypsum dissolution. Some uranium may be released with the gypsum dissolution (possible uranium incorporation in the gypsum) based on geochemical modeling difficulties using just uranium desorption (Johnson et al. 2022). Uranium sorption parameters were similar for the three PeSCS zones, indicating that sorption properties of the sands and gravels at the site did not vary significantly and could potentially be used as one value in a sitewide model, at least in the study area.

In Johnson et al. 2022, the use of different influent water allowed for confirmation that the uranium sorption parameters derived using geochemical modeling are inherent to the solid phase. However, uranium release can change based on the influent water. This change is accounted for with the geochemical modeling and is a valuable tool for testing possible remedial fluids before doing any field tests. A main conclusion is uranium release from the unsaturated zone PeSCS at the Grand Junction site would be greater from a river water flooding event than a large precipitation event (Johnson et al. 2022). Thus, the flood control dike at the Grand Junction site is delaying natural flushing.

Multiple column tests were completed for the Riverton site (no PeSCS Project funded, but via site funding). To date, these columns have been used to empirically determine natural flushing rates (DOE 2022a). Geochemical modeling of the Riverton site column data has not been finalized yet. Empirical analyses used a selected core with identified PeSCS that was tested with influent waters that are typical of field conditions. Riverton site column testing focused on

PeSCS release from saturated zone sediments below the former tailings area (Figure 4) and unsaturated zone sediments from the downgradient discharge area (Figure 6).

When gypsum is not present in saturated zone sediments uranium is released and declines in concentration, typical of desorption processes. For saturated zone sediments with gypsum, uranium is released, declines, and then maintains a relatively constant concentration. Based on the solid-phase analyses, while gypsum is present, these sediments have uranium that is associated with aluminum oxyhydroxides. Future geochemical modeling of these Riverton site columns may help determine the geochemical mechanisms for the uranium release. These results highlight the complexity of the geochemistry, as the collocation of gypsum and elevated uranium concentration and the potential incorporation of uranium in gypsum at the Grand Junction site may not be as relevant for the Riverton site.

For the unsaturated zone Riverton site sediments (Figure 6, type E), uranium is rapidly released up to 0.93 milligrams per liter (mg/L) with the addition of deionized water. These results are similar to data collected in multilevel wells after flooding (DOE 2019), which confirms the new conceptual model for the site (Dam et al. 2015). Sands and gravels underlying the evaporite-related PeSCS have lower solid-phase uranium concentrations and release less uranium in column testing than downgradient sediments that are finer grained and strongly reducing (less oxygen) (Figure 6 type D, also referred to as NRZs). Empirically, these sediments have larger PeSCS concentrations (up to 22 mg/L) and larger release concentrations (up to 5.8 mg/L for uranium) when adding oxic river water or oxic background groundwater (DOE 2022a). However, actual field conditions tend to maintain reducing conditions in this area, which is not recreated in the laboratory. Geochemical modeling and additional column testing of these organic-rich sediments under anoxic conditions has been proposed (DOE 2022b), as the potential for desorption of uranium even under anoxic conditions exists (Bone et al. 2017). Thus, it is still unclear if the PeSCS release parameters derived from an oxic column test can be applied to anoxic field conditions.

5.3 Field Tracer Testing

A significant recommendation from the Plume Persistence Project was determining whether the PeSCS release rates in column tests could be upscaled to the field. This was tested as part of the PeSCS Project at the Grand Junction site (Figure 10) (DOE 2020a [work plan]) using single-well push-pull tracer testing (Johnson et al. 2023) and cross-hole tracer testing (Johnson et al. forthcoming). Grand Junction site field scale testing also included infiltration of traced river water into the unsaturated zone in an area with known PeSCS (Johnson et al. 2023). The Grand Junction tracer testing results were simulated using a reactive transport modeling program (Johnson et al. 2023; Johnson et al. forthcoming). The results indicate similar mechanisms and reactive transport parameters for the column and the saturated zone tracer tests. Infiltration tracer testing at the Grand Junction site released PeSCS similar to column tests (Johnson et al. forthcoming). Required geochemical parameters for field testing included uranium sorption parameters, calcite dissolution, and cation exchange (Johnson et al. 2023; Johnson et al. forthcoming), which was the same as for the column testing (DOE 2018; Johnson et al. 2022).

In general, the geochemical parameter values derived from the column and field testing were the same (Johnson et al. forthcoming). One exception was a low value for uranium sorption in a cross-hole field test where fast aquifer flow paths with less sorption capacity were a possibility

(Johnson et al. forthcoming). As previously discussed, gypsum is needed at all scales to adequately simulate sulfate dissolution. Inclusion of gypsum dissolution as a source of uranium could not be quantified, but appeared likely (Johnson et al. 2022). Reactive transport modeling was able to determine a PeSCS release rate from the unsaturated zone to the saturated zone, but cannot simulate the heterogeneities that exist in the unsaturated zone (Johnson et al. forthcoming).



Figure 10. Photo of Grand Junction Site Field Tracer Testing

The main conclusion from the Grand Junction site field tracer work is that column data can be upscaled to the field, if that scale includes similar geologic and geochemical conditions. Understanding this scale relies on detailed site knowledge and requires a judgement call by subject matter experts. For example, gypsum dissolution in one area cannot be applied sitewide, because gypsum precipitation may not occur sitewide. Similarly, the need for inclusion of more heterogeneous flow pathways is difficult to know. If the scale of heterogeneity is not exceeded, the biggest advantage of field-scale tracer testing is a direct measurement of contaminant dispersivity and the ability to maintain in situ geochemical conditions that may be more difficult to maintain in a laboratory setting (e.g., anoxic conditions and high carbon dioxide concentrations). Diffusion of PeSCS out of layers with lower hydraulic conductivity can be a possibility with large geologic variability, but was not a specific part of the PeSCS Project.

Field tracer testing at the Riverton site focused on saturated zone sediment below the former tailings area (Figure 4, type B) and downgradient unsaturated zone sediments (Figure 6, type E). This included single-well injection drift testing (Figure 11) and testing with downgradient well galleries from saturated zone injections and unsaturated zone infiltration experiments (Figure 12). Details on the Riverton site tracer testing procedures and the resulting data can be found in DOE (2023a). DOE (2023a) provides initial observations, but the data are still being analyzed for geochemical mechanisms and parameters for use in reactive transport modeling.

These data confirm the complexity of determining the mechanisms of uranium release from material below the former tailings area. When background, oxidized groundwater is added to the subsurface, uranium release is greater than preinjection aquifer concentrations (DOE 2023a). Based on solid-phase analyses from Sultana et al. (forthcoming), it is reasonable that this uranium release is related to its association with minerals precipitated below the former tailings (iron and aluminum precipitates). If uranium is sorbed or incorporated into these precipitates, the injection fluid creates geochemical conditions that favor greater desorption. Determining the likely geochemical mechanisms that release PeSCS at the Riverton site is part of ongoing research at the University of Wisconsin-Milwaukee under a National Science Foundation grant. This ongoing effort will use data analysis procedures and reactive transport modeling like those used for the Grand Junction site (Johnson et al. 2023; Johnson et al. forthcoming).



Figure 11. Riverton Site Single-Well Field Tracer Testing with University of Wisconsin-Milwaukee Students



Figure 12. Riverton Site Unsaturated Zone Infiltration Field Tracer Testing with a Downgradient Well Gallery

6.0 Application of PeSCS-Project Approaches to Other LM Sites

Section 5.0 discusses the approaches and results from testing at the Grand Junction and Riverton sites. Other LM sites may or may not have similar hydrogeology or geochemical conditions. However, the series of decisions on performing solid-phase analyses, column testing, or field tracer testing discussed in this section provides a consistent method of evaluating the need for these techniques at any LM site. The ultimate objective from PeSCS evaluations at any LM site is to understand the potential PeSCS-release rates under various conditions to select the best site remediation option; thus, allowing for a scientific basis in evaluating the costs and benefits of various remedial actions before selecting a final remedy.

6.1 Solid-Phase Analyses

Any site characterization must include source zone characterization first, in this case, direct coring and measurement of total PeSCS concentrations. This is the first step in developing a reasonable conceptual site model for understanding the potential influence of PeSCS on long-term groundwater quality. Total digestion of the sample with PeSCS analysis is often selected, but a milder leaching approach is adequate, if the same approach is used consistently. In addition, these analyses should include other constituents besides PeSCS, if they could potential control the PeSCS mobility (e.g., calcium and total inorganic carbon [substitute for alkalinity], as both can influence uranium mobility).

Sequential extraction is typically recommended on a subset of samples that at least represents every PeSCS type that is discovered (e.g., PeSCS with evaporites, organic carbon, iron precipitates). Exact extraction techniques will vary depending on objectives and PeSCS form. At a minimum, sequential extraction testing should determine the amount of mobile versus immobile PeSCS that can be released under reasonably expected environmental conditions (e.g., contact with rainwater, river water, background groundwater, or contaminated groundwater). For the PeSCS and Plume Persistence Projects, using a 5% nitric acid leaching solution provided a reasonable first estimate of the maximum amount of PeSCS that may be mobile under field conditions (DOE 2018).

Results from sequential extraction can be used as a guide for deciding on additional solid-phase analyses, like fission-track radiography and SEM analyses. If PeSCS concentration differences between total digestion and a weaker extraction technique are relatively consistent across the site, or can reasonably be explained, then additional analyses might not be warranted. This decision could also be revisited after column or field testing (note: always retain archived solid-phase material). If column or field-testing results are difficult to explain, fission-track radiography and SEM analyses might help determine unique uranium associations that could not easily be explained with modeling. A limitation of fission-track radiography and SEM analyses is the results often determine contaminant association, but may not determine mobility controls (e.g., mineral surface sorption versus coprecipitation). Other solid-phase analyses such as XRD and X-ray fluorescence may be useful in determining minerals and major elements that may have PeSCS mobility controls (like calcite, gypsum, and calcium). However, typical PeSCS concentrations at LM sites are too low to be detected by these methods. Overall, an iterative approach between modeling and additional solid-phase analyses may be required to determine exact PeSCS mobility controls.

6.2 Column Testing and Field Tracer Testing

Beyond solid-phase analyses, column testing provides a quantitative way to determine PeSCS release rates once the types and locations of PeSCS are identified. Column data can be used in mass balance calculations to estimate natural flushing rates (DOE 2021; DOE 2022a) before doing any modeling. This approach provides a good “first cut” on natural flushing times for comparison with any modeling results. Column testing is also a good technique for testing various remedial fluids before doing any field-scale pilot testing. As mentioned before, one limitation of column testing is not being able to maintain field conditions, most notably with the introduction of oxygen and the possible degassing of carbon dioxide from influent groundwaters externally or from within the column. This is less of an issue for unsaturated zone columns, but testing of columns that are from saturated zone areas with anoxic conditions might require completion within a glove box where the atmospheric conditions can be controlled. Another limitation of column testing is the omission and misrepresentation of capturing subsurface heterogeneities that may exist. Theoretically, with appropriate geochemical modeling, column testing in the laboratory can be used for different geochemical setting (i.e., field conditions) if all the input parameters are known. However, to the author’s knowledge, this has not been fully tested.

Field tracer testing provides information on hydrology and geochemistry. With the injection of a nonreactive tracer, the movement of that tracer in the groundwater can be used to determine aquifer hydraulic conductivity and dispersivity that are not provided by column testing. Injection of different fluids (typically river water or background groundwater) creates changes in the geochemistry that are tracked by continued groundwater sampling. The resulting data and modeling provide information on the geochemical reactions that can influence the release of contaminants from the solid phase, along with the resulting contaminant mobility. In addition, the injection fluids can be amended with chemical to either enhance or reduce the mobility of selected contaminants. These procedures test the hydrogeology and geochemistry at a scale that cannot be done in the laboratory. Likewise, field tracer testing in a single well only tests a small area, whereas testing with cross-hole injection and pumping or with well galleries may incorporate heterogeneities that do not exist at a single well scale. However, if larger scale heterogeneities are not likely, then single well testing may be adequate. Such scale decisions will need to be made on a site-by-site basis along with associated costs and benefits.

With a goal of developing a sitewide reactive transport model, typically, some empirical data on PeSCS release is required to determine appropriate sitewide model input parameters. Too much remaining uncertainty after the calibration of a sitewide reactive transport model can indicate the need for additional column and field testing to reduce that uncertainty. Evaluating “data worth” during site characterization efforts is a new approach (proposed AS&T project) that can use an uncalibrated sitewide reactive transport model to test the need for additional solid-phase characterization, column, or field testing (see Section 6.4).

To derive sitewide reactive transport parameters, the column or field data are simulated with local-scale reactive transport modeling (Johnson et al. 2022; Johnson et al. 2023; Johnson et al. forthcoming), which can be upscaled to a sitewide application, as appropriate. As discussed in Section 5.0, reactive transport parameters appear to be similar at the microscopic, laboratory, and field scale, if the resulting parameters from each scale continue to be applied in zones with similar hydrogeologic and geochemical conditions (e.g., parameters derived from saturated zone sands and gravels with small amounts of sorbed PeSCS should not be applied to contaminated

unsaturated zone silts). Appropriate upscaling relies on a good conceptual site model, where zones of different hydrogeologic and geochemical conditions have been identified. Even with a good conceptual site model, upscaling may contain heterogeneities that were not previously recognized (e.g., Johnson et al. [forthcoming] showed less uranium sorption in sandy gravels at a larger scale, likely due to higher permeability groundwater flow paths with less sorption potential).

The question in developing a sitewide reactive transport model is whether to derive the input parameters from calibration to existing conditions (i.e., groundwater plume), or column testing, or field tracer testing, or a combination of these. The answer depends upon: (1) modeling goals, (2) whether calibration to existing conditions has too much uncertainty [mentioned above], (3) whether column testing can maintain geochemical conditions that are representative of the field, and (4) availability of existing wells or ease of installation for additional wells. Modeling goals and final calibration uncertainty can be quite variable, but a pure mass balance of PeSCS release from the unsaturated after a recharge event is one example where column data alone might be adequate (DOE 2021). For anoxic, saturated zone conditions, using existing wells or completing easily installed well(s) (e.g., Geoprobe installation in sands and gravels less than 25 feet below ground surface) might provide a better, more cost-effective testing approach where in situ anoxic conditions can be maintained.

Overall, a careful cost-benefit approach of deciding on column or field tracer testing must be considered on a site-by-site basis. This section provides references from the Grand Junction and Riverton sites that provide the techniques and experiences in using and applying column and field tracer testing. Key considerations are the PeSCS type, PeSCS location in relation to the water table (with likely oxic or anoxic conditions), existing well locations, and ease of adding additional wells. Final decisions on appropriate site testing to get reactive transport parameters should involve the input and review by subject matter experts. The next section discusses how PeSCS identification and related column work was used in designing a uranium transport model at the Monticello, Utah, Processing Site (<https://www.energy.gov/lm/monticello-utah-disposal-and-processing-sites>).

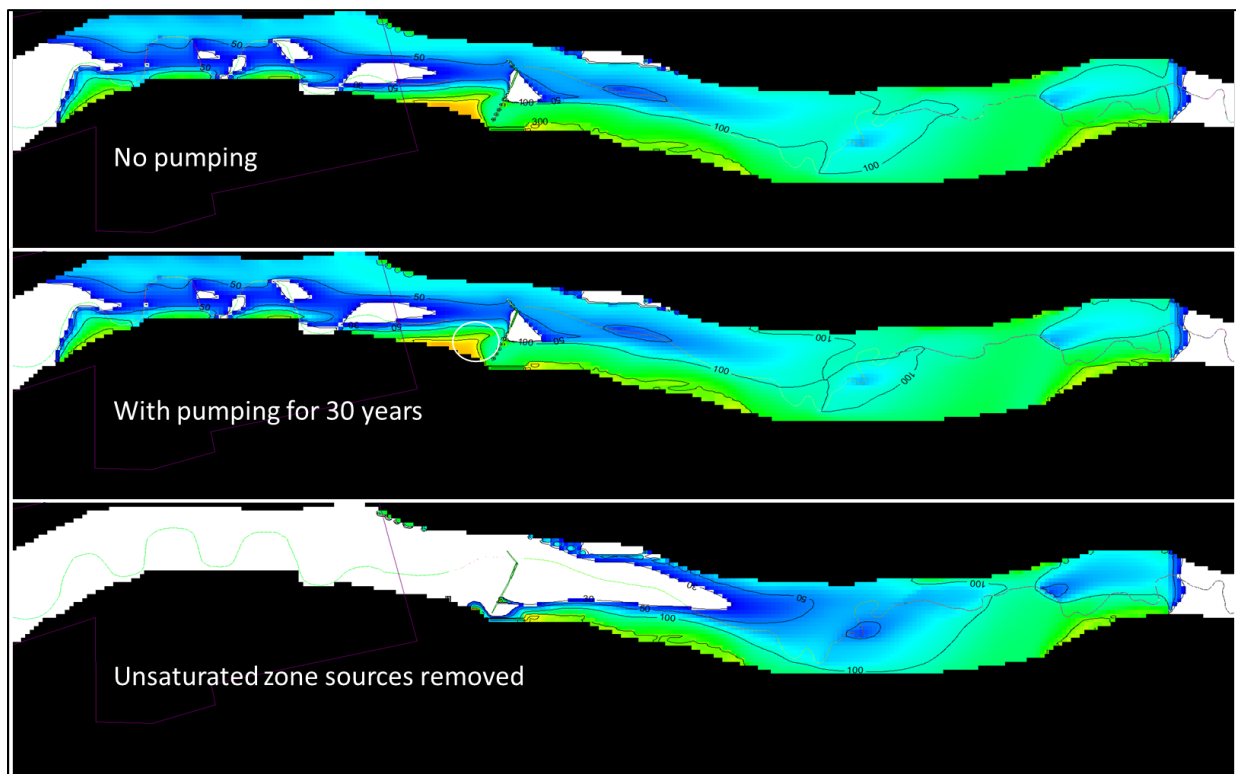
6.3 Monticello Example

The initial question for the Monticello site was whether to continue an aquifer pump-and-treat approach for 30 years and why this system was not performing as expected (DOE 2021). Thus, the first step was to identify whether any PeSCS were providing ongoing contaminant input that was not considered in the original conceptual model and may not be captured by the pumping system. Site work began with 32 boreholes with solid-phase analyses (total sample digestion) followed by column testing on specific core material with high PeSCS concentrations (DOE 2020c). This work identified approximately 9700 pounds (lb) of potentially mobile uranium in the mill-site unsaturated zone and 8200 lb of mobile uranium in the site's saturated zone compared to a removal of only 200 lb of uranium from the extraction wells over a 14-year period (DOE 2021). In addition, groundwater monitoring data indicated PeSCS release in the spring just after snow melt recharge (DOE 2021).

To predict future natural flushing time frames, contaminant concentrations with 30 years of pumping, and to test possible mass removal scenarios, the column data were used to provide PeSCS release rates as input into a contaminant transport model (DOE 2021). These release rates

were tied to the amount of predicted infiltration. Model results indicated a natural flushing time of approximately 2200 years with no change in flushing times with 30 years of pumping (Figure 13) (DOE 2021). Predictions with PeSCS removal from mill-site unsaturated zone sources indicated a reduction of the flushing times to near 340 years (Figure 13) (DOE 2021). PeSCS release from the saturated zone was simulated using an equilibrium sorption coefficient (K_d).

For the Monticello site, the use of empirical column data was adequate for evaluating if continued pumping is reasonable. Because a significant portion of the PeSCS were in the unsaturated zone, column data could reasonably represent oxidized conditions, with release of PeSCS after infiltration events. Thus, the combination of identifying PeSCS locations, amount, and release rates as input into a uranium transport model provided an approach that fit the site needs.



Note: The white circle in the middle panel indicates the pumping area.

Figure 13. Simulated Uranium Concentrations for the Monticello Site 100-Years in the Future Using Reactive Transport Modeling

Currently, the remedial actions that might involve the use of injected fluids to mobilize or immobilize contaminants have not been evaluated for the Monticello site. If this becomes a need, the choice of laboratory versus field testing will need to be revisited. The use of column testing allows for a relatively quick way to compare various remedial fluids if adequate amounts of core material are available. A key site feature are wetlands at the headwaters of Montezuma Creek, which flows through the site. These wetlands can retain uranium and vanadium after release from upgradient PeSCS sources in the unsaturated zone (DOE 2020c). While column data with different remedial fluids may be the most reasonable way to test unsaturated zone PeSCS release, maintaining the anoxic conditions found in the wetlands during core collection and laboratory testing is not easy. Thus, the use of existing wells or easily installed additional wells (sediments

are less than 15 feet thick) with field tracer testing may be a more appropriate for testing remedial fluid in the saturated zone sediments.

6.4 Reactive Transport Modeling Approaches at LM Sites

Regardless of the exact regulatory setting, conceptual site model, or proposed remedial plans, every LM site will need to evaluate a natural flushing scenario. This means every site will need a numerical model that simulates the hydrogeologic and geochemical conditions and provides predictions of flushing times. Thus, every LM site with ongoing groundwater contamination will have to consider (1) the occurrence of PeSCS; (2) PeSCS release rates, if they exist; and (3) how to simulate PeSCS release and transport rates to evaluate a natural flushing scenario. The best way to achieve point 3 is with reactive transport modeling that incorporates site geochemical conditions. Such modeling will need input parameters that can be informed by (1) direct solid phase sampling and (2) evaluation and modeling of PeSCS release rates and transport through column or field testing.

Evaluating remedial actions will require the addition of changing geochemical conditions to the natural flushing model. Such additions can be done through reactive transport modeling from both column testing and field tracer testing, which are then used to update the inputs of the natural flushing reactive transport model. This is a forward approach, where site-scale modeling is not done until after site data are collected and analyzed. An alternative “data worth” approach is a valuable method that can be done before or during data collection. Data worth analysis approximates the reduction in predictive uncertainty that can be achieved by incorporating new data into a model, and it can be performed before the new data are collected (Doherty 2015). This approach assumes that enough site characterization has been done such that a preliminary, uncalibrated reactive transport model can be completed. With an iterative approach, this model can be used for data worth analysis early on, thereby focusing efforts on collecting data that will be most informative for simulating PeSCS release and subsequent transport. The result is the workflow provided in Figure 14 with the double-headed arrows indicating iterative processes. Data worth analyses are part of a new AS&T project proposal that can be applied to the selection of column versus field tracer testing for use in reactive transport modeling (DOE 2023b).

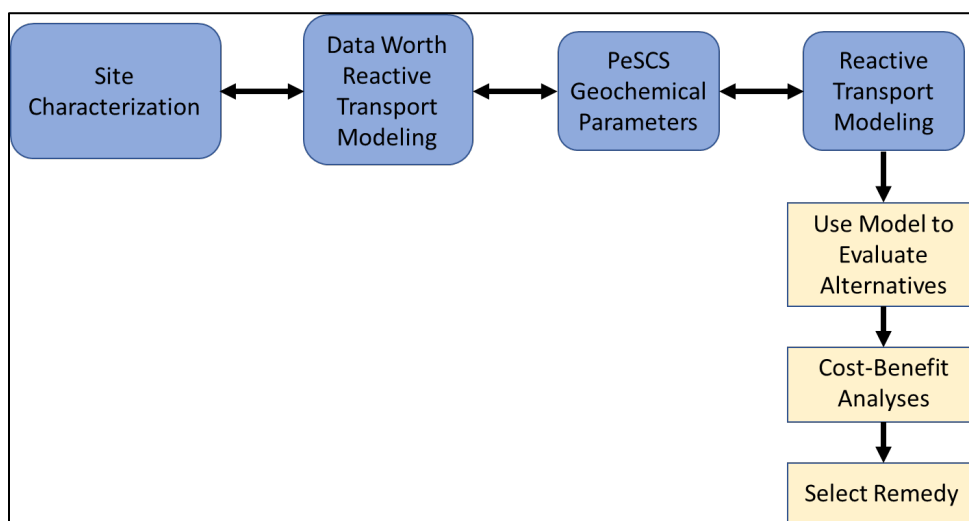


Figure 14. Conceptual Workflow for Evaluating PeSCS and Using Reactive Transport Modeling at an LM Site

7.0 Conclusion

The overall goal of the PeSCS Project is to provide a toolbox for getting necessary parameters to simulate PeSCS release rates. Multiple techniques with various considerations have been provided throughout this report. However, it is impracticable to be totally prescriptive, because the use of this toolbox needs to be considered carefully on a site case-by-case basis by subject matter experts. In any case, a final PeSCS Project goal is to minimize redoing any site data collection by recognizing likely PeSCS locations, doing the necessary solid-phase characterization, and understanding modeling release rates such that site decisions can be made appropriately. While some iterations will inevitably be necessary, the goal is to avoid major revisions to conceptual site models, as was the case when PeSCS were not identified (Dam et al. 2015). This report provides a current state-of-the-art toolbox to derive the necessary data for use as input into reactive transport models. These models can then be used to simulate future site conditions with or without active remediation that can guide site management decisions.

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