Evaluation of Perched Water Post-Extraction Remedy Technologies: Interim Status Report

September 2018

SA Saslow       MMV Snyder
AR Lawter       L Zhong
BN Gartman      KJ Cantrell
F Zhang         CF Brown
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Prepared for
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Pacific Northwest National Laboratory
Richland, Washington 99352
Executive Summary

In the 200-DV-1 Operable Unit at Hanford, a perched water zone is located in a fine-grained unit a few meters above the water table within the B, BX, and BY Tank Farms area. The perched water contains elevated concentrations of uranium (U), technetium-99 (99Tc), and nitrate (NO₃), and serves as a future flux of contaminated water into the groundwater. Currently, a pumping system is used for removal of contaminant mass from the perched water zone to decrease the total contaminant mass transported into the groundwater. As the perched water zone is desaturated through pumping, removal of the contaminated perched water will become more difficult over time. Water extraction cannot remove all of the contaminant mass from this zone, nor can it stop the recharge-driven flux of remaining contaminants toward the groundwater because the flux will continue under unsaturated conditions. Thus, contamination that will remain after pumping needs to be addressed with post-extraction mitigation approaches along with appropriate monitoring and selection of a suitable remediation endpoint.

This report documents candidate post-extraction remediation options for the perched water zone once pumping is no longer a viable option for treatment. In addition to identifying post-extraction options, methods for enhancing pumping rates for the perched water zone were investigated. Candidate technology evaluations initiated in FY18 included bench-scale screening of chemical and physical immobilization approaches for the perched water contaminants. Two bench-scale tests were investigated for remediation of the co-located contaminants, U, 99Tc, and NO₃: (1) a sequential reductive and sequestration approach, and (2) permeation grouts for immobilization. In addition, a quasi-3D cylindrical model was developed and calibrated against pumping tests to identify potential extraction enhancements for the current pump-and-treat system as well as to support future scale-up of the remediation technologies. Removal of the perched water via enhanced pumping is of value to decrease the total contaminant mass that will eventually move into the groundwater.

The two-step treatment process for a sequential reductive sequestration approach involves first creating an anaerobic environment to reduce contaminants so that they are degraded (nitrate) or precipitate in situ. The second step in the sequential approach is to armor the precipitated contaminant with a mineral that will be stable under oxidizing conditions. Zero valent iron, sulfur modified iron and calcium polysulfide were examined for their use in the reductant phase of the sequential technology approach. For the sequestration phase, an alkaline treatment as well as apatite and calcite formation were investigated. Preliminary results identified the two-step in situ treatment as a viable approach in the perched water zone. Although preliminary results indicate the need to use higher concentrations of reductants to fully reduce contaminants in the batch-scale tests, the sequestration technologies, particularly apatite and calcite precipitation, nominally decrease the rate of contaminant remobilization as oxidative conditions return. Experiments are ongoing, and the long-term stability of the contaminants will continue to be evaluated as the batch reactors become fully oxidized. In addition, an alternative method for stimulating calcite precipitation was investigated with the injection of CO₂ gas. Preliminary results suggest that this may be a cost-effective approach to promote calcite precipitation for contaminant sequestration.

Colloidal silica, acrylamide based chemical grouts and Portland-based cements were also investigated for their potential for solidifying and immobilizing contaminants in the perched water zone. The first phase of testing focused on injectability of the permeation grout materials. Only the colloidal silica and acrylamide products have the low injection viscosities, controllable gel times, and a propensity to fill the small void space in fine sediments that would be needed to be effective in the perched water. Additional testing for these grouts would focus on permeability reduction of treated sediment columns to quantify their ability to sequester perched water contaminants.
To support pump-and-treat enhancements and post-extraction treatment technologies, a cylindrical model of the perched water system was developed and calibrated to data from three pump tests. Preliminary simulations demonstrate that the radius corresponding to the lateral extent of drawdown within the perched water aquifer varied from 12 to 47 m. The results show that the extraction volume and extent of impact of an extraction well are strongly dependent on the hydraulic conductivity of the lithofacies. Based on these findings, simulations will be conducted to investigate the potential for enhancing the extraction rate of water in the perched water zone.
Acknowledgments

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<table>
<thead>
<tr>
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<th>Description</th>
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<tbody>
<tr>
<td>CCU</td>
<td>Cold Creek Unit</td>
</tr>
<tr>
<td>CCUz</td>
<td>Cold Creek Unit silt</td>
</tr>
<tr>
<td>CCUg</td>
<td>Cold Creek Unit gravel</td>
</tr>
<tr>
<td>COPC</td>
<td>contaminant of potential concern</td>
</tr>
<tr>
<td>CPS</td>
<td>calcium polysulfide (CaSₓ)</td>
</tr>
<tr>
<td>DDI</td>
<td>double de-ionized</td>
</tr>
<tr>
<td>DVZ</td>
<td>deep vadose zone</td>
</tr>
<tr>
<td>IC</td>
<td>ion chromatography</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma optical emission spectroscopy</td>
</tr>
<tr>
<td>NQAP</td>
<td>Nuclear Quality Assurance Program</td>
</tr>
<tr>
<td>nZVI</td>
<td>nano zero valent iron</td>
</tr>
<tr>
<td>OU</td>
<td>operable unit</td>
</tr>
<tr>
<td>PVDF</td>
<td>polyvinylidene fluoride</td>
</tr>
<tr>
<td>SMI</td>
<td>surface modified iron</td>
</tr>
<tr>
<td>SPW</td>
<td>synthetic perched water</td>
</tr>
<tr>
<td>ZVI</td>
<td>zero valent iron</td>
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1.0 Introduction

Perched water conditions exist a few meters above the water table beneath the B-Complex in the vadose zone in the 200-DV-1 Operable Unit (OU) at the Hanford Site. In this area, the Cold Creek Unit (CCU) is made up of low-permeability sediments, creating a perched water zone that intercepts contaminant movement through the vadose zone. The B-Complex perched water aquifer contains high concentrations of comingled contaminants, including technetium-99 (99Tc), uranium (U), and nitrate (NO3), and serves as a long-term source of contamination to the underlying aquifer.

Water extraction is underway under a CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) removal action for the perched water (DOE/RL-2014-34). Consistent but low extraction rates have been maintained over the operational lifetime of the pumping system, but it is unknown when desaturation will occur, and the pump-and-treat system will no longer be effective. Because there are physical limitations that prevent full dewatering of the perched water by this method, other options to decrease contaminant flux to groundwater need to be identified. Thus, contamination that will remain after pumping needs to be addressed with post-extraction mitigation approaches along with appropriate monitoring and selection of a suitable remediation endpoint. To this end, in situ technologies for the perched water system can address contamination that the pump-and-treat system cannot remove.

Remediation options are limited within the perched water due to the considerable depth of the zone, as well as the challenges posed by the physical and hydrogeologic properties of the perched water (Dresel et al. 2011). Key factors unique to the perched water zone include (a) the contaminant mixtures (99Tc, U, and NO3); (b) contaminant concentrations that are much higher in the perched water relative to the Central Plateau groundwater (maximum concentrations measured in 2016 were 50,100 pCi/L, 150 mg/L, and 1730 mg/L for 99Tc, U, and NO3, respectively; DOE/RL-2016-69); and (c) the potential for slow re-oxidization (once reduced during a response action) due to diffusion limitations of O2 into the perched water.

To address the complex biogeochemistry of contaminant mixtures, laboratory and modeling efforts were initiated in FY18 to better characterize the perched water zone and screen potential in situ remedial alternatives. Specifically, modeling efforts are focused on estimating the effective longevity of the current perched water extraction system, evaluating alternative extraction scenarios, and determining possible remediation endpoints. Laboratory studies are being conducted to screen potential in situ remedial alternatives. These include both chemical and physical immobilization approaches. Specifically, technologies include strong chemical reductants, such as zero valent iron (ZVI), chemical precipitates, such as apatite, and a reactive gas (i.e., CO2). Additionally, permeation grouts are being evaluated for their potential to sequester remaining contamination within a low-conductivity solid matrix. Results from these tests will be used to develop site-specific treatment strategies that address the specific contaminant mixtures in the perched water zone.

1.1 Perched Aquifer

The perched water zone is present in the deep vadose zone at the B-Complex Area located in the Inner Area of the Hanford Site (Figure 1). The perched zone is relatively thin (< 5 m [15 ft]) and is located a few meters above the unconfined aquifer, on top of a low-permeability zone perching unit. The perched water zone is estimated to extend from the east-central portion of the BX Tank Farm northeast to the 216-B-8 Crib and to include the northwest portion of the B Tank Farm (Figure 2). The Cold Creek Unit (CCU) silt (CCUz) in the area with perched water is composed of a lower perching silt (CCUz lower), a high sand content zone (CCUz sand), and upper silt zone (CCUz upper) (see Figure 3). The underlying
Cold Creek Unit gravel (CCUg) contains the regional groundwater aquifer and is underlain by basalt (Truex et al. 2013). The top of the perched water zone is approximately 68.6 m (225 ft) below ground surface and extends to approximately 4.6 m (15 ft) above the water table at its lowest point.

**Figure 1.** Location of the Hanford Site and Central Plateau (from SGW-58147).
Perched water was initially detected in this area in 1991 during drilling of Resource Conservation and Recovery Act of 1976 (RCRA) wells to characterize groundwater contamination in the underlying unconfined aquifer. Significant perched water was encountered during the drilling of well 299-E33-344 in January 2008, which was completed with a screen in the perched water. Extraction of the contaminated perched water began in August 2011 to collect information on the perched zone and to reduce migration of contamination to the unconfined aquifer (DOE/RL-2011-40). In 2014, a removal action was initiated (DOE/RL-2014-34). As part of the removal action, two 200-DV-1 OU perched water wells were drilled in fiscal year (FY) 2014 (wells 299-E33-350 and 299-E33-351) and have been added as the extraction wells.
1.2 Sequential Reductive Sequestration Approach

Reduction and sequestration processes can be used to immobilize subsurface contaminants that are otherwise mobile in pore water or groundwater. Introduction of a reductant to the system can cause the contaminant to transform to a geochemically reduced form and adsorb to sediments or be incorporated into a solid phase. However, technologies that singularly use reductants for immobilizing contaminants are dependent on minimal re-oxidation of the reduced contaminant (e.g., chromium) or maintenance of static reduced redox state for contaminants that are readily re-oxidized (e.g., uranium and $^{99}$Tc).

Re-oxidation of redox sensitive contaminants, such as uranium and $^{99}$Tc, may typically occur via diffusion of dissolved or gas-phase oxygen. The rate at which contaminants remobilize is dependent on the redox potential needed to maintain the reduced form of the contaminant and the rate of re-oxidation. Downward migration of oxidized pore water or oxygen diffusion at the water table are mechanisms relevant to the thin perched water aquifer. Consequently, sequential application of multiple remediation technologies may be needed to decrease contaminant mobility more effectively. Hence, technologies that incorporate contaminants into precipitates or coat surface contaminants with other precipitates that are not sensitive to dissolution with oxygen present can be used to further stabilize a contaminant in situ. With
this type of precipitate, immobilization is dependent on the solubility of the newly formed precipitate, but not the redox conditions. Remobilization of a contaminant after reductant or sequestration treatment in sediment can be evaluated by laboratory-scale batch tests that introduce the reductant and then a sequestration compound, and then measure contaminant stability when the system is oxidized.

### 1.3 Permeation Grouting

Permeation grouting is a long-established and widely used grouting technique that involves the filling of voids in the pore spaces of soils, aggregates or other porous media. Permeation grouting involves injecting a liquid grout into pore spaces that then gels to form a solid void-filling material. Grouting attempts to sequester subsurface contaminant by physically or chemically binding or encapsulating contaminants (Truex et al. 2011). The objective is to fill a void space without displacement of the formation or any change in the void configuration or volume. This requires that grout hole spacing be sufficiently close to provide some overlap of grout penetration. Grouting effectiveness is usually determined by the level of reduced permeability achieved. While permeation grouting is standard practice in the installation of vertical subsurface barriers (e.g., dam foundations), there are uncertainties associated with applying grouting for in situ contaminant stabilization (Kaback et al. 2006).

Several U.S. Department of Energy sites have evaluated, tested, and/or implemented in situ grouting for shallow waste immobilization. In the 1990s, several in situ near-surface waste barrier applications were investigated at the Hanford Site (e.g., Persoff et al. 1994; Dwyer 1994; Heiser et al. 1994; Heiser and Dwyer 1997; DOE/RL 1995). Shallow permeation grouting was also investigated at the Oak Ridge Site to reduce hydraulic conductivity (ORNL 1997). Holdren et al. (2007) provides a thorough review of in situ grouting for shallow waste sites at Idaho National Laboratory, including the use of grout to stabilize waste in near-surface sites (Loomis et al. 2003). The Savannah River Site has also implemented in situ grouting for shallow waste sites such as the F Area seepage basins (DOE 1999).

Acrylamide and silicate grouts were recommended for application to the deep vadose zone at Hanford in a comprehensive review of grouts (Truex et al. 2011). Both materials were identified because they can be formulated for low injection viscosities (1–5 cP), have long gel times that can be controlled, and are may be able to penetrate fine-grained sediment layers at the Hanford.

### 1.4 Enhanced Pump-and-Treat

The presence of perched water enables the use of a pumping system for mass removal. Removal of contaminated water decreases the total contaminant mass that will eventually move into the groundwater. Although removal of perched water via pumping is of value, as the height of the perched water declines over time, the removal of water from the perched zone will become more difficult with time. Removal of the contaminated perched water has been slow due to the low permeability of the silty sand that contains the contaminated water. During a 4-year period between 2011 and 2015, approximately 1,140,000 L (300,000 gal) of perched water was extracted and treated, removing approximately 68.5 kg (151 lb) of uranium, 2.1 g (4.6 × 10-3 lb) of technetium-99, and 583.1 kg (1285 lb) of nitrate from the perched zone (CHPRC 2015).

Perched groundwater is seldom considered in groundwater modeling of water extraction. Modeling the perched water system at the B-Complex previously presented in Truex et al. (2013) and Oostrom et al. (2013) focused on the features that control perched water formation and flux of contaminants toward the groundwater, not on pumping effectiveness. These studies used 1D scoping calculations to evaluate a range of recharge and perched-layer hydraulic conductivity conditions that created the perched water zone. These results contribute to establishing the range of conditions consistent with the observed perched
water height, but further detail is needed to establish alternative pumping rates to enhance contaminant extraction.

### 1.5 Scope, Report Content, and Organization

This report documents batch-scale laboratory screening tests and computer modeling that support evaluation of remediation approaches for the perched water zone at the B-Complex at Hanford. Evaluated contaminant immobilization technologies are presented in Sections 2 and 3. Section 2 presents interim results for a sequential reductive sequestration approach. Section 3 presents initial evaluation of permeation grouts for the perched water. Section 4 provides a description of a model developed to investigate alternative pumping scenarios that can enhance contaminant removal in the perched water zone. A summary of all results to date and recommended future efforts is presented in Section 5, followed by a description of the quality assurance in Section 6.
2.0 Combined Reductant and Sequestering Chemical Treatment

Batch experiments are being performed to assess the potential effectiveness of a number of technologies as part of the remediation strategy for comingled contaminants in the 200-DV-1 OU perched water. Testing includes sequential application of reductive and sequestering technologies for remediation of U(VI), \(^{99}\)Tc, and NO\(_3\)-. Technologies selected for evaluation include Fe and S based reduction, sequestration through mineral precipitation and incorporation, and/or coatings. Specifically, the reduction technologies currently being tested include ZVI, sulfur modified iron (SMI), and calcium polysulfide (CPS). Concurrently, the sequestering technologies being evaluated include apatite formation, calcite formation, and an alkaline treatment (NaOH). Table 1 contains the matrix for evaluation of these combined technologies.

<table>
<thead>
<tr>
<th>Reductive Treatments</th>
<th>Sequestering Treatments</th>
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<tr>
<td>Zero Valent Iron (ZVI)</td>
<td>Apatite</td>
</tr>
<tr>
<td>Sulfur Modified Iron (SMI)</td>
<td>Calcite</td>
</tr>
<tr>
<td>Calcium Polysulfide (CPS)</td>
<td>NaOH</td>
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2.1 Reductive Treatments

2.1.1 Zero Valent Iron

The use of chemical reduction with granular ZVI as a remediation approach is advanced, with a large body of research conducted to support this technology and many documented field deployments in groundwater (ITRC 2005). Most early applications have been in the form of permeable reactive barriers in groundwater to treat a variety of chlorinated organic compounds, metals, and radionuclides. As of 2005, nearly 120 ZVI-based permeable reactive barriers have been installed, 83 of which are considered full scale (ITRC 2005). Metals and/or radionuclides that have been treated by ZVI include chromium, uranium, arsenic, technetium, lead, cadmium, molybdenum, mercury, phosphorous, selenium, and nickel (ITRC 2005). Removal of metals and metalloids by ZVI permeable reactive barriers occurs primarily through reductive precipitation on the surfaces of the ZVI, or as co-precipitates with iron oxyhydroxides that form on the surfaces of the ZVI. Sorption onto iron oxyhydroxides formed during the oxidation of the ZVI can provide an additional mechanism by which metals and metalloids are removed from solution.

2.1.2 Sulfur Modified Iron

Under typical groundwater conditions, soluble pertechnetate (\(^{99}\)TcO\(_4\)\(^-\)) is reduced by ZVI to less-soluble TcO\(_2\)·nH\(_2\)O, but this oxide is highly susceptible to reoxidation. Fan et al. (2013) investigated sequestration of Tc as a sulfide under sulfidogenic conditions in the presence of nano zero valent iron (nZVI). In this study, abiotic sulfide was used to simulate biotic sulfate reduction. Their results demonstrated that sulfidation of nZVI could be effective for favoring the formation of Tc sulfide phases. Results showed increasing Tc removal rates as S/Fe ratios increased between 0 and 0.056, but decreased as S/Fe ratios increased above 0.224. The more favorable Tc removal kinetics at low S/Fe was likely due to a higher affinity of TcO\(_4\)\(^-\) for FeS than iron oxides. X-ray absorption spectroscopy revealed that as S/Fe increases, the pathway for Tc(IV) formation shifted from TcO\(_2\)·nH\(_2\)O to Tc sulfide phases. Recent work
by Lawter et al. (2018) demonstrated that both ZVI and SMI were nearly equally effective at removing Tc(IV) from a Hanford synthetic vadose zone pore water.

### 2.1.3 Calcium Polysulfide

Calcium polysulfide (CPS) or CaSx (where x ranges from 3 to 7) has been used for in situ reduction of Cr(VI) for more than 30 years at sites throughout the United States, as well as a few sites in Europe and Australia (SGW-38255 2009). A historical review of in situ reduction of Cr(VI) using CPS, including several case studies and their relevance to the Hanford Site, was presented in SGW-38255 (2009). These prior efforts have shown that the addition of a carbon source prevents excess sulfate formation and allows the reducing effect to last longer. Monitoring at these sites has shown that remobilization of chromium from the trivalent form via re-oxidation is not a significant factor. The most effective delivery system for the reductant depends on site hydrogeologic conditions. Remediation can be accomplished in both the unsaturated and saturated zones, but remediation of the saturated zone is typically easier to accomplish.

### 2.2 Sequestering Treatments

#### 2.2.1 Apatite

Apatite \([\text{Ca}_{5}(\text{PO}_{4})_3(\text{F,OH,Cl})]\) is a relatively insoluble mineral that can be used to sequester metal and radionuclide contaminants through co-precipitation and adsorption. Phosphate in various forms has been used to sequester selected metal and radionuclide contaminants at the Hanford Site. At the 300-FF-5 Operable Unit in the 300 Area of the Hanford Site, polyphosphate solutions were used to sequester uranium and reduce its mobility in the vadose zone, periodically rewetted zone, and top of the aquifer (Vermeul et al. 2009; Wellman et al. 2011; SGW-59614, Rev. 0). At the 100-N Area of the Hanford Site, treatability tests were performed using a solution containing calcium citrate and phosphate (Vermeul et al. 2010; Fritz et al 2011; SGW-56970, Rev. 0) with jet injection of phosphate and pre-formed apatite into the vadose zone (Szecsody et al. 2010a; SGW-47062, Rev. 0) to sequester Sr-90.

#### 2.2.2 Calcite

ZVI barriers are known to promote the precipitation of calcite and aragonite (along with other phases) due to an increase in pH resulting from oxidation of the ZVI to ferrous iron (Furukawa et al. 2002). As a result of this phenomena, the use of reductants (ZVI or SMI) and calcite-forming solutions to simultaneously remove aqueous Tc(VII) and iodate via reduction and incorporation, respectively, was investigated (Lawter et al 2018). It was found that most of the aqueous iodate was transformed to iodide faster than it could be incorporated into calcite, and therefore I remained in the aqueous phase. However, this two-step approach of reduction followed by calcite precipitation was shown to be highly effective for technetium removal from solution. Additionally, trace amounts of uranium are known to occur in natural calcite (e.g., Kelly et al. 2003), suggesting that precipitation of calcite could potentially be used to sequester uranium.

An alternative approach to chemically precipitating calcite in situ is to promote calcite dissolution using CO₂ gas. CO₂ gas injection into unsaturated sediment results in an acidic pH as low as 5.4 and is dependent on the water content, with lower water content resulting in lower pH values (Szecsody et al. 2010b). Exposing sediments to 100% CO₂ greatly increases carbonate concentrations in the sediment pore water relative to natural conditions. Both the increased carbonate and acidic pH is expected to increase uranium mobilization by forming more Ca-U-CO₃ aqueous complexes and reducing adsorption. Other minerals, such as iron oxides, are also likely partially dissolved at lower pH. After the CO₂ is allowed to
dissipate, the pH will increase, resulting in precipitation of calcite, uranium, and other phases. The precipitated calcite can coat sediment minerals, limiting their interaction infiltrating fluids and/or gases.

### 2.2.3 Sodium Hydroxide

Alkaline gas treatment of low-water content Hanford sediments has been shown to be effective for reducing the mobility of water leachable uranium (Szecsody et al. 2010b, 2012). Reductions of 85% in water leachable uranium in Hanford sediments have been reported (Zhong et al. 2015), with a range of 50% to 90% decrease in uranium mobility. Ammonia treatment significantly decreased the amount of U present as adsorbed and aqueous species in field contaminated sediments. The idea of alkaline treatment with NH₃ gas in the vadose zone has been extended into water-saturated systems using both NH₄OH and NaOH (Emerson et al. 2017, 2018), where it has been shown that uranium immobilization is much more effective in the presence of aqueous carbonate (i.e., Ca-uranyl-carbonate species).

### 2.3 Experimental Methods

A series of batch experiments were conducted to evaluate (1) the reductant(s), (2) sequestering technologies, and (3) a combination of the reductant and sequestering technologies for remediation efforts of the perched water zone. A uranium contaminated sample from the CCU was selected for use in these batch tests. The sample was collected from borehole C9488 at a depth of 217.3 to 218.3 feet below ground surface. The sample (219.3-220.3 ft) had been previously characterized as a sandy mud, with a uranium concentration of 599 μg/Kg (Szecsody et al. 2017). The sample was sieved and the < 2mm fraction was used for testing. Moisture content analysis was also conducted on the as received (field moist) sample and the < 2mm fraction. 10 g of material was added to each batch reactor receiving sediment; the batch reactors were then placed in an environmentally-controlled chamber to avoid exposure to oxygen during the reduction phase.

A synthetic perched water (SPW) solution was used as the aqueous medium for all tests (Table 2). The SPW was spiked with the three contaminants of concern (COCs) and thoroughly mixed to ensure homogeneity. Concentrations of the COCs used for these tests were 150 mg/L uranium, 167 nCi/L ⁹⁹Tc, and 124 mg/L nitrate. COC concentrations were selected to mimic concentrations previously measured in the perched water zone (DOE/RL-2016-69). The spiked SPW was bubbled with N₂(g) to remove oxygen prior to moving it into the anaerobic chamber.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Mmol/L</th>
<th>g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHCO₃</td>
<td>10.7079</td>
<td>0.8995</td>
</tr>
<tr>
<td>KHCO₃</td>
<td>0.3095</td>
<td>0.0310</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>2.7031</td>
<td>0.6662</td>
</tr>
<tr>
<td>CaSO₄·2H₂O</td>
<td>0.5608</td>
<td>0.0965</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>1.7441</td>
<td>0.2477</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.3006</td>
<td>0.1929</td>
</tr>
</tbody>
</table>

Add 100 μL of 2M HCl to 1L solution to lower pH to ~8.2

Phase I experiments focused on bracketing the reducing capacity of ZVI, SMI, and CPS on U(VI), Tc(VII), and NO₃⁻ in simulated perched water. This was accomplished by evaluating each reductant at two ratios. ZVI (Hepure FeroxTarget) and SMI (North American Hogan) were both added as solids and evaluated at ratios of 0.1 and 1.0% by weight. CPS was added as a solution (29% CPS, Agua-Clear) and was evaluated at ratios of 0.5 and 5.0% by weight. Batch reactors were prepared for testing using a
sediment to SPW ratio of 1:10 (10 g CCU sediment:100 mL SPW). A 100 mL volumetric flask was used to measure out spiked SPW for all reactors. All batch reactors were equilibrated in the chamber for 5 days prior to adding the reductants.

After the initial equilibration period, the ZVI, SMI, and CPS were added to the respective batch reactors receiving the reducing treatments. Samples were taken periodically from the reactors, filtered with a 0.22-µm polyvinylidene fluoride (PVDF) filter, and analyzed to monitor changes in concentrations of COCs. Screening analyses for Tc⁹⁹ and U(VI) filter, and analyzed to monitor changes in concentrations of COCs. Screening analyses for Tc⁹⁹ and U(VI) were done by liquid scintillation counting (LSC) and kinetic phosphorescence analysis (KPA), respectively. Samples were also analyzed for pH, anions by ion chromatography (IC), major cations by inductively coupled plasma optical emission spectroscopy (ICP-OES), and Tc and U by inductively coupled plasma mass spectrometry (ICP-MS).

Batch reactors were exposed to the reducing chemicals for 1 month prior to starting the second phase of testing (sequestration). Apatite was added as a series of chemicals targeting a Ca/P ratio of 1.67 for the formation and precipitation of apatite in solution. Calcite was precipitated by adding equimolar concentrations of ammonium carbonate and calcium chloride (final concentrations of 0.05 M). NaOH was added as a solution (final concentration was 0.05M). After a week of equilibration in the anaerobic chamber, the reactors were taken out of the chamber, opened to allow contact with atmospheric oxygen, resealed, and shaken gently to allow slow reoxidation of the solutions. This process was repeated weekly throughout the sequestration phase of the experiments to represent anticipated field conditions where the perched water zone is slowly re-oxidized via diffusion of oxygen from the vadose zone. Periodic sampling of the reactors was conducted to monitor concentration changes of contaminants using ICP-OES, ICP-MS, and IC. Additionally, solution pH was measured in all sample aliquots. All samples collected were filtered with a 0.22-µm PVDF filter. Ongoing sampling was conducted to monitor long-term contaminant remobilization within the reactors.

In addition to chemical precipitation of calcite, batch experiments were conducted to determine if dissolved uranium could be removed through dissolution and re-precipitation within carbonate minerals following CO₂ injection. Testing involved aqueous tests and aqueous plus Hanford-relevant sediments to better determine the effectiveness of this technology at the Hanford Site. Uncontaminated material from the CCU, was crushed to < 2mm for use in the aqueous plus sediment experiments. Batch experiments were conducted in high-density polyethylene (HDPE) bottles containing 2 g of CaCO₃ or 5 g of CCU material along with double de-ionized (DDI) water or SPW spiked with 1 mg/L uranium. The batch reactors were fitted with lids that have an inlet to allow injection of CO₂ as well as an outlet to avoid the buildup of pressure. Inside the reactor, the inlet tube extended into the solution, but did not reach the bottom of the reactor where the solid was located. The CO₂ hydrated by flowing through a bottle containing water prior to entering the batch reactors to minimize solution loss due to evaporation. One sample of the solution was taken prior to CO₂ injection. CO₂ injection occurred for ~24 hours. After CO₂ injection ended, sampling occurred at intervals of approximately 0, 2, and 6 hours, and 1, 3, 7, 14, and 21, 28, and 49 days. Previous studies (Lawter et al. 2015a, 2015b; Wang et al. 2017) have shown that the pH and aqueous Ca concentrations (presumably due to carbonate dissolution) tend to reach steady value in < 7 days (and many reached steady state in < 1 day) of CO₂ injection. After the CO₂ injection period stopped, 2 mL of solution was sampled from each reactor, filtered (0.2 µm, Pall), analyzed for pH, and submitted for uranium analysis via ICP-MS.
2.4 Results

2.4.1 Zero Valent Iron (ZVI) Treatment

Figure 4A shows uranium solution concentrations as a function of time in the batch reactors. The ZVI High (1.0%) treatment was effective at reducing nearly all the uranium within the 28-day test; conversely, the ZVI Low (0.1%) treatment only reduced approximately 20% of the uranium over the same time frame. Both ZVI treatment ratios were effective at reducing pertechnetate in the batch reactors; nearly all the Tc was removed from solution within the first 2 weeks (Figure 4B). Nitrate reduction is following a similar trend to the uranium data, in which the 1.0% ZVI treatment reduced most of nitrate, while the 0.1% ZVI treatment only reduced approximately 20% of the nitrate over the same time period data available for 13 days. Low-concentration ZVI had a low but significant effect on reducing nitrate within 13 days.
Figure 4. Reducing capacity of ZVI for each contaminant of interest.

2.4.2 Sulfur Modified Iron (SMI) Treatment

Figure 5 illustrates the concentration changes over time for U, Tc, and NO₃⁻ in batch reactors containing either 0.1 or 1.0% SMI. Like the ZVI treatments, the two SMI treatment ratios were chosen to bracket the reducing capacity needed to fully reduce all the comingled contaminants. The reduction of U by SMI was similar to the ZVI treatment (Figure 5A); however, the SMI Low (0.1%) treatment showed better
performance (~40% reduction in 28 days) than the low-concentration ZVI treatment (~20% reduction in 28 days). Like the ZVI treatment, Tc was reduced the fastest of the three COCs (Figure 5B) by SMI, with only a slight difference in removal rates between the low and high ratio treatments. Unlike the ZVI treatment, SMI did not reduce nitrate in the 0.1% treatment tests within 13 days. Approximately 45% of the nitrate was reduced after 13 days in the 1.0% SMI treatment tests.

Figure 5. SMI reducing capacity for U(VI), Tc⁹⁹, and NO₃⁻.
2.4.3 Calcium Polysulfide (CPS) Treatment

Figure 6 shows the reduction of U, Tc, and NO₃⁻ by CPS as a function of time. The high-concentration (5%) CPS treatment was highly effective at reducing both U and Tc, with complete reduction occurring almost immediately (Figure 6A and Figure 6B). Tc reduction was observed in the 0.5% CPS treatment tests; however, both the percentage reduced and rate of reduction were lower than in the 0.1% ZVI and SMI treatments. The 0.5% CPS treatment was ineffective at reducing U, and neither CPS solution ratio was effective at reducing nitrate (Figure 6).
2.4.4 Sequestering Technologies for U(VI) and Potential Mobility Impact

After 28 days of exposure to the reducing chemicals, sequestering chemical treatments were added to all the batch reactors to evaluate if a two-step treatment process could limit re-oxidation of the three major contaminants of interest. For this portion of testing, time \( T = 0 \) represents the point when the sequestering
chemical treatments were added to the reactors. (Note: This occurred 28 days after reductants were added to the reactors.) To simulate re-oxidation, the reactors were removed from the environmentally-controlled chamber after 7 days, opened to expose the system to atmospheric oxygen, and then thoroughly mixed to help diffuse the oxygen throughout the reactors. This was performed weekly throughout the sequestering chemical testing phase to mimic re-oxidizing conditions within the perched water zone. Approximately 20 days of the sequestration treatment is reported herein. (Additional monitoring of treatments is ongoing and will be reported separately.)

2.4.4.1 Apatite Amendment

Uranium in solution after 28 days of contact with the low ratio reducing solutions (0.1% ZVI, 0.1 SMI, and 0.5% CPS treatments) quickly decreased upon addition of the apatite forming chemicals (Figure 7); however, the rate of removal was more rapid in the 0.5% CPS reactors than in the 0.1% ZVI and 0.1% SMI reactors. Uranium was also efficiently removed from solution in the reactors receiving just the apatite forming chemicals with no CCU sediment (Apatite Only in Figure 7), indicating the formation of apatite is effective at sorbing and/or precipitating uranium. Additional monitoring of treatments is ongoing and will be reported separately.

![Ca/P Amendment for U(VI)](image-url)

**Figure 7.** Ca, P treatment on U(VI) as a sequestering mechanism.
2.4.4.2 Calcite Amendment

Calcite precipitation was evaluated as a uranium sequestration technology (via coprecipitation) as well as for its potential to coat reduced sediment particles, limiting their interaction with oxygen diffusing into the reactors. For this treatment, ammonium carbonate and calcium chloride were added at final concentrations of 0.05 M each. As shown in Figure 8, calcite precipitation had limited effectiveness at removing residual uranium from solution in the calcite only, 0.1% ZVI, 0.1% SMI, and 0.5% CPS reactors, and uranium concentrations may be slowly rebounding in these reactors. Conversely, uranium solution concentrations remained low in all the high ratio treatment tests, indicating that the systems may have remained reduced even after the addition of atmospheric oxygen to the reactors. Additional monitoring of treatments is ongoing and will be reported separately.

![Calcite Amendment on U(VI)](image)

**Figure 8.** Calcite treatment and the effect on U(VI) treatment with time.

2.4.4.3 Alkaline (NaOH) Amendment

As hypothesized, uranium is rapidly removed from solution following the addition of NaOH (Figure 9). The concentration of uranium remaining in solution quickly decreased (i.e., within the first 7 days) for the reductant-treated reactors, and continued to decrease or remained suppressed throughout the duration of the 28-day test. The NaOH treatment had no effect on uranium solution concentrations in the control samples with or without sediment. Bulk solution chemistry of the reactors will need to be evaluated to
determine the impact on other minerals present in the CCU sediment throughout the re-oxidation period. Additional monitoring of treatments is ongoing and will be reported separately.

![NaOH Amendment for U(VI)](image)

**Figure 9.** NaOH amendment on U(VI) as a sequestering mechanism.

### 2.4.4.4 CO₂ Injection

In the uranium-spiked experiments, aqueous U concentrations remained near 960 ppb (958 ± 82) in the SPW reactor that received CO₂ but contained no solids, and around 830 ± 71 ppb in the reactor with SPW and CCU solids but no CO₂ injection. The U concentrations in the reactors with SPW, CCU solids, and CO₂ injection initially decreased after CO₂ injection, corresponding with the lowest solution pH measured during the test, but subsequently increased as solution pH slowly increased due to calcite dissolution, ending with a solution concentration of approximately 700 ppb by day 7 (Figure 10). The lowest U concentration was measured in the reactor containing DDI water, CCU solids, and no CO₂ injection, which continued to decrease from 650 ppb at time 0 to 320 ppb at day 14, indicating that uranium sorption to minerals present in the CCU sediment is a more effective removal pathway than dissolving and re-precipitating calcite. However, given the promising results observed in the calcite solution forming tests (Figure 8), further effort is warranted to evaluate the potential of CO₂ injection to create a carbonate coating on previously reduced COCs as part of a two-step remediation technology.
Figure 10. a) U, b) Ca, and c) pH data for test 1810 T2.
2.4.5  Sequestering Technologies for Tc-99 and Potential Mobility Impact

2.4.5.1  Apatite Amendment

Unlike U, $^{99}$Tc is not expected to incorporate into the mineral structure of apatite during precipitation. This was confirmed by the apatite only control sample, in which $^{99}$Tc concentrations remained stable throughout the duration of the test (Figure 11). As part of an in situ two-step methodology for remediation, this effort is also evaluating the ability of precipitated apatite to form coatings on surfaces hosting accumulated reduced Tc species, such as Tc(IV)O$_2$ · nH$_2$O(s), Tc$_2$S$_4$(s), or Tc$_2$S$_7$(s). The data in Figure 11 show a slight increase in the concentration of aqueous Tc for all the reduced reactors after adding the apatite forming chemicals. The only reactors that appear to be unchanged are the samples that were exposed to a high concentration (5%) of CPS. Additionally, the release rate of Tc appears to be leveling off in the SMI treated samples, indicating that the addition of apatite forming chemicals could be limiting Tc reoxidation in these reactors. Additional monitoring of treatments is ongoing and will be reported separately.

![Ca/P Amendment for Tc$^{99}$](image-url)

**Figure 11.** Impact of the Ca/P amendment on Tc$^{99}$ with time.
2.4.5.2 Calcite Amendment

Tc was not expected to be coprecipitated with calcite, as is shown in the calcite only reactor plot in Figure 12. However, the goal of evaluating this technology for in situ deployment was to determine if the precipitated calcite could form a coating on previous reduced COCs, thereby limiting their interaction with oxygen as the system slowly oxidizes. Initial results indicate that less Tc was re-dissolved in the perched water solution with time in the calcite treated reactors vs. the apatite treated reactors. Additional monitoring of treatments is ongoing and will be reported separately.

![Calcite Amendment for Tc$^{99}$](image.png)

**Figure 12.** Effects of calcite as a sequestering treatment on the reduced Tc$^{99}$. 
2.4.5.3 Alkaline (NaOH) Amendment

As seen in Figure 13, the concentration of $^{99}$Tc remained unchanged in the NaOH only test. Additionally, as seen in Figure 13, Tc concentrations in the low SMI and low ZVI treatment tests increased dramatically within two weeks of sample reoxidation, indicating that this technology may have limited effectiveness for stabilizing reduced Tc species in increasingly oxidizing systems. Additional monitoring of treatments is ongoing and will be reported separately.

![Figure 13. NaOH Amendment effect on Tc$^{99}$ over time with re-oxidation.](image)

2.5 Discussion and Path Forward

Initial results indicate that a two-step in situ treatment for remediation of comingled contaminants in the perched water zone may be viable. Testing of two end member cases has demonstrated the need to use higher concentrations of both ZVI and SMI to fully reduce the sediments and COCs. Several of the sequestering technologies tested, particularly apatite and calcite precipitation, appear to decrease the rate of COC remobilization. These experiments are ongoing and information on the long-term stability of COCs under the various treatment technologies will be presented in the future report.

Additional monitoring of treatments is ongoing and will be reported separately. Once solution concentrations stabilize in the reactors, the tests will be terminated and sediment will be recovered from the reactors to evaluate mineralogical alteration and the presence of secondary precipitates. The next
recommended step is to evaluate the best performing reduction and sequestering chemical treatment approaches will be evaluated in flow-through column experiments to quantify treatment effectiveness at field-relevant solid/solution ratios.
3.0 Permeation Grouts

The objective of this effort was to assess the effectiveness of permeation grout materials for the stabilization (i.e., immobilization) of NO₃⁻, U(VI), and Tc in the perched water zone of the 200-DV-1 OU as a means to reduce the flux of these contaminants into the underlying groundwater. Based on a review of previous testing campaigns (Truex et al. 2011) and geological properties of the Hanford CCU, colloidal silica and acrylamide based chemical grouts were determined to be the most favorable candidates for testing due to their relatively low injection viscosities, controllable long gel times, and propensity to fill the small void space in the finer sediment regions expected in the CCU. However, recent technology developments in the field of Portland-based cements warrant their consideration in the early stages of testing as well. A list of tested grouting amendments is provided in Table 3.

<table>
<thead>
<tr>
<th>Grouting Technology</th>
<th>Product(s)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colloidal Silica</td>
<td>MasterRoc® MP 325</td>
<td>BASF</td>
</tr>
<tr>
<td>(~30 wt% Silica)</td>
<td>SOL-1030NA</td>
<td>Geo40</td>
</tr>
<tr>
<td></td>
<td>Levasil CC301, Silane modified</td>
<td>AkzoNobel</td>
</tr>
<tr>
<td></td>
<td>Levasil CS30-130, Sodium Stabilized</td>
<td>AkzoNobel</td>
</tr>
<tr>
<td></td>
<td>Levasil CS30-425, Sodium Stabilized, Surface</td>
<td>AkzoNobel</td>
</tr>
<tr>
<td></td>
<td>Modified with Aluminum</td>
<td></td>
</tr>
<tr>
<td>Acrylamide</td>
<td>AV-100 Chemical Grout</td>
<td>Avanti International</td>
</tr>
<tr>
<td>Portland-based Cement</td>
<td>US Grout Ultrafine VX</td>
<td>Avanti International</td>
</tr>
</tbody>
</table>

3.1 Experimental Methods

Three testing phases involving laboratory-scale batch and column studies were designed to down select candidate grout amendments based on their performance under expected perched water zone environmental conditions. All three phases are summarized below, but details are only provided for phase one testing. Phase two and phase three tests are recommended for future efforts.

Phase One: Candidate grout amendments were tested for gel or set time using an SPW simulant in the absence of sediment. The ability to control gel and set time is key to implementing this remediation technology in the Hanford subsurface, where rapid setting may limit the treatable area of a single grouting activity, thereby requiring more injection sites. Furthermore, rapid setting may decrease uniform permeation of the grouting amendment into the subsurface, creating isolated areas where contaminants could continue to migrate towards the groundwater. The gel time of colloidal silica based candidates was assessed as a function of amendment to SPW ratio, the concentration of accelerant (a Na⁺ solution made with NaCl), and shear rate of the rheometer used to measure the viscosity of the sample. Acrylamide and Portland cement candidates were also evaluated as a function of amendment to SPW ratio. Several amendment:SPW ratios were tested to down-select candidates and to assess the operable range of specific grouting materials within the perched water zone. Gel times were evaluated according to reproducibility, controllability, and duration during the down-selection process.

Phase Two: Hydraulic conductivity before and after grouting should be evaluated using 1-D column tests as a method for quantifying the decrease in sediment permeation upon treatment. This phase would simultaneously assess laboratory-scale injection parameters (e.g., injection pressure and rate) that provide preliminary process knowledge for field-scale implementation. A separate set of 1-D columns will be prepared with glass columns to provide visual evidence of amendment permeation during injection. This second testing phase would use SPW and uncontaminated sediment analogs that closely match the...
sediment fractions characterized for selected sediment zones in the CCU. Grouting amendments that demonstrate measurable decreases in (saturated) hydraulic conductivity relative to the untreated sediments would be considered for phase three testing.

Phase Three: (To be completed in FY19) Contaminant stabilization using the down-selected grouting amendments and contaminated borehole sediments should be tested using 1-D column and/or batch experiments. Preliminary sediment characterization (e.g., moisture content analysis) should be performed (as needed) on sediments where data do not currently exist or to determine if the sediment properties have changed while in storage. The identified perched water zone contaminants of interest include U(VI), Tc, and NO$_3^−$. Therefore, preliminary testing would include sequential extractions (groundwater, magnesium-nitrate ion-exchange solution, and weak acetic acid) carried out in batch reactors to evaluate the leachability and contaminant concentrations in the untreated sediments. Where sediments do not meet the target contaminant concentrations for Tc-99 (55,000 pCi/L) and NO$_3^−$ (2000 mg/L), sediments would be contacted with SPW spiked at these Tc-99 and NO$_3^−$ concentrations for a specified period before grouting. Sediments treated with the selected grouting amendments should also be evaluated for contaminant leachability using sequential liquid extractions after treatment. Water eluted from the column during amendment injection would be analyzed for the contaminants and components of the grout materials.

Ultimately, the effectiveness of grout amendments is based on the following success criteria:

- Gel time and gel time controllability
- Permeability reduction after grout treatment through measurement of saturated hydraulic conductivity
- Nitrate, uranium, and technetium-99 retention as quantified using column studies

3.1.1 Simulated Perched Water (SPW) Synthesis

The simulated perched water used in this work was prepared according to the procedure described in Section 2.1 (Table 2).

3.1.2 Gel and Set Time

3.1.2.1 Colloidal Silica Amendments

Gel time was determined using an Anton Paar Physica MCR 101 rheometer for each colloidal silica candidate as a function of candidate to SPW ratio, accelerant (NaCl) concentration, and shear rate. A list of candidate properties is provided in Table 4 and a test matrix is provided in Table 5. Test specimens were prepared by volume or by mass. When prepared by volume, an aliquot of SPW and/or the desired colloidal silica candidate were added to a labeled 50 mL centrifuge tube, immediately followed by a specified volume of Na$^+$ accelerator (as needed, made to the required concentration with reagent grade NaCl and DDI). Once all constituents were added, the time and date were noted at the sample start time. The specimen was then capped and hand mixed before observing or adding to the rheometer sample holder (≈19 mL) and starting a rheology test using the integrated instrument program (Anton Paar Rheoplus/32 V3.62). Each sample measured with the rheometer used a test file programmed to collect viscosity measurements for 30 minutes at a shear rate of 50 s$^{-1}$, followed by a 60-minute period without mixing (shear rate = 0 s$^{-1}$). Data collection proceeded until a specimen gelled, as indicated by a maximum in measured viscosity followed by a plateau in viscosity, which was indicative of equilibrium. For some preliminary batch experiments, primarily those performed on Levasil products in the absence of an accelerator, the gel time process was observed for relative set time rather than measured. In these instances, a specimen gel time was recorded when the gelled matrix maintained its structure for
30 seconds after the 50-mL centrifuge tube was moved from a vertical position to a horizontal position on the benchtop surface.

**Table 4.** Colloidal silica candidate properties.

<table>
<thead>
<tr>
<th>Colloidal Silica Product</th>
<th>Short Name</th>
<th>Additives</th>
<th>SiO₂ wt %</th>
<th>Viscosity cP (mPa.s)</th>
<th>Density g/mL</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>MasterRoc® MP 325</td>
<td>BASF</td>
<td>-</td>
<td>15 ± 1%</td>
<td>~10</td>
<td>1.098</td>
<td>10 ± 1</td>
</tr>
<tr>
<td>SOL-1030Na</td>
<td>Geo40</td>
<td>Na Stabilized</td>
<td>~30</td>
<td>&lt;10</td>
<td>1.196 – 1.210</td>
<td>9.0 – 9.8</td>
</tr>
<tr>
<td>Levasil CS30-425</td>
<td>Levasil</td>
<td>Na Stabilized, Surface Modified with Al</td>
<td>30</td>
<td>9.8</td>
<td>1.204</td>
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<tr>
<td>Levasil CS30-130</td>
<td>-</td>
<td>Na Stabilized</td>
<td>30</td>
<td>7.5</td>
<td>1.214</td>
<td>10.8</td>
</tr>
<tr>
<td>Levasil CC301</td>
<td>-</td>
<td>Surface Modified with epoxy silane</td>
<td>28</td>
<td>4.0</td>
<td>1.187</td>
<td>6.4</td>
</tr>
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</table>
Table 5. Colloidal silica gel time test matrix.

<table>
<thead>
<tr>
<th>Colloidal Silica Product</th>
<th>Colloidal Silica Product :SPW Ratio</th>
<th>[Na⁺] ppm</th>
<th>Colloidal Silica SPW #</th>
<th>Volume of Na⁺ Accelerant (in DDI)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mL:mL</td>
<td>mL (g)</td>
<td>mL or g</td>
<td>mL</td>
</tr>
<tr>
<td><strong>Preliminary Gel Time Tests (No Accelerant [Na⁺])</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BASF</td>
<td>10:1</td>
<td>0</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>5:1</td>
<td>0</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>0</td>
<td>20</td>
<td>6.7</td>
</tr>
<tr>
<td>Geo40</td>
<td>10:1</td>
<td>0</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>5:1</td>
<td>0</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>0</td>
<td>20</td>
<td>6.7</td>
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<tr>
<td>Levasil (Levasil CS30-425)</td>
<td>10:1</td>
<td>0</td>
<td>10</td>
<td>1</td>
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<tr>
<td></td>
<td>1:1</td>
<td>0</td>
<td>15</td>
<td>15</td>
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<td>1</td>
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<tr>
<td></td>
<td>1:1</td>
<td>0</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Levasil CC301</td>
<td>10:1</td>
<td>0</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>0</td>
<td>15</td>
<td>15</td>
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<tr>
<td><strong>Preliminary Accelerant Tests (No SPW)</strong></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Geo40</td>
<td>10,000</td>
<td>30.0</td>
<td></td>
<td>10.0^</td>
</tr>
<tr>
<td>Geo40</td>
<td>5,000</td>
<td>35.0</td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>Geo40</td>
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<td>37.0</td>
<td></td>
<td>3.0^</td>
</tr>
<tr>
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<td>1,500</td>
<td>37.0</td>
<td></td>
<td>3.0^</td>
</tr>
<tr>
<td>BASF</td>
<td>1,500</td>
<td>37.0</td>
<td></td>
<td>3.0^</td>
</tr>
<tr>
<td>Levasil (Levasil CS30-425)</td>
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<td>37.0</td>
<td></td>
<td>3.0^</td>
</tr>
<tr>
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<td>1,500</td>
<td>37.0</td>
<td></td>
<td>3.0^</td>
</tr>
<tr>
<td>Levasil CC301</td>
<td>1,500</td>
<td>37.0</td>
<td></td>
<td>3.0^</td>
</tr>
<tr>
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<td>38.0</td>
<td></td>
<td>2.0^</td>
</tr>
<tr>
<td>Geo40</td>
<td>500</td>
<td>39.0</td>
<td></td>
<td>1.0^</td>
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<td><strong>Gel Time Tests with Variable Amendment:SPW ratios and Na⁺ Accelerant Concentrations</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BASF</td>
<td>1:1</td>
<td>10,000</td>
<td>18.3 (20.2)^*</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>3,000</td>
<td>19.5 (21.5)^*</td>
<td>19.5</td>
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<tr>
<td></td>
<td>1:5</td>
<td>10,000</td>
<td>6.1 (6.7)^*</td>
<td>30.6</td>
</tr>
<tr>
<td>Geo40</td>
<td>1:1</td>
<td>10,000</td>
<td>18.3 (22.0)^**</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>3,000</td>
<td>19.5 (23.4)^**</td>
<td>19.5</td>
</tr>
<tr>
<td></td>
<td>1:5</td>
<td>10,000</td>
<td>6.1 (7.3)^**</td>
<td>30.6</td>
</tr>
<tr>
<td>Levasil</td>
<td>1:1</td>
<td>10,000</td>
<td>18.3</td>
<td>18.3</td>
</tr>
</tbody>
</table>

* Measured density of BASF MasterRoc® MP 325 = 1.1039 g/mL at 21°C
**Assume reported density of 1.2 g/mL for Geo40 SOL-1030Na to convert mL to g
^ Density of SPW = 1 g/mL
^ Use a Na⁺ stock solution of 40,000 ppm; ^ Use a Na⁺ stock solution of 20,000 ppm; ^ Use a Na⁺ stock solution of 120,000 ppm
3.1.2.2 Acrylamide Amendment

AV-100 (Avanti International) is an acrylamide-based chemical grout that is mixed with a polymerization reaction activator (AV-101 Catalyst T+, Avanti International). When this solution is combined with a second solution containing the polymerization reaction trigger (AV-102 Catalyst AP) at a 1:1 ratio, the mixture gels in under a minute. However, this gel time may be longer when diluted by perched water saturating the perched water zone. To evaluate this, different volumetric ratios of the AV-100 solutions to SPW were tested to quantify changes in gel time due to dilution.

Before testing, a solution containing AV-100 and AV-101 Catalyst T+ (Solution 1) was prepared in addition to the trigger solution (Solution 2) containing AV-102 Catalyst AP using the recommended manufacturer procedure, but scaled down from field to laboratory-scale quantities. For Solution 1, 500 mL was prepared by adding 250 mL of AV-100 and 8.375 mL of AV-101 to 166 mL of DDI water, followed by the final addition of 75 mL of DDI. For Solution 2, 10.01 g of AV-102 was added to 166.27 g of DDI contained in a 500-mL volumetric flask, and then brought to a final volume of 500 mL by adding additional DDI.

To generate specimens at the desired ratios (Table 6), an aliquot of SPW was added directly into the rheometer sample holder and the collection program started to initiate mixing. After 1 minute, Solutions 1 and 2 were simultaneously added into the sample holder under continuous mixing. The viscosity of the sample was continuously mixed and viscosity data collected every 60 seconds until gelation occurred.

<table>
<thead>
<tr>
<th>Table 6. AV-100 test matrix.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>AV.100 Sol.1-Sol.2-SPW Ratio 1:1:2</td>
</tr>
<tr>
<td>AV.100 Sol.1-Sol.2-SPW Ratio 1:1:5</td>
</tr>
<tr>
<td>AV.100 Sol.1-Sol.2-SPW Ratio 1:1:10</td>
</tr>
</tbody>
</table>

3.1.2.3 Portland Cement Amendment

Set time analysis, as described in ASTM C191-13 Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle, was used to analyze the set time of US Grout Ultrafine VX (Avanti International) treated SPW at three different ratios. The test matrix used is provided in Table 7. Aliquots of Ultrafine VX were pre-weighed into plastic bags and the desired SPW was measured directly into a 2 L plastic bucket for each test batch. To prepare the grout mixtures, the desired Ultrafine VX aliquot was slowly combined with the SPW aliquot over the course of 1 to 1.5 minutes with intermittent hand-mixing with a spatula. Once all the dry material was added, the grout mixture was continuously mixed by hand until 5 minutes had elapsed since starting the Ultrafine VX material addition. Within this 5-minute period, the desired volume of USG Super Plasticizer was added after ~3 minutes of elapsed time from the start of mixing. According to manufacturer specifications, the USG Super Plasticizer is recommended to be added at 0.9 wt%; however, assuming the manufacturer reported relative density of 0.57 g/mL, the USG Super Plasticizer was added here at ~0.51 wt%.
After mixing, the grout mixture was poured into a pre-tared, pre-labeled plastic form (with lid ~3 in. diameter × 2.5 in. tall). The initial sample mass was then recorded and the specimen stored inside a plastic 5-gallon bucket with an inch of deionized water at the bottom to maintain a relative humidity >80%. Samples were elevated in the bucket to avoid contact with the deionized water and stored with the container lid loosely covering the specimen surface.

To determine set time, specimens were measured using a Vicat needle apparatus. After placing the specimen under the Vicat needle, the needle was lowered until it rested on the surface of the slurry/paste. In most instances, there was a layer of residual free liquid that was not reabsorbed by the grout slurry and covered the surface of the test specimen. For these measurements, the needle was lowered until it rested at the surface of this residual free liquid layer. Once aligned with the surface, the set screw on the apparatus was tightened and the indicator set at the top of the scale, e.g., 0 mm. To perform a measurement, the rod holding the Vicat needle was released by releasing the set screw. The needle was then allowed to settle for 30 seconds before recording the penetration depth, measurement date, and time. Subsequent measurements were made at least 5 mm from any previous measurement and at least 10 mm from the edge of the specimen container. Between measurements, the Vicat needle was cleaned by wiping with deionized water. Measurements continued at regular intervals until the specimen had set or at least 30 days had passed since specimen preparation. A specimen was considered to have set when the needle no longer made a mark in the specimen surface. When this was observed, two additional measurements were made to verify the set time and the final specimen mass was measured. Specimens that did not reabsorb residual free liquids were not considered to have set and a final specimen mass was not recorded.

**Figure 14.** Vicat needle apparatus (specimens shown are not from this test).
3.2 Gel and Set Time Results

3.2.1 Gel Time of Colloidal Silica Grout Amendments

To assess the gel time for colloidal silica treated SPW, three sets of tests were ultimately performed that measured or observed the gelation period of (1) colloidal silica treated SPW in the absence of the Na\textsuperscript{+} accelerator, (2) colloidal silica amendments spiked to variable final concentrations of Na\textsuperscript{+} accelerator and without SPW, and (3) amendment and accelerator treated SPW with variable volumetric ratios and Na\textsuperscript{+} accelerator concentrations.

In preliminary tests that studied gelation in the absence of an accelerant, the objective was to identify whether cations present in the SPW would be capable of catalyzing the gelation reaction without the addition of an accelerant. The results of these experiments are shown in Figure 15, where BASF and Geo40 amendments were used to treat SPW at volumetric ratios of 3:1, 5:1, and 10:1 (amendment:SPW). The measured viscosity was minimal and did not change over the course of ~5 hours for all tests except Geo40 treated SPW at a ratio of 10:1, although the increase in this test was less than 1 cP. In addition to the tests performed on BASF and Geo40 amendments, Levasil products CS30-425, CS30-130, and CC301 were used to treat SPW at ratios of 10:1 and 1:1. Each Levasil test was observed over several days, with little to no change in viscosity. Rheometer measurements were not performed on the Levasil samples, since the outcome relative to BASF and Geo40 tests was not expected to differ.

![Figure 15. Gel time of BASF and Geo40 treated SPW as a function of volumetric ratio (amendment:SPW) and in the absence of accelerant (e.g. Na\textsuperscript{+}).](image)

With the apparent need for an accelerant to treat the SPW with colloidal silica amendments, the next testing group studied the impact of final accelerant concentration on gel time and final viscosity of the colloidal silica amendments. These tests were performed in the absence of SPW and the results are shown
in Figure 16. Each test was performed for at least 1000 minutes (~16.7 hours), or until gelation occurred and a maximum viscosity was reached. Initially, each colloidal silica amendment was treated with Na⁺ accelerator to a final concentration of 1500 ppm Na⁺. However, only the Geo40 amendment showed indication of gelation. As such, additional Na⁺ concentrations were investigated, but only for Geo40. From these additional studies, an increase in the start and duration of the gelation period was observed as Na⁺ concentration decreased. For instance, in the presence of 10,000 ppm Na⁺, Geo40 gelled in ~5 minutes, whereas in the presence of only 1500 ppm Na⁺, gelation did not begin until ~200 minutes had passed and took ~400 minutes to reach a maximum viscosity of ~10,000 cP. Despite these changes, the final viscosity after gelation was similar for all Na⁺ concentrations tested.

Another observation worth noting in Figure 16 is the sudden increase in viscosity for Geo40 spiked to 10,000 ppm Na⁺ when the measurement was restarted 180 minutes after measuring the sample initially for 60 minutes. During the 180-minute break, the instrument spindle was no longer spinning and the mixture continued to gel. When the measurement restarted and the spindle resumed turning at a shear rate of 50 s⁻¹, the viscosity was measured at a new maximum, and then decreased. This trend in viscosity after gelling and after long pauses in rheology measurements was observed throughout nearly all of the gel time tests for colloidal silica amendments, regardless of specific products, and is attributed to shearing by the rheometer. The dependence of viscosity on shear rate and time after mixing is shown for Geo40 treated with Na⁺ accelerator (1500 ppm and 3000 ppm) in Figure 17 where at the time of gelling there was a measurable viscosity dependence on the shear rate applied for these two examples. This is due to the limited influence of shear rate on samples with low viscosities, but as they gelled and viscosity increased, the shear rate impact became measurable. A dependence on shear rate is expected to persist in the other colloidal silica candidates, although measurements have not yet been performed.

Figure 16. Gel time of BASF, Geo40, and Levasil CS30-425, CS30-130, and CC301 when treated with variable concentrations of Na⁺ accelerator (no SPW).
Finally, the gel time for colloidal silica treated SPW was investigated at two different amendment:SPW ratios, 1:1 and 1:5, and Na⁺ concentrations of 3000 ppm and 10,000 ppm to determine the impact of dilution from perched water on gel time properties. These tests were performed using the most promising of the colloidal silica candidates, Geo40, BASF, and Levasil CS30-425, and the results are shown in Figure 18. More extensive testing was performed on the BASF and Geo40 amendments due to the slow gel initiation of Levasil CS30-425. In fact, of the three Levasil products initially observed after treatment with 1500 ppm Na⁺, only CS30-425 showed any signs of gelation ~4 weeks after the tests were started.

In Figure 18, panels A and B, Geo40 and BASF results are shown for three combinations: a 1:1 ratio treated with either 10,000 ppm Na⁺ or 3000 ppm Na⁺ and a 1:5 ratio treated with 10,000 ppm Na⁺. In both systems, the 1:5 ratio was not tested with 3000 ppm Na⁺ due to the relatively long gel time measured when a 1:5 amendment:SPW ratio was treated with 10,000 ppm Na⁺. Comparatively, Geo40 and BASF behaved similarly when accelerated with 10,000 ppm Na⁺ (Figure 18C), where both have similar initiation times for gelation, ~10 minutes (when viscosity begins to increase), and reach their respective maximum viscosities within a similar period, ~90 minutes. However, the final viscosity measured for Geo40 treated SPW is nearly 5000 cP higher than that of BASF treated SPW. In fact, the Geo40 treated samples generally had higher viscosity readings compared to their BASF counterparts, which is likely due to the 50% lower silica concentration in the BASF product (Table 4). Additional work would be needed to elucidate whether this difference in viscosity translates to a difference in strength and decreased porosity in treated sediments. When the amendment:SPW ratio was increased to 1:5 while maintaining a 10,000 ppm Na⁺ concentration, the Geo40 samples began to gel later than the BASF samples, ~100 minutes compared to <~100 minutes. Finally, the most prevalent difference between the Geo40 and BASF samples was measured when the concentration of Na⁺ was dropped to 3000 ppm. Here, an nearly 1000 minute delay in gelation was observed for BASF relative to Geo40 samples, and the gelation period for the BASF samples spans ~1000 minutes rather than the ~600 minutes seen for the Geo40 samples. Finally, in Figure 18C, the similarities and differences between Geo40, BASF, and Levasil CS30-425 treated SPW (1:1 ratio) with 10,000 ppm Na⁺ are illustrated. Here the similarities between Geo40 and BASF samples, as previously discussed, are apparent in addition to the slow initiation of gelling for the Levasil CS30-425 product, which began ~200 minutes after starting the test. Furthermore, while the final viscosity measured for the Levasil CS30-425 sample was about equal to the BASF sample, the viscosity
began to decrease with time. However, this decrease may have been due to shearing effects that may also be responsible for the sudden changes in viscosity at ~1000 minutes.

Figure 18. (A) Gel time of Geo40-treated SPW as a function of amendment:SPW ratio and Na⁺ accelerator concentration. (B) Gel time of BASF-treated SPW as a function of amendment:SPW ratio and Na⁺ accelerator concentration. (C) Gel time for BASF, Geo40, and Levasil CS30-425 treated SPW at a 1:1 volumetric ratio of amendment:SPW and with the addition of accelerator to 10,000 ppm Na⁺.
3.2.2 Acrylamide Candidates

Due to the rapid gelation time (<1 minute) when AV-100 Solutions 1 and 2 were combined without SPW, testing of the acrylamide grout technology immediately focused on the impacts of SPW dilution on the gel time and final viscosity of the gelled matrix. In total, triplicate samples were analyzed for AV-100 Solution 1 and AV-100 Solution 2 at SPW ratios of 1:1:2, 1:1:5, and 1:1:10. As expected, gel initiation and gelation period increased with increased SPW fraction. At a 1:1:2 ratio, gelation began in less than 2 minutes and reached a maximum viscosity of ~10,000 cP after only 4 minutes. When the ratio was increased to 1:1:5, gelation began as early as 6 minutes and ~10,000 cP was reached within ~20 minutes. At both ratios, the maximum viscosity measured was similar to Geo40 treated SPW with 10,000 ppm Na+. However, when the SPW fraction was increased to 1:1:10, not only did gelation begin later (~20 to 30 minutes) and last longer (tens to hundreds of minutes), but the maximum viscosity measured decreased by nearly two orders of magnitude and results were not as reproducible across replicate samples. As such, this treatment technology seems most effective when displacing perched water, thus minimizing the dilution factor, and at possibly shorter gelation time scales. Furthermore, while the AV-100 treatment is recommended for phase two testing, implementation of this technology hundreds of feet below the subsurface may require short application times and consequently, cover smaller treatment areas.

![Figure 19](image.png)

Figure 19. Gel time of AV-100 treated SPW as a function of AV-100 Solution 1, Solution 2, and SPW ratio, where the ratio of AV-100 Solutions 1 and 2 was maintained at 1:1 according to manufacturer recommendations.

3.2.3 Set Time of Portland Cement Candidate

The set time for Portland based cement candidate US Grout Ultrafine VX (Avanti International) was evaluated using the ASTM C191-08, Standard Methods for Time of Setting of Hydraulic Cement by Vicat Needle. In this method, the Vicat needle was used to measure penetration into a curing cementitious matrix. When the needle no longer penetrated the surface, the cementitious matrix was considered set. For SPW applications, the manufacturer’s recommendation to include USG Super Plasticizer was adhered to in order to improve viscosity of the grout for application. Using the three samples prepared according to Table 6, the amount of SPW that could be treated by Ultrafine VX was assessed as a function of the SPW to Ultrafine VX mass ratio, 1.0, 0.8 (manufacturer recommended ratio), and 0.6.
After each sample was mixed, free liquids began to accumulate on the surface of each sample within the first day. For UFVX-0.6-P, testing at a SPW to Ultrafine VX ratio of 0.6, the residual free liquids were reabsorbed within 2 days and the sample was determined to have set after 6.9 days (Table 8 and Figure 20A and B). For samples UFVX-0.8-P and UFVX-1.0-P, the residual free liquids were not reabsorbed within the 30-day testing period (Figure 20C) and upon termination of the experiment the Viact needle was still penetrating the solid surface by 0.5 to 1 mm. As a result, no set time is reported for the 0.8 and 1.0 SPW to Ultrafine VX sample ratios. Additionally, a homogeneous matrix is preferred in order to avoid points of weakness within the solid matrix. In samples UFVX-0.8-P and UFVX-1.0-P, shown in Figure 20A, visible settling and striations were observed in these samples. Combined with a soft exterior, the Portland-based treatment is not recommended for phase two testing since it would not likely set within the saturated conditions typical of the perched water zone.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>SPW:Ultrafine VX Ratio (g/g)</th>
<th>Set Time Days</th>
<th>Residual Free Liquids Observed Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>UFVX-1.0-P</td>
<td>1.0</td>
<td>-</td>
<td>29.9</td>
</tr>
<tr>
<td>UFVX-0.8-P</td>
<td>0.8*</td>
<td>-</td>
<td>30.8</td>
</tr>
<tr>
<td>UFVX-0.6-P</td>
<td>0.6</td>
<td>6.9</td>
<td>2.0</td>
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</table>
3.3 Discussion and Path Forward

Based on the results from phase one testing, colloidal silica products SOL-1030Na from Geo40 and MasterRoc® MP 325 from BASF, as well as acrylamide amendment AV-100 from Avanti International are recommended for phase two and possibly phase three tests for hydraulic conductivity and contaminant immobilization tests. Down-selection to one colloidal silica product was not made due to the similarities between the BASF and Geo40 systems below 1000-minute testing scales, which is the timeframe when treatment would likely take place; however, between these two amendments, the Geo40 system created a more viscous matrix that may create less-permeable barriers in the perched water zone. This prediction should be tested in phase two testing when the hydraulic conductivity of treated sediment columns is measured. For acrylamide grout AV-100, this product should also move forward to phase two testing due to its competitive performance when compared to the colloidal silica materials. As previously mentioned, short gel times may become an issue with the current chemical recipe, but at these time scales, the gelation results were highly reproducible, which suggests controllably. However, this treatment may only
be effective when displacing the perched water, where the dilution factor is minimized. Finally, Portland-based cement amendments will not be further evaluated in phase two and three tests due to the long or immeasurable set times. Additional testing to evaluate the potential radius of influence of amendment injection will be reported separately.
4.0 Extraction Rate Enhancement

The purpose of this investigation is to examine approaches to enhance the extraction rate of perched water, the current approach under the removal action (DOE/RL-2014-34). As a first step, a model was developed and used to evaluate current pumping data to provide a baseline for subsequent use in evaluating alternative pumping configurations. To this end, a model of the perched water system and extraction wells has been built and calibrated to field data to prepare for its use in identifying extraction rate enhancements and to support simulating the potential deployment of the remediation technologies presented in this report.

4.1 Methods

Oostrom et al. (2013) constructed a layered geological model and investigated the hydraulic conductivity of the perched water zone using a 1D numerical model. This model was used to identify the height of the perched water zone. In this investigation, the same geological framework was used, but was extended to a quasi-3D model using a cylindrical coordinate system.

A series of quasi-3D simulations using a cylindrical coordinate system in eSTOMP (Fang et al. 2015; White et al. 2015) was conducted to establish the hydraulic conductivities of the perching layer and the perched water aquifer that would match the conditions observed in the field at the site. The hydraulic conductivities of both the perching layer and the perched water zone were determined by trial and error to match the extraction rate of approximately 800 L/day. Three field pump tests were simulated based on these hydraulic conductivities as a validation of the obtained parameters. The extent of the extraction drawdown was also evaluated in two of the pump tests.

4.2 Geology

Perched water wells 299-E33-350 and 299-E33-351 were installed within the perched water zone in March 2014 (Schulyer 2014), and well 299-E33-360 was drilled in the same general area, south of them, in August 2014 (CHPRC 2014). The generalized stratigraphy of the perched water zone near wells 299-E33-344 (C5859) and 299-E33-345 had been determined earlier (Truex et al. 2013), and confirmed by the analysis of the boreholes composite logs from wells 299-E33-350 (C8914), 299-E33-351 (C8915), and 299-E33-360. The conceptual geologic model is shown in Figure 21 and is based on the geologic framework used in Oostrom et al. (2013).

4.3 Hydraulic Properties

Table 9 lists the thickness of the perched water layers based on the analysis of the borehole logs for wells 299-E33-350 and 299-E33-351, and well 299-E33-360 (Truex et al. 2013) and the hydraulic parameters from Khaleel et al. (2001). Newcomer (2014) determined the $K_s$ of the perched water aquifer using slug tests in wells E33-350 and E33-351. The hydraulic conductivity of the near full thickness of the perched water aquifer are summarized in Table 10. The average value of $K_s$ for the CCUzs based on Newcomer (2014) is 9.2 times the value from Khaleel et al. (2001).
Table 9. Sediment layer thickness (Truex et al. 2013) and hydraulic properties (Khaleel et al. 2001).

<table>
<thead>
<tr>
<th>Sediment Layer</th>
<th>Sediment Symbol</th>
<th>Thickness (m)</th>
<th>Hydraulic Conductivity (cm/s)</th>
<th>Van Genuchten Alpha (1/cm)</th>
<th>Van Genuchten n (-)</th>
<th>Porosity (-)</th>
<th>Residual Saturation (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>H2</td>
<td>55.21</td>
<td>$1.18 \times 10^{-4}$</td>
<td>0.0157</td>
<td>1.888</td>
<td>0.252</td>
<td>0.123</td>
</tr>
<tr>
<td>CCUz Upper</td>
<td>CCUzu</td>
<td>1.83</td>
<td>$1.22 \times 10^{-5}$</td>
<td>0.0046</td>
<td>1.767</td>
<td>0.376</td>
<td>0.066</td>
</tr>
<tr>
<td>CCUz Sand</td>
<td>CCUzs</td>
<td>4.58</td>
<td>$1.18 \times 10^{-4}$</td>
<td>0.0157</td>
<td>1.888</td>
<td>0.252</td>
<td>0.123</td>
</tr>
<tr>
<td>CCUz Lower</td>
<td>CCUzl</td>
<td>1.83</td>
<td>$1.22 \times 10^{-5}$</td>
<td>0.0046</td>
<td>1.767</td>
<td>0.376</td>
<td>0.066</td>
</tr>
<tr>
<td>CCUg</td>
<td>CCUg</td>
<td>4.58</td>
<td>$3.08 \times 10^{-4}$</td>
<td>0.0061</td>
<td>1.571</td>
<td>0.121</td>
<td>0.085</td>
</tr>
</tbody>
</table>

Table 10. Field measured hydraulic conductivity of the CCUz sand layer (Newcomer 2014).

<table>
<thead>
<tr>
<th></th>
<th>299-E33-350</th>
<th>299-E33-351</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_s$ (m/day)</td>
<td>0.58</td>
<td>1.30</td>
<td>0.94</td>
</tr>
<tr>
<td>$K_s$ (cm/s)</td>
<td>6.71E-4</td>
<td>1.50E-3</td>
<td>1.09E-3</td>
</tr>
</tbody>
</table>

4.4 Field Pumping Tests

Three pump tests were conducted in 2016 (Section 5.1.2 of CHPRC 2017), and are briefly described below.

**Test 1: Baseline monitoring**

This pump test was conducted to establish barometric response functions for perched-water extraction wells to minimize barometric pressure effects in the water-level data and provide insight into the vadose zone overlying the perched water zone. During this test, each well was individually pumped for 1 hour, followed by a 30-day recovery period.

**Test 2: Single well pump testing**

This pump test was conducted to determine near – and inter-well hydrologic properties for the perched water zone. During this test, each well was individually pumped for 7 days, followed by a 14-day recovery period.

**Test 3: Multi-well pump test**

This pump test was conducted to assess the PWA extent through analysis of any observed hydrologic boundary detection and/or aquifer dewatering during the test. For the test, it was planned to pump 3 wells simultaneously on a schedule: 60 day on, 60 days off. However, the pump in well 299-E33-351 failed soon after the pumping began, so the well was only used for monitoring.

4.5 Quasi-3D Simulations

4.5.1 Simulation Configuration

The flow to an extraction well was simulated with a quasi-3D domain, using a 2-D cylindrical coordinate system that represents the domain as a cylindrical wedge. One extraction well was set at the center of the cylinder. The simulation domain radius was set at 100 m, with a 14-m-thick domain (from depth 66 m to 80 m) as shown in Figure 21. The radial coordinate was discretized into 109 grid blocks, with spacing varying from 0.05 m to 1.0 m. The vertical coordinate was discretized into 140 grid blocks with a uniform grid spacing of 0.1 m.

The diameter of the wells was set at 4 inches based on the 4-6 inch well screen diameters reported in CHPRC (2017). The extraction well was simulated with a seepage face condition at the well surface. The top boundary received a constant recharge rate and the bottom boundary was represented as a water table condition. The recharge rate was set at 60 mm/yr, representing current conditions with disturbed surface (Fayer et al. 2010).

A zero-flux boundary condition was assigned to all the side boundaries. The base thickness and hydraulic properties (Khaleel et al. 2001) of the geological units in Table 9 were used unless otherwise stated in Table 11.

4.5.2 Simulation Scenarios

Two sets of simulations were conducted, as described in the following section.
The first set of simulations (Cases Sim1 to Sim5 in Table 11) was performed to evaluate the hydraulic conductivities of the perched water zone and the perching layer.

The second set of simulations (Cases Sim6x to Sim8x in Table 11) was performed to simulate the three field pump tests. Each of these cases included two sub-cases, \( a \) and \( b \).

The base thickness and hydraulic properties (Khaleel et al. 2001) of the geological units in Table 9 were used unless otherwise stated in Table 11. The recharge rate was set at 60 mm/yr, representing current conditions with disturbed surface (Fayer et al. 2010).

Two simulations were conducted for each case, one for the steady-state run and the other for the transient run, which simulated different types of water extraction scenarios. The steady-state run was to achieve a steady-state flow condition without water extraction by running the model for 1000 years. For Sim1 through Sim4, an initial saturation condition was imposed in the CCUzs layer during the transient runs. For Sim5 through Sim8, the steady-state condition was used as the initial condition for the subsequent transient simulations.

For Cases Sim6x through Sim8x, the CCUzl \( K_s \) of \( 6.00 \times 10^{-8} \) cm s\(^{-1} \) found in Sim5 was used because it could produce a sustained perched water zone of 3.36 m, as reported in Truex et al. (2013). Each of these cases included two sub-cases, \( a \) and \( b \). For sub-case \( a \), the CCUzs \( K_s \) values were obtained by trial and error to match the observed extraction rate of approximately 800 L/day (CHPRC 2015); for sub-case \( b \), the CCUzs \( K_s \) value was the average value of the field slug tests (Table 10).

### Table 11. Summary of two-dimensional simulations.

<table>
<thead>
<tr>
<th>Simulation Case</th>
<th>Description</th>
<th>Modified ( K_s )</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sim1</td>
<td>Extraction for 30 days.</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Sim2</td>
<td>Extraction for 30 days; modified ( K_s ).</td>
<td>CCUzl ( K_s = 1.83 \times 10^{-7} ) cm s(^{-1} )</td>
<td>( K_{sat} ) of the perching layer CCUz lower was reduced ( \times 0.015 ) (See Oostrom et al. 2013).</td>
</tr>
<tr>
<td>Sim3</td>
<td>Same as in Sim1; no pumping</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Sim4</td>
<td>Same as in Sim2; no pumping</td>
<td>CCUzl ( K_s = 1.83 \times 10^{-7} ) cm s(^{-1} )</td>
<td>( K_{sat} ) of the perching layer CCUz lower was reduced ( \times 0.015 ) (See Oostrom et al. 2013).</td>
</tr>
<tr>
<td>Sim5</td>
<td>Same as in Sim1 with some ( K_s ) values adjusted</td>
<td>CCUzl ( K_s = 6.00 \times 10^{-8} ) cm s(^{-1} )</td>
<td>Match the height 3.36 m of the PWA (See Oostrom et al. 2013).</td>
</tr>
<tr>
<td>Sim6a</td>
<td>Test 1 in DOE/RL-2016-69, Rev. 0</td>
<td>CCUzl ( K_s = 6.00 \times 10^{-8} ) cm s(^{-1} )</td>
<td>Water was extracted for 1 hour followed by a 30-day recovery period.</td>
</tr>
<tr>
<td>Sim7a</td>
<td>Test 2 in DOE/RL-2016-69, Rev. 0</td>
<td>CCUzl ( K_s = 6.00 \times 10^{-8} ) cm s(^{-1} )</td>
<td>Water was extracted for 7 days followed by a 14-day recovery period.</td>
</tr>
<tr>
<td>Sim8a</td>
<td>Test 3 in DOE/RL-2016-69, Rev. 0</td>
<td>CCUzs ( K_s = 1.80 \times 10^{-4} ) cm s(^{-1} )</td>
<td>Water was extracted for 60 days followed by a 60-day recovery period.</td>
</tr>
<tr>
<td>Sim6b</td>
<td>Test 1 in DOE/RL-2016-69, Rev. 0</td>
<td>CCUzl ( K_s = 6.00 \times 10^{-8} ) cm s(^{-1} )</td>
<td>Water was extracted for 1 hour followed by a 30-day recovery period.</td>
</tr>
<tr>
<td>Sim7b</td>
<td>Test 2 in DOE/RL-2016-69, Rev. 0</td>
<td>CCUzl ( K_s = 6.00 \times 10^{-8} ) cm s(^{-1} )</td>
<td>Water was extracted for 7 days followed by a 14-day recovery period.</td>
</tr>
<tr>
<td>Sim8b</td>
<td>Test 3 in DOE/RL-2016-69, Rev. 0</td>
<td>CCUzs ( K_s = 1.09 \times 10^{-3} ) cm s(^{-1} ) (Table 10)</td>
<td>Water was extracted for 60 days followed by a 60-day recovery period.</td>
</tr>
</tbody>
</table>

*This \( K_s \) value for the perched water layer CCUz sand was obtained by trial and error to match the extraction rate of approximately 800 L/day during the period from 2011 to 2015 (Fig. 8 of CHPRC 2015).*
4.6 Results

4.6.1 Evaluation of Hydraulic Properties of CCUz Lower

The results indicate that the reported CCIzl $K_s$ value of $1.22 \times 10^{-5}$ cm s$^{-1}$ in Khaleel et al. (2001) cannot produce a perched water zone (Sim1 and Sim3). The suggested $K_s$ $1.83 \times 10^{-7}$ cm s$^{-1}$ for the CCUzl in Oostrom et al. (2013) can simulate a perched water zone, but its thickness is not sustainable (Sim2 and Sim4). An additional test (Sim5) indicates that a CCUzl $K_s$ of $6.00 \times 10^{-8}$ cm s$^{-1}$ will produce a sustained perched water zone with a thickness of 3.36 m, as reported in Truex et al. (2013). Note that the CCUzl $K_s$ value of $6.00 \times 10^{-8}$ cm s$^{-1}$ was obtained by trial and error under a recharge rate of 60 mm/yr. A different recharge rate would lead to a different CCUzl $K_s$.

4.6.2 Simulation of Field Pumping Tests

4.6.2.1 Extraction Rates

The actual extraction volume and rate of water for the three tests are summarized in Table 12. The extraction rates from the three wells varied by a factor of approximately 2 to 6, indicating large spatial variability of hydraulic properties within the perched water zone.

The simulated extraction volume and rate of water for the three tests are summarized in Table 13. For sub-case $a$, for which the CCUzl $K_s$ matched the 3.36 m perched water thickness, the extraction rates compare reasonably well with the observed values in Table 12. For sub-case $b$, for which the CCUz sand layer $K_s$ values were determined by slug tests, the simulated extraction rates tended to be higher than the observed values. Note that the geology is represented as constant thickness layers. Since the perched water zone thickness varies spatially, this would affect the match of the simulated and measured data.

<table>
<thead>
<tr>
<th>Well Name</th>
<th>Test 1</th>
<th>Test 2</th>
<th>Test 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta t$ (hr)</td>
<td>V (L)</td>
<td>$R$ (L/hr)</td>
</tr>
<tr>
<td>299-E33-344</td>
<td>1</td>
<td>67.5</td>
<td>67.5</td>
</tr>
<tr>
<td>299-E33-350</td>
<td>1</td>
<td>412.8</td>
<td>412.8</td>
</tr>
<tr>
<td>299-E33-351</td>
<td>1</td>
<td>232.0</td>
<td>232.0</td>
</tr>
<tr>
<td>Average</td>
<td>-</td>
<td>-</td>
<td>237.4</td>
</tr>
</tbody>
</table>

$\Delta t$: Extraction duration; V: Extraction volume; R: Extraction rate.

<table>
<thead>
<tr>
<th>Well Name</th>
<th>Test 1 (Sim6)</th>
<th>Test 2 (Sim7)</th>
<th>Test 3 (Sim8)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta t$ (hr)</td>
<td>V (L)</td>
<td>$R$ (L/hr)</td>
</tr>
<tr>
<td>Scenario a</td>
<td>1</td>
<td>48.9</td>
<td>48.9</td>
</tr>
<tr>
<td>Scenario b</td>
<td>1</td>
<td>268.2</td>
<td>268.2</td>
</tr>
<tr>
<td>Average</td>
<td>-</td>
<td>-</td>
<td>158.6</td>
</tr>
</tbody>
</table>

$\Delta t$: Extraction duration; V: Extraction volume; R: Extraction rate.
4.6.2.2 Extent of Extraction Drawdown

During perched water extraction, a drawdown cone was created (Figure 22). The maximum drawdown varied from 0.83 m (Sim7a) to 1.01 m (Sim8b). The drawdown of the perched water relative to the maximum value after 7-days (Sim7a and Sim7b) and 60-days (Sim8a and Sim8b) of extraction is shown in Figure 23. The radius corresponding to the relative drawdown of 0.05 is also shown in Figure 23 as a measure of the lateral extent of the drawdown. This radius varied from 12 m (Sim7a) to 47 m (Sim8b). Assuming that the volume of the drawdown cones is the same as the cylinder’s height, the radius of the cylinder varies from 5.3 m to 19.6 m.

**Figure 22.** Depth of the perched water table after 7-day (Sim7a and Sim7b) and 60-day (Sim8a and Sim8b) extractions.

**Figure 23.** Drawdown of the perched water table relative to the maximum value after 7-day (Sim7a and Sim7b) and 60-day (Sim8a and Sim8b) extractions. The numbers in the plot are the radii in meters corresponding to the relative drawdown of 0.05.
A series of simulations was conducted to obtain a representative model that can be used for investigating enhanced extraction rates in the perched water zone. To this end, three pump tests were simulated for model calibration. The results show that a CCUzl $K_s$ value of $6.00 \times 10^{-8}$ cm s$^{-1}$ will produce a perched water zone with a thickness of 3.36 m, and a CCUzs $K_s$ of $1.80 \times 10^{-4}$ cm s$^{-1}$ could match the observed extraction rate of approximately 800 L day$^{-1}$ (33 L hr$^{-1}$) during the period from 2011 to 2015. When the CCUzs $K_s$ values from slug tests were used in the simulation, extraction rates were overestimated. The radius corresponding to the relative drawdown of 0.05 was used as a measure of the lateral extent of the drawdown, which varied from 12 m to 47 m. The results show that the extraction volume and extent of impact of an extraction well are strongly dependent on the hydraulic conductivity of the CCUz sand layer. The baseline simulations reported herein provide verification that the modeling approach can be used to test alternative pumping scenarios in the future.
5.0 Conclusions

This report provides an interim status report on candidate post-extraction remediation options for the perched water zone in the B-Complex at Hanford that can be used to treat high concentrations of U, Tc\textsuperscript{99}, and NO\textsubscript{3}: The candidate technology evaluations included a sequential reductive and sequestration approach and permeation grouts for immobilization. In addition to identifying post-extraction options, a numerical model calibrated against pumping tests was developed with the purpose of optimizing the current extraction system to hasten the timeframe for implementing the post-extraction remedies and decrease the total contaminant mass that will eventually move into the groundwater.

Zero valent iron, sulfur modified iron, and calcium polysulfide were examined for their use in the reductant phase of the sequential technology approach. For the sequestration phase, an alkaline treatment as well as apatite and calcite formation were investigated. The alkaline treatment was screened out as a viable approach to sequestration, whereas other methods for reduction and sequestration are still being evaluated.

Colloidal silica, acrylamide based chemical grouts, and Portland-based cements were also investigated for their potential for solidifying and immobilizing contaminants in the perched water zone. The first phase of testing has been completed, and resulted in screening out the Portland-based cements. The colloidal silica and acrylamide products will move into the next phase of testing focused on permeability reduction, since they both demonstrated low injection viscosities, controllable gel times, and a propensity to fill the small void space in fine sediments.

A cylindrical model of the perched water system was developed and calibrated to data from three pump tests. Future simulations will support optimization of the current pump-and-treat system, as well as provide support for assessing the viability of post-extraction treatment technologies.
6.0 Quality Assurance


Two quality grading levels are defined by the NQAP:

**Basic Research** - The required degree of formality and level of work control is limited. However, sufficient documentation is retained to allow the research to be performed again without recourse to the original researcher(s). The documentation is also reviewed by a technically competent individual other than the originator.

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

The work supporting the results presented in this report was performed in accordance with the *Basic Research* grading level controls.
7.0 References


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