ESTCP
Cost and Performance Report

(ER-200913)

Baseline (water-based dye tracer)	Shear-Thinning Fluid (600 mg/L xanthan w/ tracer)

70: K_{sat} = 12 Darcy

40/50: K_{sat} = 72 Darcy

12/20: K_{sat} = 503 Darcy

30/40: K_{sat} = 148 Darcy

zones with cross-flow
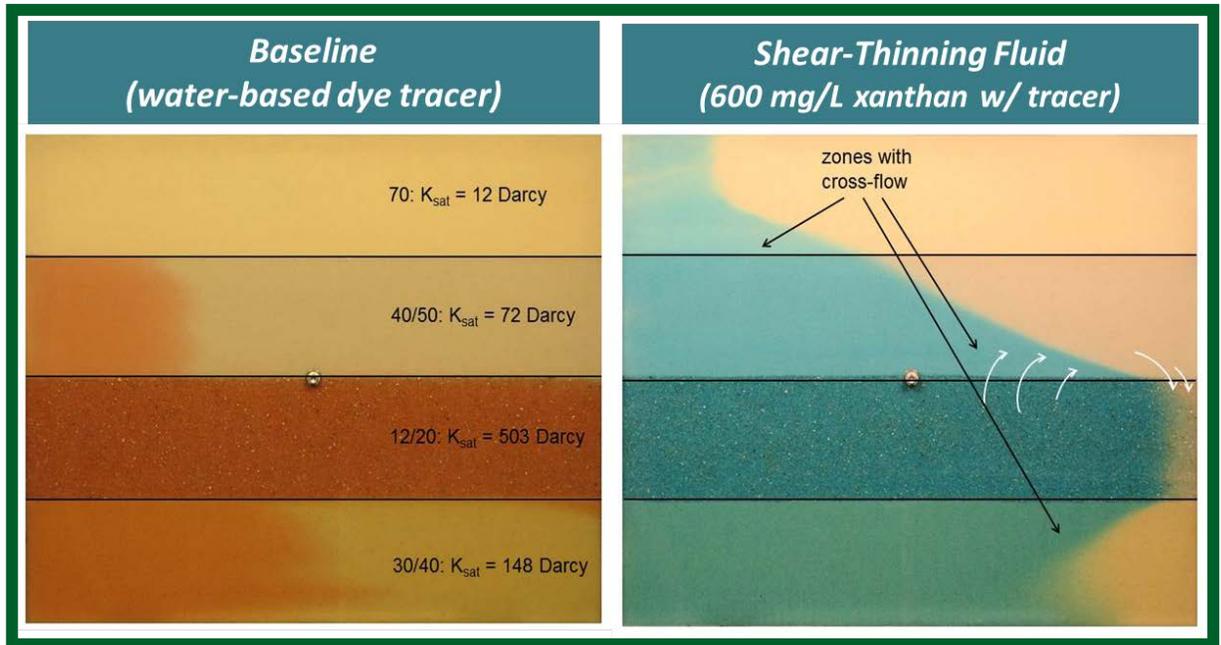
Enhanced Amendment Delivery to Low Permeability Zones for Chlorinated Solvent Source Area Bioremediation

October 2014

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ESTCP

ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

COST & PERFORMANCE REPORT
Project: ER-200913

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ACRONYMS AND ABBREVIATIONS

2D	two-dimensional
AATDF	Advanced Technology Demonstration Facility
AFCEC	Air Force Civil Engineer Center
bgs	below ground surface
cDCE	*cis*-1,2-dichloroethene
CMT	continuous multichannel tubing
cP	centipoise
CPT	cone penetration testing
CVOC	chlorinated volatile organic compound
DG	downgradient
DI	de-ionized
DNAPL	dense non-aqueous phase liquid
DoD	Department of Defense
EBF	electronic borehole flowmeter
ERT	electrical resistivity tomography
ESTCP	Environmental Security Technology Certification Program
g/L	grams per liter
gpm	gallons per minute
GSI	GSI Environmental Inc.
high-k	high-permeability
HPT	hydraulic profiling tool
ISCO	in situ chemical oxidation
ITRC	Interstate Technology & Regulatory Council
JBLM	Joint Base Lewis-McChord
kg/m^3	kilograms per square meter
low-k	low-permeability
µg/L	micrograms per liter
MCL	maximum contaminant level
m/d	meters per day
mg/L	milligrams per liter
MIP	membrane interface probe
MNA	monitored natural attenuation
mV	millivolts

MW	monitoring well
NAPL	non-aqueous phase liquid
NAVFAC	Naval Facilities Engineering Command
ND	non-detect
ORP	oxidation-reduction potential
PNNL	Pacific Northwest National Laboratory
psi	pounds per square inch
PV	pore volume
RACER	Remedial Action Cost Engineering and Requirements
RPD	relative percent difference
SEAR	surfactant enhanced aquifer remediation
SERDP	Strategic Environmental Research and Development Program
STF	shear-thinning fluid
STOMP	Subsurface Transport Over Multiple Phases
TCE	trichloroethene
TOC	total organic carbon
UIC	underground injection control
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
VC	vinyl chloride
VOC	volatile organic compound

ACKNOWLEDGEMENTS

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EXECUTIVE SUMMARY

OBJECTIVES OF THE DEMONSTRATION

The shear-thinning technology is designed to enhance delivery of remedial amendments to low-permeability (low-k) zones for which treatment is typically limited when standard amendment delivery processes are utilized. Improved distribution of injected fluids is achieved by exploiting the rheological properties of shear-thinning fluids (STFs) during injection and transport within a formation, such as cross-flow from high-permeability (high-k) to low-k zones. The overall goal of this project was to demonstrate and validate the use of shear-thinning delivery fluid for enhanced delivery of bioremediation amendments at a chlorinated solvent-impacted site and to develop guidance for its use at other sites.

TECHNOLOGY DESCRIPTION

The term "shear-thinning" is applied to fluids to describe their dynamic viscosity-reducing behavior when shear rates are increased. Shear-thinning fluids are non-Newtonian, meaning that their viscosities exhibit a temporary drop when the applied shear rate is increased. A viscosity-modifying shear force can be applied using methods as simple as mixing or shaking of the solution, or—in the context of subsurface delivery—by injecting the fluid through a well screen and into porous media. For the enhanced amendments delivery process, a non-toxic biodegradable polymer, such as xanthan gum, is added to the injection solution to form a non-Newtonian fluid with shear-thinning properties. The shear-thinning behavior causes a more significant viscosity reduction to the fluid flowing through the lower-k zones relative to the viscosity reduction of the fluid flowing in higher permeable zones, i.e., the fluid mobility in the higher-k zone is controlled. Therefore, the preferential flow through the more permeable zones is significantly reduced while the flow into the lower-k zone is increased. In addition, mobility reduction behind the viscous injection fluid front in a higher-k layer creates a transverse pressure gradient that drives cross-flow of viscous fluids into adjacent less permeable layers. These mechanisms result in an improvement in the sweep efficiency within a heterogeneous system. The remedial amendments added to the shear-thinning solution can then be delivered to low-k zones, which otherwise would be bypassed.

Once injection stops, the injected fluid viscosity increases and creates a more stable zone for biodegradation reactions because the amendment-laden fluid with high viscosity is not as easily displaced by flow from upgradient groundwater. The persistence of the delivered amendment helps to minimize inefficiencies associated with supplying sufficient electron donor to reduce competing electron acceptors, and the appropriate conditions for promoting microbial growth and activity can be maintained over a longer period of time. Over time, the xanthan gum will degrade and is anticipated to act as a long-term carbon source as the treatment zone returns to pre-treatment hydraulic conditions.

DEMONSTRATION RESULTS

The technology demonstration was performed using a combination of xanthan gum (shear-thinning polymer) and ethyl lactate (carbon substrate) to promote biological reductive dechlorination in a low-level trichloroethene (TCE) plume at Joint Base Lewis-McChord

(JBLM). The formation consisted of mixed glacial till and outwash with considerable small-scale heterogeneity and preferential pathways.

An evaluation of project results yielded the following key conclusions:

- Relative to a comprehensive baseline injection using a water-only solution, the STF injection resulted in improved breakthrough and distribution characteristics in the majority of monitoring locations. The percentage of the treatment zone covered by the amendment after pumping just over 1 pore volume increased from 49% without the STF to 69% with the STF, representing an improvement in the sweep efficiency of 41%.

- The STF injection successfully distributed measurable levels of organic carbon to the treatment zone, including the majority of lower-k layers. A significant portion of the amendment persisted through the end of the 8-month performance monitoring period, with evidence for enhanced persistence in the lower-k zones relative to higher-k zones.

- The amendment resulted in the complete degradation of the parent compound (TCE) throughout the heterogeneous treatment zone, with no evidence of rebound.

IMPLEMENTATION ISSUES

Based on the results of this demonstration and other applications, this technology is most appropriate for aquifers with permeability contrasts less than two orders of magnitude and/or thin low-k layers (< 0.5 meters [m]) unless distribution to the center of the layer is unnecessary (e.g., interface treatment to reduce flux). This permeability contrast would be equivalent to silt layers present within a sand matrix, but not clay layers. Other recommendations include: 1) a default static viscosity of approximately 100 cP for STFs in the absence of supporting data; and 2) adjusting STF injection rate based on a pre-determined maximum pressure limit.

There are no significant regulatory or end-user concerns with using this technology, primarily due to its similarity to an existing treatment technology (in situ bioremediation).

Cost modeling demonstrated that costs for this technology are moderate on a per injection event basis because of its similarity to conventional bioremediation. Primary requirements are extra time for hydration of the polymer solution and the cost of the material itself. However, there is a potential for significant life-cycle cost savings due to fewer injection events (i.e., the viscous polymer is more persistent in the subsurface) and shorter remediation timeframes (i.e., more effective treatment as a result of improved substrate distribution).

1.0 INTRODUCTION

1.1 BACKGROUND

Heterogeneity of hydraulic properties in aquifers may lead to dissolved and sorbed contaminants residing in lower-permeability (low-k) zones, primarily due to diffusive mass flux (Chapman and Parker, 2005; Sale et al., 2013). Contaminants residing in low-k zones have the potential to cause persistence of plumes and increase the remediation timeframe (i.e., the time required to reach regulatory concentration goals) because of diffusion-controlled release of contaminants back into transmissive zones (i.e., matrix or back diffusion). Reviews of source remediation (Stroo and Ward, 2010; Kueper et al., 2014) and other studies have highlighted the potential impact of this process (Ball et al., 1997; Liu and Ball, 2002; Parker et al., 2004; Chapman and Parker, 2005; Parker et al., 2008; West and Kueper, 2010; Seyedabbasi et al., 2012).

For in situ bioremediation, delivery of amendments using traditional injection approaches distributes amendments primarily to higher-permeability (high-k) zones. Back diffusion of contaminants from low-k zones has been reported to inhibit the success of site remediation as reported in pump-and-treat systems (Mackay and Cherry, 1989; Rivett et al., 2006), surfactant-enhanced aquifer remediation (Saenton et al., 2002), and injection of amendments for bioremediation (Damgaard et al., 2013). In addition, bioremediation of chlorinated solvents is also limited by biological reactions that compete or interfere with the contaminant degradation process and by advective movement of amendments out of the target zone prior to utilization.

Methods of providing more uniform distribution of injected fluids (i.e., enhancing sweep efficiency) through mobility control have been widely implemented by the petroleum industry (e.g., Sorbie, 1991; Jackson et al., 2003). Injection of a viscous fluid into a heterogeneous aquifer induces cross-flow, enhancing transverse movement between higher-k and lower-k layers as described by Silva et al. (2012). Mobility reduction behind the viscous injection fluid front in a higher-k layer creates a transverse pressure gradient that drives cross-flow of viscous fluids into adjacent less permeable layers. Polymer solutions of non-Newtonian fluids exhibiting shear-thinning (pseudoplastic) behavior have been used to create viscous injection fluids. The viscosity of a shear-thinning fluid (STF) decreases as a function of the shear rate applied to the fluid. In porous media, shear rates of injected fluids varies with fluid velocity and the hydraulic characteristics of the porous media. Due to high velocities near the injection well, shear rates are relatively high and STFs help maintain lower injection pressures than would occur with injection of a non-STF of the same static viscosity (Silva et al., 2012; Truex et al., 2011a). STFs have been investigated in laboratory and field studies to facilitate remedial amendment delivery for subsurface remediation (Zhong et al., 2008, 2011; Smith et al., 2008; Vecchia et al., 2009), as a stabilizer to enhance delivery of particulate suspensions used in remediation and improve recovery of non-aqueous phase liquids (NAPL) (Martel et al., 1998a, 2004; Truex et al., 2011a,b; Tiraferri et al., 2008, Tiraferri and Sethi, 2009; Comba et al., 2011; Comba and Sethi, 2009; Oostrom et al., 2007; Crimi and Ko, 2009). Xanthan gum is an example of a biopolymer that can be used to form a STF. It has been shown to enhance the delivery of remedial amendment into low-k zones in laboratory two-dimensional (2D) flow cell systems (e.g., Zhong et al., 2008; 2013; Chokejaroenrat et al., 2013).

The proposed use of shear-thinning fluids as a delivery technique for bioremediation represents a further advancement in promoting efficient treatment of low-k zones. The delivery technique addresses limitations due to diffusion process in low-k zones and advective processes within high-k zones. The technology is expected to deliver amendments to low-k zones for which treatment is typically limited by matrix diffusion effects when standard amendment delivery processes are utilized. In addition, the enhanced amendment delivery can reduce overall costs by decreasing treatment time, promoting efficient bioremediation through the temporary exclusion of competing electron acceptors, and potentially serving as a long term carbon source.

1.2 OBJECTIVE OF THE DEMONSTRATION

The overall goal of this project is to demonstrate and validate the use of shear-thinning delivery fluid for enhanced delivery of bioremediation amendments at a Department of Defense (DoD) site where chlorinated solvents are present. The specific objectives for the project are the following:

- Demonstrate that use of a STF improves delivery of amendments into the lower-k zones of a heterogeneous site compared to injection solutions without a shear-thinning modifier.

- Quantify the increased bioremediation efficiency due to STF enhanced delivery in terms of rate and extent of bioremediation for the targeted treatment zone, in particular for the lower-k zones, and the duration over which the fluid helps maintain suitable dechlorination conditions through diversion of competing electron acceptors and biodegradation of the shear-thinning agent.

- Determine the cost factors for applying the STF enhanced delivery technology and compare these costs to baseline bioremediation practices.

These objectives were achieved through the completion of a pilot-scale demonstration at a single site, as outlined in the subsequent sections of this document.

1.3 REGULATORY DRIVERS

Cleanup of chlorinated solvent source zones has proven to be difficult and expensive at DoD sites, in part because federal drinking water standards (0.005 milligrams per liter [mg/L] or less) are often two to five orders of magnitude below pre-treatment concentrations at sites. A series of projects funded by Strategic Environmental Research and Development Program (SERDP) and ESTCP (McGuire et al., 2006; McGuire, 2014) evaluated the actual performance of in situ source zone treatment technologies and showed that the median reduction in source zone concentration was only about one order of magnitude (e.g., 90%). Therefore, improving the performance of treatment technologies is required to meet the most stringent cleanup objectives. The proposed technology aims to more efficiently deliver bioremediation amendments to aquifers with low-k zones for which treatment is typically limited when standard amendment delivery processes are utilized. As a result, the technology targets these zones that serve as long-term contributors to low-level groundwater impacts via back diffusion.

2.0   TECHNOLOGY

2.1   TECHNOLOGY DESCRIPTION

The proposed technology is focused on treatment within low-k zones of heterogeneous subsurface environments. A STF is used to distribute a bioremediation amendment (e.g., lactate) around an injection well such that the solution is able to penetrate and deliver the amendments to both high- and low-k zones. When injected at a relatively high velocity compared to natural groundwater flow velocities, the shear-thinning nature of the solution allows it to flow readily.

The term "shear-thinning" is applied to fluids to describe their dynamic viscosity-reducing behavior when shear rates are increased. STFs are non-Newtonian, meaning that their viscosities exhibit a temporary drop when the applied shear rate is increased. A viscosity-modifying shear force can be applied using methods as simple as mixing or shaking of the solution, or—in the context of subsurface delivery—by injecting the fluid through a well screen and into porous media. STFs are typically water-soluble organic polymers, such as xanthan gum. Due to their solubility, they are ideally suited for subsurface remediation applications where injections of water-based amendment solutions are frequently used.

For the enhanced amendments delivery process, a non-toxic biodegradable polymer, such as xanthan gum, is added to the injection solution to form a non-Newtonian fluid with shear-thinning properties. The shear-thinning behavior causes a more significant viscosity reduction to the fluid flowing through the lower-k zones relative to the viscosity reduction of the fluid flowing in higher-k zones, i.e., the fluid mobility in the higher-k zone is controlled. Therefore, the preferential flow through the more permeable zones is significantly reduced while the flow into the lower-k zone is increased. In addition, mobility reduction behind the viscous injection fluid front in a higher-k layer creates a transverse pressure gradient that drives cross-flow of viscous fluids into adjacent less permeable layers. These mechanisms result in an improvement in the sweep efficiency within a heterogeneous system. The remedial amendments added to the shear-thinning solution can then be delivered to low-k zones, which otherwise would be bypassed.

Once injection stops, the injected fluid viscosity increases and creates a stable zone for biodegradation reactions because the amendment-laden fluid with high viscosity cannot be readily displaced by flow from upgradient groundwater. Thus, groundwater will be diverted around the injection zone until the xanthan gum biodegrades to the point when viscosity is considerably decreased. Consequently, inefficiencies associated with supplying sufficient electron donor to reduce competing electron acceptors are minimized, and the appropriate conditions for promoting growth and activity of dechlorinating populations can be maintained over a long period of time. Additionally, the amendments will not move downgradient and out of the targeted treatment zone. Over time, the xanthan gum will degrade and is anticipated to act as a long-term carbon source as the treatment zone returns to pre-treatment hydraulic conditions.

Multiple laboratory studies and intermediate-scale flow cell research on this enhanced delivery technology have been completed as part of this project as well as other studies (Zhong et al., 2008; Oostrom et al., 2014), and demonstrate several advantages of the treatment technology, including:

- ***Enhanced sweep efficiency.*** Flow cell studies (Figure 1) were applied to investigate the sweep efficiency comparison between water flood (upper set of panels) and shear-thinning fluid flood (lower set of panels) and showed that, the displacing front is straighter across the low-k zones in the STF flood.

- ***Enhanced amendment delivery.*** Improved sweeping of low-k zones and enhanced amendment delivery to those zones were demonstrated in the tests using sodium phosphate as the amendment for delivery (Oostrom et al., 2014).

- ***Enhanced persistence of amendment solution in low-k zones after injection.*** The shear-thinning polymer solution containing the amendment will tend to remain in the low-k zones during the natural groundwater flow (Figure 2). Zhong et al. (2013) observed significant xanthan degradation in 2 weeks when the polymer solutions were in contact with field sediments. Xanthan gum may also serve as a long-term carbon source to support dechlorination.

- ***Stabilized displacing front.*** Density differences as low as 0.8 kilograms per square meter (kg/m^3) can induce unstable displacement (Schincariol and Schwartz, 1990), resulting in preferential and non-uniform flow. The displacement stability can be improved by manipulating the viscosity of the displacing fluid (Lake, 1989; Shook et al., 1998). Figure 1 shows the difference between an unstable fluid displacement front (upper set of panels) and a stabilized displacing front when the shear-thinning solution was applied (lower set of panels).

In layered heterogeneous systems, cross flow between layers is the primary mechanism leading to increased sweeping efficiency (Silva et al., 2012). This was further demonstrated in experiments described in Oostrom et al. (2014) that were conducted in flow cells containing four layers of porous media with a larger range of hydraulic conductivities and using a packing sequence consistent with a portion of the injection interval at the demonstration site for this project. A dye tracer experiment (no STF, Figure 3a) shows independent horizontal transport in each of the layers with limited transverse fluid migration between layers. A total of 9 pore volumes (PV) (27 hours) was needed to sweep the whole flow cell. However, when a xanthan STF was injected, mobility reduction in the higher-k layers, due to an increased viscosity, resulted in considerable cross-flow of viscous fluids from the higher-k into lower-k layers. In addition, pore-water ahead of the advancing polymer solution cross-flows from the lower-k into the higher-k layers. The combination of both cross-flow phenomena, evident in Figure 3b, result in an improved sweep-efficiency. For instance, after injection of 0.67 PV (Figure 3b), the sweep efficiencies for the tracer and xanthan injections, expressed as a fraction of the total pore space, were approximately 0.4 and 0.65, respectively. Examples of the cross-flow zones during STF injection are indicated in Figure 3b. In this experiment, only 2 PVs (6 hours) were needed to completely occupy all the layers with the STF.
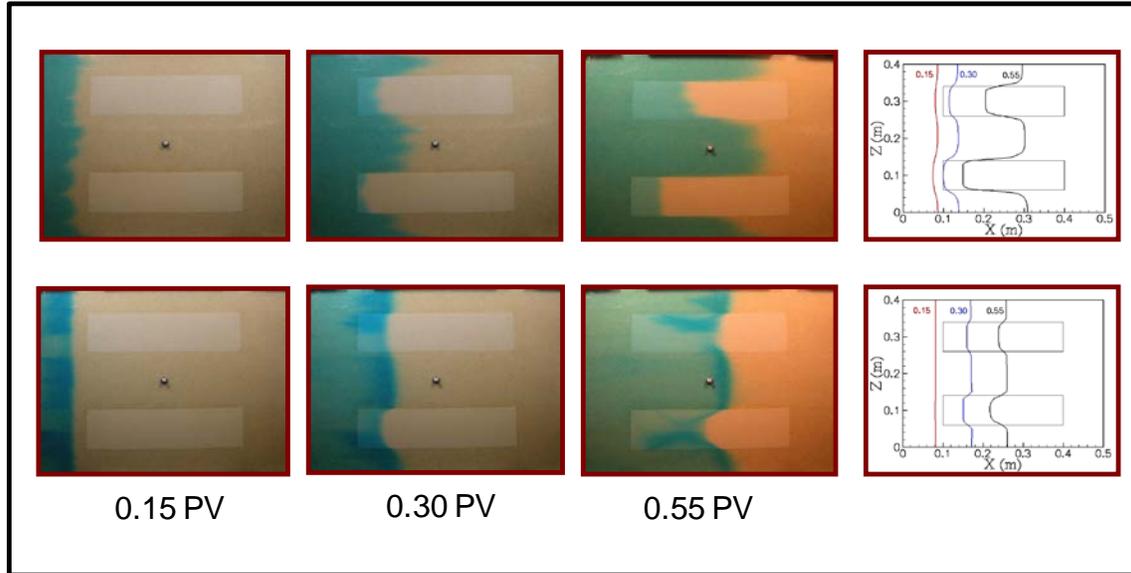
Figure 1. Sweeping efficiency comparison during lab-scale testing.
A heterogeneous porous media system is flushed with blue-dyed water (*top row of panels)* and with blue-dyed xanthan gum polymer solution with viscosity of 46 cP (*bottom row of panels*) at a shear rate of 0.5 sec^{-1}. The media system consists of high-k sand (20/30) containing two embedded cells of lower-k sand (30/40 in top cell; 40/50 in bottom cell). Simulation results (using Subsurface Transport Over Multiple Phases [STOMP]) at the same PVs are shown.
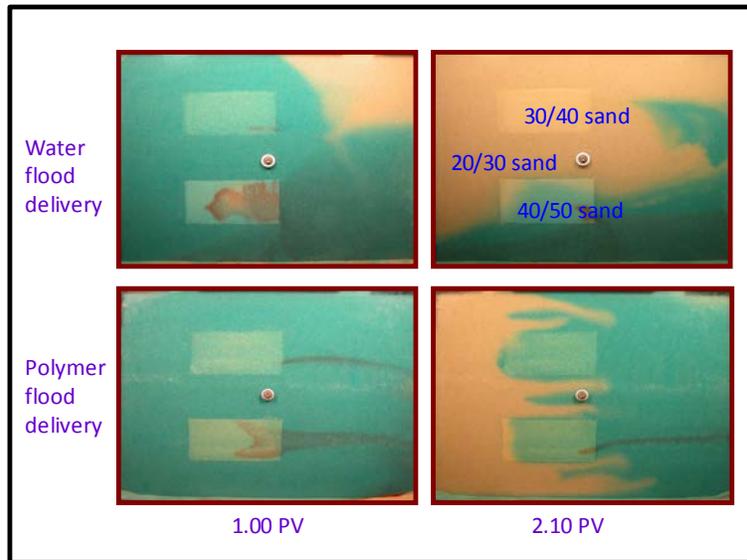
Figure 2. Long-term persistence of remedial amendment delivered to the low-k zones by polymer solution during lab-scale testing.
The upper two pictures display the persistence of phosphate-containing fluids when injected solely via water flooding, and the lower pictures display the persistence of fluids when injected as a polymer solution. After 1 PV of phosphate solution (blue) was injected, water flow was used to displace the solution.
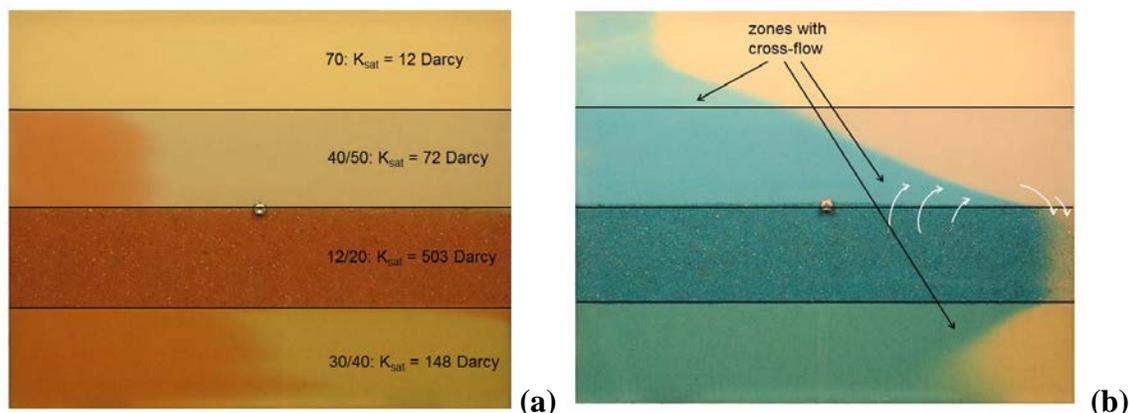
Figure 3. Fluid distribution in flow cell experiments after injection of 0.67 PV.
(a) tracer transport in Experiment I, and (b) xanthan transport in Experiment II. The white arrows represent an example of a dynamic flow system associated with cross-flow mechanism.

The STF technology is expected to be applicable at a wide variety of sites. This includes sites where in situ bioremediation is being considered as a remedy (e.g., for either source or plume control), as well as sites with a distinct low-k strata in contact with (or embedded in) the targeted groundwater bearing unit. The use of shear-thinning polymers is intended to improve distribution within heterogeneous aquifers. However, given the mechanisms involved, it should not be considered as a method to directly inject solutions into low-k materials (e.g., clays). The applicability of the technology is aided by its similarity to conventional in situ bioremediation. The primary difference is that the amendment formulation includes a polymer. Because most bioremediation applications already use liquid, food-grade compounds, the addition of a polymer with similar characteristics (such as xanthan gum) is not expected to pose any limitations to its use. Furthermore, injection well configurations for the technology are essentially identical to those for existing bioremediation applications.

2.2   TECHNOLOGY DEVELOPMENT

The proposed technology represents a combination of two technologies that have been used in subsurface remediation, specifically *bioremediation and STF* for mobility control and enhanced delivery. Bioremediation of chlorinated solvent source zones is considered a mature technology (Air Force Civil Engineer Center [AFCEC]/Naval Facilities Engineering Command [NAVFAC]/ESTCP, 2004; Interstate Technology & Regulatory Council [ITRC], 2005; McGuire et al., 2006; ITRC, 2008; Stroo and Ward, 2010) with several hundred applications across the country. And detailed technology guidance documents for field practitioners (AFCEE/NAVFAC/ESTCP, 2004; ITRC, 2008). A brief chronology of work related to the shear-thinning technology for injection of amendments for in situ remediation processes is presented in Table 1.

Many early lab-scale applications focused on the use of STFs for enhancing recovery of dense non-aqueous phase liquid (DNAPL). Their potential to aid the delivery of other remedial amendments (carbon-based substrates, oxidants) has only recently been recognized. Specifically, Zhong et al. (2008) reported increased efficiency on delivery into lower-k zones after conducting a series of tests designed to demonstrate the use of STFs for improved delivery of remedial

amendments. Another study examined the use of a number of different shear-thinning polymers to enhance in situ chemical oxidation as opposed to surfactant enhanced aquifer remediation (SEAR) (Smith et al., 2008). The authors made it clear that the objective of this research was to demonstrate the utility of STFs for improving treatment of low-k zones. This study established that combinations of xanthan gum and potassium permanganate were most successful at maintaining desired fluid viscosity while promoting significant contaminant oxidation. Of note is that both of these studies emphasized that a key advantage of shear-thinning polymers is the minimization of flow-bypassing of low-k zones that typically occurs during injection-based subsurface remediation. More recently, Silva et al. (2012) reported a study on improved sweeping over layered heterogeneous systems using STF injection. Fluid cross flow among the layers was identified as the major mechanism of sweeping enhancement. In a series of flow cell experiments using xanthan gum solution to deliver permanganate, Chokejaroenrat et al. (2013, 2014) presented a set of data supporting that the use of xanthan is a means of enhancing MnO_4^- delivery into low-k zones for the treatment of dissolved trichloroethene (TCE). In one case, they were able to demonstrate 90% improvement in sweep efficiency when including the shear-thinning polymer (Chokejaroenrat et al., 2014).

Table 1. Chronological summary of the development of the technology.

Time Period	Description of Technology Development
1960s – 1970s	• Widespread adoption of shear-thinning polymer solutions in subsurface applications (enhanced oil recovery for petroleum reservoir management)
1980s	• First uses of shear-thinning polymers as part of field-scale SEAR projects, with objective of NAPL recovery (summarized in Pennell and Abriola, 1997; Simpkin et al., 1999)
1990s	• Successful lab-scale studies demonstrating enhanced recovery of contaminant mass when surfactants and polymers used in combination (Martel et al. 1998a, 1998b, 1998c, 1998d; Dwarakanath et al. 1999) • Publishing of guidance documents for SEAR, including use of shear-thinning polymers to improve mobility control (e.g., Advanced Technology Demonstration Facility [AATDF], 1997)
2000s	• Additional guidance documents for SEAR, including use of shear-thinning polymers to improve mobility control (ITRC, 2003) • Additional successful lab-scale studies for combined surfactant/cosolvent/polymer systems (Dwarakanath and Pope, 2000; Giese and Powers, 2002; Darwish et al., 2003) • Successful lab-scale studies demonstrating enhanced delivery of other remedial amendments by using shear-thinning polymer solutions as part of the injection fluid (Zhong et al., 2008; Smith et al., 2008)
2010-present	• Additional laboratory and modeling studies to demonstrate mechanisms for enhanced sweep efficiency and distribution of injected fluids (Silva et al., 2012; Chokejaroenrat et al., 2013, 2014; Zhong et al., 2013) • Field studies to demonstrate performance of shear-thinning amendments for in-situ chemical oxidation (ISCO) (Crimi et al., 2013) and in situ bioremediation (Smith, 2014)

In addition to the project described in this report (ER-200913), the DoD has funded several other projects through SERDP/ESTCP that are related to the use of polymers in enhancing subsurface amendment delivery. This includes ESTCP ER-200912, a field demonstration that focused on the use of xanthan gum polymer to improve sweep efficiency of permanganate additions while also providing additional carbon for biostimulation. The results of this project showed that sweep efficiency improved from 37% when permanganate was used alone to 67% when permanganate

was injected as a STF in combination with xanthan gum and sodium hexametaphosphate (as a stabilizer). This project was preceded by several SERDP projects (ER-1484 and ER-1686) by the same research group that provided fundamental information on the behavior of polymers as a part of remedial amendment delivery systems.

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The proposed technology is an in situ treatment method for chlorinated solvents and other subsurface contaminants with emphasis on treating zones with contaminants in low-k zones. Therefore, the advantages and limitations of this technology should be evaluated in relation to similar in situ approaches (conventional bioremediation, chemical oxidation, thermal treatment, surfactant-enhanced remediation). These are summarized in Table 2. Technology performance is a function of site properties. Performance of STFs for enhancing delivery of amendments to low-k zones is most effective when permeability contrasts between high- and low-k zones differences are about one or two orders of magnitude.

Table 2. Advantages and potential limitations of the technology.

Advantages	Limitations
Increased ability to treat low-k matrices with potential for increased substrate persistence	Unproven in field applications
Similar in design to in situ bioremediation (established technology)	Design must be tailored on a site-by-site basis (consistent with most bioremediation designs)
Appropriate for source zones	May not be suitable for use in DNAPL source zones.
Utilizes non-toxic chemicals with no special handling requirements	Difficult to track polymer degradation by-products using standard analytical methods
Can be implemented by experienced engineers with no special training	
Costs are known or easy to estimate	

3.0   PERFORMANCE OBJECTIVES

For the purposes of evaluating the cost and performance of the field demonstration, the following performance objectives were envisioned (Table 3). A full description of the various components of the proposed approach that are listed in Table 3 is provided in Section 5.0 (Test Design). Additional detail on the evaluation of these objectives is provided in Section 6.0

Table 3. Performance objectives for the field demonstration.

Performance Objective	Data Requirements	Success Criteria	Success Criteria Achieved?
Quantitative Performance Objectives			
Quantify Improved Distribution of Amendment to Lower- k Zones	Tracer/amendment arrival and concentration in all multi-level wells located in injection zone; in-test ERT data; amendment volume used during STF stage versus baseline stage	Improvement (> 50%) in volume of amendment delivered to lower-k zones within cell during STF versus baseline phases	**YES**, as quantified below.
		Improvement (> 50% decrease) in ratio of tracer arrival between high- and low-k zones during the STF stage relative to the baseline stage	• STF injection distribution was more uniform within the target injection zone, which included low-k zones, based on the volume injected compared to the radial distance of tracer breakthrough. ERT data show an improvement of about 41% for STF distribution compared to the baseline within the monitored 2D cross section.
		Measurable tracer concentrations (> 10% of concentration in injection solution) in CMT ports within low-k zones for the STF stage	• The ratio of tracer arrival in high- and low-k zones decreased by 50% in CMT-2 and by 28% in CMT-1. Thus, this criterion was met in CMT-2 and partially met in CMT-1.
		Measurable amendment penetration in low-k zones (>10% of concentration in injection solution) in CMT ports within low-k zones for the STF stage	• Tracer concentrations in 4 of 5 monitored low-k zones were >10% of the injected concentration and were improved with STF versus baseline and worse at one. • Amendment concentration (as TOC) in 4 of 5 monitored low-k zones were >10% of the injected concentration.
Determine Effectiveness in Enhancing Concentration Reduction in Low-k Zones	Pre- and post-treatment groundwater contaminant concentrations in all wells, with focus on wells screened in lower-k zone	Improved parent compound concentration reduction (>50%) in low-k zone	**YES** • Pre-treatment parent compound concentrations were reduced by >70% in all low-k zones following treatment, including 100% reduction in 4 of 5 monitoring locations
		Measurable concentration of one or more dechlorination daughter products (Sum > 25% of initial parent compound concentration) in low-k zone	• Sum of daughter product concentration following treatment was > 25% of initial (pre-treatment) parent compound in all five monitored low-k zones • Criteria were also met in fully-screened wells in the treatment zone and all high-k monitoring locations

ERT = electrical resistivity tomography
CMT = continuous multichannel tubing
TOC = total organic carbon

Table 3. Performance objectives for the field demonstration (continued).

Performance Objective	Data Requirements	Success Criteria	Success Criteria Achieved?
Quantitative Performance Objectives			
Determine Effectiveness in Enhancing Persistence of Amendment and Effects	Pre- and in-test <u>contaminant</u> and <u>amendment</u> concentrations in groundwater within treatment cell and upgradient of treatment cell	6-month duration for lactate, by-products, and depleted competing electron acceptors within treatment zone	**YES** • Elevated TOC was still present in low-k zone locations after 8 months, with little change between 5 and 8 months • Sulfate was depleted by average of >99% after 8 months • Daughter product production maintained through 8 months • Persistence not dependent on distance from injection well
Qualitative Performance Objectives			
Ease of use	Feedback from field personnel on ease of handling and injecting polymer fluids	Single mobilization required for injection	**YES**, STF injection required a single mobilization using essentially standard injection equipment and protocol. However, the STF must be mixed the day before injection and allowed to hydrate.

4.0 SITE DESCRIPTION

4.1 SITE LOCATION AND HISTORY

Joint Base Lewis-McChord (JBLM) is located in northwest Washington within the Puget Sound region. It was established in 2010 following the merger of Fort Lewis (established in 1917) and McChord Air Force Base (established in 1947) (Figure 4). The area of interest for this demonstration is the American Lake Garden Tract, Area D site, which is located at the northwest edge of JBLM. A TCE plume has persisted at Area D for more than 15 years despite the imposed pump-and-treat remedy using three extraction wells placed at three locations along the axis of the plume downgradient of the source. Available information indicates that former waste disposal site 5/39 is the source of the TCE plume and apparent continuing source during pump-and-treat operations. Subsurface contamination at waste site 5/39 may be present over an areal extent of 2 to 3 acres. The area is currently being used as the golf course for the base.

Figure 4. Location of JBLM.

The area of interest for this demonstration includes a portion of Area D that has been characterized extensively over the past five years to support an assessment of bioremediation as a long-term remedial approach. As such, the area includes several existing monitoring wells and injection wells, as shown in Figure 5. These characterization efforts form the basis for the geologic characteristics described below.

Figure 5. Site map showing existing wells at the test site (prior to the start of the current demonstration project).
Well IDs in parentheses are those used for this demonstration.

4.2   SITE GEOLOGY AND HYDROGEOLOGY

Past field investigations, groundwater monitoring, and modeling activities have provided a conceptual hydrogeologic model in the vicinity of the Area D site where the field demonstration was conducted. Borden and Troost (2001) recently described the aquifer system beneath JBLM. The upper unit in the subsurface, termed the Vashon Unconfined Aquifer (Vashon Aquifer), comprises a nominally 100-foot-thick zone. The Vashon Aquifer is composed of inter-layered outwash and till that, in general, overlie older glacial outwash termed the Pre-Olympia drift. In some areas, non-glacial deposits referred to as the Olympia beds are present between the Vashon outwash/till and Pre-Olympia deposits. Distinct hydrologic layers in the Vashon Aquifer include the Steilacoom Gravel at the top followed by several alternating layers of laterally continuous to discontinuous glacial till and outwash. A mixture of Pre-Olympia drift, Olympia beds, and/or lacustrine beds is present toward the bottom of the aquifer. The field demonstration at Area D was conducted within the Vashon Aquifer. Within Area D, the bottom of the aquifer primarily consists of Olympia beds and/or lacustrine beds of variable thickness.

A representative geologic cross section for the Vashon Aquifer in the area and depth intervals of interest is presented in Figure 6. Glacial outwash and till features with varying silt content and consolidation are present at the site with a wide range of permeability values. Reported outwash hydraulic conductivity values range from 10 to 50+ meters per day (m/d) while till values range from 0.5 to 6 m/d (Vermeul et al., 2000; Truex et al., 2006; U.S. Army Corps of Engineers [USACE], 2002; Ebasco Environmental, 1991). A representative bulk hydraulic conductivity for test site wells with screens intersecting the upper Steilacoom Gravel unit is approximately 15

m/d (Ebasco Environmental, 1991). The bulk hydraulic conductivity of the targeted injection interval, based on analysis of a constant-rate discharge test conducted in the injection well, was estimated at ~3 m/d. Pump testing was performed using a 3-inch diameter submersible pump installed near the bottom of the wellbore in well DA-37, with pressures were monitored in the stress well (INJ-1) and two observation wells (monitoring well [MW]-1 and MW-2) using submersible pressure transducers, and well water levels were verified using manual depth-to-water measurements.
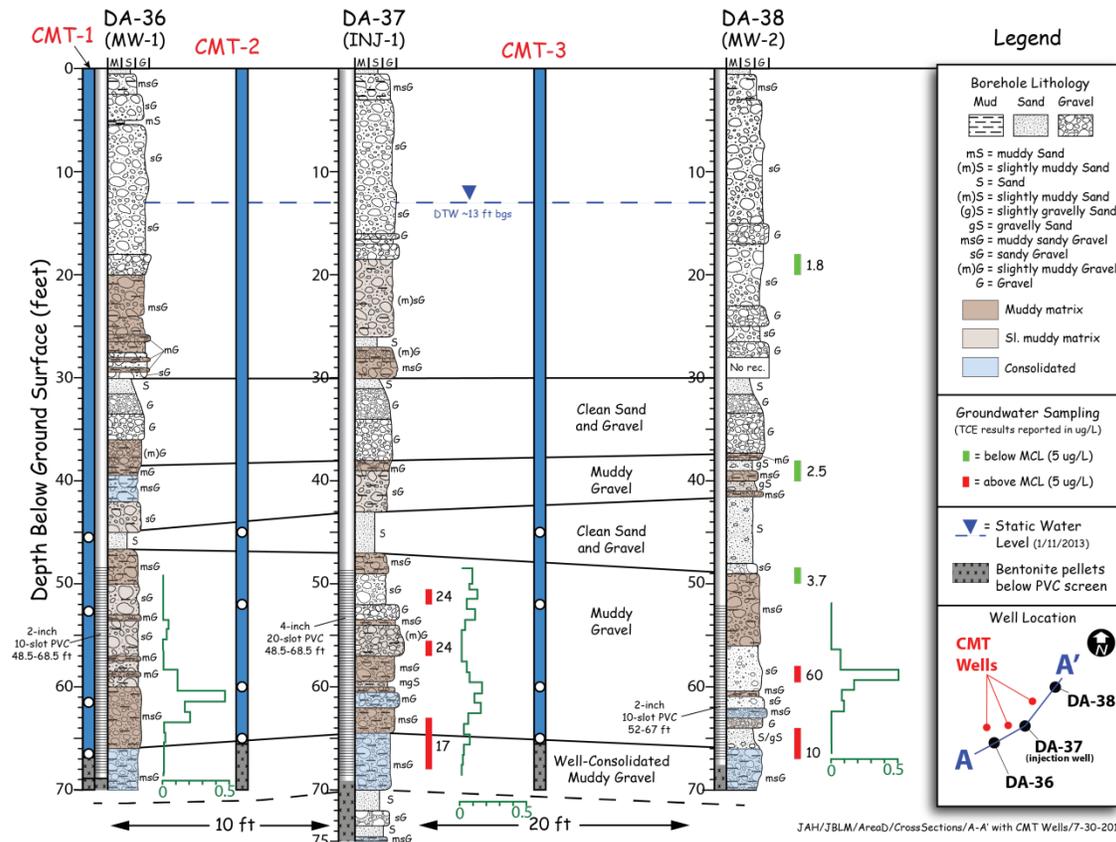
Figure 6. Cross section at the test site.
See Figure 5 for transect location. Contaminant distribution from groundwater sampling and vertical distribution of relative hydraulic conductivity (see text below) are also shown.

Groundwater in the aquifer generally flows in a west-northwest direction at the demonstration site. Groundwater is first encountered at about 4 meters below ground surface (bgs), and hydraulic gradient is nominally 0.001. Given the range in hydraulic conductivity of 3 to 15 m/d, estimated groundwater velocity would range from 0.015 to 0.075 m/d.

4.3   CONTAMINANT DISTRIBUTION

Based on the characteristics of the persistent plume and recent characterization data, residual contamination is present within till or higher silt zones of the aquifer with highest remaining concentrations in the 50-70 feet bgs interval. Figure 6 illustrates an example cross section of existing subsurface contaminant data (from 2013) at the location of the test site (groundwater

flow is perpendicular to this cross section). A plan-view depiction of the evolution of the Area D TCE plume in the Vashon Aquifer as of 2009 is shown in Figure 7. As indicated, TCE primarily migrates in a west-northwesterly direction with a plume above the maximum contaminant level (MCL) about 800-meters long. This figure also shows the approximate location of the field demonstration site. These data confirm that current concentrations in the source zone are relatively low, with concentrations in the clean gravel and sand in the aquifer above the interbedded muddy gravel/till zone below the MCL for TCE. These characterization data support the conceptual model of a continuing source of TCE to the downgradient plume caused by TCE migration from muddy gravel zones with potential contributions from TCE in the consolidated till zones. The TCE contribution from the consolidated till is expected to be smaller than from the muddy gravel zones because of the low hydraulic conductivity of the till units. These data also indicate relatively high concentrations of TCE reductive dechlorination daughter products (*cis*-1,2-dichloroethene [cDCE] and vinyl chloride [VC]) in a few of the samples. Thus, some dechlorination processes appear to be occurring in isolated portions of the source area.
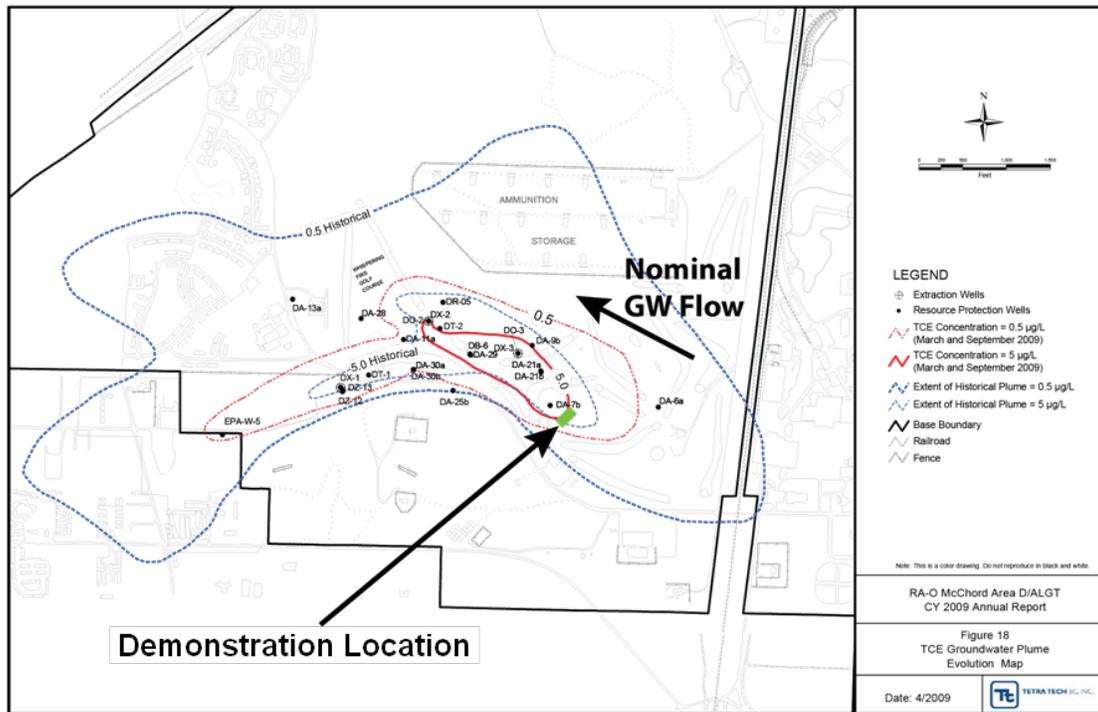
Figure 7. TCE groundwater plume evolution at Area D.
The field demonstration site is at the downgradient edge of the suspected source zone
(adapted from Tetra Tech EC, Inc., 2010).

5.0   TEST DESIGN

5.1   CONCEPTUAL EXPERIMENTAL DESIGN

The field demonstration included installation and operation of a test cell in a chlorinated solvent plume at the JBLM site. Following the completion of characterization activities (Section 5.2), the demonstration was conducted in three distinct stages:

1. ***Baseline Stage:*** Step and constant-rate injection tests with water were completed to verify suitability of the selected injection parameters (e.g., rate, pressure) for the test. A bromide tracer solution was then injected to evaluate distribution of soluble amendments through the heterogeneous aquifer under typical injection conditions (i.e., using a Newtonian fluid that does not exhibit shear-thinning characteristics).

2. ***STF Injection Stage:*** About 3 weeks after the baseline stage, an amendment solution injection containing soluble amendment (ethyl lactate) and tracer (chloride) in STF (xanthan gum) was injected to evaluate the impact of STF on substrate distribution patterns within the heterogeneous aquifer.

3. ***Performance Monitoring (Treatment Stage):*** After the STF stage, performance monitoring was conducted over a period of approximately 8 months to assess the impact of the shear-thinning amendment on contaminant removal followed by post-test characterization.

The well network consisted of an injection well for amendment distribution, upgradient and downgradient monitoring wells, and several treatment zone monitoring wells, including multi-port wells for vertically discrete groundwater monitoring. Amendment, contaminant and competing electron acceptor concentrations for the treatment cell was evaluated by comparing concentrations at the various monitoring wells. In addition, ERT was applied for a 2D cross section between the injection well and monitoring well MW-1 and used to map amendment distribution for both the baseline and STF injections. The groundwater and soil sampling specifically targeted an interval with significant heterogeneity to evaluate the relative impact of STF in improving amendment distribution and promoting faster and more complete remediation.

5.2   BASELINE CHARACTERIZATION ACTIVITIES

Existing characterization data were augmented by installation of CMT wells and subsequent collection of groundwater concentration data, a hydrogeologic evaluation using electronic borehole flowmeters (EBF), and an ERT survey. The locations of the relevant monitoring and/or injection locations are shown in Figure 8.
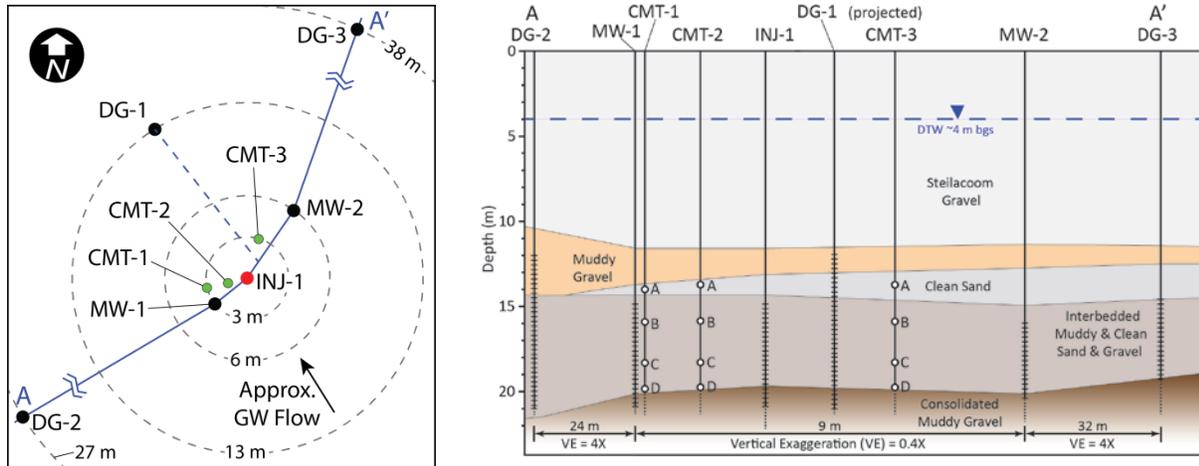
Figure 8. Layout of treatment cell.
Three CMT wells were installed at distances between 1.5 and 3 meters from the injection well.
CMT screened interval depths were selected to monitor higher permeability and lower
permeability zones within the 15-21 meter depth interval, as well as the higher permeability
sediments in the 10-15 meter depth interval.

EBF testing was completed at wells MW-1, MW-2, and INJ-1 at a spatial resolution of 0.3 meters over the screened interval of each well (approximately 50 to 70 feet bgs using standard EBF profiling protocols (Young et al., 1998; Flach et al., 2000). In each case, the peak hydraulic conductivity was noted within a relatively narrow interval around 60 feet bgs (Figure 9). Within INJ-1, a similarly high hydraulic conductivity was noted within the 50 to 55 feet bgs interval. While this approach is not necessarily able to characterize the full magnitude of permeability contrast encountered across the profiled interval, it is able to demonstrate the relative degree of heterogeneity at the tested well locations and identify primary inflow zones. A comparison of the EBF data shown in Figure 9 with the contaminant data are consistent with the presence of elevated levels of contamination in the lower-k regions of the groundwater-bearing unit.
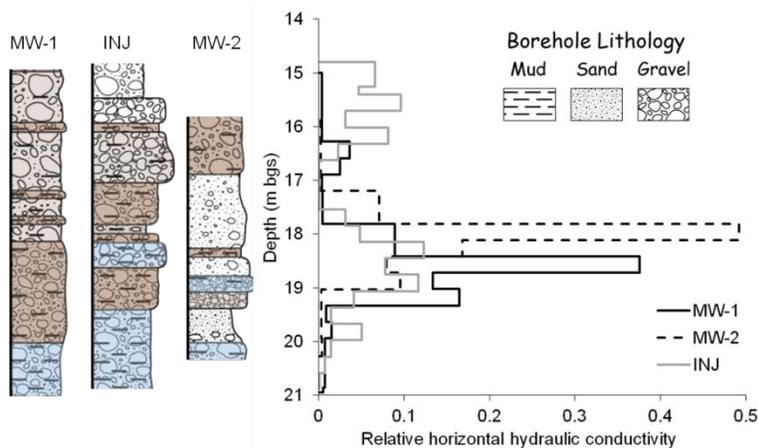
Figure 9. Borehole geologic log in well screen interval and EBF data interpreted as the vertical distribution of relative horizontal hydraulic conductivity at each individual well.
Borehole log brown shading indicates silt content with darker zones showing more silt. Borehole log blue shading indicates zones of more consolidated materials.

CMT wells were installed at three locations (CMT-1, CMT-2, and CMT-3) within the test site (Figure 8; Figure 10). An injection well that was suitable for the purposes of this demonstration was available at the test site (INJ-1; note that this well also served as an additional monitoring well following injection). In addition, there were two other fully-screened wells within the expected area of influence of the injection (MW-1 and MW-2), and additional surrounding monitoring wells.

Figure 10. CMT well installation during field demonstration.
Photos illustrate several key steps (not all steps shown).

CMT wells were placed in a pattern with one or two on each side of the injection well. Each location contained sampling ports at four different depths, with approximately the same depths used at each location (e.g., the A channel was screened at approximately 14 meters bgs at CMT-1, CMT-2, and CMT-3). The goal was to have channels at four distinct, evenly-spaced depths within a heterogeneous aquifer to provide more depth-discrete information than can be obtained with longer-screened monitoring wells. Because of the non-uniform pattern of outwash and till, both standard fully-screened monitoring wells and CMT wells were used for monitoring contaminant concentrations and solutions injected during the tests. Screened intervals for the three CMT wells were selected to monitor within a sandy layer above the targeted treatment zone

(Channel A) and then within three relatively evenly spaced vertical locations (Channels B, C, and D) within the treatment zone.

Important findings from baseline groundwater sampling of the well network included the following:

- Total chlorinated volatile organic compound (CVOC) concentrations were below 100 micrograms per liter (µg/L) at all sampling points, despite the fact that the wells are located near the presumed source. These low levels are consistent with other recent investigations at the site and reflect significant attenuation over time. TCE was generally present at higher concentrations than cDCE, particularly at the fully-screened wells (e.g., MW-1, MW-2).

- While the presence of detectable levels of cDCE at most sampling points suggests that reductive dechlorination is an active pathway, there is little evidence for dechlorination beyond cDCE. VC was present at only one location (C3A, 2.3 µg/L). Similarly, only one location contained detectable levels of ethene (C2A, 18 µg/L).

- Geochemical conditions are consistent with the observed patterns in dechlorination products. In general, groundwater appears to be mildly reducing with evidence of more oxidizing conditions in the fully-screened wells, suggesting that there are zones where anaerobic activity is less favorable. pH values are near neutral to slightly basic. Methane is present but at relatively low levels (<0.1 mg/L). Sulfate concentrations range between 6.7 and 100 mg/L, meaning that there is only moderate competition between sulfate reduction and reductive dechlorination. Finally, little TOC is present throughout the treatment area, such that the injection of the STF amendment should: 1) result in discernible levels of organic carbon (i.e., high levels relative to background); and 2) stimulate pre-existing biological activity.

5.3 LABORATORY STUDY AND DESIGN FACTORS

Laboratory studies were conducted during an early phase of the project to provide information on the rheological properties of potential shear-thinning polymer solutions. The goal of the studies was to generate data to support and optimize the field design (details are presented in Zhong et al., 2013).

The shear thinning behavior of the xanthan in de-ionized (DI) water solutions is shown in Figure 11a. The viscosity at high shear rate (200 s^{-1}) was more than one order of magnitude lower than that at low shear rate (0.3 s^{-1}). At low shear rate the solution viscosity increased linearly with the increase of xanthan concentration within the range from 300 mg/L to 2000 mg/L (Figure 11b). This concentration range should cover the concentrations that will be applied in field remediation injections.
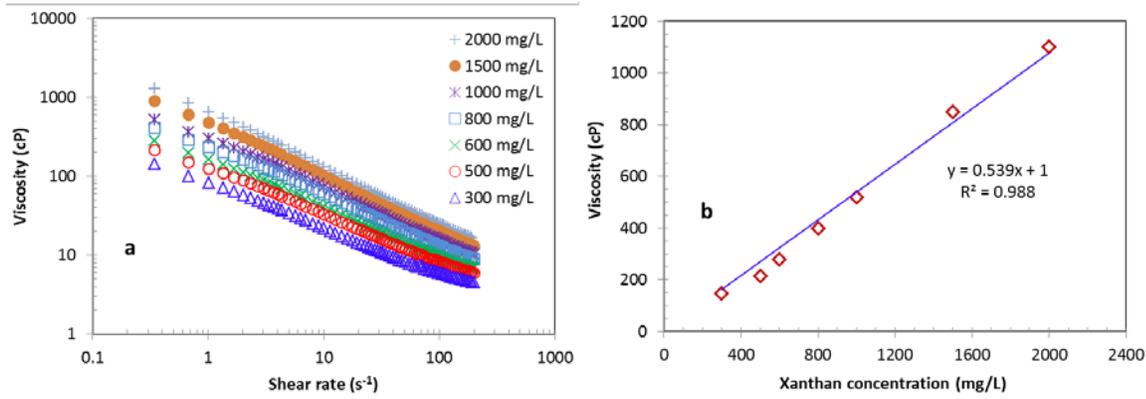
Figure 11. Xanthan gum concentration influence on fluid viscosity and rheology.
(a) Viscosity as a function of shear rate, and (b) Viscosity at low shear rate (0.3 s^{-1}) for several xanthan concentrations. All solutions were made in DI water.

Xanthan rheology was influenced by solution ionic strength and specific ions in solution. When cations were initially added to the ion-free xanthan solution, the viscosity decrease was significant, and further addition of ions to the system resulted in less impact on viscosity. Both groundwater and the remedial amendments to xanthan solutions might contain ionic and non-ionic compounds and change the ionic strength, therefore alter their rheological behavior. Sodium lactate and ethyl lactate (both at 10 grams per liter [g/L]) lowered the viscosity of 700 mg/L xanthan gum solutions while the solutions still showed shear thinning behavior (Figure 12). Sodium lactate lowered the viscosity at 0.3 s^{-1} shear rate by 76% and the ethyl lactate decreased the viscosity by 25% (Figure 12). The significant difference between the viscosity impacts of the two substrates was presumably due to the presence of Na^+ in the sodium lactate ($C_3H_5NaO_3$) while there was no salinity in ethyl lactate ($C_5H_{10}O_3$). When higher viscosity is desired for substrate delivery in corresponding to the aquifer heterogeneity settings, ethyl lactate is preferred over sodium lactate. Therefore, ethyl lactate was selected for the JBLM site demonstration.
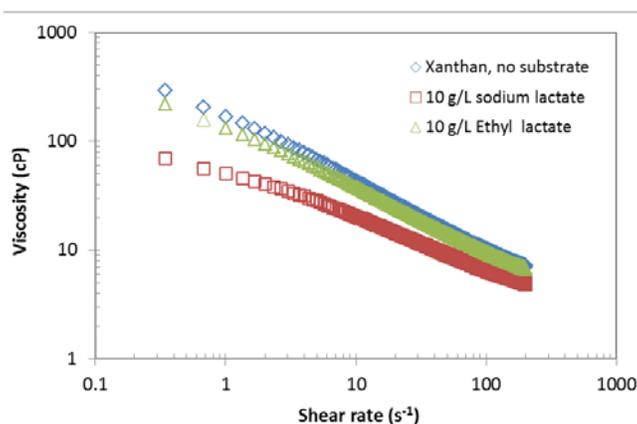
Figure 12. Influence of remedial amendment lactate on xanthan solution rheology.

Key design considerations for use of STF are managing the injection pressure and inducing distribution of amendment into lower-permeability zones in the subsurface. These design considerations impact selection of the appropriate STF rheology, and therefore, concentration of

STF polymer (e.g., xanthan) to use. The injection pressure for the STF will be the baseline injection pressure (water only) multiplied by the viscosity of the STF under the injection conditions. There is typically high shear rate near the injection well such that an upper bound for the viscosity is the measured viscosity at a shear rate of 150/s. In the field, observed initial pressure increases from STF have been only about 20% of this value, although the injection pressure increases with time. For pressure management in the field, monitoring of pressure to a pre-determined maximum based on system constraints may be needed where pressure can be decreased, if needed, by decreasing the injection flow rate.

While the injection pressure consideration leads to the need for keeping viscosity as low as possible, viscosity is needed to induce distribution of amendment into low permeability layers (e.g., through the cross flow phenomena). Generally, more viscosity leads to more cross flow between layers. However, there are diminishing returns as viscosity increase. Figure 13 shows results of model simulations performed as part of this project to examine the relation between viscosity and improved distribution to low permeability layers. In these simulations, using a radial simulation grid to approximate fluid movement from an injection well, a 5-foot thick low-k layer was imposed at the middle of a 20-foot well screen interval. The contrast between the high-k and low-k zone hydraulic conductivities was either 10 (Figure 13a) or 100 (Figure 13b). STF was injected at 30 gallons per minute (gpm) to a target ideal cylindrical injection radius of 15 feet (12 hours). The swept volume fractions are computed by dividing the swept volume of STF delivered in the low permeability layer by the total volume of this layer out to a 15 foot radius. The red line represents the total swept volume fraction and the blue line represents the swept volume fraction resulting from cross flow only. The difference between the two lines represents the swept volume fraction resulting from direct well flow into the low-k zone. It is difficult to explicitly model most sites due to uncertainties in the actual layer permeability contrasts and the configuration of layering. Thus, a rule of thumb for applying STF with a static viscosity of near 100 cP is suggested. If more detailed assessment is warranted for a specific site, modeling approaches such as described by Oostrom et al. (2014) or Silva et al. (2012) can be applied.

(a) **(b)**
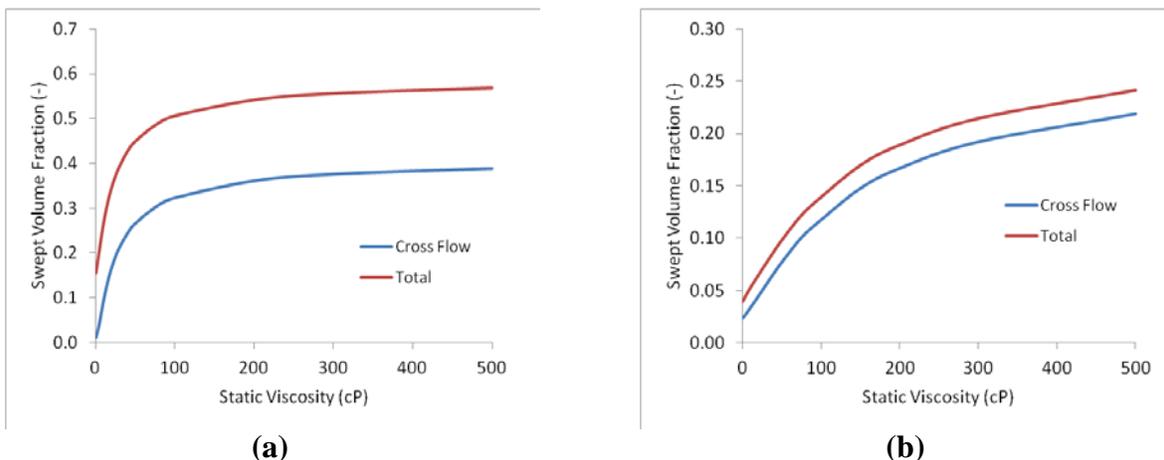
Figure 13. Results of simulations examining the relation between viscosity and improved distribution to low-k layers.
The contrast between the high-k and low-k zone hydraulic conductivities was either 10 (Figure 13a) or 100 (Figure 13b). The red line represents the total swept volume fraction and the blue line represents the swept volume fraction resulting from cross flow only. See text for simulation details.

5.4 FIELD TESTING

The field portion of this project involved three stages as outlined in Section 5.1.

5.4.1 Baseline Injection Stage

The objective of the baseline injection stage of the demonstration was to evaluate the distribution of an injected aqueous solution in the absence of a shear-thinning polymer. In this regard, it mimics a conventional injection approach for in situ bioremediation, with the distribution of amendments highly influenced by the heterogeneity near the injection well.

Following the site characterization (described in Section 5.2), the first step was completion of step and constant-rate injection tests. The injection well was sealed with an inflatable packer, fitted with a pressure gauge and pressure relief valve, and connected to the injection water supply via flexible tubing. Injection solutions were transferred via this line using a centrifugal pump. To minimize the potential for formation fracturing, the injection pressure was checked against allowable injection pressures estimated based on pore pressures within the formation.

Hydraulic properties were estimated during these initial injection trials by monitoring pressure heads in nearby monitoring wells. A step injection test was conducted first by sequentially increasing the injection flow rate and observing the pressure response. Based on these data, an injection rate for the constant-rate test was selected. During the constant-rate injection test, pressure heads were monitored for analysis of aquifer hydraulic properties. The change in the water level is a function of the spatial distance between the observation well and the injection well, aquifer thickness, storativity/specific yield, and the aquifer hydraulic conductivity. Data from the field tests during injection was used to establish the hydraulic properties of the groundwater-bearing unit (Kruseman and de Ridder, 1991).

The second and primary step during the baseline injection stage involved the injection of a bromide tracer solution to monitor the distribution of soluble compounds in a heterogeneous formation in the absence of a shear-thinning polymer.

For the baseline injection, the concentrated sodium bromide stock solution was prepared in a 1900 liter polyethylene tank (Figure 14). The solution was delivered into the injection stream via a stainless-steel 2-horsepower centrifugal pump, mixed with water from a nearby fire hydrant, and routed through an inline static mixer prior to injection (Figure 15).

The test consisted of the injection of bromide at a concentration of 250 mg/L (320 as sodium bromide) at a rate of approximately 30.4 gpm. Solution preparation was completed on-site and utilized make-up water supplied by the site (fire hydrant). As described in Section 5.4.4, separate tanks with appropriate mixing capabilities were used for stock solutions and injection solutions. All solutions were metered separately to reach the desired injection concentrations.

The tracer (bromide) was injected to ensure that a target radius of influence of 10 to 20 feet was achieved. Injection occurred until breakthrough was observed at MW-2 and sufficient volume was injected (61,300 liters) for distribution of the injection solution to an ideal cylindrical radius of ~13 feet (i.e., clearly past the radial distance of MW-1 and the CMT wells). At the conclusion

of the tracer injection, a clean water flush was completed using 40,000 liters of bromide-free water injected at an average rate of 29 gpm.

Downhole ion-specific or specific conductance probes were used to monitor tracer arrival in the field; aqueous samples were also collected periodically at these locations as guided by the probe results. Arrival at locations within lower and higher permeable intervals were compared using aqueous samples collected from the CMT wells. Sampling frequency was adjusted as required based on observed arrival response during injection; less frequent sampling was completed for wells screened within the less permeable zones. At the end of injection, a complete round of samples was collected.

During and at the conclusion of the tracer test, cross-hole ERT surveys were conducted as a time series to evaluate tracer movement (using the tracer as a resistivity signal).
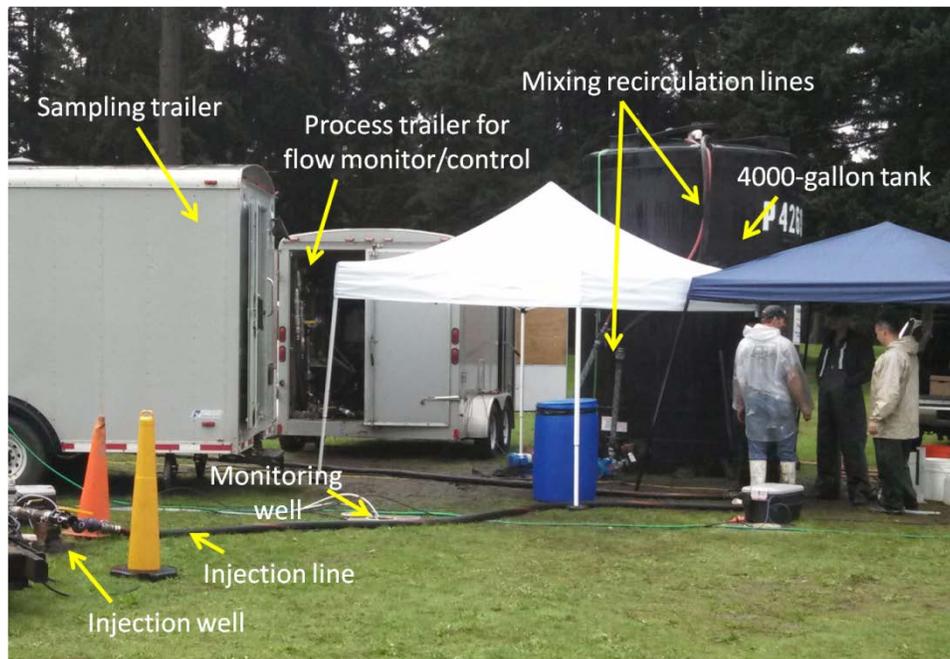
Figure 14. Injection and monitoring equipment layout.
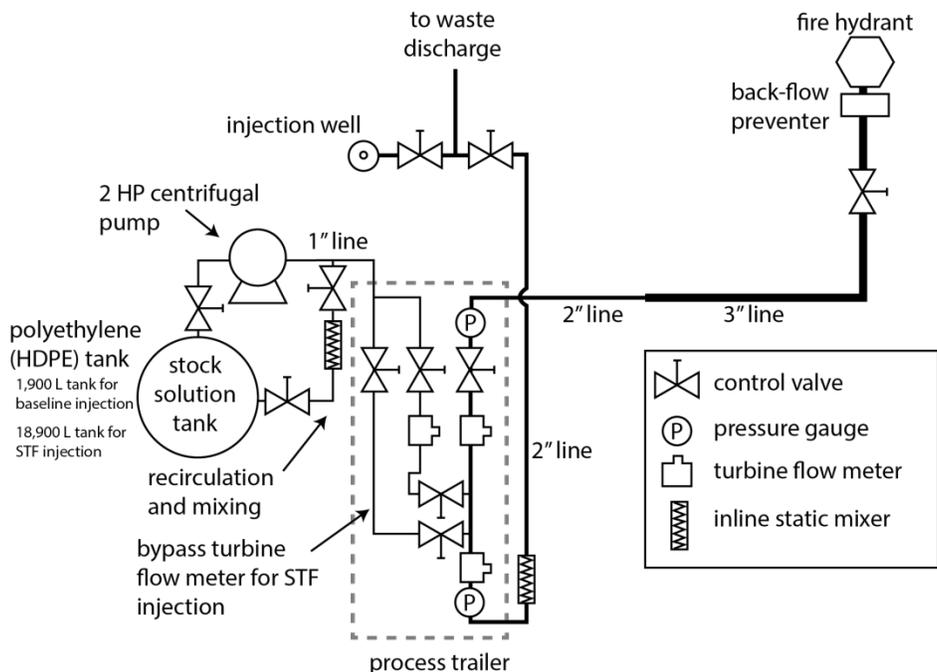
Figure 15. Schematic of the process and injection equipment for the baseline and STF injections.

5.4.2 STF Injection Stage

Following the completion of the baseline injection stage, injection of the shear-thinning solution was completed to start the treatment phase of the demonstration. The injection rate and nominal injection duration were evaluated in advance using design simulations with adjustments based on aquifer response to injection flow during the tracer test. The lactate-xanthan gum solution was prepared at a polymer concentration to provide rheological properties determined based on pre-injection numerical simulations. The STF amendment consisted of diluted ethyl lactate, potassium chloride tracer, and xanthan gum polymer. The target lactate concentration in the aquifer (following injection) was 1000 mg/L. This represents a relatively low concentration injection solution that is well-suited to stimulate the desired reductive dechlorination reactions for the site contaminant levels, and also to provide a reasonable response in fermentation and terminal electron acceptor processes to track biological processes. Xanthan was added at a final (mixed solution) concentration of 800 mg/L. Chloride was used as the tracer for this phase at a concentration of 230 mg/L (480 mg/L as potassium chloride).

STF injection required pre-mixing of a xanthan stock solution with sufficient hydration to ensure appropriate rheological properties and uniformity of the solution. The xanthan stock solution was mixed with hydrant water, potassium chloride, and ethyl lactate in 1900-liter batches and then transferred to an 18,900-liter temporary storage tank (Figure 16). Mixing and hydration of each batch was accomplished using two electric variable-speed mixers with multi-bladed impellers. The xanthan stock solution was recirculated within the storage tank for several hours to provide additional mixing using the same inline static mixer and centrifugal pump setup used in the baseline injection, and then allowed to hydrate overnight prior to the injection. The xanthan stock

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was delivered into the injection stream using the same equipment configuration as the baseline injection (Figure 15).

The injection process and monitoring followed the protocol described previously, using an injection rate of 31.7 gpm. At the conclusion of the test, the injection volume (106,400 liters) was about twice the injection volume for the baseline injection, resulting in a targeted cylindrical radius of ~17 feet. During injection, downhole ion-specific or specific conductance probes were used to monitor tracer arrival in the field. Arrival at locations within lower and higher permeable intervals were compared using aqueous samples collected from the CMT wells. At the end of injection, a complete round of samples was also collected. Once the desired amendment volume was injected, a small volume (< 500 liters) of xanthan solution with no lactate was pumped to flush out the distribution lines and well casing. During and at the conclusion of the STF injection test, surface and cross-hole ERT surveys were also conducted as a time series to evaluate tracer/amendment movement (using the tracer as a resistivity signal).

At the conclusion of the injection test, groundwater samples for volatile organic compound (VOC) analysis were collected from each of the monitoring locations (as well as the injection well).
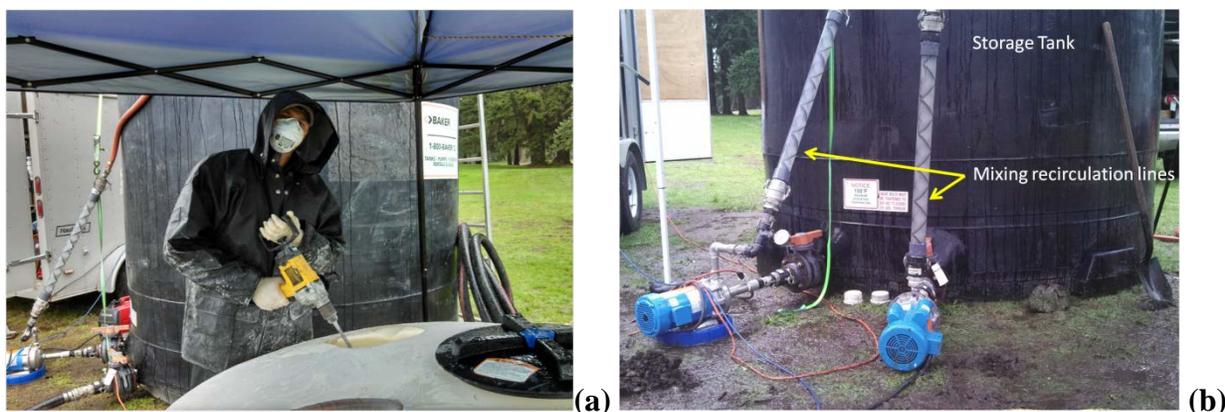
Figure 16. Preparation of the xanthan stock solution.
a) initial mixing and b) continued hydration with additional recirculation mixing in the storage tank.

5.4.3   Performance Monitoring (Treatment Stage)

Performance monitoring was completed in the period following the amendment injection to determine if the amendment were effective in achieving treatment of contaminants. In addition, the persistence of the amendment within the treatment area using the temporal data.

Performance monitoring events were completed in February 2014 and May 2014. Scheduling for the performance monitoring events was intended to be dynamic and relied on an assessment of progress of the test. Ultimately, the duration of the monitoring period (8 months) was consistent with the duration that was assumed prior to the start of the test (approximately 6 to 9 months). The last performance monitoring event essentially replaced any separate post-test characterization step.

5.5   SAMPLING METHODS

Similar sampling protocols were followed for the baseline characterization event (Section 5.2) as well as three additional comprehensive groundwater monitoring events: 1) event completed immediately after the end of the STF injection test; 2) performance monitoring event completed in February 2014; and 3) performance monitoring event completed in May 2014.

During the injection tests, groundwater samples were also collected at frequent intervals (every 2 to 10 minutes) to quantify tracer concentrations. While these samples were typically collected using low-flow purging techniques, the high frequency of sampling occasionally necessitated the use of grab sampling to ensure that no data were missed.

Samples were collected and analyzed following the program outlined in Table 4 and Table 5 at appropriate commercial laboratories.

Table 4. Summary of sampling plan for field demonstration.

Project Component	Matrix	Collection Method	Number of Samples	Analyte(s)	Location(s)
Pre-Test Baseline Characterization	Groundwater	Low-flow w/ peristaltic pump	20	CVOCs, ethene, methane, sulfate, TOC, bromide, field parameters[1,2]	Four intervals at each CMT well, MW1, MW2, INJ1, DA31-DA35,
	Groundwater	Pressure transducer	Up to six	Static water level	All fully screened wells in test area
	Soil/groundwater resistivity	ERT	N/A	Resistivity	Surface electrodes and in-well electrodes at INJ1, MW1, MW2
	Groundwater	EBF	Every 0.3 vertical meters per location	Relative Hydraulic conductivity	INJ1, MW1, MW2
Injection Monitoring	Groundwater	Low-flow w/ peristaltic pump	2-20 per screen interval to assess tracer arrival during each injection test	Bromide (during baseline test), chloride (during amendment injection)	Four intervals at each CMT well, MW1, MW2, DG1
	Groundwater	Down-well probe	N/A	Bromide (during baseline test), chloride (during amendment injection)	MW1, MW2, MW3
	Injection solution	Sample valve	Minimum of three during each injection test	Bromide (during baseline test), TOC, chloride (during amendment injection)	Injection line
	Groundwater	Low-flow w/ peristaltic pump	Up to 20 at end of amendment injection	CVOCs, ethene, methane, sulfate; bromide/chloride, TOC, field parameters[1,2]	Four intervals at each CMT well, MW1, MW2, INJ1, DA31-DA35

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Table 4. Summary of sampling plan for field demonstration (continued).

Project Component	Matrix	Collection Method	Number of Samples	Analyte(s)	Location(s)
Injection Monitoring (continued)	Soil/groundwater resistivity	Electrical Resistivity	N/A; repeated at end of each injection test	Resistivity	Surface electrodes and in-well electrodes at INJ1, MW1, MW2
	Groundwater	Low-flow w/ peristaltic pump	Up to 15 collected at the end of amendment injection	Rheologic properties	Four intervals at each CMT well, MW1, MW2, INJ1
Performance Monitoring	Groundwater	Low-flow w/ peristaltic pump	Up to 20 per event (two events; conducted 5 and 8 months after injection)	CVOCs, ethene, methane, sulfate; bromide/chloride, TOC, field parameters[1,2]	Four intervals at each CMT well, MW1, MW2, INJ1, DA31-DA35

Notes: (1) Field parameters for groundwater include temperature, pH, oxidation-reduction potential (ORP), electrical conductivity, and dissolved oxygen; (2) Not all analytes may be included in all monitoring events at all locations.
N/A = not applicable
DG = downgradient

Table 5. Summary of analytical methods for samples collected during field demonstration.

Matrix	Analyte	Method	Container and Preservative	Laboratory
Groundwater	CVOCs	USEPA 8260	3 40-mL glass vials; HCl to pH < 2	ESC Lab Sciences
	Ethene, ethane, methane	RSK175	3 40-mL glass vials; no preservative	ESC Lab Sciences
	Inorganic anions (sulfate, chloride, bromide)	USEPA 300.0	500 to 1000 mL plastic bottle; no preservative	ESC Lab Sciences
	Bromide/chloride	Specific conductance meter	> 100 mL; no preservative	Not applicable (field measurement)
	Field parameters (dissolved oxygen, electrical conductivity, ORP, pH, temperature)	YSI Mulitmeter or equivalent	> 100 mL; no preservative	Not applicable (field measurement)
	Rheology	Rotational rheometer Physica MCR 101	20 mL; no preservative	PNNL
	TOC	USEPA 9060A or SM 5310D	500 mL plastic bottle; H_2SO_4 to pH < 2	ESC Lab

mL = milliliter
PNNL = Pacific Northwest National Laboratory
USEPA = U.S. Environmental Protection Agency

5.6   SAMPLING RESULTS

Results related to the performance of the shear-thinning fluid amendment relative to the baseline control test are presented in this section. Note that the results of the baseline characterization were presented in an earlier section (Section 5.2) and are used here for comparative purposes.

Data from initial injection of only water were used to estimate a ~3 m/d bulk hydraulic conductivity of the targeted injection interval. Injection pressure and flow rate monitoring during the field injections demonstrated that, at the same rate of injection, the STF resulted in approximately 1.75 times greater injection pressure than for the baseline solution near the end of the injection period (Figure 17). Thus, the high shear rate from injection resulted in shear thinning that significantly reduced the viscosity of the STF solution from its static viscosity of about 130 cP, as would be expected based on the shear-thinning response of the injection solution determined using laboratory rheological measurements with a rotational rheometer (Physica MCR 101, Anton Paar USA Inc., Ashland, VA) (Figure 18). Under these field injection conditions, the STF injection pressure was approximately 10 m (~14 psi) above ground surface at the injection well. It was expected that the well seal would be sufficient for this pressure range. However, after injection of about 58,300 liters (528 minutes elapsed injection time), the injection pressure dropped abruptly, a strong indication that the well seal was breached and that part of the injected fluid was being discharged into the upper, high-k Steilacoom Gravel formation. Thus, while pressure increases during STF injection are much lower than would be predicted from the static STF viscosity, the additional pressure for injection puts stresses on the injection well seal that need to be considered in design of the injection well.
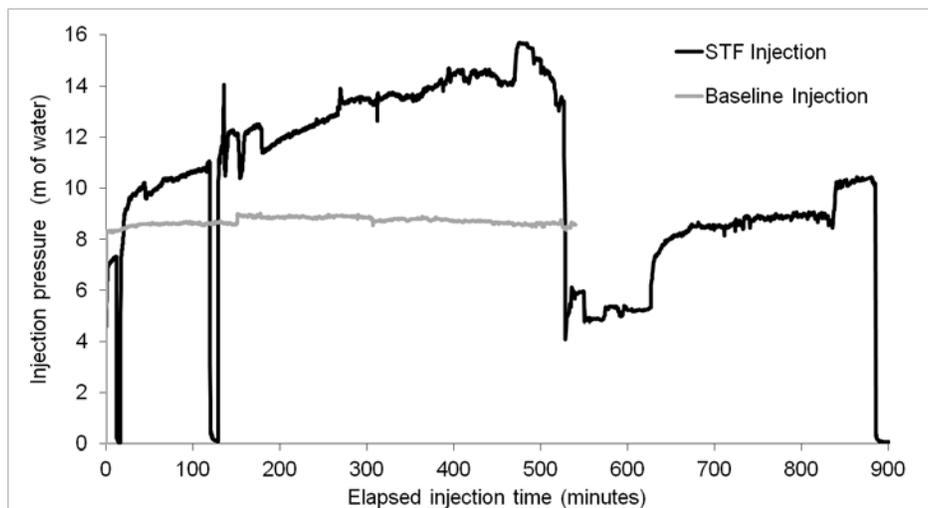
Figure 17. Injection pressure recorded during the baseline (control) and STF injection tests.
Pressure is reported as meters of water above the static water table.
The STF injection pressures are normalized to the average injection flow rate for the baseline injection of 115 liters per minute. The average flow rate for the STF injection was 120 liters per minute.
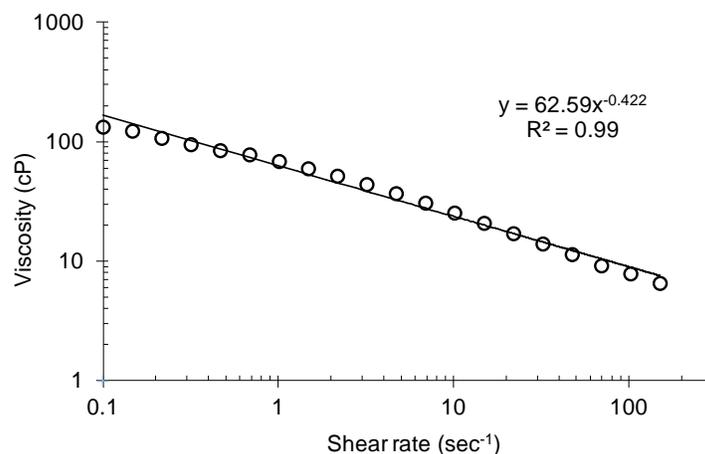
Figure 18. Rheology of STF injection solution used in the field demonstration.
The data in the power-law region have been fitted with an Ostwald-De Waele relationship
according to Lopez et al. (2003).

As observed in Figure 17, the STF injection pressure increases over time, in comparison to a stable pressure for the baseline injection. This effect is attributed to: 1) lower interstitial velocities and, therefore lower shear rates, causing viscosity of the injected solution to increase as a function of distance to the well; and 2) an increasing volume of viscous fluid in the subsurface over time as the injection volume expands radially. These conditions lead to higher pressures required to maintain the same flow rate.

A volume of 61,300 liters of tracer solution was injected during the baseline test, and a total of 106,400 liters of tracer solution containing the lactate-xanthan gum amendment was injected during the shear-thinning fluid test. Due to the well seal breach, the STF breakthrough analysis focuses on data up to that time with a corresponding injection volume of 58,300 liters, comparable to the baseline injection volume of 61,300 liters. Based on the pressure in the injection and monitoring wells after the breach, it was estimated that about 33% of the injected solution was distributed to the targeted well screen interval and 67% flowed into the overlying high-k Steilacoom gravel formation. Using this estimate, the total STF volume injected to the targeted well screen interval was 74,200 liters of the total 106,400 liters injected.

Tracer arrival at the various sampling points was monitored throughout the injection period. Breakthrough was defined as the volume associated with reaching 50% of the observed arrival concentration at a given well location after fitting data to a Sigmoid curve (TableCurve 2D, Systat Software Inc., San Jose, CA) or, where appropriate, using in a linear fit. For the baseline injection test, Figure 19 displays the volume of the tracer solution that had been injected at the time of tracer breakthrough at the most relevant monitoring locations and depths, as well as the observed tracer concentration at the end of the test relative to the concentration in the injection solution.
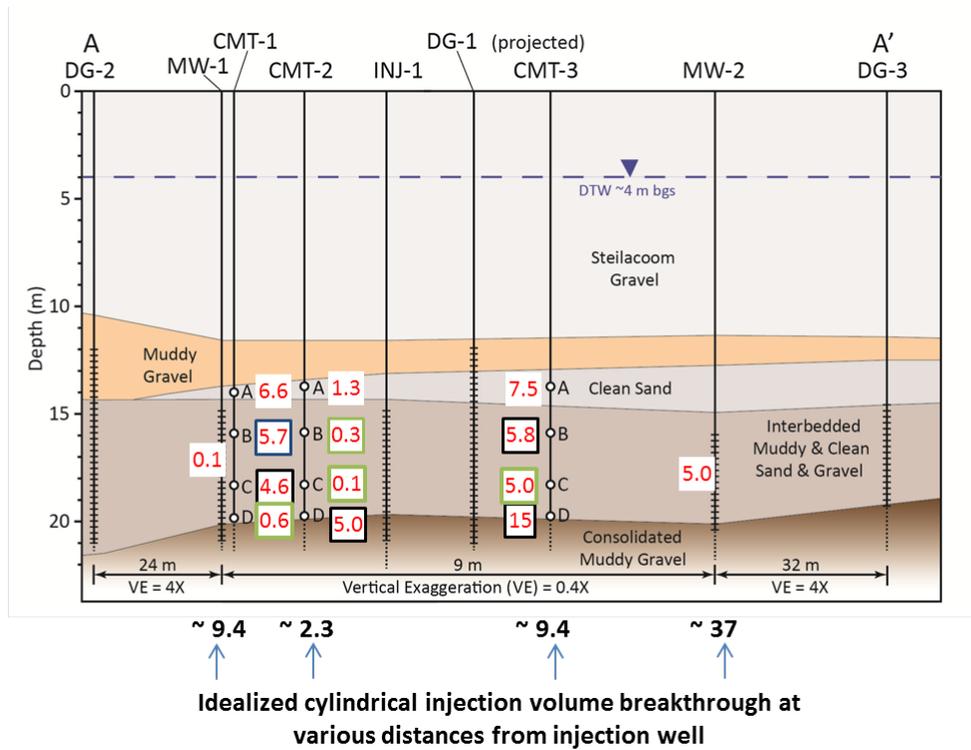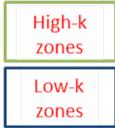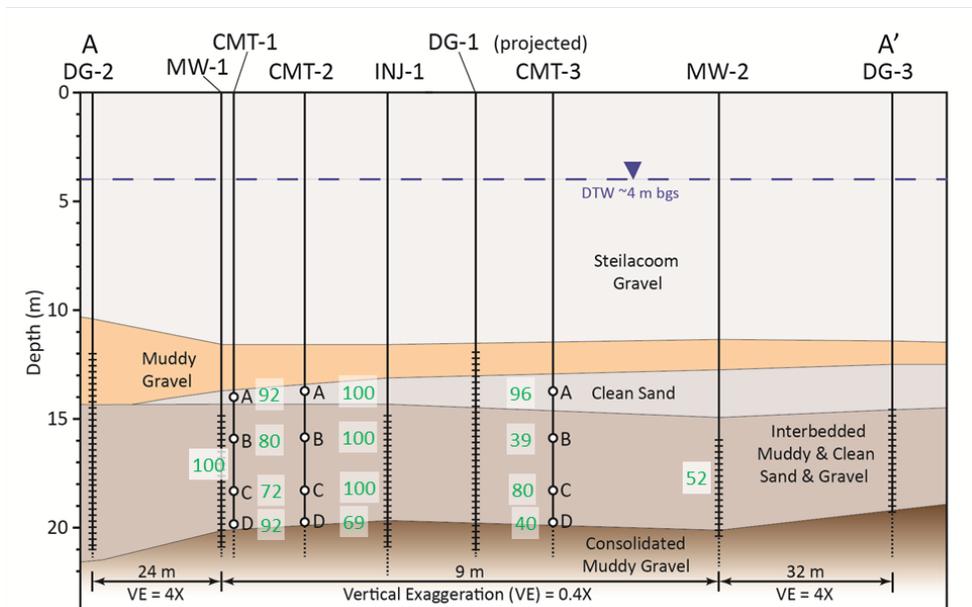
Figure 19. Cross-section of treatment zone with tracer distribution during baseline injection test.
(a) tracer breakthrough volumes with classification of locations as high-k versus low zones based on breakthrough; (b) tracer concentration.

Breakthrough of injected solution at a given monitoring location was computed based on a percentage of the idealized cylindrical injection volume required to reach the location. The idealized volume represents a cylindrical pore volume extending to the radial distance of the monitoring location from the injection well. Percentages lower than 100% provide indication of faster transport and tracer arrival than would be expected for a homogeneous and radially symmetric system. A larger percentage is indicative of slower transport and a delayed tracer arrival. Assuming an ideal cylindrical distribution, the total volumes injected during both the baseline and STF tests were sufficient to fully reach the monitoring locations at 1.52- and 3.05-meters (5 and 10 feet), but not the 6.1-meter (20-foot) location. Observed tracer concentrations at the end of the injection period were compared to the injection concentration and percentages computed to provide a metric for distribution effectiveness (Table 6). The "A" zone monitoring locations are above the injection well screen and, ideally, injected fluid would not reach these locations.

Table 6. Summary of differences between amendment distribution during baseline injection test and STF injection test.

Location ID	Permeability Classification (based on results from baseline test)	Breakthrough Volume (as % of idealized volume)		Tracer Concentration (as % of injection solution concentration)		Viscosity (as % of injection solution viscosity)
		Baseline	STF	Baseline	STF	STF
C1A	Overlying Sand (high-k)	70%	96%	93%	82%	10%
C1B	low-k	61%	30%	81%	91%	70%
C1C	low-k	49%	38%	73%	100%	68%
C1D	high-k	6%	12%	93%	100%	100%
C2A	Overlying Sand (high-k)	56%	450%	100%	100%	88%
C2B	high-k	14%	29%	100%	100%	90%
C2C	high-k K	2%	17%	100%	100%	64%
C2D	low-k	213%	56%	69%	69%	No data
C3A	Overlying Sand (high-k)	80%	>170%	97%	2%	4%
C3B	low-k	62%	124%	39%	65%	85%
C3C	high-k	53%	104%	81%	74%	46%
C3D	low-k	165%	>170%	40%	5%	54%
MW-1	NA (screened in multiple zones)	1%	7%	89%	100%	No data
MW-2	NA (screened in multiple zones)	13%	>43%	53%	2%	No data

CMT monitoring locations were categorized using the data from the baseline injection (the control test) as representing a relatively high-k transport pathway, a low-k pathway, or as monitoring within the sand "A" zone location above the targeted treatment zone (Table 6, Figure 19). This approach was selected because sediment type and associated permeability vary significantly over short vertical and lateral distance (i.e., the subsurface is not comprised of laterally-extensive layers). Based on this approach, CMT locations C1D, C2B, and C2C were categorized as representing relatively high-k transport pathways because the breakthrough

volume for the baseline injection was 7 to 50 times lower than the ideal cylindrical volume required to reach these monitoring locations (Table 6). Consistent with the results for breakthrough at well MW-1, these CMT location results indicate that significant high-k pathways in the radial direction toward MW-1 exist at the test site. A similar, though less pronounced, pathway is also evident in the radial direction toward MW-2 (Table 6).

Data from the two injection tests at the fully-screened monitoring wells MW-1 and MW-2 demonstrate key differences in injected fluid movement in a heterogeneous subsurface environment induced by the use of a STF injection solution (Figure 20). These data are based on injected volumes of 61,300 to 74,200 liters. This volume range represents 1.7 to 2.1 pore volumes for a cylinder extending to the MW-1 radius and 0.43 to 0.52 pore volumes extending to the MW-2 radius. Thus, an ideal injection would fully distribute solution to MW-1, and no solution would reach MW-2. As shown in Table 6, 100% distribution of STF was achieved at MW-1 compared to 89% distribution of tracer from the baseline injection. While the breakthrough volumes for both the baseline solution and the STF solution indicate rapid tracer movement between the injection well and MW-1 (i.e., very early tracer arrival), the STF slowed flow in the dominant flow paths (Table 6): 7% versus 1% of the idealized cylindrical volume at 50% breakthrough) and improved the final distribution (percent of injected concentration) of the injected solution. At MW-2, breakthrough during the baseline test was achieved at a volume that was equivalent to 13% of the idealized radial volume, reaching a final tracer concentration 53% of the injected concentration. In contrast, during the STF injection, tracer arrival was not observed at MW-2, consistent with a more uniform distribution of the injected solution within the heterogeneous formation due to the presence of the STF.
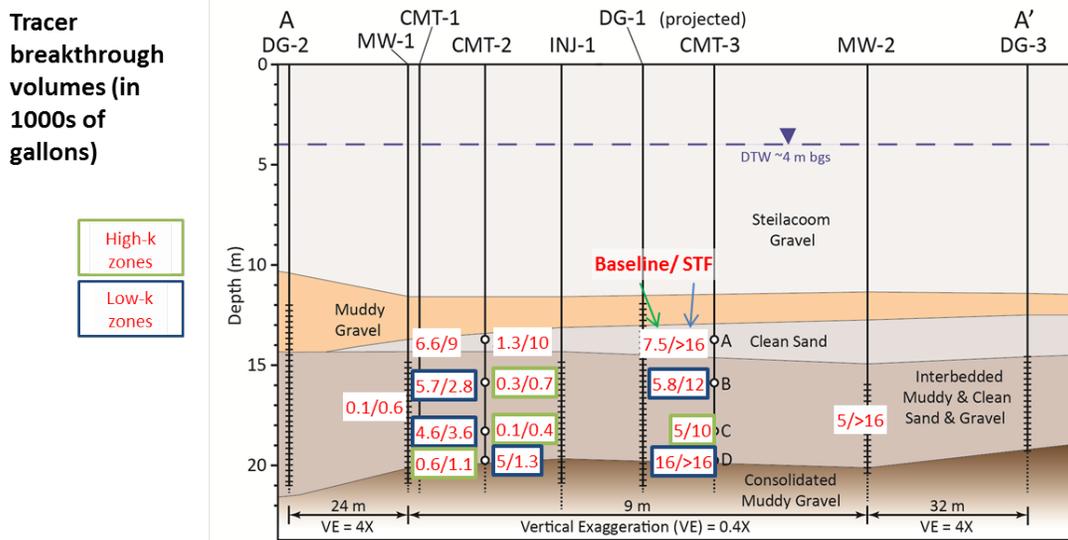
Figure 20. Cross-section of treatment zone with tracer distribution during baseline injection test versus STF injection test.
Volumes for baseline test represent breakthrough of bromide tracer while volumes for shear-thinning test represent breakthrough of chloride tracer.

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A comparison of breakthrough and distribution at the CMT monitoring locations for the baseline and STF injections is summarized in Table 7. The table presents the relative percent difference (RPD) in the breakthrough volume between the STF and baseline tests, as well as the RPD in the percentage of the injected tracer concentration for each test.

Table 7. Comparison of baseline (control) injection versus STF injection performance.

Location ID	RPD for Breakthrough Volumes	RPD for % Injected Tracer Concentration
Above Treatment Zone		
C1A	36%	-11%
C2A	709%	0%
C3A	>113%	-98%
Low Permeability Zones		
C1B	-51%	13%
C1C	-21%	38%
C2D	-74%	46%
C3B	100%	67%
C3D	>3%	-88%
High Permeability Zones		
C1D	89%	8%
C2B	108%	0%
C2C	572%	0%
C3C	96%	-9%

Notes: (1) Values are the RPD of the STF data compared to the baseline data (calculated as [[STF-baseline]/baseline] x 100); (2) Positive values represent a larger breakthrough volume (slower arrival) or higher percent of injected concentration for STF versus baseline injection; (3) Yellow shaded cells show where the metric indicates STF performance was not equal to or better than baseline performance.

To evaluate the potential benefit of the STF on distribution, it is important to distinguish between the anticipated shear-thinning response for higher-k zones versus those anticipated for lower-k zones within a radius of 3.05 meters (10 feet) from the injection well:

- For higher-k zones, the inclusion of an STF would be expected to cause slower transport than observed for the baseline injection and the same or better distribution of the injected solution.

- For lower-k zones: the inclusion of an STF would be expected to cause faster transport and a higher percentage of the injected tracer concentration (i.e., better delivery of injected solution to low-k zones) than observed for the baseline injection.

All of the high-k monitoring locations showed higher breakthrough volumes (slower arrival) with the STF injection (Table 7). Distribution (based on an evaluation of the percentage of injected concentration) was the same for the STF versus the baseline test at the CMT-2 monitoring locations, all of which are 1.52 meters (5 feet) from the injection well. At the 3.05-meter (10-foot) monitoring radius (CMT-1 and CMT-3), the STF showed improved distribution at location C1D, but a worse distribution at location C3C. For the lower-k pathways represented by the C1B, C1C, C2D locations, the STF injections achieved the expected improvements of faster transport and a higher percentage of the injected tracer concentration (Table 7). At location C3B, STF injection transport was slower but resulted in a higher percentage of the injected tracer concentration. STF injection showed slower transport and worse distribution than the baseline

injection at location C3D, contrary to the positive results at the other locations. Finally, slower transport and a lower percentage of the injected tracer solution are the preferred outcome for the "A" zone wells, which are located in a relatively higher-k sand layer above the well screen and outside the targeted treatment zone. The STF injection showed these improvements for all "A" zone wells, except that 100% of the injected concentration was observed at the C2A location 1.52 meters (5 feet) from the injection well for both STF and baseline injections (Table 7).

A second method for demonstrating the impact of the STF on remedial amendment distribution and delivery effectiveness is to examine the ratios between the fastest and slowest breakthrough at each monitoring location. The inclusion of a STF is expected to promote a more uniform sweep of the injected solution through the heterogeneous formation, such that the ratio between the fastest and slowest breakthrough would be less than that observed during the baseline test. Evidence of this positive effect was observed at both CMT-1 and CMT-2. At CMT-2, a 50:1 ratio between the fastest and slowest breakthrough volumes was observed during the baseline test, followed by a decrease to 25:1 during the STF injection. At CMT-1, the ratio during the baseline test was 11:1 and decreased to 8:1 during the STF injection. Note that at CMT-3, the lack of breakthrough at all monitoring locations during the STF injection precludes this evaluation.

A third method for demonstrating the improved distribution following the STF amendment injection is the electrical resistivity data. Figure 21 shows ERT data collected for the 2D cross section between the screened intervals of the injection well and well MW-1 at the end of the baseline and STF injections. Areas of the cross section with elevated conductivity (red/yellow shades) are caused by the higher ionic strength of the injected solutions compared to the background. In both cases, a dominant path of injected fluid distribution is observed in the interval between 18-19 meters bgs. However, the injected fluid distribution for the STF injection is more uniform across the cross section, although regions remain where the formation materials are bypassed by the amendment solution. Based on integrating the electrical resistivity data at the end of the injection period, the percentages of the ERT cross section indicating the presence of injected tracers are 49% and 69% for the baseline and STF injections, respectively. This demonstrates the improved distribution of amendment into the lower-k zones of a heterogeneous aquifer using STF.
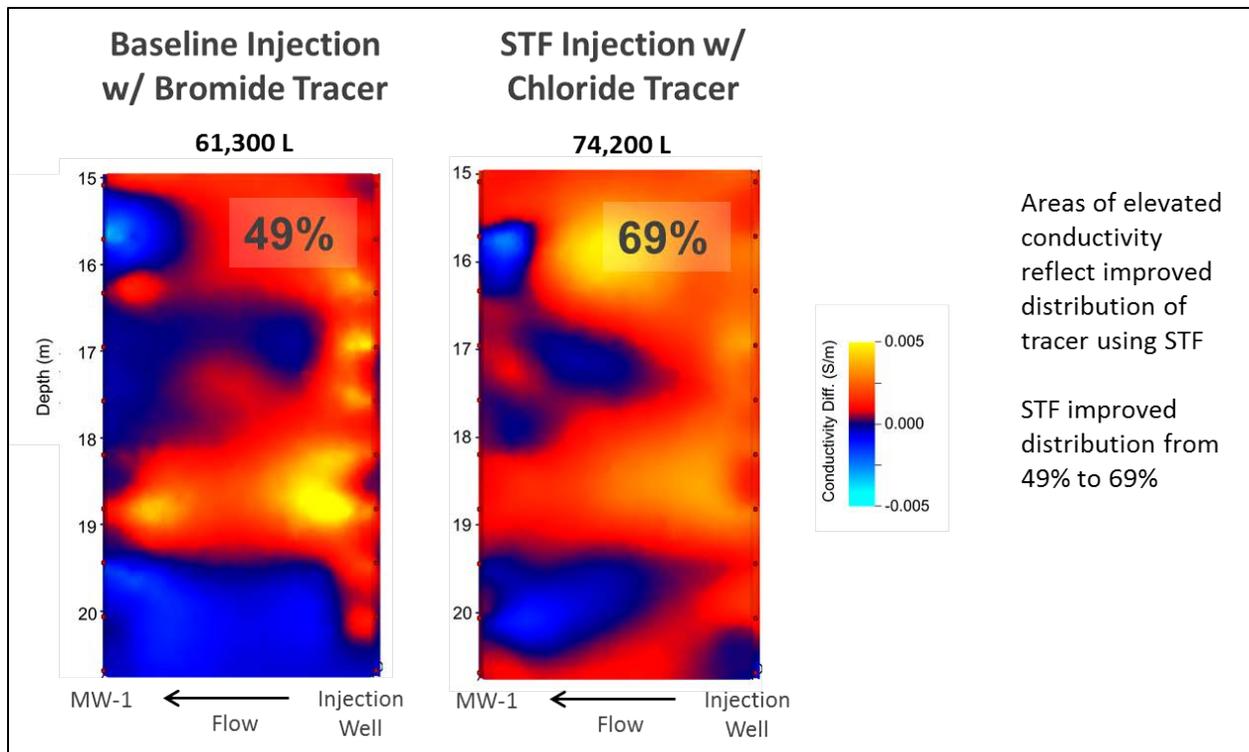
Figure 21. Comparison of amendment distribution using the ERT images.
Each panel shows the distribution of the higher electrical conductivity (red/yellow shades) solutions as a
conductivity difference between the baseline injection (left panel) and STF injection (right panel) over the depth
interval of the screen. Well MW-1 is located at a radial distance of 3.05 meters from the injection well. At the time
of these measurements, the injection volumes for both baseline and STF injections were sufficient to reach a
cylindrical radial distance of 4.0 and 4.4 meters, respectively.

As noted previously, post-injection performance monitoring was completed to assess amendment
persistence as well as effectiveness in achieving treatment of contaminants. Performance
monitoring events were completed in February 2014 and May 2014, such that the total duration
of the monitoring period was 8 months. The results for the May 2014 event are summarized in
Figure 22). Data supporting the performance objectives are tabulated in Tables 8 and 9.
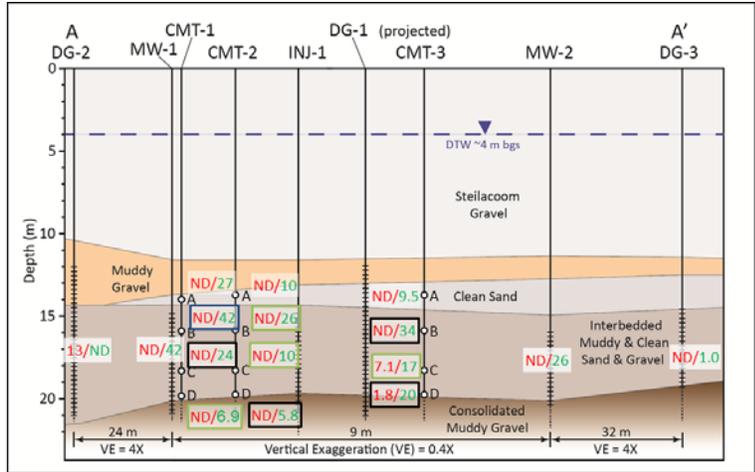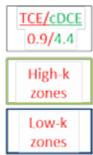
**Figure 22. Groundwater sampling results from performance monitoring –
8 months post injection.**
The location of cross-section A-A' is shown in Figure 9.

Table 8. Comparison of parent compound concentration reductions achieved during post-injection performance period.

Location ID	Pre-Injection: August 2013 Parent Concentration (µg/L)	5 Months Post-Injection: February 2014 Parent Concentration (µg/L)	5 Months Post-Injection: February 2014 % Change from Initial Parent Concentration	8 Months Post-Injection: May 2014 Parent Concentration (µg/L)	8 Months Post-Injection: May 2014 % Change from Initial Parent Concentration
Above Treatment Zone					
C1A	1.9	0.86 J	-55%	ND	-100%
C2A	8.6	0.7 J	-92%	ND	-100%
C3A	0.9	0.96 J	+7%	ND	-100%
Low Permeability Zones					
C1B	7.9	0.6 J	-92%	2.8	-65%
C1C	13	ND	-100%	ND	-100%
C2D	ND	0.48	+100%	ND	-100%
C3B	14	ND	-100%	ND	-100%
C3D	28	11	-61%	1.8	-94%
High Permeability Zones					
C1D	4.2	ND	-100%	ND	-100%
C2B	7.5	0.51 J	-93%	ND	-100%
C2C	7.8	ND	-100%	ND	-100%
C3C	27	11	-59%	7.1	-74%
Multiple Zones (Fully-Screened Wells)					
MW-1 (side-gradient)	11	ND	-100%	ND	-100%
MW-2 (side gradient)	7.6	1	-87%	ND	-100%
MW-3 (side-gradient)	14	NS	--	NS	--
DG-1 (down-gradient)	5	4.2	-16%	3.9	-22%
DG-2 (down-gradient	9.9	18	+82%	13	+31%
DG-3 (down-gradient)	1.1	1.3	+18%	ND	-100%
DA-31 (up-gradient)	9.4	16	+70%	14	+49%

Notes: (1) ND = non-detect; NA = not available (sample damaged upon receipt at lab); NS = not sampled; (2) Concentrations include J flag results where indicated (estimated values below the detection limit).

Table 9. Comparison of amendment persistence indicators during post-injection performance period.

Location ID	Pre-Injection: August 2013				5 Months Post-Injection: February 2014				8 Months Post-Injection: May 2014			
	TOC (mg/L)	ORP (mV)	Sulfate (mg/L)	Methane (mg/L)	TOC (mg/L)	ORP (mV)	Sulfate (mg/L)	Methane (mg/L)	TOC (mg/L)	ORP (mV)	Sulfate (mg/L)	Methane (mg/L)
Above Treatment Zone												
C1A	6.8	-196	43	0.03	19	-150	0.65	ND	9.1	-110	1.5	0.21
C2A	12	82	78	0.027	120	-110	ND	0.23	43	-79	ND	1.8
C3A	6.1	-135	24	0.04	22	-170	6.7	0.024	3.3	-115	0.5	0.14
Low Permeability Zones												
C1B	10	-222	95	0.027	170	-175	ND	0.053	97	-56	0.17	0.64
C1C	5.5	-195	72	0.024	240	-168	0.47	0.07	100	-105	0.48	1.7
C2D	NA	NA	NA	NA	56	-293	22	0.037	230	-90	3.6	1.3
C3B	21	-43	200	0.021	290	-159	0.71	0.077	320	-47	ND	0.87
C3D	7.9	-72	62	0.02	47	-188	0.14	ND	19	-112	0.5	0.058
High Permeability Zones												
C1D	5.1	-165	61	0.015	210	-116	0.8	0.17	69	-45	0.41	1.7
C2B	22	-78	120	0.031	380	-109	ND	0.13	160	-65	ND	5.6
C2C	4.6	-17	26	0.016	120	-165	ND	0.21	40	-68	ND	2.8
C3C	13	-69	74	0.021	95	-180	0.22	ND	14	-55	2.2	0.083
Multiple Zones (Fully-Screened Wells)												
MW-1 (side-gradient)	0.62	525	13	ND	100	-46	ND	ND	32	19	ND	0.25
MW-2 (side gradient)	0.46	240	12	ND	200	-107	0.094	ND	140	-33	0.26	0.31
MW-3 (side gradient)	0.63	160	16	ND	NS	NS	NS	NS	NS	NS	NS	NS
DG-1 (down-gradient)	0.48	142	8.4	ND	3.3	26	7.3	ND	0.48	83	17	ND
DG-2 (down-gradient)	0.49	266	6.7	ND	0.21	88	6.2	ND	0.48	351	7.2	ND
DG-3 (down-gradient)	0.95	162	8.6	ND	0.58	-60	7.3	ND	0.37	89	8.7	0.022
DA-31 (up-gradient)	0.46	246	8.1	ND	0.2	6	7.4	ND	0.51	-20	10	ND

Notes: (1) ND = non-detect; NA = not available (sample damaged upon receipt at lab); NS = not sampled; mV = millivolts; (2) Concentrations include J flag results (estimated values below the detection limit).

Important findings include the following:

- In locations where substrate was distributed during the STF injection, there was evidence that a portion of the substrate persisted through the 8 month monitoring event. For this evaluation, TOC concentration was used as a surrogate for the STF. Within the CMT wells in the treatment zone, TOC concentrations were consistently greater than pre-test background levels, and generally greater than 20 mg/L. The exceptions were C3C and C3D, which also saw relatively low levels immediately following STF injection. The measured TOC concentrations are suitable for supporting sustained treatment via biological reductive dechlorination. The finding that a portion of the substrate persisted for 8 months is promising given that the primary substrate (ethyl lactate) is readily degradable, although the presence of the shear-thinning polymer likely improved amendment persistence. It should be noted that the design of the shear-thinning amendment was based primarily on rheologic properties during injection and not long-term stability.

- There was evidence of increased persistence in lower-k zones relative to higher-k zones. After 8 months, the average TOC concentration in the five low-k CMT locations was 153 mg/L, while the average TOC concentration in the four high-k CMT locations was 71 mg/L. In addition, the average TOC concentration in the low-k locations had changed little between 5 months (151 mg/L) and 8 months (153 mg/L), while a significant decrease in the average TOC concentration was observed in the high-k CMT locations between 5 months (201 mg/L) and 8 months (71 mg/L). This pattern highlights the benefits of improving distribution to lower-k zones through the use of shear-thinning fluids; once amendment has been delivered to the lower-k zones, it is less subject to flushing and thus should persist for longer periods.

- Little TOC was measured in downgradient wells (e.g., DG-1, DG-2, DG-3), a pattern that is consistent with the persistence of the amendment within the treatment zone.

- Relatively rapid tracer breakthrough was observed during the baseline injection test at MW-2, a well that is located in a direction lateral to the regional groundwater flow direction. In contrast, tracer breakthrough was not observed at MW-2 during the STF injection test, and the TOC concentration immediately after injection was only 22 mg/L. This provided evidence that the STF resulted in a more uniform distribution that minimized preferential pathways in the direction of MW-2. However, a significant increase in the TOC concentration at the side-gradient well MW-2 was observed during the 5 month performance monitoring event (200 mg/L), and only a slight decrease was observed after 8 months (140 mg/L). This indicates a portion of the amendment was being transported out of the treatment zone via advection due to localized hydraulic gradients.

- The presence of TOC was positively associated with the establishment of proper reducing conditions for reductive dechlorination. The majority of locations maintained ORP readings that were well below zero throughout the 8-month performance monitoring period.

- Sulfate was below detection limits at the majority of locations throughout the performance monitoring period. While pre-injection sulfate levels were generally low

(24 to 200 mg/L in the treatment zone), the fact that nearly 100% removal was achieved and maintained is promising with respect to controlling influx of competing electron acceptors.

- Methane production within the treatment zone was relatively limited, although there were some notable increases in several high-k locations in the period between 5 and 8 months. Given the low baseline concentration of methane and slow methanogenic growth rates, the data suggest that the methanogenic population within the treatment zone is initially low.

- Complete removal of TCE was observed in the majority of wells in the treatment zone by 5 months, and no rebound in TCE concentrations was observed after 8 months of monitoring. TCE concentrations in downgradient wells were largely similar to pre-injection levels, while the TCE concentration in the upgradient well increased slightly (from an initial level of 9.4 µg/L to 14 µg/L after 8 months).

- Increases in cDCE concentration in all treatment zone wells provided confirmation that the reductions in the parent compound (TCE) were attributable to reductive dechlorination rather than dilution. At both the 5-month and 8-month monitoring events, cDCE represented 100% of the total CVOCs measured in the majority of wells in the treatment zone. The exceptions were C3C and C3D, which were locations that saw lower TOC concentrations immediately after the end of the STF injection (i.e., poor distribution). However, these two wells were still characterized by increased cDCE concentrations after injection, such that cDCE represented 70% or more of the total CVOC concentration by the end of the 8-month monitoring period.

- Vinyl chloride was detected in only one location (C3A) during both the 5-month (3 µg/L) and 8-month (3.4 µg/L) monitoring events. Similarly, ethene was detected at a limited number of locations (C2A and C2D) at trace levels. This pattern was observed even though TCE had been largely removed from the treatment zone within 5 months. The results suggest a limitation in the native microbial population with respect to the capacity for complete dechlorination given that other commonly-cited factors for cDCE stall (e.g., TCE inhibition, competing electron acceptors, pH) were not applicable. Consequently, bioaugmentation would likely need to be evaluated for a full-scale design for this site.

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6.0   PERFORMANCE ASSESSMENT

A summary of the performance objectives for this demonstration, along with an overview of technology performance, was presented in Section 3. This section includes a detailed assessment of technology performance based on the quantitative data presented in Section 5. Following completion of the sampling and analysis program, the data were reviewed to determine whether the success criteria for each performance objective have been met. The evaluation of each individual performance objective is discussed below.

6.1   QUANTIFY IMPROVED DISTRIBUTION OF AMENDMENT TO LOWER-PERMEABILITY ZONES

Success Criteria Achieved? **YES**

The highest-priority objective of this technology was to demonstrate that the injection of amendments, such as a STF, results in improved distribution to lower-k zones relative to conventional approaches (e.g., lactate or other carbon source diluted in water). Distribution was monitored for both baseline (conventional injection) and STF injections using a tracer solution (baseline and STF), and TOC and viscosity measurements (STF only) that were taken at the multiple radial distances from the injection well and, at selected locations, within vertically discrete monitoring intervals. ERT data was also collected as part of both injection phases for a 2D cross section between the injection well and monitoring well MW-1 located 10 feet from the injection well. The ERT monitored the screen depth interval (20 feet) within this cross section and provided an indication of the 2D distribution of injected solution based on the increased electrical conductivity of the injection solution compared to the background.

The objective was considered achieved if the STF injection results in measurable evidence that the STF and associated amendments and tracer has penetrated the low-k zones and at higher concentrations (>50% volumetric improvement in distribution) relative to the water-only injection. Another related criterion was to demonstrate an improvement (> 50% decrease) in the ratio of tracer arrival between high- and low-k zones during the STF stage relative to the baseline stage, an indicator of improved uniformity of distribution (sweep efficiency). Success was also evaluated based on whether the concentration of the tracer and amendment in monitored low-k zones reached 10% of the concentration of the tracer in the injection solution. Indications of success in meeting these objectives are listed below.

- An ideal injection would fully distribute solution to MW-1, and no solution would reach MW-2. 100% distribution of STF was achieved at MW-1 compared to 89% distribution of tracer from the baseline injection. At MW-2, tracer arrival was not observed at MW-2 during the STF, but breakthrough during the baseline test was achieved at a volume that was equivalent to 13% of the idealized radial volume. Monitoring in a sandy zone above the targeted injection interval showed less STF distribution upward than was observed for the baseline injection. Thus, more of the injected volume was maintained within the targeted injection radius, including low-k zones, with use of STF. ERT data show that injection solution, as measured by increased bulk conductivity, was present in 69% of a 2D cross section over the first 3 meters from the injection well for

STF versus 49% for the baseline injection. This is equivalent to a ~41% improvement in distribution for the STF stage.

- At CMT-2, a 50:1 ratio between the fastest and slowest breakthrough volumes was observed during the baseline injection, followed by a decrease to 25:1 during the STF injection, a 50% decrease. At CMT-1, the ratio during the baseline injection was 11:1 and decreased to 8:1 during the STF injection, a 28% decrease. Thus, this criteria was met in CMT-2 and partially met in CMT-1

- Tracer concentrations in four of five monitored low-k zones were >10% of the injected concentration and were improved with STF versus baseline and worse at one. Tracer concentrations in four monitored low-k zones as a % of injected tracer concentration were for the STF and baseline stage were (STF/baseline) 91%/81%, 100%/73%, 100%/69%, 65%/39%, and 5%/40%.

- Amendment concentration (as TOC) in four of five monitored low-k zones were >10% of the injected concentration. Amendment concentration (as TOC) in monitored low-k zones were 84%, 91%, 41%, 33%, and 1% of the injected concentration.

6.2 DETERMINE EFFECTIVENESS IN ENHANCING CONCENTRATION REDUCTION IN LOW PERMEABILITY ZONES

Success Criteria Achieved? **YES**

A primary goal of any remediation effort is to achieve a reduction in the concentration (or mass) of the target contaminant. In the case of the shear-thinning technology, the improved distribution of the amendment should lead to an improved ability to treat contaminants present in the lower-k zones of the treatment area. Therefore, the performance evaluation focused on data from the CMT wells screened in locations that had been identified as lower-k zones. Concentrations from the pre-treatment monitoring event were then compared to concentrations measured during performance monitoring events, particularly during the final event (8 months after the STF injection). The primary objective was to achieve >50% reduction in parent compound concentration in the majority of low-k zone locations. A second objective was based on achieving a daughter product concentration that was > 25% of the initial (pre-treatment) parent compound concentration.

Both of these sub-objectives were successfully achieved. A 100% reduction in the parent compound (TCE) concentration occurred in three of the five locations screened in low-k zones. Even at the locations where TCE was still present after 8 months, the reduction from pre-treatment concentrations was 65% to 94%. Similar patterns were observed in the fully-screened wells and in the CMT wells screened in higher-k zones, confirming that treatment effectiveness was relatively uniform. Importantly, there was no evidence for rebound in parent compound concentrations in the period between the final two monitoring events. The wells where incomplete parent compound reduction was achieved were wells where lower TOC concentrations were measured after injection (C3C and C3D). This confirmed that treatment effectiveness was a function of amendment distribution.

The success criterion for the second sub-objective was also met. Specifically, the daughter product concentration at each low-k zone monitoring location was > 25% of the initial parent compound concentration during each monitoring event. The same condition was met at all other monitoring locations within the treatment zone. Because this criterion was developed prior to the pre-treatment monitoring event, it eventually became clear that it was a relatively low threshold for success. Therefore, the secondary metrics for success that were evaluated were: 1) the daughter concentration was also > 25% of the parent compound concentration measured during individual monitoring events; and 2) the percentage of the total CVOC concentration represented by daughter compounds increased throughout the performance monitoring period. Both of these secondary criteria were also successfully achieved.

Note that in addition to the amendment distribution, the treatment effectiveness is a function of site-specific conditions. At Area D of JBLM, pre-demonstration data suggested that there was dechlorination beyond cDCE. Therefore, the fact that complete dechlorination to ethene was not observed following injection of the STF, reflects deficiencies in the native microbial population, rather than a limitation in the technology.

6.3   DETERMINE EFFECTIVENESS IN ENHANCING PERSISTENCE OF AMENDMENT AND EFFECTS

Success Criteria Achieved? **YES**

The purpose of this performance objective was to evaluate if the beneficial influence of the STF persisted over an extended period of time. Conventional amendments for in situ treatment technologies typically require repeated injections. In the case of enhanced bioremediation, soluble substrates such as lactate are often injected at intervals of several weeks to several months. The STF that was used as the amendment for this demonstration was not specifically designed to serve as a long-lasting substrate; if so, a semi-soluble or emulsified carbon source would have been more appropriate choice than ethyl lactate. However, the technology is designed to improve delivery of the substrate to the lower-k intervals within the treatment area. As such, the technology takes advantage of the relative persistence of amendments that have been successfully delivered into low-k zones because advective flushing is minimized.

The sub-objectives that were developed for this evaluation used a minimum of a 6-month period that these benefits persisted; the final monitoring event was completed 8 months after the STF injection. Success was based on the continued presence of the amendment (in the form of TOC concentrations) and dechlorination products, as well as favorable geochemical conditions and diverted electron acceptors throughout the entire performance monitoring period. As such, this objective focused on the temporal patterns in the monitoring data, with particular attention to the impacts in the lower-k zones.

All sub-objectives that were developed as part of this evaluation were met. The primary criterion was elevated TOC concentration in monitoring locations in low-k zones relative to the TOC concentrations that were present prior to injection. In these five monitoring locations, the average concentration increased from 11 mg/L (pre-injection) to approximately 600 mg/L immediately after injection. During the performance monitoring period, the average concentration in these five locations dropped to 151 mg/L after 5 months but was maintained at 153 mg/L after 8

months. The pattern in the four CMT locations screened in high-k zones was slightly different, with a decrease from approximately 900 mg/L immediately post-injection to 200 mg/L after 5 months of monitoring and then 71 mg/L after 8 months of monitoring. Consequently, the results confirmed enhanced persistence of the STF within low-k zones. In addition, there was no indication that groundwater entering the treatment zone was resulting in more rapid decreases in TOC concentrations in wells located in the upgradient portions of the treatment cell relative to those located farther downgradient.

Other sub-objectives were based establishing proper reducing conditions within the treatment area due to the long-lasting presence of the amendment and its ability to divert competing electron acceptors. Sulfate concentrations decreased to nearly non-detectable levels during the performance monitoring events. At most monitoring locations, the oxidation-reduction potential were relatively similar to pre-treatment readings, but consistently negative and supportive of reductive dechlorination. Methane concentrations were relatively low (generally < 1 mg/L) but did increase at the majority of locations as a result of the amendment injection.

Finally, treatment effectiveness via amendment persistence was part of this performance objective. The criterion of increased cDCE production throughout the entire monitoring period was achieved. There was a notable lack of rebound in parent compound concentrations during the demonstration despite the fact that the test consisted of a single injection with a relatively limited footprint. Despite these constraints, there was sustained activity within the treatment zone for at least 8 months.

6.4   EASE OF USE

Success Criteria Achieved? **YES**

The purpose of this performance objective was to confirm that the methods could be implemented with minimal additional effort relative to more conventional methods. While there are certain extra steps that are necessary in including shear-thinning polymers in an amendment solution, the techniques are not highly dissimilar to those already familiar to practitioners. Because the use of STFs require slightly more time (and material/equipment costs) relative to conventional injection, the success criterion for this performance objective was demonstrating that the STF injection could be completed in a single mobilization using standard equipment.

The success criterion was met. The shear-thinning injection was completed in a single mobilization, using a pumping period of approximately 15 hours to achieve an idealized radius of influence of > 4 meters. A pumping rate of 30 gpm was sustainable, and this rate is within the typical range for amendment injections based on the project team's experience. Hydration of the xanthan gum to create the STF was completed the day before pumping started, but this type of 1-day preparation period is typical for any in situ injection-based technology (and in the case of this demonstration, it overlapped with the equipment set-up period). Collectively, the project demonstrated that the field methods are easy to implement and can be completed in a timely manner.

7.0 COST ASSESSMENT

A key objective of this project was to track costs associated with this technology demonstration in order to provide a basis for estimating costs of a full-scale implementation of the technology. To aid the evaluation, implementation costs were incorporated into various scenarios and then compared to various alternatives.

7.1 COST MODEL

As part of the demonstration, the cost of implementing the field program was carefully tracked and this cost data was used to estimate the cost that would be associated with implementing this methodology at a generic site. These are summarized in Table 10. Only those elements that are unique to this technology were included as part of the cost assessment and comparison. This means that costs that are standard to injection-based treatment methods (e.g., in situ enhanced bioremediation) were tracked but have not been included in the cost assessment. Finally, costs that were incurred during this demonstration with the objective of obtaining a more comprehensive dataset than would be expected during a standard implementation were tracked but not included in the cost model.

Table 10. Cost model for the shear-thinning technology.

Cost Element	Tracked Data
Laboratory and/or modeling studies	Labor, materials, analytical costs
Baseline characterization	Detailed vertical stratigraphic characterization of targeted groundwater-bearing unit using one of several different methods: • EBF used for this demonstration • Cost model assumed that high-resolution baseline data was available for either STF application or conventional in situ bioremediation
Injection/monitoring well installation	No unique requirements, although multi-level monitoring well clusters are recommended if not otherwise installed for conventional in situ bioremediation applications
Amendment injection	Labor associated with shear-thinning amendment injection as basis for comparison to conventional amendment injection • Includes labor associated with amendment preparation • All other costs are standard for injection
Material cost	Polymer as component of amendment formulation • Cost for conventional substrate (ethyl lactate) not included Tank and other equipment rental
Long-term monitoring	No unique requirements
Operations and maintenance	No unique requirements
Waste disposal and decommissioning	No unique requirements

7.1.1 Technology-Specific Cost Elements

The following descriptions focus on the cost elements that are specifically associated with the shear-thinning technology. There are other cost elements associated with the various scenarios that were part of the scenario-based cost model, but these are not discussed separately here.

Laboratory and/or Modeling Studies: In order to determine the optimum polymer formulation and injection design, a limited set of studies are recommended. Costs associated with this task are primarily labor required to complete laboratory studies and/or modeling, but also include materials and analytical costs. Bench-scale studies to understand the rheologic properties, or at minimum the static viscosity of various potential amendment formulations, are recommended. Supplemental studies using multi-phase flow modeling (STOMP, UTCHEM) may be beneficial for understanding the expected distribution of injected amendments, using known or estimated bulk permeability values within relevant layers of the targeted groundwater-bearing unit. However, it is anticipated that this step may not be included in many applications. Therefore, the cost estimate includes only bench-scale testing of amendment formulation rheology or static viscosity. Static viscosity may be sufficient, if a formulation similar to those for which rheological properties are published in scientific literature. Otherwise, testing of rheological behavior is important to ensure that the formulation will perform as expected in the field injection.

Baseline Characterization: A complete understanding of the site stratigraphy and contaminant distribution is a required element prior to implementing this technology. For the purposes of the cost model, it is assumed that sufficient characterization data has been collected to develop a conceptual site model that supports the remedy being implemented, i.e., in situ bioremediation.

Further, the cost model assumes that existing characterization efforts indicate that a level of geologic heterogeneity exists at the site, such that the use of the shear-thinning technology would be beneficial. Therefore, it is anticipated that a full-scale implementation would rely on existing data from groundwater and soil sampling.

The only recommended addition to conventional characterization efforts would be the use of one or more high-resolution methods to provide more detailed spatial information (particularly in the vertical direction) on contaminant distribution and permeability within the treatment area (Adamson et al., 2013; Sale et al., 2013). Depending on the site, there are a number of methods that may be appropriate, including (but not limited to) cone penetration testing (CPT), membrane interface probe (MIP), GeoProbe hydraulic profiling tool (HPT) or MiHPT, Waterloo[APS], passive flux meters, and various geophysical approaches. For this demonstration site, the presence of very coarse-grained soils precluded the use of tools that rely on direct-push methods. Therefore, the primary characterization method utilized during this project was the EBF to obtain a vertical permeability profile within several of the monitoring wells at the site. These data proved useful for identifying permeability contrasts and preferential flowpaths, such that the cost model assumed that a similar level of effort would be included in most applications of this technology. For the purposes of the cost comparison, however, it was assumed that both conventional in situ bioremediation and in situ bioremediation with STF would rely on existing baseline characterization data. Note that the high-resolution data are of interest because the STF is targeting treatment of those lower-k zones that are not effectively treated with conventional in situ bioremediation.

Injection/Monitoring Well Installation: STFs can be injected through wells that are designed for conventional amendment solutions. As such, there are no unique cost considerations relative to most in situ bioremediation applications. However, careful attention to the well annular seal is

needed to accommodate the injection pressures. In addition, the use of permanent injection wells—as opposed to temporary wells and/or direct-push boreholes—is strongly recommended due to the higher injection pressures that will be experienced in comparison to conventional injection. Monitoring requirements are also similar to conventional in situ bioremediation, although the use of multi-level wells is generally recommended to better evaluate amendment distribution.

Amendment Injection: The techniques used for injecting the shear-thinning polymer solution are identical to those for soluble (and most semi-soluble carbon substrate amendment solutions), assuming that a strategy of monitoring tracer breakthrough is employed to confirm that the desired radius of influence is achieved. The primary unique cost for this technology is polymer preparation, which requires additional time for sufficient hydration of the xanthan gum within the polymer solution. The cost model include labor for experienced personnel to complete the polymer preparation and injection, as well as assumptions of injection duration and frequency over the course of the project lifetime (see Sections 7.1.2 and 7.1.3).

In addition, the technology requires pressure testing of the injection well using a step-injection test along with monitoring of adjacent wells, and it can be completed within a short period of time (<1 day) prior to the start of the full-scale amendment injection. Because similar procedures are used during most injection-based remedial technologies to test the efficacy of the well design, separate cost tracking for these tests were not included. Other applications of this technology may include a limited tracer test or comprehensive tracer test using a water-based (non-shear thinning) solution as a first step to confirm flow in the absence of the polymer. However, this option was not included in this cost model.

Material Cost: The primary costs associated with materials are the shear-thinning polymer and the equipment required to prepare the shear-thinning polymer solution. All other costs (e.g., purchase of a carbon substrate for bioremediation) are not unique to this technology. For this demonstration, these costs included xanthan gum, an additional tank and metering pump (for preparation of the concentrated polymer solution), and proper mixing equipment.

Note that the cost model assumes that there are no permanent installations at the site. Injections were completed as one-time events using rented equipment that required no automated process control system. As such, there were no additional labor costs for installation (labor associated with polymer preparation was included in the *Amendment Injection* cost element described above.

Long-Term Monitoring: Monitoring requirements are identical those for most in situ bioremediation applications. The analyte list for all monitoring programs should include TOC measurements (in groundwater samples) as a surrogate for the STF.

Operations and Maintenance: There are no unique costs associated with operations and maintenance of the technology. As noted above, the cost estimates presented here are based on the assumption that injections were completed as discrete events (i.e., not continuous) without the use of automated process control systems.

Waste Disposal and Decommissioning: The technology generates no additional waste beyond that typical of in situ bioremediation projects, assuming that the entire volume of STF is injected into the subsurface. There are no special decommissioning requirements since the technology utilizes conventional injection and monitoring wells. Note that there were several requirements for decommissioning the CMT wells installed as part of this demonstration (based on Washington Department of Ecology regulations). However, these were specific to the monitoring network installed as part of this demonstration, which is not required for all applications of this technology. Consequently, these costs are not included in this model.

7.1.2 Cost Scenarios

The cost elements described above were incorporated into several scenarios for illustrating the costs associated with this technology.

- ***Scenario 1: Cost of Single Injection of STF Amendments versus Conventional Amendments for In-Situ Bioremediation.*** The goal was to establish how much additional short-term cost would be associated by implementing the shear-thinning technology relative to similarly-sized treatment systems that used conventional amendments. In this case, the potential long-term benefits of the technology are not incorporated into the evaluation.

- ***Scenario 2: Project Lifetime Costs of In-Situ Bioremediation using STF versus Conventional Amendments.*** This scenario assumes that the better distribution of substrate achieved through the use of STFs results in fewer injection events over the project lifetime and leads to site closure within 5 years. Conventional in situ bioremediation also leads to an alternative outcome, where post-treatment management of the site using monitored natural attenuation (MNA) is required over the course of the next 25 years.

7.1.3 Assumptions

The various assumptions used to develop the cost model and generate cost estimates for the various scenarios are described below:

- Site characteristics and the scale of the treatment system were assumed to be similar to those for this demonstration project. This ensured that cost tracking performed for the project would be useful and representative. This means that the treatment consisted of a single injection well with sufficient volume to achieve an idealized radius of influence of 10 feet based on pore volume estimates and 20-feet thick treatment interval. As a result, the soil treatment volume was estimated to be 6280 cubic feet (233 cubic yards) for the baseline case.

- Distribution to the majority of treatment zone (i.e., improved sweep efficiency) could be achieved by injecting 2 pore volumes of STF. This is based on the finding that a sweep efficiency of 69% was achieved during this demonstration using an injection volume that represented slightly greater than 1 pore volume, as well as the relatively moderate permeability contrasts at the test site. While 100% sweep efficiency is unlikely (some tailing sweep efficiency was noted during the demonstration), for modeling purposes it

was assumed that 2 pore volumes would achieve sufficient sweep efficiency to treat significant mass in the low-k zones, such that a decrease in the remediation timeframe would occur. For the case in Scenario 2 where STF is compared to conventional amendments, it is assumed that a 2 pore volume injection of conventional amendments would not achieve the same sweep efficiency, such that incomplete treatment would occur and the remediation timeframe would be dictated by matrix diffusion effects.

- An injection rate of 30 gpm could be achieved, such that the entire amendment volume could be injected over the course of two work shifts (16 hours). Note that the cost model includes injection rate as an input parameter for the purposes of sensitivity analysis.

- An additional day was required for initial preparation of the STF. Injection testing was assumed to occur during the prep day, and process monitoring was completed during the course of the amendment injection period. During the 2-day, 3-shift work phase (preparation plus injection), a total of three people were needed (one engineer/geologist, two technicians).

- For Scenario 1, the unit cost for conventional in situ bioremediation was assumed to $100/cubic yard. This value is based on median technology-specific unit costs compiled as part of ESTCP ER-201120 (involving several PIs from this project; McGuire, 2014) and represents primarily the treatment phase of full-scale in situ bioremediation projects. Therefore, we feel that this typical unit cost represents an appropriate baseline. Given that the scale of the project evaluated here is smaller than the majority of projects in the ESTCP ER-201120 cost and performance survey, additional evaluation of the influence of scale is presented in Section 7.3. Because the cost model used the injection frequency as an input value, the $100/cubic yard unit cost was assumed to apply to two full-scale injection events for a moderately persistent substrate. A unit cost adjustment of 25% per injection event was used to account for scenarios with less than or greater than two injection events (e.g., the single injection envisioned in Scenario 1).

- For Scenario 2, the unit cost for in situ bioremediation using STF amendments was again estimated in terms of the incremental cost associated with the technology. In other words, the costs associated with those elements unique to the technology were added to the typical unit cost for more conventional applications.

- For Scenario 2, two injections of the STF and four injections of the conventional substrate (lactate without polymer) were assumed. The STF amendment was expected to persist for approximately 1 year, such that the second injection for each case occurred approximately 1 year after the first injection. The conventional amendment was expected to be less persistent, such that additional injection events were necessary over the same project lifetime.

- For Scenario 2 that involves a comparison of outcomes, the costs associated with any additional characterization efforts during the remedy selection period were not considered. For example, additional characterization may occur immediately prior to the start of in situ bioremediation to optimize the design. These costs can vary widely based on site-specific considerations and thus were not included in this cost assessment.

- For Scenario 2, long-term monitoring involved bi-annual (twice yearly) monitoring of wells for CVOCs and TOC. The number of wells is based on the size of the treatment area (one well per 1600 square feet, plus one background and one downgradient compliance well). The monitoring period for MNA was assumed to be 30 years (i.e., including monitoring during the active treatment period). For the case where the use of STF led to site closure, long-term monitoring to provide confirmatory evidence for site closure was assumed to be 5 years.

7.2 COST ANALYSIS

This section provides a cost comparison for each of the scenarios described above. The costs were compiled using a combination of the demonstration data, information from similar projects, vendor quotes, literature values, and the Remedial Action Cost Engineering and Requirements (RACER) software. Drillers and analytical laboratories that were part of the demonstration were used where applicable. The cost breakdown for each scenario is presented in Table 11 and summarized below.

Table 11. Summary of cost modeling results.

Cost Element	Scenario 1 Single Injection of STF (Duration = 3 days)	Scenario 2 STF Injections Followed by Site Closure (Duration = 5 years)	Scenario 2 Conventional Amendment Injections Followed by MNA (Duration = 30 years)
Task 1. Laboratory study and amendment selections	$6200	$6200	$0
Task 2. Conventional in situ bioremediation	$17,444	$23,259	$34,889
Task 3. STF preparation and injection (costs beyond conventional in situ bioremediation	$10,736	$21,472	$0
Task 4. Modeling	$0	$0	$0
Task 5. Other characterization/ reporting in support of remedy selection/design	$0	$0	$0
Task 6. Well installation (monitoring wells, injection wells, extraction wells)	$0	$0	$0
Task 7. Treatment system design and installation	$0	$0	$0
Task 8. Treatment system operations and maintenance	$0	$0	$0
Task 9. Long-term monitoring	$0	$32,310	$133.860
Task 10. Closeout and decommissioning	$0	$0	$0
Task 11. Final reporting	$0	$0	$0
Contingency	**$5157**	**$12,486**	**$25,312**
Total cost	**$39,538**	**$95,728**	**$194,061**
Cost per injection location	**$39,538**	**$95,728**	**$194.061**
Cost per foot	**$1977**	**$4786**	**$9703**
Life-cycle cost per cubic yard treated	**NA**	**$412**	**$834**

Notes: (1) Costs were not included for tasks that are not applicable or where there were no unique costs for the STF technology relative to conventional in situ bioremediation.

Scenario 1: The cost of implementing a small-scale injection of the shear-thinning technology (single well, single injection event) was estimated to be approximately $40,000. Approximately 51% of this cost was associated with conventional enhanced bioremediation; 31% was associated with the extra field time for preparing the STF and injection testing; and the remaining 18% was associated with lab-scale tests and other work to support the STF formulation and design. In other words, the inclusion of STF increased the cost of conventional bioremediation by approximately a factor of two for this scenario. It should be noted that this cost estimate is highly scale-dependent. For example, increasing the treatment volume by a factor of three (i.e., three injection wells required) would increase the total cost to $81,000. However, the cost associated with using STF is approximately $21,000 in this case, representing an incremental cost of 34% over conventional enhanced bioremediation.

Scenario 2: For the case where the shear-thinning technology was used (at a single site at a scale similar to that used for this project) to support site closure after 5 years, the total life-cycle cost was $96,000 (or $412 per cubic yard). Approximately 33% of this cost was associated with the use of the STF (including costs for lab-scale testing), while long-term monitoring represented 39% of the cost. The total life-cycle cost associated with the alterative—conventional enhanced bioremediation leading to MNA—was estimated to be $194,000 (or $834 per cubic yard). For the latter option, approximately 79% of the cost was associated with long-term monitoring obligations. As a result, the total life-cycle cost of the remedy that incorporated the shear-thinning technology was 51% less than the baseline case.

The primary cost benefit of the shear-thinning technology is the decrease in the remediation timeframe for the site, which greatly reduce the long-term monitoring obligations. For the scenario evaluated here, the cost savings more than compensates for the short-term incremental costs of adding the shear-thinning polymer to the in situ bioremediation design. These benefits are largely the result of providing enhanced treatment of the contaminants in the low-k zones, such that only a short monitoring period (4 years after the end of active treatment) is required for compliance purposes. Under the alternative scenario, a 26-year period of MNA is required to ensure that mass diffusing from low-k zones has decreased below the acceptable endpoint. An additional cost benefit of the shear-thinning technology is the reduction in the number of injection events to complete the active treatment phase.

7.3   COST DRIVERS

The total costs of implementing this technology are primarily associated with the scale of the remediation performed at a site. Key cost drivers include the volume of the treatment zone, the injection rate for the STF, and the polymer concentration used in the STF. All of these parameters were included in the following sensitivity analysis for Scenario 1. In addition, the effect of treatment volume was evaluated for Scenario 2.

7.3.1   Sensitivity to STF Injection Rate

The baseline scenario in the cost model used an STF injection rate (30 gpm) that was identical to that for non-STF injections. This condition was met during the demonstration project, with the understanding that site-specific injection pressures may dictate using lower injection rates for the STF. This sensitivity analysis compared costs using the injection rate for an STF relative to the

injection rate for a non-STF. Assuming all other inputs remained unchanged, the estimated costs associated with the STF injection rate were evaluated for Scenario 1. The results are shown in Figure 23.


Figure 23. Sensitivity of cost of shear-thinning technology to injection rate.
(Scenario 1: single injection)

As expected, the total costs increase if the injection rate must be decreased to compensate for the inclusion of the STF. However, the cost increases are relatively marginal (10%) even if the injection rate is halved, primarily because the materials cost remain constant regardless of the injection rate. More significant changes in the cost curve can be observed when the STF injection rate decreases to 25% of the baseline rate. This injection rate corresponds to 7.5 gpm, which is on the lower-end of what would be considered technically practical for selecting injection-based in situ treatment technologies.

7.3.2   Sensitivity to Polymer Concentration

The baseline scenario in the cost model assumed that a polymer concentration of 800 mg/L was selected for the STF, i.e., the same concentration used for this demonstration project. Purchasing polymer represents an incremental cost relative to conventional bioremediation, and the results of the sensitivity analysis on this input parameter for Scenario 1 are shown in Figure 24.

The cost curve clearly demonstrates that the impact of material costs on the total project costs are relatively minimal for the scenario that was evaluated. In part, this is a function of the scale of the project being considered. While site-specific considerations might dictate a higher or lower polymer concentration than the concentration used during this project, it is our experience that greater than order-of-magnitude adjustments would be unusual.
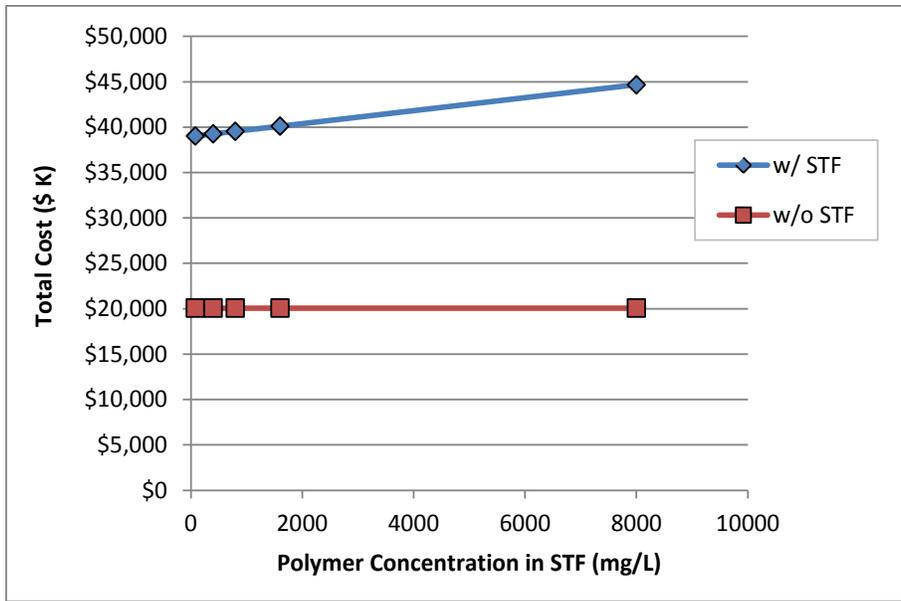
Figure 24. Sensitivity of cost of shear-thinning technology to polymer concentration.
(Scenario 1: single injection)

7.3.3 Sensitivity to Volume of Treatment Zone

To provide a basis for comparison to the demonstration project, the baseline scenario in the cost model assumed that the site represented a relatively small treatment volume of 6280 cubic feet (233 cubic yards). The unit costs that resulted from this assumption (Table 11) are a reflection of the limited scale. At larger sites, a higher number of injection points and greater amendment quantities would be required. Larger sites would also require a more intensive monitoring program during the long-term monitoring phase of the project. The impacts of changes to the treatment volume for Scenario 1 are shown in Figure 25a, while the changes for the costs in Scenario 2 are shown in Figure 25b.

As expected, increasing the treatment volume has significant cost implications. However, relative to the baseline case, increasing the treatment volume has limited direct cost impacts for the shear-thinning technology (assuming that the similar injection rates are possible). This is because material costs, including the incremental costs from using the shear-thinning polymer (xanthan gum), represent a modest percentage of the overall project costs. In Scenario 1 (Figure 25a), the marginal difference in the slopes between the baseline case versus the STF injection reflects that changes in treatment volume have a similar influence over both cases.

For Scenario 2 (Figure 25b), there is always a life-cycle cost savings when the STF is used. The incremental cost savings becomes progressively higher when the size of the site increases from the combined effects of fewer injection events and a shorter monitoring period. When the cost savings is expressed as a percent of total cost, the effect diminishes at larger sites. This is because the shorter-term costs associated with the treatment itself represent a larger portion of the total costs as the treatment volume increases, while the longer-term beneficial effects of the STF (reduced monitoring costs) become a less important cost driver.

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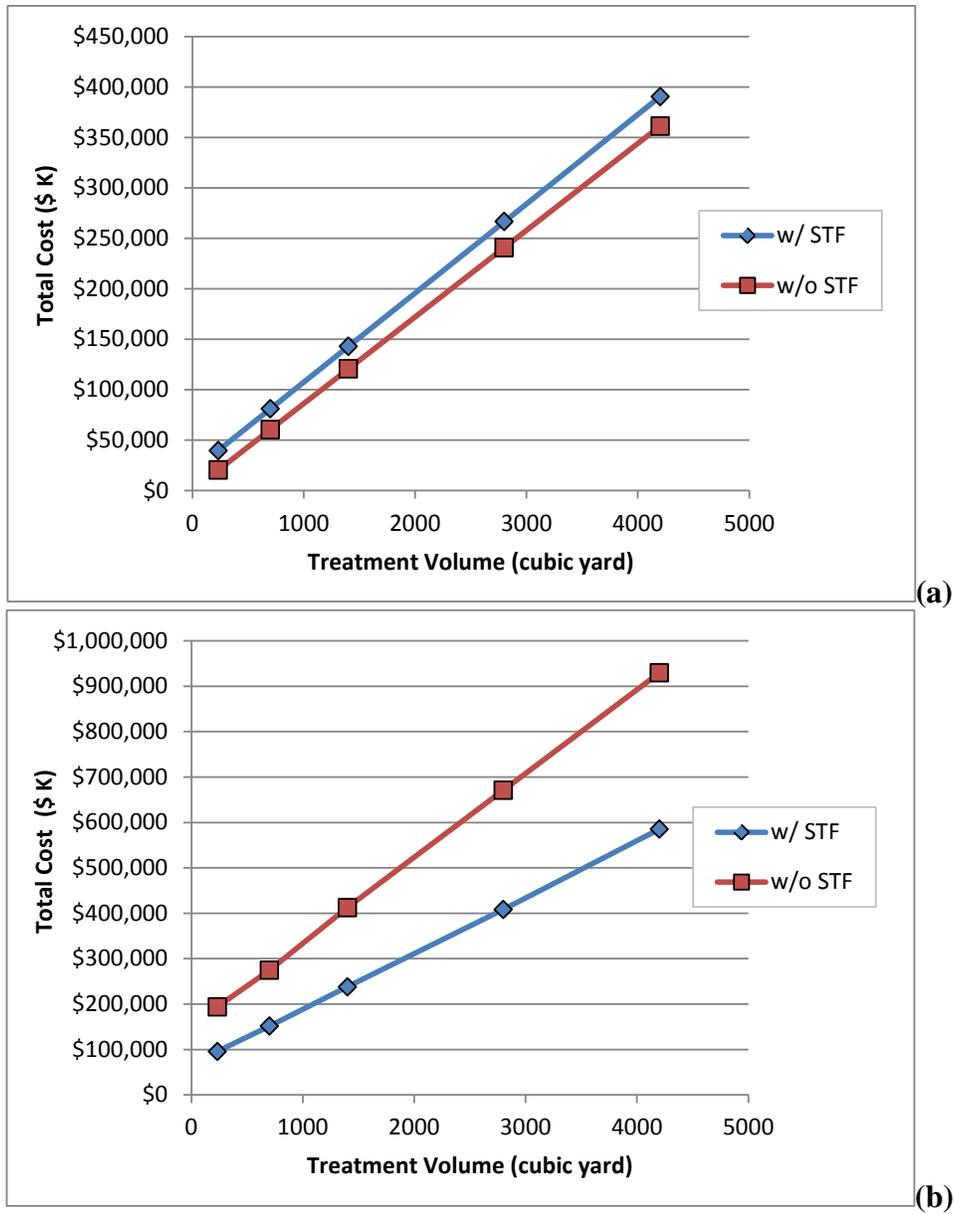
Figure 25. Sensitivity of cost of shear-thinning technology to volume of treatment zone.
(a) Scenario 1: single injection; (b) Scenario 2: life-cycle cost comparison between two outcomes.

8.0   IMPLEMENTATION ISSUES

8.1   REGULATIONS AND PERMITS

The project demonstrated the use of STFs to improve subsurface distribution of remedial amendments. Shear-thinning fluids are generally food-grade organic compounds and similar in nature to substrates used for enhanced bioremediation. Consequently, the regulatory issues associated with full-scale technology implementation are the same as those for enhanced bioremediation. Given the familiarity of enhanced bioremediation to federal and state agencies, there are not expected to be significant regulatory impediments to using the technology.

In many cases, an underground injection control (UIC) permit may be necessary when using the shear-thinning technology, particularly if groundwater recirculation is used in the design. The technology does not result in discharge of wastewater or discharge to air. Waste generation is minimal and primarily related to the installation of injection and/or monitoring wells. As with most technologies involving injection of chemicals to the subsurface, every effort should be taken to inject the entire volume of the prepared fluid.

8.2   END-USER CONCERNS

Therefore, the shear-thinning technology is expected to be applicable at a wide variety of sites where enhanced bioremediation is being used or considered, particularly those with low-k strata in contact with (or embedded in) the targeted groundwater bearing unit.

Acceptance of this technology requires that end-users can achieve distribution of amendment into lower-k zones using a remedial design that is safe and effective. It will not be effective if used to directly inject solutions into low-k materials (e.g., clays). Instead, STFs promotes cross-flow from high-k zones into low-k zones (except near the injection well). Cross flow is less effective in moving fluid into the low-k layer as the distance from the low-high permeability interface increases. Amendments will be more difficult to distribute to the center of thicker low-k layers. However, there may be applications where distributing the amendment along a thin interface of a thick low-k layer would be effective for reducing matrix diffusion. While site-specific conditions and treatment goals should always dictate remedial decision-making, a rule of thumb would be to target aquifers with permeability contrasts < 2 orders of magnitude, and/or for low-k layers thinner than about 0.5 m, if distribution to the center of the layer is necessary to meet goals. This permeability contrast would be equivalent to silt layers present within a sand matrix, but not clay layers. A similar recommendation is reported by Crimi et al. (2013) in their demonstration of shear-thinning polymers in combination with chemical oxidants.

Shear-thinning fluids are injected at a relatively high velocity compared to natural groundwater flow velocities, such that the shear-thinning nature of the solution allows it to flow readily. An estimate should be made of the injection pressure at the design injection rate (or range of rates) for water-only injection. A water-only injection test or step-drawdown and constant rate extraction test can be used to obtain expected injection pressures. The injection pressure for the STF will be this baseline injection pressure multiplied by the viscosity of the STF under the injection conditions. There is typically high shear rate near the injection well, such that an upper bound for the viscosity is the measured viscosity at a shear rate of 150 meters per second. In the

field, observed initial pressure increases from STF have been only about 20% of this value, although the injection pressure increases with time. Thus, this range of injection pressures should be considered in the design. For the current demonstration, average injection pressures for the STF over the course of the test was similar to those for water solutions, but there was an evident increase over time for the former case. For all applications of this technology, it is recommended to monitoring pressure continuously and use a pre-determined maximum pressure limit based on system constraints. If field pressures approach this limit, pressure can be decreased by decreasing the injection flow rate.

If injection pressure becomes a limiting factor, then the rheological properties (i.e., viscosity) of the STF can be modified. Viscosity is needed to induce distribution of amendment into low permeability layers (e.g., through the cross flow phenomena), and in general, higher viscosity leads to more cross flow between layers. However, there are diminishing returns as the viscosity of the injection fluid increases. More detailed modeling approaches are available to support more thorough site-specific assessments (Silva et al., 2012; Oostrom et al., 2014), though it may be difficult to explicitly model some sites due to uncertainties in the actual layer permeability contrasts and the configuration of layering. Given this limitation, a rule of thumb is to use a static viscosity of near 100 cP for the STF when applying the technology.

Shear-thinning fluids increase in viscosity after the injection (shear force) is completed, and this property increases their persistence in the subsurface and promotes sustained treatment. In some cases, end-users may be concerned about long-lasting secondary effects on groundwater quality. However, these shear-thinning fluid mixtures are not infinitely stable and can be expected to decrease in viscosity over the course of weeks to months. The STF formulation used in this demonstration was persistent over 8 months, but there was no evidence of excessive deterioration of groundwater quality (e.g., acidification, biofouling).

As noted above, the inherent similarity of the technology to conventional in situ bioremediation should help to minimize potential end-user concerns. The primary difference is that the amendment formulation includes a polymer that must be mixed into the injection solution. Injection designs already familiar to most site managers (e.g., injection wells configured in a grid or barrier pattern) are also applicable to this technology.

8.3   PROCUREMENT

There are no procurement issues related to the use of this technology. Materials, including shear-thinning polymers, are readily available and relatively similar to those already familiar to environmental remediation professionals. There are a number of technology specialists and other service providers that are experienced at performing these types of injections.

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