Field Demonstration of Polymer-Amended In Situ Chemical Oxidation (PA-ISCO)

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1. Abstract

The methods and results of the first field-scale demonstration of polymer-amended in situ chemical oxidation (PA-ISCO) are presented. The demonstration took place at MCB CAMLEJ (Marine Corps Base, Camp Lejeune) Operable Unit (OU) 15, Site 88, in Camp Lejeune, North Carolina between October and December 2010. PA-ISCO was developed as an alternative treatment approach that utilizes viscosity-modified fluids to improve the in situ delivery and distribution (i.e. sweep-efficiency) of chemical oxidants within texturally heterogeneous contaminated aquifers. The enhanced viscosity of the fluid mitigates the effects of preferential flows, improving sweep-efficiency and enhancing the subsurface contact between the injected oxidant and the target contamination within the treatment zone. The PA-ISCO fluid formulation used in this demonstration included sodium permanganate as oxidant, xanthan gum biopolymer as a shear-thinning viscosifier, and sodium hexametaphosphate (SHMP) as an anti-coagulant. It was the goal of this demonstration to validate the utility of PA-ISCO within a heterogeneous aquifer. An approximate 100% improvement in sweep-efficiency was achieved for the PA-ISCO fluid, as compared to a permanganate-only injection within an adjacent control plot.

1. Introduction

Viscosity-modification as a technique to mitigate the effects of permeability heterogeneities and improve the subsurface delivery and distribution of injected in situ remediation fluids has gained increased attention in recent years. Viscosity-modification is the addition of water-soluble polymers or other fluid thickening agents to groundwater remediation fluids to increase the viscosity of the injected fluid. The increased viscosity improves sweep efficiencies within heterogeneous aquifer sediments by reducing the mobility of the fluid within higher permeability strata during injection operations. This reduced mobility (i.e. increased resistance to flow) within more permeable strata promotes enhanced transverse fluid movement (i.e. cross-flow) into adjacent lower permeability strata, mitigating preferential flow and bypassing of lower permeability strata that often limits the effectiveness of remedial treatments ([Jackson et al., 2003](#)). The net result is a more uniform fluid propagation front during injection operations and improved distribution of that fluid within heterogeneous formations. A recent detailed discussion of the physics of viscosity-modified flow, as well a bench-scale evaluation of the utility of the technique was recently presented ([Silva et al., 2012, 2013](#)).

Mobility control methods, including viscosity-modification, have a long history of research and application in the petroleum industry ([Littmann 1988](#); [Lake 1989](#); [Sorbie 1991](#)). In petroleum engineering applications, the goal is to reduce the injected fluid mobility to match or be less than the mobility of the target oil deposit to promote displacement and enhance oil recovery. In environmental application, the goal of polymer amendment is to enhance in situ treatment effectiveness by improving the sweep-efficiency and contact between the remedial fluid and the contaminant. Environmental applications of this technique have generally focused

on the coupling of water-soluble polymers and surfactants to further improve the recovery of nonaqueous phase liquids (NAPLs) (Martel et al. 1998, 2004; Robert et al. 2006; Young et al. 2002; Zhong et al. 2008). However, other applications have been proposed and demonstrated, including the use of polymer-amended solutions to improve the suspension and subsurface distribution of zero-valent iron (Cantrell et al. 1997; Oostrom et al. 2007; Truex et al. 2011; Velimirovic et al., 2014) and to enhance water-flooding efficiencies and recovery of coal tar and creosote NAPL (Giese and Powers 2002). More recently, Truex et al (2015) reported improved sweep-efficiency for a shear-thinning tracer solution injected into a heterogeneous aquifer at the field-scale, the results of which indicated reduced rate of flow within higher permeability pathways and increased sweep within lower permeability strata. Additional treatment applications can be imagined, including the use of viscosity-modification to improve the delivery and subsurface distribution of bioremediation agents, and for enhanced waterflooding applications to sweep dissolved-phase contaminants from lower permeability strata within large plumes (i.e., enhanced pump-and-treat).

Polymer-amended in situ chemical oxidation (PA-ISCO) was developed as a novel variation on existing ISCO groundwater remediation technologies to combat challenges associated with subsurface permeability heterogeneity and poor ISCO fluid delivery by the addition of water-soluble polymers and polyphosphates to the ISCO solution formulation. Polymer-amendment provides an enhanced solution viscosity and shear-thinning rheology that, upon injection into porous media, combine to provide in situ mobility control and improve the injectivity of the solution (Silva, 2012; Martel, 1998). Smith et al (2008) demonstrated the compatibility (i.e. oxidation resistance) of xanthan gum biopolymer and permanganate oxidant in aqueous solution, suggesting that viscosity-modification is indeed applicable to ISCO.

An additional permanganate ISCO challenge is the management of manganese dioxide (MnO_2) particles, which are a byproduct of the reaction of permanganate with organic contaminants and naturally reduced subsurface materials. These particles have the potential to deposit in the well and subsurface and impact flow in and around the well screen, filter pack, and the surrounding subsurface formation. This is particularly challenging for sites with excessive oxidant consumption due to the presence of natural materials or large masses of non-aqueous phase liquids (NAPLs). Polyphosphates are added to the PA-ISCO formulation as particle stabilizers and anti-coagulants to mitigate the deposition, aggregation, and accumulation of MnO_2 particles to further improve fluid injectivity and subsurface delivery.

Herein, we report the methods and results of the first field-scale application of Polymer-Amended ISCO (PA-ISCO) which took place during October-December 2010. The primary objective of this field demonstration was to validate the effectiveness of PA-ISCO to improve the subsurface delivery and distribution of permanganate oxidant within a texturally heterogeneous contaminated aquifer.

2. Materials and Methods

2.1 Site Description and Well Field Layout

The site selected for PA-ISCO demonstration was located on Marine Corps Base Camp Lejeune (MCB CamLej), Operable Unit (OU) 15, Site 88, in Camp Lejeune, North Carolina. Site 88 is the former location of the base dry-cleaning facility that was in operation beginning in the 1940's until 2004, thereafter operations ceased and the building was eventually demolished. Historic operating practice included the disposal of spent dry-cleaning fluids (including perchloroethene (PCE)) into floor drains within the facility. These drains led to a buried sanitary

sewer line from which PCE entered the shallow aquifer underlying the facility as non-aqueous phase liquid (NAPL) and provided a source for dissolved-phase contamination. Contaminants of concern at the site included PCE and the degradation products trichloroethene (TCE), cis-dichloroethene (DCE), and vinyl chloride (VC).

As shown in Figure 1, the hydrogeologic setting beneath Site 88 consists of a water table aquifer that extends from ground surface to approximately 6 meters (m) below ground surface (bgs). The aquifer sediments are composed of interbedded fine to very-fine sands and silt that overlay a layer of silty clay that serves as an aquitard supporting the water table aquifer above. The aquitard varies in thickness between 1.5 m and 4 m across the site. Sediments beneath the shallow aquitard consist of a generally coarsening-downward series of interbedded silts and to fine-grained silty sands overlying a series of poorly sorted fine to medium-grained sands. These sediments represent the shallowest extent of the upper Castle Hayne aquifer unit (CH2M Hill, 2008) that extends further to a depth of 25 m bgs in the area and is water-saturated throughout its thickness. Previous sediment cores collected within the vicinity of the site provided evidence of a layer of calciferous cemented sands existing between 15 and 18 m bgs. Data collected from previous hydraulic tests indicated this cemented sand interval possessed low vertical hydraulic conductivity, and therefore would serve as an adequate lower confining unit for this demonstration. The portion of the upper Castle Hayne aquifer existing between the upper confining clay aquitard and the lower confining cemented sands was selected as the target treatment interval for the PA-ISCO demonstration. Previous hydraulic investigations within the upper Castle Hayne aquifer indicated that ground water flows slowly to southwest, along a 4×10^{-4} m/m gradient with hydraulic conductivities reported to range between 0.3 and 3.4 meters/day (m/d) (CH2M Hill, 2008).

Figure 1. Projected subsurface cross section (A) and well installation layout (B). Red dashed lines in (A) designate the target treatment interval and numbers indicate the location of discrete groundwater sampling intervals.

The well field selected for this demonstration (Figure 1) consisted of two side-by-side plots, both containing a central injection well separated by a 4.6 m (15 ft) design treatment radius (DTR). The pore volume of each demonstration plot was calculated to be 158,987 L (42,000

gallons), based on the dimensions of plots, a 7.6 m (25 ft) saturated thickness, and an average porosity of 0.32. Along the perimeter of the DTR, multi-level sampling wells (Solinst continuous multichannel tubing (CMT) wells) were installed as sentry wells to monitor the arrival of the permanganate solution during injection operations. All wells were installed using Roto-sonic drilling techniques. Injection wells (IW) were constructed with 4-inch diameter, 6 m long, stainless steel screens (20-slot) affixed to schedule 80 polyvinyl chloride (PVC) risers. The well screens were positioned within the target treatment interval between 10.7 and 16.8 m (35 and 55 feet) bgs. CMT well sampling intervals were selected to monitor the distribution of injected fluids within the treatment interval (i.e. between the less permeable silty sands and underlying fine-medium sands) and within the cemented sand unit. Each CMT well sampling interval was isolated from the port above by bentonite seals. Analyses of sediment samples collected during well construction indicated that pre-treatment sorbed-phase TCE and PCE concentrations within the control plot were as high as 1.3 and 10 mg/kg, respectively. Sorbed-phase TCE and PCE concentrations within the test plot pre-treatment samples were as high as 2.08 and 16.3 mg/kg, respectively. Pre-treatment PCE groundwater concentrations within the target treatment interval ranged between 1 and 5 mg/L. NAPL was not observed in sediment cores collected from within the treatment zone.

2.2 PA-ISCO Fluid

The PA-ISCO fluid selected for demonstration included xanthan gum biopolymer (Keltrol® T, CP Kelco) as a viscosifier, sodium permanganate (NaMnO_4 , Remox® ISCO reagent, Carus Corp.) as oxidant, and sodium hexametaphosphate (SHMP) as a particle stabilizing agent. Xanthan gum biopolymer was selected based on previous work demonstrating compatibility (i.e. resistance to oxidation) with permanganate oxidants ([Smith et al, 2008](#); [Silva, 2011](#)). NaMnO_4

was selected because it was commercially available in a concentrated liquid form that simplified oxidant preparation in the field. SHMP was selected as a particle stabilization aid (i.e., anticoagulant) to mitigate the deposition and accumulation of manganese dioxide (MnO_2) particles generated as a reaction product of MnO_4 oxidation (Crimi et al. (2009); Crimi and Ko (2009)) that can reduce media permeability during subsurface injections. Determining an optimal mixture of these components was a key design goal for this PA-ISCO demonstration. Sodium permanganate (RemOx® L ISCO Reagent, Carus Corp., LaSalle, IL) was shipped to the site in six 996 L (263 gallon) liquid chemical transportation totes as a 40 % (by volume), or 40,000 mg/L, solution concentrate. Xanthan gum (Kelzan-T, CP Kelco, Houston, TX) and SHMP (Carus Corp., LaSalle, IL) were delivered to the site in dry powder form within 22.7 kg (50 lb) bags.

2.3 Pre-Demonstration Design and Treatability Testing

The design of this first PA-ISCO field-scale demonstration relied on experience gained from previous laboratory batch, column, and two-dimensional (2D) tank-scale research (Smith, et al. 2008, Crimi et al., 2009, Crimi and Ko, 2009; Silva et al. 2012, 2013). However, up-scaling the approach required additional laboratory treatability tests and in-field hydraulic testing to ensure successful field-scale application. During the installation of the well field, samples of aquifer sediment and groundwater were collected for use in treatability testing.

Specific treatability testing goals included: (1) determining permanganate oxidant demand for polymer and sediment organic carbon in excess of contaminant demand to optimize permanganate concentration and deliver the PA-ISCO fluid to the DTR, (2) characterizing polymer/permanganate solution rheology and rheologic stability, and (3) performing one-dimensional (1-D) column tests to evaluate PA-ISCO solution injectivity and permeability

reduction potentials within site sediments. A detailed description of the methods utilized and results of the entire treatability testing work scope has been provided in Section S.1 of the Supplemental Materials.

As a part of the well-field installation work scope, additional hydraulic testing was performed to provide a more detailed assessment of degree of permeability heterogeneity and bulk hydraulic properties within the target treatment interval. Prior to the well field installation, pneumatic slug testing was performed at discrete depth intervals within the upper Castle Hayne aquifer utilizing direct-push technology (DPT) methods. Following the wellfield installation, step injection tests were performed utilizing the injection wells within both demonstration plots. Hydraulic data provided were used in design calculations to determine optimal and maximal injection rates.

Given the enhanced viscosity of polymer-amended remedial fluids, and the proximity of the target treatment interval to ground surface in the present case, it was important to first determine a maximum injection pressure ($P_{\max}$) for the demonstration formation to avoid formation damage during injection operations. This information was then used to optimize the injection flow rate to fall below $P_{\max}$ while maximizing sweep-efficiency improvement for the PA-ISCO fluid. Details of these design calculations, including the hydrostatic evaluation used to determine $P_{\max}$ and the approach used to determine the optimal injection flow given the shear-thinning rheology of the PA-ISCO solution used are presented in Section S2 of the Supplemental Materials.

A schematic of the process equipment used during the PA-ISCO demonstration is provided in [Figure 2](#). The equipment was constructed as three separate skid-mounted systems: a process flow control system, a dry polymer mixing system, and an injection control system. Potable water was supplied by a nearby fire hydrant and inlet pressure was regulated prior to entering the system.

The process flow control unit regulate the rate of NaMnO_4 and xanthan gum/SHMP solution concentrate dosing into the main process line during injection operations and monitored injection pressures, process flow rates, and other alarm and telemetry systems to allow for overnight injection operations. Field photographs and additional details relating to the operation of the process flow control system are presented in Section S.3 of the Supplemental Materials.

2.4 Test Operations

Within the two side-by-side demonstration plots, test fluids were introduced to the central injection wells at the same constant rate of injection. This constant injection rate was maintained until achieving a one pore-volume injection within each demonstration plot. The PA-ISCO solution was introduced to the test plot and a permanganate-only solution was introduced to the control plot, thereby providing a means of comparing resulting sweep-efficiencies.

Maintaining a constant rate of injection was important for this demonstration, not only to provide a proper comparison of sweep-efficiencies between the two demonstration plots, but also to provide a steady in situ mobility reduction potential for the PA-ISCO fluid to maximize sweep-efficiency improvement within the test plot at that flow rate. Quality control monitoring, at startup and throughout the injection period, included the onsite analyses of permanganate concentration and/or PA-ISCO fluid rheology from liquid samples collected from a sampling port located on the injection wellhead manifold. Samples were also collected from additional points along the process flow and injection system during the initial phases of injection operations to help adjust and fine-tune the rate of permanganate and/or PA-ISCO solution dosing to maintain design conditions.

Immediately following injection operations at both demonstration plots, a DPT rig was used to collect continuous soil cores within the treatment interval to characterize the post-injection

distribution of permanganate. These continuous cores were collected along three radial transects within each demonstration plot, each intersecting the central injection wells. The cores were logged for soil stratigraphy and the presence or absence of permanganate as indicated by the purple staining of the soil. Soil samples were also collected for offsite analysis of permanganate concentration and the concentration of contaminants (see Section S.4 Supplemental Materials) to confirm reduction in contaminant mass where permanganate contact was made.

3. Results and Discussion

3.1 Pre-Demonstration Design Testing

3.1.1 Evaluating Oxidant Demands

A detailed description of the methods and results of the NOD and NOD kinetics evaluation has been previously presented ([Crimi et al., 2013](#)). Briefly, instantaneous NOD measured for permanganate solutions absent of xanthan gum (540 – 600 mg/kg) were somewhat lower than for those containing xanthan gum (800 – 900 mg/kg) for sediment samples collected from the same depth interval. However, the percentage of the total NOD that was instantaneous was found to be generally similar regardless of whether xanthan gum was included in the solution, suggesting that permanganate oxidant demand for xanthan gum was low compared to the sediment NOD. A low permanganate oxidant demand for xanthan gum was also observed by [Smith et al. \(2008\)](#).

These results, as well as hydraulic and dimensional information for the demonstration plot, were included as input parameters for the Conceptual Design for ISCO (CDISCO) spreadsheet design tool ([Borden et al, 2010](#)). The results of CDISCO simulations indicated a 4,500 mg/L permanganate concentration would be sufficient to deliver permanganate to the 4.6 m (15 ft) DTR and preserve a 100 mg/L permanganate concentration at the DTR during the first pore

volume. However, a 5,000 mg/L permanganate concentration was ultimately selected to account for oxidant demand uncertainties within the treatment volume and add a factor of safety with respect to treatment and delivery.

3.1.2 PA-ISCO Solution Rheology

As shown in [Figure 3](#), all PA-ISCO solutions evaluated exhibit a shear-thinning rheology. These measurements were made within one hour of preparing the solutions and at a constant temperature of 25°C, using an AR-G2 cone-and-plate rheometer (TA Instruments, New Castle, DE) and a 40 millimeter stainless-steel cone with a 2 degree angle. It is interesting to note that PA-ISCO fluid rheology was largely insensitive to NaMnO₄ concentration. This is the result of the solution cationic strength provided by the SHMP and NaMnO₄ added to the solutions which help to stabilize fluid rheology ([Wyatt and Liberatore, 2009](#), [Silva et al, 2013](#)). Providing a stable fluid rheology during initial injection operations greatly improves the delivery of co-injected remedial fluids within heterogeneous geomedias. For PA-ISCO, this improved stability is particularly beneficial as permanganate is utilized in situ, to maintain favorable cross-flow potentials. The results of the Meter's equation (Meter and Bird, 1964 and Section S.2 Supplemental Materials) fits to the measured data are presented as an insert within [Figure 3](#). These parameters were used in design calculations to account for the effects of a shear-thinning rheology on solution injectivity, as described in Section 2.4.

Figure 3: PA-ISCO fluids demonstrating shear-thinning rheology. All test solutions contained 3,000 mg/L SHMP.

3.1.3 Rheological Stability

A detailed description of the methods and results of the rheological stability evaluation has been previously presented (Crimi et al., 2013). Briefly, increasing the concentration of permanganate oxidant resulted in an overall reduction of solution viscosity (i.e., increased loss of rheological stability) over time (Smith et al, 2008). For the solutions containing 10,000 mg/L permanganate, 80 to 93 percent of the initial fluid viscosity was lost over the 6-day measurement period. The most rheologically stable solutions were those in which the permanganate concentrations were less than or equal to 500 mg/L permanganate. However, these lower oxidant concentrations were determined to be insufficient to overcome the unproductive oxidant demand for the aquifer. Solutions containing the optimal 5,000 mg/L permanganate concentration

exhibited reasonable viscosity retention (i.e. a 20 to 30% viscosity reduction) over the 6-day measurement period.

It is important to note that these experiments were performed utilizing batch methods in which the oxidant concentration continually exists in excess. That is, throughout the duration of these measurements, there was always an abundance of oxidant to continue oxidizing portions of the xanthan gum molecule that allows these large linear molecules to self-associate and provide solution viscosity. Given the oxidant demand observed for the Castle Hayne sediments, upon injection in situ NOD reactions will reduce permanganate concentrations and help further stabilize the rheology of these fluids as they propagate from the point of injection.

3.1.4 PA-ISCO Solution Injectivity

One-dimensional column experiments were performed to characterize the potential for permeability reduction as a result of polymer entrapment and/or manganese dioxide plugging during PA-ISCO fluid injection. A detailed discussion of the methods and results of PA-ISCO solution injectivity testing was previously presented ([Crimi et al, 2013](#)). These results are summarized in [Table 1](#). Briefly, the results of these column experiments demonstrated that the addition of xanthan gum to a 5,000 mg/L NaMnO₄ solution resulted in a factor of 1.2-1.5 reduction in the permeability of the upper Castle Hayne aquifer sediments tested. However, when SHMP was added to the formulation, it was reduced by a factor of 1.02-1.06. These results stress the importance of including SHMP in the PA-ISCO fluid formulation at this site, in that SHMP-induced MnO₂ particle stabilization greatly improved the overall injectivity of the solution.

Table 1. Results of Bench-Scale Injectivity Testing

Test Condition	Injected Pore Volumes	Original Hydraulic Conductivity (m/sec)	Original Media Permeability (darcy)	Final Conductivity (m/sec)	Final Media Permeability (darcy)	Permeability Reduction Factor
Column 1 (Oxidant Only)	8	4.2E-05	4.2	4.2E-05	4.2	1
Column 2 (Xanthan/MnO ₄)	8	3.8E-05	3.8	1.5E-06	3.2	1.2
Column 3 (Xanthan/MnO ₄)	20	4.0E-05	4	1.1E-06	2.6	1.5
Column 4 (Xanthan/MnO ₄ /SHMP)	20	3.4E-05	3.4	1.7E-06	3.3	1.02
Column 5 (Xanthan/MnO ₄ /SHMP)	20	3.7E-05	3.7	1.8E-06	3.5	1.06

Note: In all cases concentrations of xanthan gum, MnO₄ and SHMP are 1,000 mg/L, 5,000 mg/L, and 3,000 mg/L, respectively

3.2 Hydraulic Testing

The results of in-field hydraulic testing are provided in [Table 2](#). Depth-discrete slug testing performed prior to the well installation within the target treatment interval provided hydraulic conductivity values that ranged from 5.2 to 0.3 m/day (17.0 to 1.0 ft/day) (permeability in the range of 6 to 0.35 darcy) with a mean value of 2.2 m/day (7.2 ft) (mean permeability of 2.6 darcy). This range of media permeability provides a permeability contrast ($k_{\text{high}}/k_{\text{low}}$) of 17, and a 0.95 variance in the natural logarithm of permeability, indicating a moderate degree of heterogeneity ([Clayton and Borden, 2003](#)). This degree of permeability heterogeneity was consistent with the degree of textural heterogeneity (i.e., sands, silty-sands, silts) observed for the upper Castle Haynes sediments, confirming that the site was a good candidate for demonstrating sweep-efficiency improvement.

Table 2. Summary Results of Hydraulic Testing within the upper Castle Hayne aquifer unit.

Parameter	Value
Max Hydraulic Conductivity (slug testing, ft/day)	17
Min Hydraulic Conductivity (slug tests, ft/day)	1
Mean Hydraulic Conductivity (slug tests, n = 9, ft/day)	7.2
Estimated Permeability Contrast for Castle Haynes	17
Variance in natural log of permeability ($\sigma_{\ln k}^2$)	0.95
Control Plot Average Hydraulic Conductivity (step injection tests, ft/day)	4.9
Test Plot Average Hydraulic Conductivity (step injection tests, ft/day)	6.3
Average Porosity	0.32

Step-injection testing provided hydraulic conductivity values of 1.5 ± 0.03 and 1.9 ± 0.09 m/day (4.9 ± 0.11 and 6.3 ± 0.3 ft/day) for the control plot and the test plot, respectively. These differences reflect a 21% variation in permeability heterogeneity between the two demonstration plots, and was considered acceptable for a side-by-side comparative evaluation of sweep-efficiency and sweep-efficiency improvement between both demonstration plots. For each step increase in injection flow rate, the wellhead pressure response stabilized within 1.5 hours. The results of the step-injection tests provided hydraulic conductivities that are within the range of values measured using alternative methods (e.g., slug testing). However, the results of the step-injection tests were considered to be most appropriate for demonstration design purposes because they were measured under direct injection and provide a more meaningful integrated average conductivity across the injection well screens.

3.3 Design Calculations

Design calculations centered on optimizing concentrations of permanganate, SHMP, and xanthan gum as components of the PA-ISCO formulation, and to optimize the rate of PA-ISCO fluid injection. Using the calculated parameters presented in [Figure 4](#), $P_{\max}$ was estimated to be 68 psi (4.69×10^5 Pa) (i.e., pressure measured at the well head). A 40% factor of safety was

thereafter applied to account for potential well completion irregularities and errors associated with the selection of the soil friction angle. This reduced the design injection pressure (P_{design}) to 50 psi (3.45×10^5 Pa). Therefore, the injection system, and all associated plumbing, for this demonstration were designed to accommodate, at minimum, a 50 psi backpressure at the wellhead.

Figure 4. Schematic of the upper Castle Hayne aquifer and calculated parameters used in maximum injection pressure calculations. Not to scale.

Steady-state wellhead pressure response profiles were then prepared (an example of which is provided as Figure 5), utilizing the calculations described in Section 2.4, to evaluate the effect of injection flow rate and xanthan gum concentration on the wellhead pressure response. These results include the effects of permeability reduction (Table 1) but do not account for the loss of solution viscosity due to slow oxidation of the polymer over time or anticipated rheological stability improvements resulting from NOD reactions reducing oxidant concentrations in situ (as described in Section 3.1.3).

Figure 5. Calculated steady-state wellhead pressure response to injection flow rate (1 gallon per minute or GPM = $6.31 \times 10^{-5} \text{ m}^3/\text{sec}$)

In the absence of xanthan gum, wellhead pressures increase linearly with increasing flow rate, up to and including 75.7 LPM (20 GPM), without exceeding P_{design} . In contrast, shear-thinning fluids (like those containing xanthan gum biopolymer) will exhibit a non-linear increasing wellhead pressure response with increasing flow rate. Increasing the concentration of xanthan gum (i.e. increasing the solution viscosity) was shown to reduce the maximum allowable injection flow rate, as regulated by the maximum design pressure constraint. For the demonstration site, a PA-ISCO solution containing 1000 mg/L xanthan gum would be limited to a 22.7 LPM (6 GPM) injection rate, and a solution containing 500 mg/L xanthan gum would be limited to a 62.5 LPM (16.5 GPM) rate of injection.

The design analysis was continued to provide steady-state shear rate and in situ viscosity profiles, examples of which are provided as [Figure 6](#). In situ shear rates will decrease with

distance from the injection well, in proportion to the decrease in interstitial velocity (Equation 3), resulting in an increased fluid viscosity with distance from the point of injection for a shear-thinning fluid. In the cases presented, PA-ISCO solutions containing between 500 mg/L and 1,000 mg/L xanthan gum were determined to provide sufficient viscosity enhancement to achieve sweep-efficiency improvement regardless of the rate of injection, within a range of 22.7 and 62.5 LPM (6 and 16.5 GPM).

However, practical considerations related to the preparation of the xanthan gum solutions during the field demonstration also had to be included in selection of the design injection flow rate. As the pore volume for the demonstration plots were estimated to be 158,987 L (42,000 gallons), a 22.7 LPM (6 GPM) rate of injection would require 4.9 days to achieve a one pore-volume injection, and a 16.5 GPM (62.5 LPM) injection rate would require 1.8 days to achieve one pore-volume. In the field, xanthan gum was to be prepared as a separate solution concentrate in 1,893 L (500 gallon) batches and stored in a larger 9,464 L (2,500 gallon) tank. During injection operations, additional 1,893 L (500 gallon) batches were to be prepared and added to the storage tank, as needed, to facilitate continuous 24-hour injection throughout the demonstration. It became clear that preparing enough xanthan gum solution to achieve a one pore-volume injection in 1.8 days would not be practical, even as a solution concentrate to be diluted prior to subsurface injection. Therefore, the lower 22.7 LPM (6 GPM) flow rate was ultimately selected as the design flow rate, which would provide slightly greater in situ viscosities for the solutions being considered and allow sufficient time to prepare polymer solutions on-site.

Figure 6. Example steady-state shear rate and in situ viscosity profiles for PA-ISCO solutions containing a) 500 mg/L and b) 1000 mg/L xanthan gum.

Selecting the optimal xanthan gum concentration for use in this field demonstration involved evaluating the in situ viscosity profiles while considering the results of solution rheological stability testing. Ultimately, the final PA-ISCO solution formulation selected for this demonstration included 500 mg/L xanthan gum, 5,000 mg/L NaMnO_4 , and 3,000 mg/L SHMP.

3.4 Field Operations

3.4.1 Injection Operations

Control plot operations began on 28 October 2010 with the injection of potable water at the 22.7 LPM (6 GPM) design flow rate until well pressures stabilized, at which point the permanganate metering pump was set to dose the sodium permanganate concentrate at a rate that provided a 5,000 mg/L permanganate concentration leaving the process system. Control plot injection operations were terminated on 02 November 2010, which provided a 5-day (1 pore volume) continuous injection duration.

Test plot operations initiated on 08 December 2010, following the repair of the polymer mixing pump that was found to be damaged. Throughout the injection period, polymer solution was prepared as a concentrate, containing 5,000 mg/L xanthan gum and 30,000 mg/L SHMP. The polymer metering pump was set for a 1/10 dilution of the polymer concentrate solution, providing a 500 mg/L xanthan gum and a 3,000 mg/L SHMP solution upon exiting the process flow system. As was the case for the control plot, the permanganate concentrate was metered down to deliver a 5,000 mg/L concentration upon exiting the process flow system. Likewise, a 22.7 LPM (6 GPM), rate of injection was maintained. Test plot injection ended on 13 December 2010 for a 5-day (or 1 pore volume) continuous injection duration.

The wellhead pressure response to injection that was recorded during control plot and test plot operations is shown in [Figure 7](#). The sharp decrease in wellhead pressures observed for both demonstration plots were, in both cases, the result of a temporary shutdown for system maintenance. During control plot operations (i.e. permanganate-only injection), wellhead injection pressures were much greater than the calculated steady-state estimate of 5 psi (3.45×10^4 Pa) calculated for the 22.7 L/min (6 GPM) design injection rate ([Figure 5](#)). This result

suggests a greater degree of MnO_2 production and permeability reduction had occurred during injection at the field-scale than was captured in the results of laboratory column testing.

Figure 7. Results of wellhead pressure monitoring during injection operations (1 PSI = 6895 Pa)

Conversely, the wellhead pressure response recorded during test plot injection operations was consistently lower than the calculated 26 psi (1.79×10^5 Pa) steady-state design estimate throughout the injection period. As this estimate included the effects of PA-ISCO solution viscosity, shear-thinning rheology, and permeability reduction derived from bench-scale measurement, the lower wellhead pressure observed could have resulted from discrepancies in the hydraulic conditions assumed in the estimate, including (1) the integrity of the lower cemented sand layer as a true lower confining unit, and (2) the fact that the screened portion of the injection wells were not fully penetrating. The slow and steady increase in wellhead pressure throughout the injection period, also suggests that a steady-state pressure condition was not achieved during injection operations in both cases.

During control plot operations, permanganate did not arrive at MLS-4 (positioned at the northeastern boundary of the control plot) at any depth interval during the injection period. Permanganate did arrive at MLS-3 (positioned to the northwest of the injection well and 1.5 m (5 feet) within the control plot boundary) beginning day 2 of the injection period, at the 11.3-12.8 m (37-42 ft) depth interval, but was not encountered within groundwater samples collected from the remaining depth intervals throughout the remainder of the injection period. Similarly, permanganate, as a component of the PA-ISCO solution, was not encountered in any of the groundwater samples collected from MLS-1 and MLS-2 during test plot operations.

3.4.2 Post-Injection Sediment Cores

Figure 8 includes an example of the post-injection soil cores collected at the completion of injection operations. As shown, the presence/absence and vertical distribution of permanganate within these cores was easily discerned by visual examination. The locations of individual DPT cores and cross-section locations are identified in Figure 9. The boring logs generated for each soil core were used to prepare transect cross-sections to better visualize differences in the subsurface distribution of permanganate within both demonstration plots. Examples of these cross-sections are presented in Figures 10 and 11. Additional post-injection cross-sections were prepared and are presented in Section S.5 in the Supplemental Materials.

During core collection the upper Castle Hayne sediments were observed, in some cases, to be very loose and fluidic, resulting in incomplete recovery. In these cases, when permanganate was observed to be present above and below the missing core section of the same sediment textural category, the presence of permanganate was interpolated to exist between the missing sections and identified as ‘probable MnO_4 ’. This approach was applied equitably to both the control plot and the test plot sediment cores and cross-sections.

Figure 8. Post-injection soil cores showing presence/absence of permanganate.

Figure 9. Locations of post-injection DPT cores and prepared cross-sections.

Figure 10. DPT core cross section showing stratigraphy and permanganate presence for control plot (1 m = 3.28 ft).

Figure 11. DPT core cross-section showing stratigraphy and permanganate presence for test plot (1 m = 3.28 ft).

For the control plot injection, permanganate appeared to have propagated predominantly within the sediment sand fraction (i.e., fine to medium sands) and along preferential flow paths within a given sediment textural category. These results demonstrate that the existing permeability heterogeneity greatly affected the subsurface distribution of permanganate within the upper Castle Hayne test interval. For the test plot, injection of the PA-ISCO fluid resulted in a much more uniform vertical distribution of permanganate than was observed in the absence of polymer-addition, particularly with distance from the injector. Some by-passing of sediments was observed with distance from the injector. However, an overall enhanced vertical and radial distribution of permanganate was achieved for the PA-ISCO solution compared to the permanganate-only treatment.

3.5 Sweep-Efficiency Improvement

To provide an estimate of sweep-efficiency for permanganate delivery within individual demonstration plots, the results of soil core permanganate concentration analyses were combined with the permanganate absence/presence data collected during DPT coring and the used to generate a permanganate concentration dataset for each DPT core location. These data were then input to the Groundwater Modeling System (GMS, Aquaveo, Inc.) software to provide individual scatter-point datasets, as shown in [Figure 12](#). Ordinary kriging was then applied to both datasets to provide a three-dimensional (3D) volumetric representation of the distribution of permanganate within both demonstration plots, the results of which are provided in [Figure 13](#). In both cases, the experimental variogram was a general semi-variogram fit consisting of 8 lags and a 0.61-meter (2-foot) separation distance. GMS could not provide a cylindrical grid space to represent the control volume for each demonstration plot. Therefore, a square (or cube) grid

space of similar dimension ($X = 8.5$ m (28 ft), $y = 8.5$ m (28 ft), $z = -10.7$ m (-35 ft)) was used to represent the treatment volume of each demonstration plot.

Figure 12. Three-dimensional scatterpoint datasets of permanganate concentration derived from DPT soil cores and analyses of soil core subsamples.

Figure 13. Results of ordinary kriging of the post-injection permanganate data representing the distribution of permanganate within the control and test plots after a 1 pore volume injection. Integrated sweep efficiency (volume contacted by permanganate divided by total volume) was 33% for the control plot and 67% for the test plot.

Based on this treatment of the data, the significant improvement in sweep-efficiency provided by the PA-ISCO solution is clear. During control plot operations, injected permanganate did not propagate to the eastern, southern, and western edges of the control plot volume. Rather, it appears that the injected permanganate preferentially flowed toward and exited the control volume along the northern edge of the control plot in the vicinity of core CP-DPT12 and between multi-level wells MLS3 and MSL4 (Figure 9). This observation is

consistent with lack of permanganate arrival at MLS4 and the absence of permanganate within core CP-DPT5 (Figure 10) that is located at the western boundary of the control plot. The significant preferential flow of injected fluids out of the treatment volume highlights the degree to which permeability heterogeneity can control the distribution of injected fluids within even a moderately heterogeneous aquifer such as the upper Castle Hayne. In contrast, the PA-ISCO fluid is shown to have achieved a more uniform lateral and vertical distribution within the test plot treatment volume. Some preferential flow was captured at the end of the injection period, where the reduced mobility of the PA-ISCO solution did not yet have a chance to develop a sufficient cross-flow potential (Silva et al, 2012) during the 5-day (1 pore volume) injection period selected for this demonstration.

Integration of the isosurface contours within the grid domain (for permanganate concentrations > 10 mg/L) provided the total volume swept within the control volume. Sweep efficiency was calculated by dividing the total permanganate swept volume by the total volume for each demonstration plot (i.e. 233,339 L (59,000 gallons)) and dividing by 100 to provide a percent volume swept. The volumetric sweep efficiency for the control plot injection was thus determined to be 33%. The volumetric sweep efficiency for the test plot PA-ISCO solution injection was determined to be 67%, representing an approximate 100% (or factor of 2) sweep-efficiency improvement over the permanganate-only control plot injection.

The apparent preferential flow path observed from the results of the control plot injection highlights the degree to which permeability heterogeneities can control the distribution of injected fluids, even at this small scale. However, this result complicates our objective of demonstrating PA-ISCO sweep-efficiency improvement in that it is unclear as to whether the test plot pore volume also accessed this preferential pathway. Still, viscosity-modification and other

mobility control methods have been used by the petroleum industry since the 1960's to combat the effects of heterogeneity (Littmann 1988; Lake 1989; Sorbie 1991). Likewise, recent work in laboratory 2-dimensional (2-D) sand tanks have clearly demonstrated the degree to which viscosity-modified fluids can improve sweep efficiencies in heterogeneous strata (Zhong et al., 2008; Silva et al., 2011; Silva et al., 2012).

As a demonstrative example, the results of the 2-D tank experiment presented as Figure 14 possessed a maximal permeability contrast of 82.5/5 darcy, or 16.5, which is similar to the range of maximum permeability contrast observed for the upper Castle Hayne aquifer during hydraulic testing (i.e., a factor of 10 to 17 permeability contrast). These results clearly demonstrate the effects of the cross-flow mechanism to mitigate the effects of permeability heterogeneity and reduce the number of pore volumes required to achieve 100% sweep. In this experiment, 100% sweep of the sand pack required a 1.5 pore volume injection. Therefore, given the similarities in overall permeability contrasts between this experiment and the demonstration treatment zone, it is possible that an optimal sweep efficiency improvement for the treatment volume would require a 1.5 to 2 pore volume injection period. However, as the experimental system shown in Figure 14 is a simplified representation of a more complicated 3D permeability heterogeneity structure for the upper Castle Hayne aquifer, the optimal injection volumes provided by these experiments cannot be truly predictive.

Figure 14. Example of experimental and simulated (UTCHEM model) polymer-improved sweep-efficiency within a two-dimensional sand tank (from Silva et al., 2011).

4. Conclusions

A field-scale demonstration was performed to evaluate the benefits of viscosity-modified fluids to improve the subsurface distribution of injected permanganate ISCO solutions. Within adjacent side-by-side demonstration plots, viscosity-modification of permanganate ISCO fluids was observed to mitigate preferential flow and significantly improved the overall sweep efficiency of the PA-ISCO fluid compared to a conventional permanganate treatment within a control plot of similar permeability heterogeneity. For a one pore volume (i.e. 158,987 L (42,000 gallon)) injection, calculated sweep-efficiencies for the control plot (i.e. permanganate-only treatment) was 33%, whereas sweep-efficiency for the PA-ISCO treatment was 67%, or a 103% improvement for the PA-ISCO treatment. As a result, a greater percentage of the aquifer was contacted by the aquifer.

Implementing PA-ISCO at the field-scale requires consideration of a number of site-specific and fluid-specific factors that can affect successful in situ application. Site-specific factors include understanding the sub-surface heterogeneity structure and determining safe injection pressures achievable for the viscosity-modified fluid being considered. Fluid-specific factors include selecting polymer rheological characteristics to maximize sweep-efficiency improvements, optimizing injected oxidant concentrations to overcome oxidant demands, selecting appropriate polymer-oxidant pairings that provide stable in situ rheological characteristics during the injection period, and evaluating the injectivity of these solutions to minimize injection pressures and ensure enhanced delivery.

The results of the test plot injection demonstrate that the viscosity-modified PA-ISCO fluid mitigated the effects of preferential flow pathways to provide an improved distribution of injected fluids within the treatment zone. The results of the control plot permanganate-only

injection exemplifies the degree to which preferential flow can affect the delivery of remedial fluids during injection operations, even for a moderately heterogeneous aquifer system like the upper Castle Hayne. PA-ISCO represents an alternative treatment approach that focuses on improving contact efficiency by improving sweep-efficiency within texturally heterogeneous contaminated aquifers. PA-ISCO can require a longer period of sustained injection than is commonly the case for traditional permanganate treatments. However, cost savings can be realized by achieving more effective treatment via improved contact efficiency, a lower number on injection points, and a more efficient use of oxidant.

When considering viscosity-modification, it is important to remember that solution viscosities need not be excessive to achieve optimal sweep-efficiency improvement. In the present case, the static solution viscosity was 36 cP (0.036 Pa•sec), similar to that of linseed oil or propylene glycol. However, the shear-thinning character of the xanthan gum solution used in this case results in a near-water viscosity near the injection well (i.e. where pore velocities are greatest) with a gradationally increasing viscosity with distance from the injector, theoretically approaching the static viscosity at the injection radius of influence where in situ pore velocities approach zero. Therefore, within the treatment volume, solution viscosities less than 36 cP (0.036 Pa•sec) were shown to provide sufficient cross-flow potentials to achieve improved sweep-efficiency within the upper Castle Hayne aquifer

Finally, it is also important to realize that, in certain cases, the effect of heterogeneity and heterogeneity structure on sweep-efficiency can be mitigated but not altogether eliminated. For example, polymeric viscosity-modified fluids are unlikely to penetrate clay and silty-clay strata, regardless of the cross-flow potential imposed. These strata are typically less hydraulically connected to the primary flow field and can be subject to permeability reductions resulting from

pore filtering and plugging processes associated with the polymer, co-injected remedial amendment, or by-products of amendment reactions at the surface or interfaces of these strata that can further isolate these media. Generally, viscosity-modification in environmental applications have been observed to be beneficial for geomedia ranging from silts/silty sands to coarse sands/gravelly sands, and will likely be most beneficial, in terms of achieving maximal sweep efficiency while minimizing the number of injected pore volumes required, when the target aquifer possesses an overall permeability contrast ($k_{\text{high}}/k_{\text{low}}$) between 4 and 20 (Silva et al., 2012).

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