Development and Characterization of Controlled-Release Permanganate Gel

for Groundwater Remediation

A thesis presented to

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This thesis titled

Development and Characterization of Controlled-Release Permanganate Gel

for Groundwater Remediation

by

NEHA GUPTA

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ABSTRACT

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Development and Characterization of Controlled-Release Permanganate Gel for Groundwater Remediation

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This study focused on furthering the development of a novel, cost-effective scheme to remediate large, dilute plumes of DNAPLs in groundwater through the in-situ, well-based emplacement of concentrated permanganate solution mixed with a gelling agent. The controlled-release permanganate gel (CRP-G) solution was developed so that it may be injected and flow with groundwater and subsequently increase in viscosity over time to remain emplaced and slowly release MnO$_4^-$ in a long-term, controlled release fashion.

This study characterized CRP-G gelation and release mechanisms of MnO$_4^-$ in saturated porous media through the execution of batch experiments, viscosity tests, and column tests. Specific attention was devoted to use of colloidal silica within the CRP-G.

Results of batch tests indicated that gelation times can be modified on the order of 5 min to over 10 dys; dilution by flowing water in the subsurface will be a consideration upon gel engineering. Results of column tests in open water indicated that release of MnO$_4^-$ from CRP-G occurred within 24 hrs. In column tests conducted with saturated, sandy media, gelation occurred within 1, 3, and 6 hrs when using CRP-G solution 25.0, 23.0, and 22.9 g/L of KMnO$_4$. Permanganate mass flux approached values that are near the benchmark for this study ($\approx$ 850 µg/day), with release lasting up to 3 dys. This release was characterized as rapid short-term release followed by a longer, stabilized release
phase. Impact of dilution of the injected CRP-G solution in the subsurface will be a consideration upon gel formation.

The use of colloidal silica as a controlled-release material for the CRP-G is promising. Further studies are warranted for the development of a novel remediation scheme using the CRP-G.
I would like to thank my advisor, Eung Seok Lee, for giving me the opportunity to work on this research and present it at a conference this year. I would also like to thank my thesis committee, Dina Lopez and Douglas Green, as well as my labmates, Lizhi Tong, Thomas Antonacci, and Tim Eyerdom, for their insight, advice, and assistance throughout the last two years.

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This work was done with the funding of the SERDP Program of the Department of Defense and GRL program of Korea, in conjunction with Frank Schwartz and Utku Solpuker of the Ohio State University, without whom completion of this project would not have been possible.

Finally, I would like to thank my family and my boyfriend, Andrew Austin, for their continued love and support throughout graduate school.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract .................................................................................................................. 3</td>
</tr>
<tr>
<td>Acknowledgements .................................................................................................... 5</td>
</tr>
<tr>
<td>List of Tables ........................................................................................................... 8</td>
</tr>
<tr>
<td>List of Figures ......................................................................................................... 9</td>
</tr>
<tr>
<td>Chapter 1: Introduction ............................................................................................. 11</td>
</tr>
<tr>
<td>Chapter 2: Characteristics of ISCO Using Permanganate ........................................ 15</td>
</tr>
<tr>
<td>2.1 Use of Permanganate to Treat Groundwater Contamination ................................ 15</td>
</tr>
<tr>
<td>2.2 Oxidation of Chlorinated Ethylenes by Permanganate ....................................... 16</td>
</tr>
<tr>
<td>2.3 Use of Controlled-Release Permanganate in ISCO ............................................. 17</td>
</tr>
<tr>
<td>Chapter 3: Characteristics of Colloidal Silica ......................................................... 19</td>
</tr>
<tr>
<td>3.1 Selection of Colloidal Silica as Vehicle for CRP-G ............................................ 19</td>
</tr>
<tr>
<td>3.2 Properties of Colloidal Silica ............................................................................... 19</td>
</tr>
<tr>
<td>3.3 Use of Colloidal Silica in Porous Materials ....................................................... 20</td>
</tr>
<tr>
<td>3.4 Use of Colloidal Silica for Controlled-Release Purposes .................................... 21</td>
</tr>
<tr>
<td>Chapter 4. Materials and Methods .......................................................... 22</td>
</tr>
<tr>
<td>4.1 Materials and Devices .......................................................................................... 22</td>
</tr>
<tr>
<td>4.2 Gelation Tests ...................................................................................................... 24</td>
</tr>
<tr>
<td>4.2.1 Effect of Ionic Strength Upon Gelation Time ............................................... 24</td>
</tr>
<tr>
<td>4.2.2 Effect of Dilution Upon Gelation Time ............................................................ 26</td>
</tr>
<tr>
<td>4.3 Release characteristics of CRP-G in Open Water ............................................. 26</td>
</tr>
</tbody>
</table>
4.4. Characterizing spreading, gelation, and release of CRP-G in saturated, porous media........................................................................................................................................28

Chapter 5: Results and Discussion........................................................................................................................................30

5.1 Gelation of CRP-G solution........................................................................................................................................30

5.2 Permanganate release in water: Column tests........................................................................................................38

5.3 Column Tests in Media........................................................................................................................................45

5.3.1. Dynamics of CRP-G in Saturated Sands: Column Tests with Media........................................................................55

Chapter 6: Conclusion........................................................................................................................................65

References..............................................................................................................................................................67
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Reaction rate constants for degradation by MnO₄⁻</td>
<td>17</td>
</tr>
<tr>
<td>4.1</td>
<td>Characteristics of Colloidal Silica</td>
<td>22</td>
</tr>
<tr>
<td>4.2</td>
<td>Gel solution concentrations in batch tests</td>
<td>25</td>
</tr>
<tr>
<td>4.3</td>
<td>Gel solution concentrations in diluted batch tests</td>
<td>26</td>
</tr>
<tr>
<td>5.1</td>
<td>Details of release from CRP-G in column tests conducted in open water</td>
<td>39</td>
</tr>
<tr>
<td>5.2</td>
<td>Column test with media results</td>
<td>46</td>
</tr>
<tr>
<td>5.3</td>
<td>Details of release from CRP-G in column tests conducted in saturated, porous media</td>
<td>48</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic of sol-gel process</td>
<td>20</td>
</tr>
<tr>
<td>4.1</td>
<td>Viscolite 700</td>
<td>23</td>
</tr>
<tr>
<td>4.2</td>
<td>UV-Visible Spectrophotometer</td>
<td>23</td>
</tr>
<tr>
<td>4.3</td>
<td>Gelation Batch Test</td>
<td>24</td>
</tr>
<tr>
<td>4.4</td>
<td>Column test in open water schematic</td>
<td>27</td>
</tr>
<tr>
<td>4.5</td>
<td>Picture of actual column test in progress</td>
<td>28</td>
</tr>
<tr>
<td>4.6</td>
<td>Column test with media schematic showing horizontal flow</td>
<td>29</td>
</tr>
<tr>
<td>5.1</td>
<td>Gelation of 20.0 mg/L gel solution through time</td>
<td>31</td>
</tr>
<tr>
<td>5.2</td>
<td>Gelation of 25.0 mg/L gel solution through time</td>
<td>32</td>
</tr>
<tr>
<td>5.3</td>
<td>Effect of KMnO₄ concentration upon gel time</td>
<td>35</td>
</tr>
<tr>
<td>5.4</td>
<td>Effect on dilution upon gelation time</td>
<td>36</td>
</tr>
<tr>
<td>5.5</td>
<td>Mass flux and cumulative release from 9.0 mgL⁻¹ gel.</td>
<td>40</td>
</tr>
<tr>
<td>5.6</td>
<td>Mass flux and cumulative release from 10.0 mgL⁻¹ gel.</td>
<td>41</td>
</tr>
<tr>
<td>5.7</td>
<td>Mass flux and cumulative release from 16.0 mgL⁻¹ gel.</td>
<td>42</td>
</tr>
<tr>
<td>5.8</td>
<td>Mass flux and cumulative release from 20.0 mgL⁻¹ gel.</td>
<td>43</td>
</tr>
<tr>
<td>5.9</td>
<td>Mass flux and cumulative release for 25.0 mgL⁻¹ gel.</td>
<td>44</td>
</tr>
<tr>
<td>5.10</td>
<td>Estimated gelation times in column test with media</td>
<td>47</td>
</tr>
<tr>
<td>5.11</td>
<td>Mass flux and cumulative release from 20.0 mg L⁻¹ gel</td>
<td>50</td>
</tr>
</tbody>
</table>
Figure 5.12. Mass flux and cumulative release from 21.8 mg L\(^{-1}\) gel. ..........................51

Figure 5.13. Mass flux and cumulative release from 22.5 mg L\(^{-1}\) gel. .........................52

Figure 5.14. Mass flux and cumulative release from 22.9 mg L\(^{-1}\) gel. .........................53

Figure 5.15. Mass flux and cumulative release from 23.0 mg L\(^{-1}\) gel. .........................54

Figure 5.16. Mass flux and cumulative release from 25.0 mg L\(^{-1}\) gel. .........................55

Figure 5.17. Optical data from 22.5 mgL\(^{-1}\) trial.........................................................58

Figure 5.18. Optical data from 22.9 mgL\(^{-1}\) trial.........................................................59

Figure 5.19. Optical data from 23.0 mgL\(^{-1}\) trial.........................................................60

Figure 5.20. Optical data from 25.0 mgL\(^{-1}\) trial.........................................................61
CHAPTER 1: INTRODUCTION

Chlorinated ethylenes such as perchloroethylene (PCE), trichloroethylene (TCE), and dichloroethylene (DCE) are currently considered the most prevalent organic contaminants of groundwater (Baird and Cann, 2008). Due to their relatively low solubility (1.28 g/L) and high density (DCE: 1.213 g/cm³; TCE: 1.463 g/cm³; PCE: 1.623 g/cm³; MSDS, 2012), these dense nonaqueous phase liquids can reside as thick residual Dense Non-Aqueous Phase Liquids (DNAPLs) or form DNAPL pools in aquifers. These accumulations provide long-term sources of direct and indirect contamination that can remain in place for hundreds of years under natural conditions (e.g., Baird and Cann, 2008; Schwartz and Zhang, 2003; Aulenta et al., 2007; US EPA, 1987).

Residual DNAPLs can often yield large, dilute (<0.1 mg/L), or deep dissolved plumes of DNAPLs in groundwater. The problem of large, dilute plumes is very difficult to address, with few cost-effective solutions. Typically, the volume to be treated precludes active, long-term control of remediation (e.g., pump and treat, flushing) for cost reasons. Particular problems posed by deep aquifer systems can also be identified, where traditional passive systems such as reactive barriers lose their cost advantage. Therefore, a more cost-effective treatment scheme is needed to treat large, dilute, or deep DNAPL plumes in groundwater.

Previous attempts to treat groundwater contamination by DNAPLs were generally ex-situ in nature, such as the pump-and-treat method in which groundwater is pumped to the surface to be treated. This method is costly; annual national expenses are estimated to be $2.7-4.5 billion for treatment (SERDP CU-1290, 2006). As a result, focus has shifted
to more cost efficient in-situ treatment methods designed to reduce the volume and mass of DNAPLs in the subsurface. Typical in-situ methods of interest include fluid flushing with water, surfactants or cosolvents; thermal treatments using steam, resistance or conductive heating; and chemical treatment by oxidation or reduction (US EPA, 2003).

Permanganate ($\text{MnO}_4^-$) is an oxidant used in many site remediation schemes as an in-situ chemical oxidant (e.g. Siegrist et al., 2001; Yan and Schwartz, 1999, 2000). Permanganate has been shown to be effective in treating contamination chlorinated ethylenes in the subsurface. However, manganese dioxide ($\text{MnO}_2$) is formed as a solid reaction product during the treatment of chlorinated ethylenes and results in an impermeable layer that may block contact between contaminant and oxidant (e.g. Lee et al., 2003). To attenuate the problems of $\text{MnO}_2$ precipitation and the resulting fluid bypassing, controlled-release permanganate (CRP) was developed as an alternative treatment option.

To further develop the novel remediation scheme using the CRP, this study focused on developing and characterizing controlled release $\text{MnO}_4^-$ gel (CRP-G) solution, a hypersaline KMnO₄ solution that can be introduced via well-based injection and gelate in the subsurface to form a long-term source of in-situ $\text{MnO}_4^-$ release. The CRP is implemented in the subsurface via well-based injection to facilitate lateral spreading. The CRP-G in this study was manufactured using colloidal silica, a material that results in formation of a gel through the sol-gel process.

This study tested whether the sol-gel process applied to CRP-G gelation and release mechanisms of $\text{MnO}_4^-$ in saturated porous media can meet the requirements for an effective in-situ remedial scheme for large and dilute plumes of dissolved DNAPLs.
Specifically, this study tested the hypothesis that colloidal silica, through the sol-gel process and its modifiable gelation times, provides a suitable diffusional matrix and adequate gelation and release times for the CRP-G scheme. The desired CRP-G solution is expected to have an initial viscosity that is low enough (~ 4 cP) to allow for well-based injection and gelation times of more than 3 d so that the CRP-G solution may spread from the injection wells to surrounding areas. At an ambient groundwater flow rate of 0.4 m/day in a typical unconsolidated sandy gravel aquifer, this would result in a treatment zone with a diameter larger than 2.4 m. A treatment zone this large is assumed to negate the necessity for multiple, laterally adjacent wells. Therefore, 3 d was chosen as the benchmark gelation value in this study. The desired CRP-G solution would form a gel barrier that can release MnO$_4^-$ at a rate that allows months to years for the complete release; Minimum release rates of 850 µg/day was chosen as a benchmark release rate within this study. This benchmark was chosen based on the amount of MnO$_4^-$ and time required to degrade a dissolved plume TCE plume of 100 µg/L to concentrations less than the maximum contaminant level (MCL: 0.005 µg/L) in 1 L.

Key issues investigated in this study were (i) gelation and release characteristics of colloidal silica in batch tests and (ii) ) dynamics of migration, gelation, and MnO$_4^-$ release of the CRP-G in saturated, sandy media in flow-through columns. Specific objectives included: (i) identification of key constraints on the gelation of colloidal silica as a gelling agent for the CRP-G, (ii) optimization of the gelation kinetics of the CRP-G to a target value of at least 3 d or distance of 1.2 m (iii) identification of key constraints on the release of MnO$_4^-$ from the gelated CRP-G (iv) optimization of the release kinetics of MnO$_4^-$ from the CRP-G to a target mass flux of 850 µg/day, and (v)
characterization of spreading, gelation, and release dynamics of the CRP-G in saturated, porous media under flowing conditions.
CHAPTER 2: CHARACTERISTICS OF ISCO USING PERMANGANATE

2.1. Use of KMnO₄ to Treat Groundwater Contamination

An in-situ chemical oxidation (ISCO) method is explored in this study. The ISCO schemes have been widely used as treatments for chlorinated ethylenes through the introduction of chemical oxidants into the subsurface to reduce groundwater contamination (Siegrist et al., 2001; SERDP CU-1290, 2006; SERDP, 2006). The introduction of a strong oxidizing agent such as MnO₄⁻ readily transforms chlorinated ethylenes into environmentally innocuous byproducts such as chloride and carbon dioxide gas through a series of reactions, resulting in the complete dechlorination of chlorinated ethylenes (Yan and Schwartz, 1999; Lee and Schwartz, 2007; Huang et al., 2001).

The introduction of MnO₄⁻ into groundwater systems contaminated by chlorinated ethylenes has been proposed as an effective in-situ remedial measure (e.g. Lee and Schwartz, 2007; Huang et al., 2001; Siegrist et al., 2001; Yan and Schwartz, 1999). Permanganate is an inorganic compound that is both a strong oxidizing agent and highly water soluble. Its extensive uses include gas purification, wastewater treatment, hazardous waste remediation, slag quenching or food processing (Carus Corporation, 2011). Permanganate is relatively stable in the subsurface, effective over a wide pH range, and is relatively inexpensive (Yan and Schwartz, 1999, 2000).
2.2. Oxidation of Chlorinated Ethylenes by Permanganate

Oxidation of chlorinated ethylenes by MnO$_4^-$ is well documented in the literature (Huang et al., 2001; Yan and Schwartz, 2000). The overall reaction of TCE is summarized as follows: As a metal-oxo reagent, MnO$_4^-$ attacks the double carbon-carbon bond of TCE to initially form a cyclic hypomanganate (V) ester intermediate. Depending on the pH of the medium the reaction can then take a number of pathways. Hydrolysis reactions dominate in neutral and alkaline media while oxidation reactions dominate in acidic media. In neutral to weakly acidic conditions, the cyclic hypomanganate ester is degraded to a number of intermediates, including glycolic acid, glyoxylic acid, oxalic acid, and formic acid. The end products of these intermediates are carbon dioxide gas and chlorine atoms. The overall net equation is shown below (Yan and Schwartz, 1999; Yan and Schwartz, 2000; Huang et al., 2001).

\[
C_2HCl_3 + 2MnO_4^- \rightarrow 2MnO_2 (s) + 2CO_2 + 3Cl^- + H^+ \quad (1)
\]

The reaction kinetics is second-order overall, and first order in regards to TCE and all chlorinated ethylenes except vinyl chloride (VC). The reaction follows pseudo first-order kinetics in the ISCO scheme, when MnO$_4^-$ concentrations can be considered to be constant. Activation parameters are documented in literature and can be found in Yan and Schwartz (1999) as well as Huang et al. (2001). Pseudo-first order and second order rate constants listed in literature are shown in Table 2.1.
Table 2.1. Reaction rate constants (first order $k_1$, second order $k_2$) for degradation by MnO$_4^-$ (from 1: Huang et al, 2001; 2: Yan and Schwartz, 1999)

<table>
<thead>
<tr>
<th></th>
<th>PCE</th>
<th>TCE</th>
<th>cis-DCE</th>
<th>trans-DCE</th>
<th>1,1-DCE</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$ ($\times 10^{-4}$ s$^{-1}$)</td>
<td>0.48</td>
<td>11.32</td>
<td>16.8</td>
<td>632</td>
<td>25.4</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.45 ± 0.03</td>
<td>6.5 ± 0.1</td>
<td>9.2 ± 0.5</td>
<td>300 ± 20</td>
<td>23.8 ± 1.3</td>
<td>2</td>
</tr>
<tr>
<td>$k_2$ (M$^{-1}$ s$^{-1}$)</td>
<td>0.03</td>
<td>0.72</td>
<td>1.06</td>
<td>40</td>
<td>1.61</td>
<td>1</td>
</tr>
</tbody>
</table>

2.3. Use of Controlled-Release Permanganate in ISCO

Typical ISCO methods using MnO$_4^-$ involve active flushing of contaminants through the injection of highly concentrated MnO$_4^-$ solution. However, this process forms manganese dioxide (MnO$_2$), a solid reaction by-product that can plug pores and causes fluid bypassing that can considerably reduce the treatment efficiencies (e.g. Lee et al., 2003). The ISCO method of interest in this study involves the use of a controlled release system (CRS) in which KMnO$_4$ granules are dispersed in a diffusion-controlled, polymeric matrix through which it will slowly release, maintaining a predetermined concentration over time. Though MnO$_2$ will still be formed as a reaction product of the oxidation of chlorinated ethylenes, the amount is assumed to be severely reduced as to allow continuous reactions between the oxidant and contaminant.

Advantages of a controlled-release permanganate (CRP) over active flushing processes include lower cost, easy handling, persistent duration, and lower risk of secondary contamination (Lee and Schwartz, 2007). It was, however, suggested that the use of a CRP solid would require multiple adjacent wells to promote lateral spreading to treat contaminant plumes (Lee et al., 2008). In order to reduce the number of wells needed, focus has shifted to a delayed-gelation approach in which a permanganate
solution that gradually increases in viscosity (CRP-G) is injected into groundwater using wells to construct slow-release $\text{MnO}_4^-$ gel in situ for long-term treatment of dissolved plumes of chlorinated ethylenes.
CHAPTER 3: CHARACTERISTICS OF COLLOIDAL SILICA

3.1. Selection of Colloidal Silica as Vehicle for CRP-G

A previous study examined compatibility and gelling properties of chitosan, aluminosilicate gels, silicate gels, and colloidal silica gels as potential gelling agents for the CRP-G (Olson, 2011). Compatibility tests were conducted to measure the rate and extent of degradation of gelling material upon its exposure to a strong oxidant such as MnO$_4^-$- . Gelling tests included monitoring the increase in viscosity of the gelling agents through time. Release tests were conducted to monitor the net mass release from suitable gel forms in water.

Through a series of compatibility and gelling tests, colloidal silica and sodium silicate were identified as potentially suitable gelling agents for the CRP-G. Colloidal silica was chosen as the primary material of interest in this study over sodium silicate gels due to its low initial viscosity and modifiable gelation times. It is also compatible and miscible with MnO$_4^-$-, nontoxic, chemically inert, water insoluble, and can provide a matrix in which diffusion can occur.

3.2. Properties of Colloidal Silica

Colloidal silica is a highly polymerized species of silica that contains amorphous silica particles in suspension in a liquid phase (sol). As a sol, the particles are stably dispersed in liquid. Through the sol-gel process, the colloidal solution (sol) forms an integrated network in which the solid particles form a continuous solid skeleton in which the colloidal particles enclose a continuous liquid phase (gel; Figure 3.1). Through the
gelation process, the amorphous silica particles link together in branched chains that fill the entire volume of the sol (Iler, 1979).

![Diagram of sol-gel process](Figure 3.1. Schematic of sol-gel process (modified from Brinker and Scherer, 1985)).

Although there is no increase in the concentration of amorphous silica, the overall medium becomes highly viscous and solidifies through the coherent network of particles that retain liquid through capillary action. Gelation can be considered a rapid solidification process in which the polymer essentially “freezes” in viscosity at the gel point. The gelation rate of colloidal silica is primarily affected by the ionic strength of the solution and pH, and is secondarily impacted by temperature and concentration of SiO₂ in the silicate sol (Iler, 1979).

3.3. Use of Colloidal Silica in Porous Materials

Colloidal silica has been investigated for use in natural materials (soil, groundwater), primarily in grouting and soil stabilization applications. Jurinak et al.
(1989) investigated the in-situ application of colloidal silica gel as applied to oil field fluid-flow control systems. Colloidal silica has also been investigated for use in soil stabilization studies in areas prone to soil liquefaction (e.g. Gallagher et al., 2007; Gallagher and Lin, 2005); to form secondary containment systems around oil storage tanks and underground storage of contaminants (e.g. McCartney et al., 2011; Persoff et al., 1999); and to form horizontal barriers to halt the migration of contaminants in the subsurface, such as LNAPLs and DNAPLs (Durmusoglu and Corapcioglu, 2000). Its nontoxic properties and initial low viscosity make it an ideal material to use in the subsurface to treat an area with a relatively large radius. The large treatment radius is also practical in implementation procedure to ensure the solution does not form a gel close to the injection well and result in pore clogging within the media and block flow near the injection well.

3.4. Use of Colloidal Silica for Controlled-Release Purposes

Colloidal silica has been the subject of relatively recent research regarding its use as a drug-delivery system, particularly for antibiotics (Vancomycin) and analgesics (Bupivacaine) (e.g. Barbe et al., 2004; Radin et al., 2001; Radin et al., 2008). In the studies of Radin et al. (2001), the use of sol-gel silica gel for antibiotic release was observed to result in a fast initial first order release with subsequent zero-order release to result in steady, long-term (~ 42 days) release. Colloidal silica has been shown to be compatible with biological systems, thus reducing chances for secondary toxicity in groundwater contamination applications (Barbe et al., 2004).
CHAPTER 4: MATERIALS AND METHODS

4.1 Materials and Devices

Granular KMnO₄ was purchased from Sigma-Aldrich and Bindzil 1440. Colloidal Silica was purchased from Wesbond Corporation (Table 4.1). Batch tests were conducted in various HDPE containers with dimensions L x ID = 6.0 cm x 3.5 cm. Column tests were conducted in KONTES Chromaflex Columns with dimensions 15, 60, or 120 cm x 4.8 cm (L x ID) oriented either vertically or horizontally. Water was pumped into column using a peristaltic pump (Cole-Parmer Masterflex L/S).

Table 4.1. Characteristics of Colloidal Silica

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Diameter (nm)</td>
<td>14</td>
</tr>
<tr>
<td>SiO₂, wt %</td>
<td>40</td>
</tr>
<tr>
<td>Na₂O, wt %</td>
<td>0.5</td>
</tr>
<tr>
<td>pH at 25°C</td>
<td>10.4</td>
</tr>
<tr>
<td>Viscosity at 25°C (cP)</td>
<td>15</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Viscosity of select gels was measured using Viscolite 700 (Vindum Engineering; Range 0-10.0 cP; Figure 4.1). Permanganate concentrations were measured using the UV-Visible Spectrophotometer (UV-1800 Schimadzu; Figure 4.2) at wavelength of 525 nm.
Figure 4.1. Viscolite 700 (from Vindum Engineering).

Figure 4.2. UV-Visible Spectrophotometer
4.2 Gelation Tests

For gelation tests, colloidal silica and KMnO₄ granules were mixed in variable ratios (Figure 4.3; Table 4.2) and the subsequent viscosity increase was monitored over time to determine the effect of ionic strength on the gelation rate. The modification of additional water, i.e. dilution, to the gelation of the system was studied in diluted batch tests and column tests conducted with saturated media.

4.2.1 Effect of ionic strength upon gelation time

The gelation process was monitored as the viscosity increased through time, and was assessed both quantitatively and qualitatively in batch and viscosity tests. Gelation in batch tests smaller than 200 mL was assessed relatively as the resistance of insertion and movement of a glass rod as well as visual observation of the state of the solution. A qualitative parallel for this method was established with data from the viscometer and is shown in the following section. The use of qualitative methods to measure gelation is
common in colloidal silica grouting applications (e.g. Persoff et al., 1999; Syndansk, 1990). In the aforementioned studies, gelation was assessed visually and according to resistance to flow, which is considered analogous to the method used in this study.

Gelation was characterized for a simple colloidal silica/KMnO₄ system. Though encapsulation by paraffin wax was considered as a method, proprietary methods and equipment limitation restricted the feasibility of exploration of this modification. The effect of varying ionic strength due to KMnO₄ upon gelation rate of the system was determined through varying concentration of gel solutions. Table 4.2 shows the various gel concentrations manufactured in order to gain an understanding of the nature of the effect of ionic strength upon gelation. Volume of fluid, including water and colloidal silica, was kept constant in these trials while the mass of KMnO₄ added to the solution was altered systematically in order to approach a gelation time of three days.

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<thead>
<tr>
<th>Trial</th>
<th>Mass KMnO₄ (g)</th>
<th>Volume CS (mL)</th>
<th>Concentration (°/ℓ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.15</td>
<td>25</td>
<td>6.00</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>25</td>
<td>8.00</td>
</tr>
<tr>
<td>3</td>
<td>0.23</td>
<td>25</td>
<td>9.00</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>25</td>
<td>10.00</td>
</tr>
<tr>
<td>5</td>
<td>0.28</td>
<td>25</td>
<td>11.00</td>
</tr>
<tr>
<td>6</td>
<td>0.40</td>
<td>25</td>
<td>16.00</td>
</tr>
<tr>
<td>7</td>
<td>0.50</td>
<td>25</td>
<td>20.00</td>
</tr>
<tr>
<td>8</td>
<td>0.63</td>
<td>25</td>
<td>25.00</td>
</tr>
<tr>
<td>9</td>
<td>0.94</td>
<td>25</td>
<td>37.52</td>
</tr>
<tr>
<td>10</td>
<td>1.00</td>
<td>25</td>
<td>40.00</td>
</tr>
<tr>
<td>11</td>
<td>1.25</td>
<td>25</td>
<td>50.00</td>
</tr>
</tbody>
</table>

Table 4.2. Gel solution concentrations in batch tests
4.2.2 Effect of dilution upon gelation time

The effect of dilution upon gel formation is an important factor in ascertaining gel behavior due to the emplacement of the gel solution in flowing conditions where it will encounter dilution through advection-dispersion processes. The general effect of gel dilution with deionized water upon gelation was determined by gelation batch tests in which colloidal silica solutions were diluted with water in a 1:1 ratio (Table 4.3). The effect of dilution of the silica concentration of gels was of primary concern in these trials.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Mass KMnO₄ (g)</th>
<th>Volume CS (mL)</th>
<th>Volume H₂O (mL)</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.250</td>
<td>12.5</td>
<td>12.5</td>
<td>10.00</td>
</tr>
<tr>
<td>2</td>
<td>0.625</td>
<td>12.5</td>
<td>12.5</td>
<td>25.00</td>
</tr>
<tr>
<td>3</td>
<td>1.000</td>
<td>12.5</td>
<td>12.5</td>
<td>40.00</td>
</tr>
</tbody>
</table>

4.3 Release characteristics of CRP-G in open water

Flow through tests were conducted using glass columns (L x ID = 15 cm x 4.8cm) to measure net release rates of MnO₄⁻ from the gelated CRP-G. Deionized water was pumped through columns vertically at a machine-controlled flow rate of 200 rpm using the peristaltic pump. Water was pumped in through the bottom of column, and out throughout the top in order to achieve perfect sink conditions for MnO₄⁻ immediately around the CRP-G forms (Figures 4.4 and 4.5). Effluent of column was collected throughout the span of test, initially at 15-20 minute intervals that were adjusted throughout the course of the experiment. Effluent samples were then monitored for MnO₄⁻ concentrations using the UV-Vis. Actual flow rates were measured throughout the
span of the test to determine instantaneous flow rates during each sampling event.

Mass flux of $\text{MnO}_4^-$ from the CRP-G cylinder was calculated from measured flow rates and concentrations, and used to determine cumulative mass of $\text{MnO}_4^-$ released from the CRP-G cylinder.

Figure 4.4. Column test in open water schematic showing vertical flow of water
4.4 Characterizing spreading, gelation, and release of CRP-G in saturated, porous media

Column flow-through tests were conducted to monitor the spreading, gelation, and release of the colloidal silica-based CRP-G in the presence of saturated, porous media. Glass columns of variable length (L x ID = 60 cm X 4.8 cm , 120 cm x 4.8 cm) were oriented horizontally and packed with coarse-grained silica sand at an assumed porosity of 0.3 (Figure 4.6). Total volumes of the columns were 1.08 and 2.16 L, with estimated residence times of 7 and 14 hrs, respectively, resulting in an average flow velocity of 2.1 m/d. Flow was facilitated in the long column (L x ID = 120 cm x 4.8 cm) by loosening output end to allow free flow of water through sands due to pressure differential created between inlet and outlet of the in column for the duration of each test.
Samples were initially collected in ~ 2 hr samples during the initial periods, and adjusted throughout the remainder of the testing period.

Gels of varying KMnO$_4$ concentrations were pumped in to the column using the peristaltic pump at flow rate of 50 rpm, which yielded a total gel injection time of 24 min. Pump speed was reduced to ambient flow rate of 20, 30 rpm for 60 cm, 120 cm long column, respectively, after gel was injected into column. Gelation within column was observed via video recordings and photographs during the entire periods of column test. The formation of gels were confirmed upon excavation of media from column. Release of MnO$_4^-$ from the gel was monitored through measurements of MnO$_4^-$ concentration of the outflow samples using UV-VIS.

The initial objective of the tests was to achieve gelation within the column before progressing to delayed-gelling approaches. It was noted in batch tests that the addition of water had a dilution effect on the gels, increasing the observed gel time. Once gelation had been achieved in the column the release of MnO$_4^-$ was monitored.

Figure 4.6. Column test with media schematic showing horizontal flow.
CHAPTER 5: RESULTS AND DISCUSSION

5.1 Gelation of CRP-G solution

Gelation tests exhibited characteristic two-phase increase in viscosity: a lag phase characterized by minimal increase in viscosity followed by gelation phase in which viscosity increased rapidly until gel solidification (Figures 5.1 and 5.2.). In the 20.0 mgL\textsuperscript{-1} gel, viscosity increased gradually, remaining below 150 cP for the first 157 min (144 cP) and then underwent rapid gelation to achieve a viscosity of 820 cP by 187 min. In the 25.0 mgL\textsuperscript{-1} gel, gelation followed a similar pattern in which viscosity remained below 150 for the first 90 min (130 cP), and then rapidly gelled to achieve a viscosity of 692 cP by 119 min. This gelation pattern is consistent with other studies conducted on the aggregation of colloidal silica in which the shape of the gel curve is similar regardless of gelation times (e.g. Gallagher and Lin, 2007; Jurinak et al., 1991).
Figure 5.1. Gelation of 20.0 mg/L gel solution through time.
Figure 5.2. Gelation of 25.0 mg/L gel solution through time.

The duration of lag phase of gelation appears to be primarily affected by the salt (KMnO₄) concentration of gel. The effect appears to be logarithmic in nature, yielding increasing lag times ranging from 1 hr to 13 d with decreasing KMnO₄ concentrations of >25 g/L to 8 g/L. (Figure 5.3., 5.4.). This effect indicates that the salt is not only a solution component of gel but also the gel catalyst. This observation is consistent with
other studies (e.g. Gallagher and Lin, 2007; Jurinak et al., 1991; Kobayashi et al., 2005) that used salt, typically NaCl, to modify gel time in grouting applications.

Gelation of colloidal silica is primarily governed by kinetics of the sol-gel process. Sol-gel aggregation is affected by a number of factors, primarily ionic strength and pH, and to a lesser extent by silica concentration, particle size, and temperature (Iler, 1979). The effects of the primary variables including ionic strength, pH, and silica concentration were investigated by other grouting studies, and can be summarized as follows.

The primary focus on modifying gelation can be manipulation of ionic strength. The cation in salt of interest, K⁺, was primarily responsible for aggregation of colloidal solution (Allen and Matijevic, 1969). In the presence of natural water this mechanism is expected to be modified due to the presence of additional naturally occurring cations (Na, Ca, Mg) within the waters. It was beyond the scope of this study to determine whether the effect would be to increase the gelation rate or result in cation exchange within the gel structure, or possibly a combination of both. However, Gallagher et al. (2007) suggested that groundwater salinity had no “detrimental” effects on the gelation of colloidal silica grout, though gel times must be formulated using site water.

Silica sols bear a slightly negative charge when stabilized at high pH and a slightly positive charge when stabilized at low pH. Therefore, sols are stabilized at high pH (9-10) and at low pH (pH = 1-2) and exhibit maximum gelation rate at neutral pH or on the slightly acidic side of neutrality (Carman, 1940). Gelation rate from pH 2-6 is considered maximum (slightly acidic side of neutrality). However, most studies tend to
focus on the extremely acidic and alkaline range so this assumption has yet to be confirmed in the literature.

Silica sols are noted to be stable at high ionic strengths at low pH (Baldyga et al., 2012; Kobayashi et al., 2005). In this case gelation rates are noted in literature to be very low; this is attributed to hydrogens in water bonding to adsorbed cations rather than silanol groups. In the case of Baldyga et al. (2012), the formation of interparticle siloxane groups (gel formation) was not observed.

The colloidal silica solution used in this study was stabilized at pH 10.4 and thus bears a slightly negative charge. As injecting a highly acidic CRP-G solution (pH = 1-2) into natural waters is not considered optimal, stabilization at pH 10.4 was considered ideal. The effect of the low pH upon groundwater species is assumed to result in a highly localized effect and will have to be modeled on a site-specific basis due to its dependence on groundwater conditions.

The dilution of colloidal silica was noted to result in an overall delay in gelation (Figure 5.4). This observation is consistent with other studies in which dilution was utilized to achieve gelation over 75 days (Persoff et al., 1999; Gallagher and Lin, 2005, 2009).
Figure 5.3. Effect of KMnO$_4$ concentration upon gel time.
It has been suggested that there are “several peculiarities” in the aggregation behavior of silica sols, particularly in the presence of alkaline cations (Baldyga et al., 2012). While detailed modeling of CRP-G gelation process was beyond the scope of this study, there are explanations of the gelation of colloidal solutions at very-fine scales. A brief discussion on the mechanisms of aggregation of the gel is presented below.
The Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory has generally been used to provide a framework in the discussion of stability of colloidal suspensions (e.g. Baldyga et al., 2012; Harbottle et al., 2011; Kobayashi et al., 2005). The DLVO theory treats particle interactions within colloidal dispersions as a superposition of repulsive double-layer forces and an attractive dispersion (van der Waals) forces (Kobayashi et al., 2005). This theory predicts a critical coagulation concentration (CCC) that separates the slow aggregation and fast aggregation regime as applied to colloidal suspensions.

However, this theory has limited application in regards to silica sols (e.g. Kobayashi et al., 2005; Milonjic, 1992). It was suggested that observed aggregation rate constants of silica sols show a more complex behavior then that approximated by the DLVO theory. In general, the DLVO incorrectly predicts that the fast aggregation rate constant to be lower than observed, incorrectly predicts the aggregation rate at low pH and high ionic strength to be much higher than observed, and incorrectly predicts an increase in the aggregation rate at pH > 11 (Kobayashi et al., 2005). Additionally, it appears silica sols contain surface forces with short-range repulsion that are not accounted for in the DLVO theory (e.g. Adler et al., 2001). As a result, other hypotheses have emerged to explain the gelation of colloidal silica.

The Gel Layer model, developed by Adler et al. (2001) explains a gel layer on silica as a rigid surface swelled by water. The model proposes a gel layer composed of an unbroken silica network, in which the stress of accommodating water in the structure would limit the maximum thickness. The gel layer is observed to form rather rapidly and with an average thickness of 2.0 nm, and result in a swelled surface layer. The model also
incorporates an additional background electrostatic repulsion to predict coagulation of silica at low pH or high ionic strength. However, the model does not incorporate structural forces within gel layers and suggested that the surface of silica is quite complicated and multiples processes may be occurring.

The Hairy-Layer hypothesis was developed to explain observed anomalies of silica aggregation (Kobayashi et al., 2005). The hypothesis proposes a hairy (or gel) layer consisting of short, flexible, polymer-like poly(silicic acid) anchored to the surface. It explains the additional repulsive forces observed between silica surfaces and accounts for observed particle-size dependence of short-range forces. As a result, smaller deviations from the DLVO theory are predicted with larger particle sizes. This “hairy-layer” is also suspected to induce a strong repulsion at lower pH due to the deprotonation of silanol groups at lower pH; and is predicted to dissolve at higher pH (~12), accounting for the acceleration in gelation rate in slightly alkaline conditions.

It was suggested that at high salt levels and high pH, aggregation rates are fast and close to the diffusion-controlled value (Kobayashi et al., 2005). Diffusion-controlled aggregation occurs as a result of diffusion of particles that aggregate and form clusters or branches, represented as a fractal model of irreversible nucleation in which branches form as a result of non-linear growth process (Jensen et al., 1994; Vicsek, 1983).

5.2 Permanganate Release in Water: Column Tests

Release of MnO$_4^-$ from 25 mL CRP-G cylinders was characterized by initial peak release (0.94- 2.3 mg/min) during the first 60 – 105 min, which was followed by exponential decay of mass flux during the remainder of the testing periods (Figures 5.5 –
5.9). Duration of release from gelled CRP-G cylinder was less than 24 hrs. Details of trials are shown in Table 5.1. The observed heterogeneity in mass flux through release tests is attributed to the heterogeneity within the amorphous gel structure.

Table 5.1. Details of release from CRP-G in column tests conducted in open water

<table>
<thead>
<tr>
<th>KMnO₄ Concentration (g/L)</th>
<th>Time to Peak Release (hr)</th>
<th>Peak Release Mass Flux (mg min⁻¹)</th>
<th>Max Cumulative Release (mg)</th>
<th>Time to Max Cumulative Release (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0</td>
<td>1.0</td>
<td>0.95</td>
<td>197.4</td>
<td>12.3</td>
</tr>
<tr>
<td>10.0</td>
<td>1.3</td>
<td>0.94</td>
<td>186.6</td>
<td>12.3</td>
</tr>
<tr>
<td>16.0</td>
<td>1.0</td>
<td>1.69</td>
<td>313.8</td>
<td>10.0</td>
</tr>
<tr>
<td>20.0</td>
<td>1.0</td>
<td>2.23</td>
<td>396.3</td>
<td>20.3</td>
</tr>
<tr>
<td>25.0</td>
<td>1.8</td>
<td>1.38</td>
<td>541.2</td>
<td>20.3</td>
</tr>
</tbody>
</table>
Figure 5.5. Mass flux and cumulative release from 9.0 mgL$^{-1}$ gel.
Figure 5.6. Mass flux and cumulative release from 10.0 mgL\textsuperscript{-1} gel.
Figure 5.7. Mass flux and cumulative release from 16.0 mgL$^{-1}$
Figure 5.8. Mass flux and cumulative release from 20.0 mgL$^{-1}$ gel.
Studies have shown that there exists a relationship between the silica concentration and hydraulic conductivity of colloidal silica gel (e.g. Persoff et al., 1999) and will therefore affect the behavior of the gel in porous media. Iler (1979) describes gelled colloidal silica as network of particle chains. Within space between gelled silica particles flow can occur, the size of micropores depends on silica concentration. Flow resistance results from viscous drag on water as it flows through tangle of chains of
gelled particles. The observed low value of hydraulic conductivity in colloidal silica results from a highly divided flow path with many small pores. Decreasing silica concentration will increase the space between these chains, which may be considered as a measure of the effective radius of micropores.

In the case of Persoff et al. (1999), the pores are approximated as parallel tubes in which laminar flow of water is described by Hagen-Poiseuille equation (Equation 2).

\[ \Delta P = \frac{8\mu LQ}{\pi r^4} \]

For a fixed pressure gradient (Pa) and viscosity (Pa·s), flow (m³·s⁻¹) through each tube is proportional to the fourth power of the radius (m; approximated by the radius of pore space between chains of silica particles within the gel). Thus, flux, or Darcy velocity, is said to be proportional to the square of the radius. Reducing concentration of silica particles has the effect of increasing the separation between chains of silica particles. This is similar in effect to increasing the pore diameter: increasing permeability.

5.3 Column Tests in Media

Gelation and release times observed in column tests conducted in media do not appear to agree with data from batch tests of this study and release from solidified gel form in open water. Overall, duration of CRP-G gels within column was significantly longer than in open water tests, conceivably due to reduced flow rate through pores and
reduced contact areas between the CRP-G and pore water. Details of column test results are given in Table 5.2.

**Table 5.2. Column test with media results**

<table>
<thead>
<tr>
<th>Trial</th>
<th>Gel Concentration (g/L)</th>
<th>Flow Rate (ml/min)</th>
<th>Residence Time (days)</th>
<th>Gelation (yes/no)</th>
<th>Gelation Lag Time (Hours)</th>
<th>Release Duration (Days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.00</td>
<td>0.29</td>
<td>4.18</td>
<td>yes</td>
<td>1</td>
<td>3.88</td>
</tr>
<tr>
<td>2</td>
<td>23.00</td>
<td>0.58</td>
<td>3.20</td>
<td>yes</td>
<td>3</td>
<td>2.61</td>
</tr>
<tr>
<td>3</td>
<td>22.90</td>
<td>0.52</td>
<td>2.35</td>
<td>yes</td>
<td>6</td>
<td>2.05</td>
</tr>
<tr>
<td>4</td>
<td>22.50</td>
<td>0.94</td>
<td>2.15</td>
<td>no</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>5</td>
<td>21.80</td>
<td>0.63</td>
<td>2.79</td>
<td>no</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>20.00</td>
<td>0.43</td>
<td>2.21</td>
<td>no</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
Effect of dilution of the gel when injected into the column appears to be sensitive to dilution factor of column, which was not experimentally determined. Gelation times were increased when injected into column packed with porous media containing flowing water (Table 5.2; Figure 5.10). In the gelation batch tests, the 25.0 mgL\(^{-1}\) gel gelled in 0.5 hrs, while in the column test the time to gelation was estimated at ~ 1 hr (including injection time). This is a significant increase (100%) in the gelation time from the batch.
tests. However, in diluted gel tests with 100% gel dilution, gel time for the 25.0 mgL\(^{-1}\) gel was 20 hrs.

Release of MnO\(_4^-\) out of gel followed similar pattern to that of open water tests: rapid initial peak release followed by exponential decay. Column tests in media also exhibited an asymptotic release phase after exponential decay of mass flux. This asymptotic release was the longest phase observed in column tests, lasting 20-70 hrs. This asymptotic release is favorable due to the potential to provide a long-lasting method of release of MnO\(_4^-\) into groundwater once emplaced. As with open water tests, mass flux exhibited heterogeneity that is attributed to amorphous structure of silica gel. Details of mass flux in column tests in media are shown in Table 5.3

\textit{Table 5.3. Details of release from CRP-G in column tests conducted in saturated, porous media. }*Time measured after release from gel began.*

<table>
<thead>
<tr>
<th>KMnO(_4) Concentration (g/L)</th>
<th>Time to Peak Release (hr)*</th>
<th>Peak Release mass flux (mg min(^{-1}))</th>
<th>Max Cumulative Release (mg)</th>
<th>Time to Max Cumulative Release (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>1.8</td>
<td>0.38</td>
<td>358.6</td>
<td>530</td>
</tr>
<tr>
<td>21.8</td>
<td>9.2</td>
<td>0.53</td>
<td>382.0</td>
<td>67.1</td>
</tr>
<tr>
<td>22.5</td>
<td>3.2</td>
<td>0.38</td>
<td>348.7</td>
<td>51.6</td>
</tr>
<tr>
<td>22.9</td>
<td>4.8</td>
<td>0.56</td>
<td>479.6</td>
<td>76.9</td>
</tr>
<tr>
<td>25.0</td>
<td>8.2</td>
<td>0.95</td>
<td>450.8</td>
<td>100.2</td>
</tr>
</tbody>
</table>

Gels were optically monitored to assess the relative concentration down the length of column and characterize gel flow. In gels that did not solidify, such as 20.0, 21.8, and 22.5 mgL\(^{-1}\) gels, mass transport appeared to be confined to advective and dispersive transport only (Figures 5.11-5.13). Gels that gelled within column were observed to have
characteristic release patterns (Figures 5.14-5.16). It was noted that gels tended to have initial high concentration in small area before advective transport down column during the peak and exponential decay portion of release. Once gel solidified, \( \text{MnO}_4^- \) mass flux appeared to be driven by diffusion. Mass transport after solidification appears to have an additional diffusion component to mass transport and is linked to the lag phase of mass flux. Gel solidification was determined visually through assessment of the relative change in position of the gel through time, solidification was pronounced when gel appeared as a concentrated region of \( \text{MnO}_4^- \) that did not flow any further down column. Solidification was confirmed upon excavation of sands from the column. Optical data of select column test is shown in picture series (Figures 5.17-5.20)
Figure 5.11. Mass flux and cumulative release from 20.0 mg L\(^{-1}\) gel.
Figure 5.12. Mass flux and cumulative release from 21.8 mg L$^{-1}$ gel.
Figure 5.13. Mass flux and cumulative release from 22.5 mg L$^{-1}$ gel.
Figure 5.14. Mass flux and cumulative release from 22.9 mg L$^{-1}$ gel.
Figure 5.15. Mass flux and cumulative release from 23.0 mg L$^{-1}$ gel.
5.3.1. Dynamics of CRP-G in Saturated Sands: Column Tests with Media

Optical data in the form of photographs and videos were taken throughout the span of column tests to monitor the spreading, gelation and release of the CRP-G within saturated, porous media. Data are shown from select column tests in which gelation within the column is shown to have not occurred (22.5 mg L$^{-1}$) and to have occurred (22.9, 23.0, 25.0 mg L$^{-1}$).
In trial with 22.5 mgL\(^{-1}\) CRP-G, the solution evidently spread through the porous media and spread to distance of ~12 cm after injection that then spread to ~18 cm within the next 1.5 hr, with higher concentrations near gel injection point as indicated by dark purple color of MnO\(_4^-\) (Figure 5.17 a,b). After 24 hrs, solution was visible throughout the length of the column with no distinct regions of higher concentration (Figure 5.17 c,d). After 33 hrs the solution was still visible throughout the length of the column but with no trace of residual MnO\(_4^-\) remaining near gel injection point and higher concentrations near the column outlet point as indicated by dark purple color of MnO\(_4^-\) (Figure 5.17 e). After 48 hrs solution was no longer visible in column and there is no trace of residual MnO\(_4^-\) remaining in column (Figure 5.17 f).

In trial with 22.9 mgL\(^{-1}\) gel, permanganate solution initially spread to distance of 10 cm after injection that then spread to ~28 cm within 2 hrs, with higher concentrations near gel injection point (Figure 5.18 a,b). Gel was observed to form ~6 hrs after injection and was still visible in column at 27 hrs past injection time, with higher concentrations still near injection point. Permanganate had obviously released down length of column and was particularly visible when viewed through bottom of column (Figure 5.18 c,d). Gel was still visible 34.5 hrs after injection time, though in noticeably lower concentrations, as indicated by light purple color, with MnO\(_4^-\) still being released down column length (Figure 5.18 e). After 53 hrs gel was no longer visible although MnO\(_4^-\) was still visible down column length as a remnant of controlled-release (Figure 5.18 f).

In trial with 23.0 mgL\(^{-1}\) gel, permanganate solution initially spread to distance of ~10 cm after injection that then spread to ~20 cm within 1 hr, with higher concentrations observed near gel injection point (Figure 5.19 a,b). Gel formation was observed ~3 hrs
after injection and was still visible in column after 26 hrs, with higher concentrations still near injection point. Likewise, MnO₄⁻ had released down length of column and was particularly visible when viewed through bottom of column (Figure 5.19 c,d). Gel was still visible 53 hrs after injection time, though in noticeably lower concentrations with MnO₄⁻ still being released down column length (Figure 5.19 e). After 72 hrs gel was no longer visible, although MnO₄⁻ was still visible down column length as a remnant of controlled-release (Figure 5.19 f).

In trial with 25.0 mgL⁻¹ gel, MnO₄⁻ solution initially spread to distance of 10 cm after injection that then spread to ~ 20 cm within 1 hr, at which point gelation was observed to result in decreased flow of gel through column (Figure 5.20 a, b). The gel was still visible in column 31 hrs past injection time, with MnO₄⁻ released down length of column and was particularly visible when viewed through bottom of column (Figure 5.20 c). Gel was still visible 51 and 72 hrs after injection time, though in noticeably lower concentrations through time with MnO₄⁻ still being released down column length (Figure 5.20 d, e).
Figure 5.17. Optical data from 22.5 mgL\(^{-1}\) trial.

A) Immediately after pumping. B) 1.5 hour after gel pumped into column. C) 24 hrs after gel pumped into column. D) 24 hrs after gel pumped into column (bottom view). E) 33 hrs after gel pumped into column (bottom view). F) 48 hrs after gel injected into column (bottom view).
Figure 5.18. Optical data from 22.9 mgL$^{-1}$ trial.

A) Immediately after pumping.  B) 2 hrs after gel pumped into column.  C) 27 hrs after gel pumped into column.  D) 27 hrs after gel pumped into column (bottom view)  E) 34.5 hrs after gel pumped into column.  F) 50 hrs after gel pumped into column.
Figure 5.19. Optical data from 23.0 mgL⁻¹ trial.

A) Immediately after pumping. B) 1 hour after gel pumped into column. C) 26 hrs after gel pumped into column. D) 26 hrs after gel pumped into column (bottom view). E) 53 hrs after gel pumped into column. F) 72 hrs after gel pumped into column
Figure 5.20. Optical data from 25.0 mgL⁻¹ trial.

A) Immediately after pumping. B) 1 hour after gel pumped into column. C) 31 hrs after gel pumped into column. D) 51 hrs after gel pumped into column (bottom view). E) 72 hrs after gel pumped into column (bottom view).
The overall pattern to emerge from the optical data of column tests conducted with saturated, sandy media is that gelation that did occur within columns tended to occur within the first 10 cm of column, or near gel injection point. In CRP-G concentrations that did not gel, there was no remnant MnO$_4^-$ solution near injection point following advective mass transport. In tests in which gelation occurred, general concentrations tended to decrease throughout the span of the test, evidenced by the degree of saturation of the purple color of MnO$_4^-$, until reaching an asymptotic release that is reflected in mass flux data collected through sampling of effluent.

Migration of the CRP-G solution in the column filled with saturated sandy media under continuously flowing condition can be described by solving the transient groundwater flow equation and the advection–dispersion equation simultaneously. Here, the transient groundwater flow equation for dense fluid in saturated porous media can be written as:

\[
\frac{\partial}{\partial t}(n\rho) = -\nabla \cdot \{\rho q\}
\]  

(3)

where \( t \) is time, \( n \) is porosity, \( \rho \) is fluid density, and \( q \) is groundwater velocity, described by:

\[
q = \frac{k}{\mu_f} (\nabla P - \rho g \nabla Z)
\]  

(4)

where \( k \) is intrinsic permeability, \( \mu_f \) is fluid viscosity, \( P \) is pressure, \( g \) is the gravitational constant and \( Z \) is vertical distance from datum.
The advection-dispersion equation is written as:

\[ (5) \]

where \( c \) is solute concentration and \( D_{ij} \) is the dispersion coefficient, described by Bear (1972).

There are some computer codes that can solve these equations. An example is MITSU3D (Ibaraki, 1998), which solves equations (1) and (3) simultaneously given some simulation domain, associated boundary, initial conditions and a set of parameters, which include intrinsic permeability, porosity, diffusion coefficient, and longitudinal, transverse and vertical transverse dispersivities, initial solute conditions (source location, initial concentration, and release rate), and initial pressure conditions. Use of computer codes to simulate migration of injected CRP-G in the column setting was prohibited, however, due to the lack of information required for defining boundary and initial conditions, hydraulic properties, and concentration data. Therefore, this study relied on optical and flow data to approximate the impact of dilution to gelation lag times in the column.

It has been noted in trials that gelation within a saturated column packed with porous media will occur in a relatively short period of time (< 8 hrs). Otherwise gelation was noted to not occur at all. This is attributed to continual dilution of the gel as time persists due to the gel spreading dispersively, reducing the gel thickness, as well as increasing the amount of water the gel encounters per unit surface area through time.
Column tests resulted in relatively rapid release of MnO$_4^-$ from cylinder, and was not shown to be an accurate representation of how the same gel would behave within porous media. This discrepancy is thought to be attributed to two factors. The first factor is a stronger diffusion coefficient at gel boundary compared to the tests conducted in porous media due to a higher flow rate and a stronger concentration gradient due to a sharp contact between the gel and water. The second factor is a differing release mechanism. The proposed method of release of MnO$_4^-$ from the solid gel form is swelling-driven release, in which the membrane undergoes a transition from the glassy to a gel state due to hydration of the surface layer. Polymer chains in the gel state are more mobile and thus would allow for the active agent to diffuse out more rapidly than in glassy state (Pothamkury, 1995). Because the gel injected in porous media may never reach the glassy state due to its presence in water, the method of release is likely different from the release through a solidified, geometric gel, and may be strongly affected by an attenuated concentration gradient.

While measuring the space between chains of silica particles is beyond the scope of this study, it is valuable to reconcile the effect of concentration upon both flow of gel through media as well as release rate. Release is theorized to occur more quickly in the presence of a diluted gel due to the larger spaces available for water to flow through. Therefore, the effect of dilution of gel is thought to be two-fold: it decreases the ability for a gel to form within saturated media as well as quicken release from gel matrix once it has formed.
CHAPTER 6: CONCLUSION

The aim of this study was to further the development of a semi-passive in-situ chemical oxidation scheme that uses a delayed in-situ gelation procedure. This study specifically conducted batch, viscosity, and column tests with colloidal silica and KMnO₄ to determine whether colloidal silica has the potential to provide adequate gelation times for the in-situ gelation of the CRP-G, and a suitable diffusional matrix for release to occur in a controlled manner.

Colloidal silica has high potential as an optimal material for the construction of the CRP-G due to the robust control on gelation times that was evidenced in batch tests as well as the asymptotic release that was observed in flow through tests conducted with saturated, sandy media. Extended gelation lag times of up to 13 d were achieved, attesting to the modifiable lag times possible so the CRP-G can flow through porous media before gelation. The original target value of 3 d gelation lag time in saturated, porous media with flowing water will need to be revisited in subsequent studies to ensure that gels can achieve gelation in that time and not become diluted to the extent that it does not achieve gelation within the aquifer. Dilution of the CRP-G in terms of ionic strength and silica concentration have been noted to be key constraints upon gelation, in agreement with other studies conducted the gelation of colloidal silica with different solutes for grouting purposes. Release from CRP-G was observed to last up to 3 d and is characterized by initial rapid short-term release that was followed by a longer, attenuated release phase. Mass flux tended to approach values that are near the desired benchmark mass flux ($\approx 850 \mu g/day$) for this study, and can likely be further reduced with an
increase in silica concentration. An increase in silica concentration may also extend the duration of MnO$_4^-$ release from the CRP-G.
REFERENCES


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