Portland State University

PDXScholar

Dissertations and Theses

Dissertations and Theses

Fall 11-16-2015

Transport of Heat Activated Persulfate and Its Application for In-situ Chemical Oxidation of Residual Trichloroethylene

Lauren Dekker Quig
Portland State University

Follow this and additional works at: https://pdxscholar.library.pdx.edu/open_access_etds

Part of the [Civil and Environmental Engineering Commons](#)

Let us know how access to this document benefits you.

Recommended Citation

Quig, Lauren Dekker, "Transport of Heat Activated Persulfate and Its Application for In-situ Chemical Oxidation of Residual Trichloroethylene" (2015). *Dissertations and Theses*. Paper 2629.
<https://doi.org/10.15760/etd.2625>

This Thesis is brought to you for free and open access. It has been accepted for inclusion in Dissertations and Theses by an authorized administrator of PDXScholar. Please contact us if we can make this document more accessible: pdxscholar@pdx.edu.

Transport of Heat Activated Persulfate and Its Application for In-situ Chemical Oxidation
of Residual Trichloroethylene

by

Lauren Dekker Quig

A thesis submitted in partial fulfillment of the
requirements for the degree of

Master of Science
in
Civil and Environmental Engineering

Thesis Committee:
Gwynn Johnson, Chair
Scott Wells
William Fish

Portland State University
2015

Abstract

In situ chemical oxidation is a promising technology for the remediation of persistent subsurface contamination. Increasingly, the persulfate ion is being studied for use in these systems, both on its own as a strong oxidant and as the precursor to the even more reactive sulfate radical. Persulfate has been shown to treat a wide range of contaminants, from traditional Superfund contaminants such as chlorinated solvents to emerging pharmaceutical contaminants. Additionally, persulfate ISCO can be tailored to site and pollutant specific characteristics based on the method of persulfate activation (e.g., energy and catalysis activation) to the sulfate radical. Thermal activation of persulfate is particularly promising because it can be easily controlled, requires no additional reagents, and commonly creates only non-toxic end products. While persulfate *in-situ* chemical oxidation technology is being commercially used, a mechanistic study of the physical and chemical processes controlling the effectiveness of this remedial approach is not well documented in the literature. Published work characterizing persulfate ISCO largely focuses on reactions in aqueous, batch systems, which fail to provide crucial design data when working with ever transient, multi-phase groundwater systems.

The purpose of this research was twofold. Initial studies characterized the overall transport behavior of unactivated and thermally-activated persulfate (20, 60, and 90°C) in one-dimensional soil column systems packed with a natural sandy porous media. This necessitated the development of a flow-through, temperature-controlled, continuous-

injection system for the delivery of heat-activated persulfate. Finally, as a proof of concept, experiments were conducted to investigate persulfate ISCO as a remedial approach for residual-phase trichloroethylene (TCE), a commonly detected, persistent subsurface contaminant.

At all activation temperatures investigated, persulfate exhibited ideal transport behavior with negligible differences in the observed breakthrough curves of persulfate ion and nonreactive tracers in miscible displacement experiments. Additionally, moment analysis of the breakthrough curves measured for persulfate ion in solution indicated negligible interaction of persulfate with the sandy material under steady-state flow (average retardation factor equaled 1.00 ± 0.021). Persulfate ISCO for residual-phase trichloroethylene (TCE) was characterized at two flow rates, 0.2 mL/min and 0.5 mL/min, resulting in two degrees of apparent persulfate activation, 39.5% and 24.6%, respectively. Both ISCO soil column systems showed an initial, long-term plateau in effluent concentrations measured for TCE indicating steady-state dissolution of pure phase TCE. Effluent concentrations of TCE began decreasing after 75 and 100 pore volumes (normalized for the residual fraction of TCE in individual soil columns) in the 39.5% and 24.6% activated persulfate columns as compared to 110 pore volumes in the control study (flushed with electrolyte only). Pseudo first-order rate constants for the decreasing TCE concentrations were calculated using log-linear regression analysis. The measured reaction rate constants for the control, the 0.2 mL/min (39.5% activation) study, and the 0.5 mL/min (24.6% activation) study equaled 0.044, 0.063, and 0.083 hr⁻¹, respectively.

Additionally, moment analysis of the complete dissolution of TCE in the persulfate/activated persulfate remediation systems indicated approximately 33% degradation/oxidation of TCE mass present.

As shown by this and other work, persulfate has enormous potential as a subsurface remediation technology. A more thorough understanding of the physical and chemical mechanisms controlling the behavior and application of persulfate in the subsurface, especially under transient conditions, is necessary for the growth of this technology. By characterizing heat-activated persulfate under dynamic conditions, describing the overall transport of persulfate/activated persulfate in a natural porous media, as well as a proof of concept for the ISCO treatment of a residual nonaqueous phase liquid, this work aids in improving the implementation of persulfate ISCO systems.

Table of Contents

Abstract	i
List of Tables	vi
List of Figures	viii
List of Symbols and Abbreviations	ix
1 Introduction	1
2 Background and Literature	5
2.1 Persistent Groundwater Contamination	5
2.2 <i>In Situ</i> Chemical Oxidation Treatment Technologies	6
2.2.1 Permanganate	6
2.2.2 Hydrogen peroxide/Fenton's Reagent	7
2.2.3 Ozone	8
2.2.4 Persulfate	9
2.3 Persulfate Chemistry	10
2.3.1 Chemical Properties of Persulfate	10
2.3.2 Methods of Persulfate Activation	11
2.3.3 Persulfate Reactivity	16
2.3.4 Persulfate and TCE	21
2.4 Purpose of Research	22
3 Materials and Methods	24
3.1 Materials	24
3.1.1 Reagents	24
3.1.2 Porous Media	24
3.2 Apparati	25
3.2.1 Batch Controls	25
3.2.2 Heat Activation	25
3.2.3 Soil Columns	26
3.3 Methods	27
3.3.1 Analysis	27
3.3.2 Batch Studies	29

3.3.3	Transport Studies	30
3.3.4	Remediation Studies	31
4	Results and Discussion	33
4.1	Batch Studies	33
4.2	Transport Studies	38
4.2.1	Physical Hydrodynamics	38
4.2.2	Temperature Effects	44
4.3	Remediation Studies	51
5	Future Work and Conclusions	58
	References	60
	Appendix A – Temperature Controller Design.....	68
	Appendix B - Experimental Set-up	70
	Appendix C – Experimental Data	71

List of Tables

Table 1: Select groundwater contaminants and their properties	5
Table 2: Redox half-reactions and potentials for common ISCO species [44]	11
Table 3: Percent mass recovery of persulfate after 9 day batch experiment under a range of conditions. Standard error given for batch reactors containing Accusand.	37
Table 4: Relevant experimental values for NRTs performed over the course of experimentation in column packings A and B.	39
Table 5: Relevant experimental values from thermal activation transport studies done in column A	44
Table 6: Apparent activation gains observed after persulfate has left the heated reservoir in elevated temperature studies	46
Table 7: System properties for remediation studies	52
Table 8: Mass removal for remediation studies	53
Table 9: Activation gains observed after persulfate has left the heated reservoir in transport and remediation studies	57

List of Figures

Figure 1: Relative concentration over time for persulfate activated at 60 and 90°C in a batch system.	33
Figure 2: Relative concentration over time for persulfate and sulfate activated at 90°C in a batch system..	35
Figure 3: Persulfate concentration in batch reactors after 9 days, normalized to starting concentration C_0	37
Figure 4a-b: (a) Arrival waves and (b) elution waves for three separate nonreactive tracers in column packing A.....	40
Figure 5a- c: Arrival and inverted elution waves for (a) NRT 1A, (b) NRT 2A, and (c) NRT 3A..	41
Figure 6a-c: (a) Arrival wave (b) elution wave and (c) arrival and inverted elution waves for nonreactive tracer in column packing B.....	42
Figure 7a-b: (a) Arrival and (b) elution waves for representative NRTs in column packings A and B	43
Figure 8a-b: Comparison of (a) arrival and (b) elution waves for persulfate at three different activation temperatures in column A.	47
Figure 9a-f: Arrival and elution wave comparisons and reproducibility for all thermal activation studies done in column A.....	48
Figure 10a-b: Comparison of (a) arrival and (b) elution waves for 20°C PS-2 and NRT 2A	49
Figure 11: Transport of persulfate (PS), sulfate (SO_4), and total sulfate species (PS + SO_4) as measured in PS 60°C-3.	50
Figure 12: Relative concentration of TCE versus dimensionless time in pore volumes scaled for initial residual TCE content.	52
Figure 13 a-c: Modeled pseudo-first order dissolution for three TCE transport studies. 55	

Figure 14a-c: Concentration of persulfate and sulfate as measured at the effluent of the heated reservoir ("Reservoir") and in the column effluent ("Effluent") as compared to measured concentration of initial persulfate stock concentration ("Initial PS"). 56

List of Symbols and Abbreviations

ATSDR	Agency of Toxic Substances and Disease Registry
BPA	Bisphenol A
BTEX	Benzene, toluene, ethylene, and xylenes
C	Aqueous phase concentration
C ₀	Initial aqueous concentration
d ₅₀	Median particle diameter
DEHP	Di-(2-ethylhexyl)phthalate
E ⁰	Standard oxidation-reduction potential
GC	Gas chromatography
ISCO	<i>In situ</i> chemical oxidation
k	First-order or pseudo first-order rate constant, units of inverse time
LDL	Lower detection limit
MCL	Maximum contaminant level
MTBE	Methyl <i>tert</i> -butyl ether
NAWQA	National Water-Quality Assessment Program
NRT	Nonreactive Tracer
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PCE	Tetrachloroethylene
PFAA	Perfluoroalkyl acids
PFBA	Pentafluorobenzoic acid
ppb	Parts per billion
ppm	Parts per million
PS	Persulfate
PV	Pore volume
R	Ideal gas constant, 8.314 kJ K ⁻¹ mol ⁻¹
T	Absolute temperature, in Kelvin
TCE	Trichloroethylene
UV	Ultra-violet
ZVI	Zero-valent iron

1 Introduction

Though hidden from sight, aquifer systems are an absolutely vital source of freshwater. Exempting the freshwater stored in glaciers and ice caps, there is nearly 100 times more freshwater stored in aquifers as compared to surface water [1]. Approximately 25 to 40% of the world's drinking water [2] and nearly 45% of water for irrigation [3] comes from subsurface systems. The top three groundwater users—China, India, and the United States — pull nearly a quarter of all their water from aquifer systems, withdrawing a combined 475 billion m³ of water per year [4]. With such a heavy dependence on subsurface systems, maintaining the health of aquifers is paramount to providing clean water for residential, agricultural, and industrial uses. Unfortunately, the inherent and complex physical qualities of groundwater systems and the wide variety of pollutants migrating to the subsurface make aquifers difficult to monitor, and when contaminated, a challenge to clean up.

A wide variety of natural occurring and anthropogenic compounds have been found at concerning levels in subsurface systems. The Agency of Toxic Substances and Disease Registry (ATSDR) lists some of the most concerning environmental pollutants at priority Superfund sites. In the top twenty contaminants of concern, a range of chemical classes are represented, including heavy metals, large organic compounds, oil and gas contaminants, and pesticides [5]. In a survey of over 6,000 drinking water wells in the United States, the National Water-Quality Assessment Program (NAWQA) found 22% had

levels of contaminants that are of concern for human health, ranging from agricultural based nitrates, to anthropogenic volatile organic compounds, to naturally occurring radon [6]. This large array of contaminant classes and associated chemistry significantly increases the difficulty in developing effective treatments for contaminated aquifer systems.

Complicating the maintenance and remediation of subsurface systems further, a focus on science and research was not prevalent until the 1970s [7] as the environmental movement gained traction in the United States and around the world. Though the technology continues to develop, traditional remedial approaches for subsurface contamination such as pump and treat and soil vapor extraction are often ineffective, time consuming, costly, and may not be appropriate for all contaminant classes ([7]–[9]). For example, the Baird and McGuire Superfund site in Holbrook, Massachusetts has had a pump and treat system in place since 1993 with no plans to end operation any time soon [10]. Costs for environmental cleanup at hazardous waste sites in the United States are projected as high as \$250 billion dollars between 2004 and 2033 for an estimated 294,000 sites [11]. With the sheer cost and volume of necessary remediation, treatment options that are cost effective, quick, and robust are more and more vital.

In situ chemical oxidation (ISCO) is a remediation technology that has gained increasing attention in recent years. ISCO systems inject a chemical oxidant directly into the subsurface to treat recalcitrant contaminant zones, either by complete mineralization of the pollutant or degradation to less harmful byproducts. There are four oxidants

commonly used: hydrogen peroxide (H_2O_2 or Fenton's reagent), permanganate (MnO_4^-), ozone (O_3), and more recently, persulfate ($\text{S}_2\text{O}_8^{2-}$). These compounds are all effective oxidizers, and two (peroxide and persulfate) can be activated to produce even stronger oxidant radical species, i.e., the hydroxyl radical ($\bullet\text{OH}$) and the sulfate radical ($\text{SO}_4^{\bullet-}$), respectively [8]. Research has shown that physical, chemical, and biological heterogeneities inherent to contaminated subsurface systems often require various and different ISCO technologies to be employed. Understanding the advantages and disadvantages of each treatment approach is crucial to designing the most effective system for remediation.

In situ chemical oxidation has been proven to successfully degrade a wide array of contaminants at the bench scale. Primarily it has been shown to degrade volatile organic compounds [12], chlorinated solvents ([9], [13]–[17]), polycyclic aromatic hydrocarbons ([8], [9], [18], [19]), aromatic compounds, petroleum products (e.g., benzene, toluene, ethylbenzene, and xylene) [9], poly-chlorinated biphenyls, pesticides ([20], [21]), and emerging contaminants such as pharmaceuticals and other personal care products ([22]–[24]). A majority of these studies have been done in batch systems, and few examine the effectiveness of the technology under dynamic (transport) conditions (i.e., in soil column systems) ([25]–[28]). Unfortunately, pilot- and field-scale studies are scarce in the literature, although some research results are available in conference proceedings and industry technical reports ([8], [9]). Though batch studies provide relevant insight for characterizing the overall applicability of ISCO for the remediation of commonly found

subsurface pollutants, more peer-reviewed work under dynamic (transport) conditions is vital to the development of working, full-scale, ISCO treatment systems.

As one of the newest chemical oxidants to be employed in ISCO systems, research characterizing the applicability and effectiveness of persulfate and/or activated persulfate for the remediation of common contaminants found in subsurface systems is needed. Though some knowledge from other chemical oxidant technologies is transferrable, particularly associated with permanganate treatment technologies [8], there are significant gaps in the understanding of persulfate's chemical oxidation behavior. For example, the effectiveness of ISCO using persulfate and its applicability to contaminated subsurface systems is expected to be a function of the various methods of persulfate activation (e.g., iron, biochar, pH, ultraviolet light, and heat), the complexities of subsurface environments, and the properties of common contaminants of concern.

This study aims to characterize the overall transport behavior of persulfate and heat-activated persulfate in a natural porous media. Soil column studies were conducted to investigate the physical and chemical processes controlling the transport of persulfate and activated persulfate under different degrees of activation as a function of activation temperature. This research included the design of a temperature-controlled flow apparatus to deliver a steady-state concentration of thermally-activated persulfate to a soil column system. Additionally, the effectiveness of thermally-activated persulfate as an *in situ* chemical oxidant for the remediation of residual trichloroethylene (TCE) in a natural porous media was characterized in a flow-through soil column system.

2 Background and Literature

2.1 Persistent Groundwater Contamination

As water becomes an ever more precious resource, the cleanup of contaminated aquifers for human use is becoming more vital. More than 80% of Superfund sites in the United States have degraded the health of local aquifers, and some 500 more sites have the possibility to adversely affect nearby supply wells [29]. The most common classes of contaminants found at Superfund sites are volatile organic compounds (e.g., trichloroethylene and tetrachloroethylene), semi-volatile organics (e.g., polycyclic aromatic hydrocarbons), and heavy metals [30]. Data for some representative subsurface contaminants are shown in Table 1.

Table 1: Select groundwater contaminants and their properties

Contaminant	ATSDR Rank [5]	Percent Frequency [5].¹	US Drinking Water MCL [31].²	Example Adverse Health Effects [31]
Arsenic	1	86.2%	0.010 ppm	Skin irritation, paralysis carcinogen
Polychlorinated Biphenyls (PCBs)	5	41.4%	0.050 ppb	Hearing/vision problems, cancer, liver damage
Benzene	6	73.5%	0.005 ppm	Anemia, carcinogen
Polycyclic aromatic hydrocarbons (PAHs)	9	30.3%	0.010-0.040 ppb ³	Endocrine disruption, carcinogen
Trichloroethylene (TCE)	16	79.0%	0.005 ppm	Liver damage, carcinogenic
Di-(2-ethylhexyl)phthalate (DEHP)	77	56.8%	0.006 ppm	Endocrine disruption, liver damage, carcinogen

(1)—Percent frequency out of 1322 NPL sites as of the release of ATSDR's 2013 Priority List.

(2)—MCL = Maximum contaminant level

(3)—Range given for PAHs with EPA MCL Values

As indicated by the high frequency of many of these pollutants, many Superfund sites are contaminated with multiple and diverse compounds. This makes cleanup even more complex, and stresses the need for treatment technologies that are effective on a wide variety of compounds. While the sheer number and complexity of contaminated sites is troubling enough, many of the pollutants at these sites also exhibit high toxicity to humans at low levels.

2.2 *In Situ* Chemical Oxidation Treatment Technologies

One treatment technology that has been increasingly studied in recent years is *in-situ* chemical oxidation (ISCO). ISCO involves the injection of a chemical oxidant species into the subsurface to degrade recalcitrant compounds susceptible to redox reactions. The oxidant species work by removing electrons from the contaminant of concern (COC), either breaking the compound down completely or transforming it into less hazardous products. The most common oxidants currently used are hydrogen peroxide (H_2O_2 or Fenton's reagent), permanganate (MnO_4^-), ozone (O_3), and more recently, persulfate ($\text{S}_2\text{O}_8^{2-}$). As with any technique, each method has its advantages and disadvantages. For reference, some of the benefits and challenges of the prominent ISCO technologies are listed below.

2.2.1 Permanganate

Permanganate is the most widely studied chemical oxidant, with literature describing the process from bench to the field scale (e.g., [7], [8], [27], [30], [32]–[34]).

Different half reactions dominate under different pH conditions, but all cases involve the oxidation of manganese present in permanganate. Permanganate has been shown to be highly effective with chlorinated alkenes, both in the aqueous and nonaqueous phase, but less so with alkanes, aromatics, and polychlorinated biphenyls. The reactivity of the permanganate ion is broad, but nonspecific. In the subsurface, this often means that permanganate use is inefficient, as the oxidant is lost to side reactions driven by natural oxidant demand. Due to its high solubility, permanganate can be injected at high concentrations, leading to density driven transport that has been shown to improve its distribution in subsurface systems [35]. A wide variety of aquifer systems, from fractured bedrock to clay-silts (e.g., [8], [30], [34]), have been successfully treated with permanganate, however, there are several byproducts, particularly solid MnO_2 and gaseous CO_2 , that can lead to inefficient mass transfer associated with decreases in the matrix permeability [36]. While subsurface biomes appear to recover quickly after permanganate ISCO, there is little data on long-term impacts to groundwater quality due to process byproducts ([8], [37]).

2.2.2 Hydrogen peroxide/Fenton's Reagent

Hydrogen peroxide when activated with ferrous iron (Fe^{2+}) can produce the hydroxyl radical ($\bullet\text{OH}$), an incredibly reactive, non-specific oxidant. The high degree of reactivity means that the radical can break down a wide variety of contaminants. For example, radical chain reactions can form new radical and ion species, such as the superoxide radical ($\bullet\text{O}_2^-$), and peroxide anions (HO_2^-), which may act as reducing agents

in the subsurface. Because of these reductive species, hydrogen peroxide systems could be designed to treat pollutants susceptible to both oxidation and reduction [8].

The rapid rate of both peroxide breakdown and radical reaction means that the long-term persistence of the oxidant in the subsurface post application is not a concern; however, that high reactivity and rapid reaction rate can make the oxidant mixture difficult to deliver far past the injection site. For example, researchers have shown that while the hydroxyl radical is highly reactive to a wide range of chemical species, it has a tendency to be scavenged by other compounds in the subsurface ([38], [39]). Additionally, some subsurface sites employing peroxide ISCO have reported higher contaminant levels after treatment due to mobilization of nonaqueous phase liquids and migration of heavy metals (e.g., [8], [34], [37]). Researchers have also reported that large quantities of heat and gas can be produced on the application of hydrogen peroxide/Fenton's reagent, causing the melting of ISCO equipment, asphalt buckling, and even fire ([34], [40]). While these byproducts can be dangerous, they have also been shown to contribute to an increase in mass transfer between the contaminant and oxidant [37].

2.2.3 Ozone

Ozone has been injected as a subsurface treatment similar to air sparging. Ozone has relatively broad reactivity, and in combination with water or hydrogen peroxide can form the hydroxyl radical as well. This broad reactivity means that ozone reacts

nonspecifically in the subsurface, and it is often consumed in non-productive side reactions by more readily-oxidized aquifer materials (e.g., cationic metals) rather than the contaminant of concern ([8], [34], [41]). Research has shown that ozone is more reactive in the gas phase, making it a valuable tool for treatment in the unsaturated zone while ozone's low aqueous solubility makes it less effective for treating contaminants in the saturated zone [8]. When injected as a gas, the formation of air channels in the subsurface is essentially random, limiting the extent of ozone delivery to target areas of concern ([41], [42]). Additionally, special equipment (e.g., 316 stainless steel and Teflon seals and gaskets) is often needed due to ozone's corrosive effect at the high pressures needed for injection as other common materials (e.g., galvanized steel, natural rubbers, polypropylene) are prone to ozone cracking and oxidation [43]. Ozone is also a regulated air pollutant and can increase volatilization of subsurface contaminants as well, making vapor control an important part of any field-scale treatment design [8].

2.2.4 Persulfate

Persulfate, or peroxydisulfate, is the most recent compound being investigated for remediation purposes. Its strong oxidant properties have been well characterized in the literature (e.g., [8], [9], [44] and sources therein). For *in situ* chemical oxidation, persulfate is an attractive reagent for several reasons, in part because of the high oxidizing potential associated with both persulfate and its associated decomposition products. While unactivated persulfate itself has a high standard potential, upon activation, persulfate decomposes to form the even more active sulfate radical ($\text{SO}_4^{\bullet-}$). The persulfate ion is

also a promising technology because of the multiple ways that activation to the sulfate radical can occur. This allows for tailoring to a specific site and compound for more effective remediation.

2.3 Persulfate Chemistry

2.3.1 Chemical Properties of Persulfate

Several characteristics of persulfate make it particularly attractive as an aquifer remedial technology. In particular, it is readily available in a salt form as sodium, potassium, or ammonium, although the sodium salt is preferred due to its high aqueous solubility and low environmental impact. With a solubility of 73 g/L at 25°C [45], highly concentrated solutions of sodium persulfate can be created, facilitating density driven mass transport in the subsurface. The byproducts of oxidation-reduction reactions with sodium persulfate are sodium and sulfate ions, two compounds without enforceable water quality standards ([46], [47]). On a weight basis persulfate is also cost-competitive at approximately \$1.20/lb. [8]. Persulfate is highly stable at ambient temperatures, with a half-life of approximately 50 days when no activation sources are present at 20°C in aqueous solution [48].

For comparison, the relevant redox reactions and reduction potentials of persulfate, the sulfate radical, and other chemical oxidants are given in Table 2. Of the common oxidants used for ISCO, only the hydroxyl radical has a higher redox potential than that of the sulfate radical.

Table 2: Redox half-reactions and potentials for common ISCO species [44]

Compound	Redox Half Reaction	Redox Potential, E ⁰
Persulfate	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	2.01 V
Sulfate Radical	$SO_4^- \bullet + e^- \rightarrow SO_4^{2-}$	2.60 V
Hydrogen Peroxide	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.77 V
Hydroxyl Radical	$OH \bullet + e^- \rightarrow OH^-$	2.70 V
Permanganate (natural pH)	$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2(s) + 2H_2O$	1.70 V
Ozone	$O_{3(g)} + 2H^+ \rightarrow O_{2(g)} + H_2O$	2.07 V

2.3.2 Methods of Persulfate Activation

Zhang et al. [44] categorized the activation methods of persulfate into two primary types: energy activation and catalyzer activation. The former indicates a system where energy is applied, as heat, radiation, or photochemically, to encourage the breakdown of persulfate to sulfate radicals. The latter, catalyzer activation, refers to processes that use another chemical species, generally transition metals, acids, or bases, to create sulfate radicals.

Energy activation systems work by providing enough energy, through heat or light, to sever the peroxy (oxygen-oxygen) bond in the persulfate ion, generating two sulfate radicals, as shown in equation (1):

Thermal activation has been studied largely at the bench scale, with promising results for a wide variety of environmental contaminants ([12], [14], [16], [22], [49]–[51]). Multiple studies have shown that higher temperatures led to a higher rate of decomposition of persulfate to form the sulfate radical ([12], [16], [48]). Studies have also shown that the reaction in equation (1) follows the Arrhenius equation (e.g., [48], [52]). While heat activation of persulfate under higher temperatures lead to a both higher potential for species oxidation and percent removal for most compounds, some researchers have shown that higher temperatures can release sulfate radicals too quickly to provide adequate remediation [9].

The characterization of heat-activated persulfate as a chemical oxidant are largely reported in the literature for batch systems, wherein researchers achieve thermal activation by simply heating the batch reservoir to temperature (e.g. [12], [22], [51], [53]). While characterizing the kinetics of chemical oxidation by persulfate, this method is highly unrepresentative of the technical approach necessary to employ persulfate as an *in situ* treatment technology in subsurface systems. For example, at the field scale it is likely that persulfate would be heat activated on the surface and then pumped into the subsurface, or that heating technologies (e.g., radio-wave heating or steam injection) would be applied to the aquifer following the injection of persulfate [16]. Ultraviolet light, most often a mercury lamp at 254 nm, and even visible light have also been used to provide the energy needed for the reaction in equation (1) to go forward. However, due to the low penetrating power of these wavelengths, most work examines the UV-

activation of persulfate for treatment of wastewater rather than subsurface contamination [44].

Outside of energy activation, the most common method of persulfate activation in ISCO systems is cationic metal catalysis. The generic reaction for persulfate activation by metal catalysis is shown in equation ((2), [44]):

Metal catalysis is slightly less efficient in its activation of persulfate, as only one sulfate radical is produced per persulfate ion. In addition, persulfate activation by metal catalysis suffers from scavenging of the sulfate radical by the same metals used for activation, as well as unproductive reactions of persulfate with metal cations as shown in equations (3) and (4), respectively [44].

Clearly, these reactions can be incredibly detrimental to treatment efficiency when using metal-activated persulfate ISCO. Several researchers have investigated the proper balance of oxidant to activation method for persulfate ISCO [e.g., 26]. For example, on activating persulfate with iron, the use of chelating agents and sequential additions of ferrous iron have been studied to decrease the extent of those reactions in equations (3) and (4) by limiting available iron. Chelating agents can also recycle trivalent iron (Fe^{3+})

back to its divalent form (Fe^{2+}), thus increasing the amount of ferrous iron able to activate persulfate by reaction (2). Iron chelation not only affects the reactivity but is also necessary to keep iron in solution at concentrations that are viable for persulfate activation ([8], [44]).

Researchers have shown various metals can act to catalyze the activation of persulfate. For example, zero-valent iron (ZVI) has also been used with success to activate persulfate ([18], [54]–[56]), as well as several other metals, such as silver (Ag^+), cobalt (Co^{2+}), and nickel (Ni^{2+}) ([33], [57], [58]). Of those metals characterized in the literature, silver has been shown to be the most effective persulfate activator [33]; however, its environmental impacts far outweigh the benefits of increased activation efficiency. Iron is the most commonly employed metal activator for several reasons. It is largely prevalent in the subsurface and has low environmental toxicity. Additionally, much research has been done using iron as an activator in other systems, primarily for hydrogen peroxide (e.g., Fenton's reagent), and some of those application techniques are transferable to the application and remediation of subsurface systems using iron-activated persulfate ISCO. Unfortunately, iron has limiting transport behavior in the subsurface, and iron activation of persulfate above ground, prior to injection, can mean significant reductions in the amount of persistent radical reaching the contaminated zone. Researchers have shown naturally occurring iron may also be effective at persulfate activation, but that science is still in its infancy ([57]–[59]).

While energy and iron activation are the most well studied activation methods for persulfate, another common technology is pH-dependent activation. Alkaline activation is achieved by increasing the pH to highly basic conditions, generally with pH greater than 10. Equation (5) describes the activation of persulfate under these conditions [60].

Under alkaline conditions, the hydroxyl radical can also be formed as shown in equation (6):

The activation of persulfate under these conditions is very rapid, so much so that it can be difficult to treat far past the injection zone. The hydroxyl radical, while very powerful (i.e., a high redox potential), also has a very short half-life in the subsurface. The rapid reaction of both radicals, as well as the stoichiometry in reaction (5), makes alkaline activation less efficient than other activation methods ([9], [44]). However, because of ease of mixing and technology transfer from the more developed Fenton's reagent technologies, this is the most common activation method in field studies and commercial applications to date (e.g. [34], [61], [62]). Unfortunately, there is little peer-reviewed literature available describing these efforts, as most sites are done by commercial rather than academic enterprises.

2.3.3 Persulfate Reactivity

Upon activation and regardless of activation method, persulfate is reactive with a broad range of common subsurface contaminants. As the sulfate radical is effective in withdrawing electrons, contaminants with substituent groups prone to electrophilic reactions are generally more susceptible to oxidation by the persulfate/sulfate radical system [44]. Persulfate has exhibited strong remediation potential for many of the key classes of compounds found at contaminated subsurface sites. This includes chlorinated alkanes and alkenes, polycyclic aromatic hydrocarbons, petroleum hydrocarbons, pesticides, and dyes. Promising research has also been done on some emerging contaminant classes, including endocrine disruptors, pharmaceuticals, and personal care product additives. Current research concerning persulfate treatment of some choice contaminant classes is discussed below.

Halogenated Compounds

As one of the more prevalent subsurface contaminants, a great deal of attention has been paid to ISCO treatment of halogenated compounds. For example, Costanza et al. showed in batch reservoirs that tetrachloroethylene (PCE) could be effectively mineralized to CO₂ and chloride ions by persulfate activated above 50°C. In soil slurries, they also observed a wide variation in PCE degradation (0%-90%) over 80 minutes of reaction time for several reference soils. The low degradation rates in some slurries are presumed to be due to those slurry soils containing large natural oxidant demand and a higher amount of reduced species all competing for sulfate radicals [17]. A similar range

of removal efficiencies was seen for PCE when persulfate was activated by a basic oxygen furnace waste slag, with greater degradation efficiencies reported for increasing ratios of persulfate to activator species [63]. Pure, nonaqueous phase PCE was also treated in a column system simulating contamination in fractured bedrock, with maximum removal rates of 2600 mg/L per day when using iron-activated persulfate and a 1.8-20% removal of total tetrachloroethylene mass. Rebound occurred after persulfate injection ceased, and significant residual concentrations remained after treatment [28].

1,1,1-Trichloroethane, a particularly recalcitrant compound, was fully degraded after 2 hours by persulfate activated at 50°C when mixed in batch ratio of 100:1, though in field applications complete degradation would likely not occur due to competitive reactions with oxidizable material in the porous matrix [64]. Huang et al. treated a mixture of 59 VOCs with 1-5 g/L of persulfate activated between 20°C and 40°C in batch systems. Their study results indicate that persulfate preferentially oxidized alkene and substituted phenyl compounds over alkanes, with 37 of 59 contaminants having 90% or greater removal efficiencies after 72 hours in solution with 5 g/L of 40°C activated persulfate [50]. Discussion of the peer-reviewed literature for persulfate's degradation of trichloroethylene is discussed further on.

Oil and Gas

Contamination from oil and gas related products is prevalent throughout the United States, and is the site of many small scale ISCO field treatments [34]. Persulfate

has proved an effective remediation tool for common contaminants found at these sites (e.g., MTBE, BTEX, PAHs, and other aromatic compounds). For example, Deng et al. [65] showed the impacts of different activation methods on the removal of MTBE, a legacy contaminant used as a gasoline additive. Heat (40°C), iron, and alkaline-activated persulfate (40.5 g/L) were able to degrade 100% of 1000 ppm MTBE within 12, 100, and 600 hours, respectively. Only heat-activated persulfate also fully oxidized the degradation products of MTBE (within approximately 300 h) [65]. Huang et al. [50] found the half-life of 5 ppm MTBE to be less than one hour at an 8 g/L persulfate dose when heated to 40°C. Another study examined aqueous solutions and soil slurries spiked with BTEX and exposed to 24 g/L persulfate activated by iron. They found half-lives for BTEX to be in the range of 3-7 days for solely aqueous systems as compared to 1-2 days in both the aqueous and sorbed-phase (i.e., soil slurries) [66]. Phenol was transformed into an insoluble polymer by persulfate at 70°C, making it an effective treatment for contaminated wastewater [51]. Other studies have shown phenol-based compounds can be mineralized by room temperature persulfate reactions [67].

Studies examining complex matrices taken from contaminated sites illustrate how site dependent and variable persulfate treatment can be. Liao et al. [19] and Zhao et al. [49] examined persulfate-based remediation of PAHs in soils from a contaminated coking site. Of the 16 PAHs studied, Liao et al. found 80 to 87% degradation in both the aqueous and sorbed-phase, although some oxidation byproducts saw an increase in concentration over the treatment period. Longer treatment and higher oxidation doses were effective

in removing those byproducts as well [19]. Zhao et al. [49] have shown that heat-activated persulfate (60°C) effectively degraded over 99% of PAHs studied, while iron-activated persulfate degraded between 73 and 83% of PAHs studied. No oxidative effects were seen when persulfate was activated in alkaline conditions [49].

In one of the few pilot-scale studies available in the literature, 2000 liters of unactivated persulfate were injected into the subsurface to remediate a gasoline source zone. Ethylbenzene, naphthalene, and petroleum hydrocarbon concentrations were reduced by approximately 40% when taking into account rebound after treatment ended. Increased concentrations in CO₂ indicate complete mineralization of contaminants [68]. In another study, sediment contaminated from oil-sand production with carboxylic acids was effectively treated by 10 g/L persulfate at ambient temperature, with 100% mineralization within 110 days [69].

Emerging Contaminants

Activated persulfate has also been shown to be an effective treatment technology for new and emerging contaminants such as pharmaceuticals and additives to personal care products. In one study, between 60 and 100% of a saturated solution of ibuprofen was degraded using heat-activated persulfate at temperatures ranging from 50-70°C [69]. Ji et al. [24] showed the effects of iron-activated persulfate on the removal of two representative antibiotic compounds at micromolar concentrations, reaching maximum

removal efficiencies of 95.8 and 74.7% after 4 hours. Other promising work has been done with other medications and antimicrobial products (e.g., [44], [70]–[72]).

Pharmaceuticals are not the only emerging contaminants that have proven responsive to persulfate oxidation. Bisphenol A (BPA), an endocrine disrupting compound found in plastics, was treated with a coupled system using ultrasound and a low concentration of persulfate. Persulfate alone was shown to completely breakdown 225 ppb BPA at 70°C within 60 minutes; paired with ultrasound, the same solution was degraded within 10 to 45 minutes [73]. In one of the few available column studies, a range of perfluoroalkyl acids (PFAAs), which are used as additives in flame retardants and other applications, were tested in a bench scale ISCO system [27]. While significant losses in mass were not observed, ISCO treatment appeared to increase sorption of the longer chain PFAAs when compared to transport behavior without oxidant present, likely due to changes in aqueous and soil chemistry (pH, ionic strength, changing soil organic matter, etc.). The lack of transformation may indicate a need for process optimization, considering promising batch studies in the literature. Other studies have shown high degrees of mineralization of micromolar concentrations of PFAAs using persulfate in aqueous systems ([74]–[76]). Heat-activated persulfate was also used to treat mature landfill leachate with high concentrations of ammonia and refractory organic compounds (measured as chemical oxygen demand), with removal efficiencies of up to 91 and 100%, respectively [77]. Polyvinyl alcohol, an additive in multiple industries from textiles to

pharmaceuticals, was completely oxidized by both thermal- and iron-activated persulfate in 30 minutes and 2 hours, respectively [56].

2.3.4 Persulfate and TCE

Trichloroethylene (TCE) is one of the most commonly detected environmental contaminants and has been the focus of a great deal of ISCO and specifically persulfate ISCO. Most research has been done in batch systems with TCE aqueous-phase concentrations at approximately 60 mg/L, a fraction of TCE's saturation concentration of 1100 mg/L. A majority of available literature on the degradation of TCE using ISCO focuses on thermal- and iron-activation of persulfate, with promising results in both cases. With few exceptions ([25], [26]), the available peer-reviewed research characterizing persulfate ISCO of TCE have been conducted in batch systems. It may be of interest to note that most of that research has been done in purely aqueous phase TCE, rather than TCE-contaminated soil systems. There are some commercial examples of field treatment of TCE by persulfate, but the details are not available due to use of proprietary technologies (e.g., [34], [61], [62]). As other studies have illustrated the effects of soil properties and chemistry on remediation attempts employing ISCO, such as changes in fraction of soil organic carbon, microbe activity, and permeability ([28], [57], [78], [79]), it is clear that the physical, chemical, and biological heterogeneities associated with contaminated subsurface systems may require various and different ISCO remediation technologies to be employed.

2.4 Purpose of Research

Persulfate ISCO is a very promising technology for a wide range of commonly found pollutants in subsurface systems. A review of the literature indicates a great deal of peer-reviewed data is lacking describing its chemistry and behavior on application in subsurface environments. The purpose of this work is to characterize the overall transport behavior and remediation effectiveness of persulfate and heat-activated persulfate in a natural porous media contaminated with pure, nonaqueous phase trichloroethylene. Heat activation of persulfate was chosen for this study due to its low environmental impact and ease of control and characterization. This research included batch studies and dynamic (transport) studies carried out in one-dimensional flow, packed soil columns. These results are expected to aide in the application and design of persulfate ISCO remediation technologies. This research was conducted in three stages: batch work on activated and unactivated persulfate; column work to investigate the overall transport behavior of activated and unactivated persulfate in natural porous media; and finally remediation studies under dynamic (transport) conditions, as proof of concept for a heat-activated persulfate ISCO treatment system. Batch work was done to quantify the degree and reaction kinetics of persulfate activation at elevated temperatures, i.e., 60°C and 90°C. These batch studies included experiments to qualify the degree of mass losses of persulfate to mechanisms other than activation, such as volatilization or sorption/interaction to natural sandy material and/or experimental apparatus. Miscible displacement experiments were done in conjunction with nonreactive tracer experiments

to determine the unique transport behavior of persulfate activated to different degrees at different activation temperatures (20, 60, and 90°C).

Column studies were conducted with TCE established at residual concentrations and flushed with 10 mM, heat-activated persulfate at two flow rates, 0.2 mL/min and 0.5 mL/min, resulting in two degrees of maximum apparent persulfate activation, 39.5% and 24.6%, respectively. These final studies served as a proof of concept for a thermally-activated persulfate ISCO remediation system for a dense nonaqueous phase liquid source zone.

3 Materials and Methods

3.1 Materials

3.1.1 Reagents

Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, 98%) was sourced from Alfa Aesar (Ward Hill, MA). Potassium iodide (KI, 99%) and sodium bicarbonate (NaHCO_3 , >99.7%) for persulfate analysis were also purchased through Alfa Aesar. Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, >99%) and sodium sulfate (Na_2SO_4 , >95%) were obtained from Thermo Fisher Scientific (Waltham, MA). Sulfa4 Powder packs for sulfate (SO_4^{2-}) analysis were obtained through Cole-Parmer (Vernon Hills, IL). Pentafluorobenzoic acid ($\text{C}_6\text{F}_5\text{CO}_2\text{H}$, 99%) was also purchased through Alfa Aesar. Trichloroethylene (C_2HCl_3 , $\geq 99.5\%$) was purchased through Sigma-Aldrich (St. Louis, MO).

3.1.2 Porous Media

Accusand, a commercially available milled silica sand (Unimin Corporation, New Canaan, CT), was used as the representative porous media for both batch and column experiments. The 40/50 mesh sand chosen has a d_{50} of 0.39 mm and a particle density of 2.65 g/cm^3 . Prior to use, all sand was cleaned via sonication and rinsed with nanopure water. Sand was sonicated for an hour, stirring every 5 minutes, in a Branson 2510 water bath sonicator (Branson Ultrasonics, Danbury, CT). The sand was then rinsed with approximately 10L of nanopure water and allowed to air dry.

3.2 Apparati

3.2.1 Batch Controls

For unactivated persulfate studies, 20-mL glass scintillation vials fitted with HPDE screw caps were used as batch reactors. These reactors were placed horizontally on a wire rack and firmly secured to prevent damage. The wire rack with reactors was then placed on a Vibrax-VXR orbital shaker (IKA, Wilmington, NC) to agitate samples over the course of the experiment.

3.2.2 Heat Activation

A temperature controlled heating apparatus was designed and built to perform controlled, steady-state heat activation of persulfate at 60 and 90°C. The heating reservoir was a 250-mL flask fitted with a rubber stopper with ports drilled for inlet and outlet tubing as well as a K-type thermocouple. A programmable REX-C100 PID temperature controller (RKC USA, South Bend, IN) connected to the thermocouple then modified voltage input to a wired outlet. This built temperature controller was equipped with a standard plug, and as such was designed to be used with any bench-top heating element, controlling the temperature within $\pm 1^\circ\text{C}$, after an initial 20 minute equilibration time. A Glas-col heating mantle (Terre Haute, IN) was used as the heating element for these experiments as it could easily be placed on a Thermix 120S stir plate (Fisher Scientific) to allow for adequate mixing in the reservoir.

For column experiments, this same temperature-controlled system was used with modifications for inlet and outlet flow. Fresh 10 mM persulfate was pumped into the

heated 250-mL reservoir at 0.5 mL/min by an AcufLOW Series II HPLC pump while heat-activated persulfate was drawn out at the same flowrate with a Q Pump (Fluid Metering Inc., Syosset, NY). This process was carried out for a minimum of two residence times (approximately 12 hours) to ensure a constant concentration of activated persulfate on the effluent end of the system. The Q pump was then switched out for a second AcufLOW Series II HPLC pump during the injection and elution portions of the soil column experiments. This system behaved as a continuously-stirred tank reactor at steady-state, allowing the delivery of uniform concentrations of persulfate/activated persulfate as influent to the soil column systems.

3.2.3 Soil Columns

All flow-through experiments were conducted in vertically-positioned, 316-stainless steel columns averaging 7.0 cm in length and 2.2 cm in diameter (Alltech Chromatography). Endcaps were fitted with 0.5- μ m thick porous frits and distribution plates to ensure uniform flow over the cross-sectional area of the column. All tubing and fittings for the HPLC pumps and soil columns were composed of 316-stainless steel. All soil columns were homogeneously dry-packed with clean Accusand. The dry packing included the positioning of discrete layers of sand, with scoring and weighted tamping between each layer to interlock those layers and ensure as much physical homogeneity as possible. For all soil column experiments, an AcufLOW Series II HPLC pump delivered the injection and elution pulses.

3.3 Methods

3.3.1 Analysis

A U-1800 UV-Visible spectrophotometer (Hitachi, Tokyo, Japan) was used for analysis of PFBA, persulfate and sulfate concentration in both batch and column experiments. PFBA analysis during nonreactive tracer (NRT) experiments was conducted using the spectrophotometer at 226 nm. Standardization of the UV-Vis for PFBA analysis included a minimum ten-point calibration curve, providing a concentration range from 525 mg/L to a lower detection limit of approximately 1 mg/L. Sample and standards with concentrations above 175 mg/L were diluted to keep absorbance within the range of the UV-Vis.

Persulfate concentrations in solution were analyzed using a modified iodometric titration method [80]. Samples were diluted as needed, and then an aliquot of sample was added to a premade solution of potassium iodide (KI) and sodium bicarbonate (NaHCO_3) at 100 g/L and 5 g/L, respectively. The ratio of sample to KI- NaHCO_3 solution was held at 1:19 (m:m). After a 20-minute reaction time, three discrete measurements of sample absorbance were taken using with the UV-Vis set at a wavelength of 400 nm. A minimum ten-point calibration curve was created on the day of analysis by serial dilutions of a stock sodium persulfate solution, detecting a range of approximately 50 to 1 mg/L of sodium persulfate after the 1:19 dilution associated with the iodometric method.

Sulfate was measured using Sulfa4 powder packs, a proprietary reagent mix. Samples were diluted below 70 mg/L sulfate as needed for a total sample volume of 10

mL. A single powder pack was then added, and the sample was allowed to sit undisturbed for a reaction period of 5 minutes. Three discrete absorbance measurements were then read on the UV-Vis set at 420 nm, as recommended by EPA method 375.4 for sulfate analysis. A minimum seven point calibration curve was created on the day of analysis by serial dilutions of a stock sodium sulfate solution. These results along with persulfate analysis were used to establish a mass balance for the heat-activated persulfate/sulfate system.

Concentrations of TCE were measured in two ways, by UV-Vis spectroscopy and by gas chromatography (GC-FID). The UV-Vis was set to read at 242.5, 400, and 420 nm for TCE. The first wavelength was used in conjunction with a calibration curve to determine TCE concentration, while the second and third wavelengths were run to determine and correct for interference with persulfate and sulfate in solution, respectively. TCE analysis by direct-inject, gas chromatography was conducted on a Shimadzu (Tokyo, Japan) GC-17A gas chromatograph equipped with a flame ionization detector and an SPB-624 glass capillary column. Discrete direct inject, aqueous-phase samples were collected in 2-mL screw-cap glass vials, filled with as little headspace as possible to minimize losses to volatilization. Standardization of the UV-Vis and the gas chromatography systems for TCE analysis included an eight-point calibration curve. Sample blanks and/or check standards for the UV-Vis and the GC-FID were run on average every 10 samples.

3.3.2 Batch Studies

Batch experiments were conducted to quantify the heat activation of persulfate at 60 and 90°C. The heat activation system described previously was used with 200 mL of 10 mM persulfate in 0.01N CaCl₂. Ports for inlet and outlet tubing controlling flow in the temperature-controlled, heated reservoir were covered during all experiments to prevent loss due to evaporation. Samples were taken periodically over the duration of the experiment in 1 mL aliquots. The 60 and 90°C studies were conducted until concentrations of persulfate remaining in solution were at the method detection limit of approximately 1 mg/L, requiring approximately 100 and 6 hours, respectively. All samples were analyzed for persulfate using the iodometric method to quantify the kinetics of persulfate degradation over time. For the batch experiment conducted at 90°C, sulfate concentrations in solution over time were also determined as a mass balance for the heat activation of persulfate.

Control experiments were done on unactivated persulfate to determine any mass loss of persulfate due to mechanisms not related to heat activation, specifically interaction with porous media or reaction and sample vessels. Clean Accusand and a solution of sodium persulfate in a 1:1 mass ratio were added to 20-mL batch reactors. A combination of concentrations (10 and 100 mM persulfate) and background solutions (0.01N CaCl₂ and DI water) were tested in five replicates for these controls. Each experiment included two replicate reactors containing only the persulfate solution. Reaction times were at minimum one week, after which an aliquot was taken from each

reactor and analyzed for persulfate. Persulfate reactivity to Accusand and/or experimental apparatus was determined by mass difference.

3.3.3 Transport Studies

Packed soil columns were saturated with 0.01N CaCl_2 using an Acuflo Series II HPLC pump (SSI, State College, PA), beginning at an average linear pore-water velocity of 11.4 cm/hr for the initial 24 hours, followed by an increase in the flow rate to 16.0 cm/hr for an additional 24 hours, and then finally 22.8 cm/hr until the total column weight remained constant for several days. Bulk density was calculated using the weight of packed media and the measured column volume. Porosity was estimated using the dry and saturated packed weights of each column system. Corrections for dead volume in the column system were made using the sand's bulk density and assuming a particle density of 2.65 g/cm³.

Nonreactive tracer (NRT) experiments were performed after saturation on each column to qualify the effects of physical heterogeneities on the overall transport behavior through the porous media. These NRTs were conducted pre- and post-persulfate injections in each column both to establish reproducibility and to ensure no physical changes in the system over its experimental life. A solution of 500 mg/L pentafluorobenzoic acid (PFBA) in 0.01N CaCl_2 was injected for approximately 10 pore volumes at 22.8 cm/hr, and then eluted with PFBA-free electrolyte (0.01N CaCl_2) solution. Samples were collected in 5-mL polypropylene test tubes and analyzed for PFBA concentrations.

Soil column experiments were performed at minimum in duplicate for heat activated persulfate at 20, 60, and 90 °C. Before injection, samples from the effluent of the heat activation system were taken to insure a constant concentration of activated persulfate had been reached. The column was then injected with the activated persulfate for a minimum of 10 pore volumes and eluted with persulfate-free 0.01N CaCl₂ electrolyte solution. All samples were collected in glass scintillation vials, capped, and then placed in an ice bath to quench the activation reaction prior to analysis for persulfate. Additionally, a mass balance for the overall transport behavior of heat-activated persulfate (60 °C) in soil was performed by measuring both persulfate and the sulfate (SO₄²⁻) concentrations in the soil column effluent using Sulfa4 powder packs as described previously.

3.3.4 Remediation Studies

To determine the effectiveness of heat-activated persulfate for *in-situ* chemical oxidation of residual pure-phase organic liquid, a solution of persulfate/heat-activated persulfate was run through saturated soil columns with established residuals of TCE. Residuals of pure phase TCE were established by imbibing approximately 20 mL of pure TCE into the vertically-positioned, saturated soil column at an average injection flowrate of 0.3 mL/min using a syringe pump equipped with a 50-mL glass, gas-tight syringe. Effluent from the column was monitored for the first appearance of pure-phase TCE and imbibing continued for additional 30 minutes. A saturated aqueous-phase solution of TCE was then injected for approximately an hour in the reverse direction (i.e., vertically downward flow) using a dedicated Acuflo Series I HPLC pump at an average flowrate of

1 mL/min. The residual fraction of pure phase TCE in the soil column was determined by mass difference (e.g., soil column mass pre- and post-establishment of residual TCE). Finally, approximately ten pore volumes of a saturated aqueous-phase solution of TCE were injected to ensure equilibrium, steady-state conditions in the residual soil columns.

Remediation studies were conducted in two discrete residually-saturated soil columns using persulfate activated at 60°C. Using the temperature-controlled system described previously, heat-activated persulfate was continuously injected into residual column A at an average linear porewater velocity of 9.1 cm/hr (0.2 mL/min) and into residual column B at 22.8 cm/hr (0.5 mL/min). Samples of column effluent were collected in a 5-mL luerlock-tipped, glass, gas-tight syringe and analyzed by UV-Vis, GC-FID, or both. Specifically, an aliquot was collected for UV-Vis, persulfate, and sulfate analysis followed by a separate aliquot for GC-FID analysis. The non-GC aliquots were placed in an ice bath for a minimum of 5 minutes to quench the persulfate activation reaction and subsampled for TCE analysis by UV-Vis. The remaining sample was used for iodometric and Sulfa4 analysis of persulfate and sulfate, respectively. Persulfate was continually pumped through the system until the concentration of TCE in the effluent reached a lower detection limit of approximately 1 mg/L.

4 Results and Discussion

4.1 Batch Studies

Batch studies characterizing the kinetics of the heat activation of persulfate were conducted at both 60 and 90°C. Pseudo first-order reaction rate coefficients were determined by regression analysis of the log-linear relative concentrations of persulfate over time (see Figure 1).

Figure 1: Relative concentration over time for persulfate activated at 60 and 90°C in a batch system. First order rate constants determined from log-linear regression analysis are $k = 0.064 \text{ hr}^{-1}$ ($R^2 = 0.9326$) and $k = 1.4 \text{ hr}^{-1}$ ($R^2 = 0.9982$) for 60 and 90°C, respectively.

Rate constants describing the kinetics of the thermal degradation of persulfate in batch equaled 0.064 hr^{-1} ($R^2 = 0.9326$) and 1.4 hr^{-1} ($R^2 = 0.9982$) for 60°C and 90°C , respectively. Johnson et al. [48] describe an empirical relationship for the temperature dependence of the rate constant for thermal decomposition of persulfate as shown in equation (7):

$$\ln k = (36.6 \pm 0.8) - \frac{134 \pm 2}{RT} \quad (7)$$

where k = thermal degradation rate constant [s^{-1}]

R = ideal gas constant, $8.314 \cdot 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$

T = absolute temperature [K]

Using equation (7), the estimated rate constants for the heat activation of persulfate at 60 and 90°C equaled $0.028 \pm 0.0021 \text{ hr}^{-1}$ and $1.5 \pm 0.20 \text{ hr}^{-1}$, respectively. These rate constants correspond to half-lives of approximately 25 hours for activation at 60°C versus 28 minutes for activation at 90°C , showing the sharp temperature dependence of persulfate thermolysis. Reaction rate constants determined from regression of experimental data measured in this study are consistent with the empirical relationship in equation (7), particularly the 90°C study.

For the batch experiment conducted at 90°C , both sulfate and persulfate concentrations in solution over time were measured as a sulfate-species mass balance for the heat activation of persulfate. Figure 2 shows the relative concentration of persulfate as it degrades upon heat activation over time, as well as the resulting appearance of

Figure 2: Relative concentration over time for persulfate and sulfate activated at 90°C in a batch system. Total sulfate species shown to illustrate mass balance achieved. Psuedo first-order reaction constants of 1.4 hr⁻¹ for persulfate decomposition and 1.3 hr⁻¹ for sulfate generation determined by log-linear regression ($R^2 = 0.9982$ and $R^2 = 0.9353$ for persulfate and sulfate, respectively).

sulfate ion in solution. As sulfate only appears in the system as persulfate decomposes, the reaction rate constants for persulfate decomposition and sulfate production should be similar. The reaction rate constant for the generation of sulfate ions in solution equaled 1.3 hr⁻¹ ($R^2 = 0.9353$) compared to 1.4 hr⁻¹ ($R^2 = 0.9982$) for the degradation of persulfate. The two coefficients differ by only 7.4%, which agrees with this chemistry. Furthermore, total mass recovery of sulfate species in solution was between 98.7% and

104.3% over the duration of the experiment, with an average of $101.3 \pm 0.3\%$. The results indicate a strong mass balance, especially considering the minimum dilutions for persulfate and sulfate analysis are 20 and 5 fold, respectively.

Batch studies were also done to test for any interaction between persulfate and the natural sandy soil and between persulfate and the glass sample vials and HPDE caps. The potential effects of the background electrolyte solution (i.e., deionized water versus 0.01N CaCl_2) were also characterized. These batch experiments were conducted at two discrete concentrations of persulfate, 10 mM (~ 2.4 g/L) and 100 mM (~ 24 g/L). Results of these batch experiments indicate negligible interaction/interference of persulfate with the natural sand as well as the apparatus (Figure 3 and the data presented in Table 3). After nine days of contact time, concentration of persulfate in all systems remained essentially constant (within $\pm 5\%$ of initial concentration). Because of the low concentration maximum of the iodometric method, high dilution factors were necessary. For example, 100 mM samples had to be diluted 800 fold, and 10 mM samples were diluted 100 fold. With these large dilutions in mind, the small deviations in final persulfate concentration are to be expected.

Table 3: Percent mass recovery of persulfate after 9 day batch experiment under a range of conditions. Standard error given for batch reactors containing Accusand.

Reaction Conditions	Percent Mass Recovery	
	With Accusand	Without Accusand
10 mM DI	102.8 ± 0.1 %	104.9%
10 mM CaCl ₂	98.7 ± 0.1 %	101.0%
100 mM DI	100.1 ± 0.5 %	100.8%
100 mM CaCl ₂	100.5 ± 0.2 %	100.0%

Figure 3: Persulfate concentration in batch reactors after 9 days, normalized to starting concentration C_0 . Reactors R1-R5 with 1:1 (m:m) sand to persulfate and reactors B1 and B2 with only persulfate in solution. Background solutions consisted of either deionized water (DI) or 0.01N CaCl₂.

4.2 Transport Studies

4.2.1 Physical Hydrodynamics

Nonreactive tracer (NRT) experiments were conducted to characterize the overall transport behavior associated with physical hydrodynamics in the various packed soil columns as well as to determine the possible changes in column physical heterogeneity over time. Column packing A was used for all temperature transport studies (i.e., dynamic experiments characterizing the transport behavior of persulfate/activated persulfate in natural porous media), as well as a remediation study. NRTs were performed before (NRT 1A), during (NRT 2A) and after (NRT 3A) the course of experimentation in Column A.

Figure 4 shows the arrival and corresponding elution waves for all three NRT studies conducted in Column A. Arrival waves plotted against the respective inverted elution waves for each NRT experiment in Column A are shown in Figure 5. The strong reproducibility in overall transport behavior across all of these tracer studies confirms that Column A underwent no major changes in physical hydrodynamics during the course of experimentation therein.

Column B was used only for a remediation study and NRT experiments were performed pre- and post-complete dissolution/degradation of residual TCE. As with Column A, these studies characterized the overall transport behavior associated with physical hydrodynamics in the homogeneously packed soil column and confirmed no changes to those parameters over the course of experimentation (see results shown in Figure 6). A comparison of representative NRTs in Column A and Column B is shown in

Figure 7 indicating the reproducibility in overall physical transport conditions across the two homogeneously packed soil columns.

Retardation factors and percent mass recovery for PFBA were determined from moment analysis of the NRT data measured in Columns A and B (Table 4). Retardation factors were all close to 1 and the percent mass recovery for each study was close to 100%, indicating near-ideal transport behavior. The retardation factor for NRT 2A is slightly high. This can also be seen in the delayed arrival of tracer for NRT 2A (see Figure 4a) and the slightly different shape of the arrival and inverted elution curves as shown in Figure 5b. This is likely due to an experimental error rather than a change to the physical structure of the column, given how well the elution tail trends with other studies and the comparable behavior in the first and last NRTs.

Table 4: Relevant experimental values for NRTs performed over the course of experimentation in column packings A and B.

Study	Date	Retardation Factor	Percent Recovery
NRT 1A	January 30, 2014	0.955	100.6%
NRT 2A	July 6, 2014	1.119	98.8%
NRT 3A	April 12, 2015	1.011	99.6%
NRT 1B	April 26, 2015	0.993	100.2%
	Average:	1.019 ± 0.030	100.2 ± 0.3%

Figure 4a-b: (a) Arrival waves and (b) elution waves for three separate nonreactive tracers in column packing A.

Figure 5a- c: Arrival and inverted elution waves for (a) NRT 1A, (b) NRT 2A, and (c) NRT 3A.

Figure 6a-c: (a) Arrival wave (b) elution wave and (c) arrival and inverted elution waves for nonreactive tracer in column packing B.

Figure 7a-b: (a) Arrival and (b) elution waves for representative NRTs in column packings A and B

4.2.2 Temperature Effects

The overall transport behavior of persulfate/activated persulfate was characterized for thermal activation at three temperatures: 20, 60, and 90°C. Table 5 details some of the experimental results from this research. The degree of apparent activation achieved in each experiment has been calculated as the percent of persulfate degraded relative to initial measured persulfate concentration in solution (~10 mM). Retardation factors and percent mass recovery were determined from moment analysis of the measured persulfate breakthrough curves. Graphics comparing representative studies for each temperature compared to a corresponding NRT in the same column can be found in Figure 8, and graphics showing reproducibility at each activation temperature are included in Figure 9.

Table 5: Relevant experimental values from thermal activation transport studies done in column A

Study	Degree of Apparent Activation	Retardation Factor	% Mass recovery (PS after activation)
PS 20°C – 1	Negligible	0.936	100.7%
PS 20°C – 2	Negligible	1.128	99.5%
PS 60°C – 1	10.3%	1.015	99.6%
PS 60°C – 2	11.0%	0.976	101.3%
PS 60°C – 3	8.7%	0.979	100.6%
PS 90°C – 1	91.8%	0.968	100.2%
PS 90°C – 2	90.6%	1.024	101.1%
	Average	1.004 ± 0.021	100.4 ± 0.3%

For all temperatures and all studies, the overall transport behavior of persulfate was highly similar and reproducible, indicating the transport of thermally-activated persulfate in homogeneously packed sandy material is independent of the degree of

activation achieved for persulfate. These results suggest that in a system where persulfate is activated at the surface prior to subsurface injection, no complications for delivery of persulfate/activated persulfate to the target/source zone should occur as a result of thermal activation. The overall average retardation factor was 1.004 ± 0.021 , and percent mass recovery was $100.4 \pm 0.3\%$. Mass recovery was calculated relative to the effective long-term average concentration of each experiment, i.e., mass recovery of persulfate ions entering the column. Mass balance and recovery with persulfate and sulfate species is discussed further on.

The largest deviation was in the 20°C studies; retardation factors for all other studies were within one standard deviation of the mean. PS 20°C-2 and NRT 2A were performed in the same time frame, and both exhibit higher retardation factors, higher than the average (1.128 and 1.119, respectively). The coupled deviations in these two experiments, shown in Figure 10, indicate some experimental error consistent for both trials, most likely an incorrectly primed pump during the injection phase. This would have added dead volume to the system that could not be accounted for in moment analysis.

The potential for continued activation after the persulfate has left the heated reservoir was also examined in the elevated temperature studies. Specifically, the degree of apparent activation measured after the heated reservoir is compared to apparent activation measured at the column effluent in Table 6. The overall gains (i.e., the observed percent increase) in activation are more apparent in the lower temperature study, simply because there is a higher concentration of persulfate available in solution phase (i.e.,

leaving the temperature-controlled influent reservoir) on activation at 60°C. However, when the overall changes in measured persulfate concentrations are compared at the two measurement points, the 90°C study shows a larger change, which agrees with the more rapid degradation of persulfate at that temperature.

Table 6: Activation gains observed after persulfate has left the heated reservoir in elevated temperature studies

Study	Percent Apparent Activation, Heated Reservoir	Percent Apparent Activation, Column Effluent	Percent Increase	Percent Change, PS Concentration ¹
PS 20°C – 1	0.0%	0.7%	--	0.7%
PS 20°C – 2	0.0%	0.3%	--	0.3%
PS 60°C – 1	9.5%	10.3%	8.4%	0.9%
PS 60°C – 2	9.7%	11.0%	13.4%	1.4%
PS 60°C – 3	8.1%	8.7%	7.4%	0.6%
PS 90°C – 1	91.6%	91.8%	0.22%	2.9%
PS 90°C – 2	90.5%	90.6%	0.11%	2.0%

(1) Percent difference in measured persulfate concentration post-reservoir and measured persulfate concentration at column effluent.

Mass recovery of persulfate/activated persulfate under dynamic (transport) conditions was characterized on one of the 60°C studies (PS 60°C-3). Specifically, sulfate and persulfate ion concentrations in the effluent of the soil column were measured and compared to those initial concentrations of sulfate species in solution (see Figure 11). The total mass of sulfate species in solution (sulfate and persulfate ions) averages 101.8% of the initial measured persulfate concentration with a standard error of 0.3%. This is in agreement with the sulfate-species mass balance performed on the 90°C batch system described previously (average $101.3 \pm 0.3\%$). These results indicate that a complete mass balance was achieved across activation temperatures (60°C and 90°C) as well as experimental methods (i.e., batch versus column study).

Figure 8a-b: Comparison of (a) arrival and (b) elution waves for persulfate at three different activation temperatures in column A.

Figure 9a-f: Arrival and elution wave comparisons and reproducibility for all thermal activation studies done in column A. Arrival waves shown for 20°C, 60°C, and 90°C in (a), (c) and (e) respectively. Elution waves shown studies, and elution waves shown for 20°C, 60°C, and 90°C in (b), (d), and (f).

Figure 10a-b: Comparison of (a) arrival and (b) elution waves for 20°C PS-2 and NRT 2A

Figure 11: Transport of persulfate (PS), sulfate (SO₄), and total sulfate species (PS + SO₄) as measured in PS 60°C-3, compared to initial persulfate concentration, showing a mass balance for all sulfate species.

4.3 Remediation Studies

Transport experiments were conducted in homogeneously packed soil columns as a proof of concept for a thermally-activated persulfate ISCO remediation system for a dense nonaqueous phase liquid source zone. These experiments aimed to characterize the effects of heat-activated persulfate *in situ* chemical oxidation on residual trichloroethylene at two levels of persulfate activation. The higher degree of apparent persulfate activation was achieved by decreasing the volumetric rate of flow through the soil column (from 0.5 mL/min in the first study to 0.2 mL/min in the second study), while maintaining a 60°C temperature and fixed volume for the reservoir in each system. Lowering the volumetric flowrate through the experimental system increased the mean residence time for persulfate in the temperature-controlled, heated reservoir, leading to an overall higher degree of persulfate activation. This had the added effect of increasing the contact time between persulfate/activated persulfate and the contaminated soil core. The TCE dissolution/degradation data measured in these heat-activated persulfate ISCO experiments was compared to TCE dissolution (the control) in the absence of ISCO (i.e., traditional pump and treat of residual nonaqueous phase liquid), from data collected earlier in this research group. All dimensionless time for these experiments was scaled to the residual content of the control data to normalize for the effect of different residual saturations achieved in the discrete packed columns. Relevant properties for each system are given in Table 7 and Figure 12.

Figure 12: Relative concentration of TCE versus dimensionless time in pore volumes scaled for initial residual TCE content.

Table 7: System properties for remediation studies

	0.2 mL/min Activated PS Study	0.5 mL/min Activated PS Study	Accusand Control Study
TCE Residual Saturation	18.7 %	17.9 %	13.6%
Pore Volume	8.0 mL	7.3 mL	7.9 mL
Porosity	34.6 %	33.5 %	37%
Percent Activation, measured at Reservoir	26.8 %	9.0 %	--
Percent Activation, measured at Effluent	39.5%	24.6%	--

The relative concentrations of TCE measured in the column effluent from the two ISCO experiments compared to the control are shown in Figure 12. All of the results show an initial, long-term, steady-state plateau in measured TCE concentrations lasting a minimum of 75 pore volumes; it is assumed that during this phase of TCE dissolution/degradation, nonaqueous, pure phase trichloroethylene remains as residual in the porous matrix allowing for equilibrium, steady-state TCE concentrations in the column effluent. The 0.2 mL/min study had the shortest steady-state phase, reaching 90% of TCE's saturated aqueous-phase concentration at approximately 75 pore volumes. In comparison, the 0.5 mL/min and control experiments reached C/C_o of 90% at 100 and 110 pore volumes, respectively. Moment analysis of the measured data was performed on the two remediation studies to quantify percent mass degradation and mass dissolution of trichloroethylene; results are shown in Table 8.

Table 8: Mass removal for remediation studies

	0.2 mL/min (39.5%) Activated PS Study	0.5 mL/min (24.6%) Activated PS Study
Mass TCE, Initial	2200 mg	1900 mg
Mass TCE, Dissolved	1450 mg	1280 mg
Percent Mass Dissolved	65.7%	68.4%
Mass TCE, Degraded	750 mg	620 mg
Percent Mass Degraded	34.3%	32.6%

In terms of pore volumes, the 0.2 mL/min study saw decreases in TCE concentration 32% sooner than in the control, compared to 9% sooner in the 0.5 mL/min study. Both remediation systems degraded approximately a third of the initial mass of TCE, but the

shorter plateau in the 0.2 mL/min study indicates that the larger degree of activation was more efficient at degrading the high concentrations of trichloroethylene present initially due to the nonaqueous-phase, residual fraction of the contaminant.

After the initial steady-state phase (i.e., the effluent concentration plateau), all studies exhibited pseudo first-order mass loss behavior. This exponential behavior was modeled for each experiment, using data from the end of the steady-state phase until relative concentration reached approximately 50%. A comparison of the modeled to measured data is shown in Figure 13. Pseudo-first order rate constants equaled 0.044, 0.063, and 0.083 hr⁻¹ for the control, 0.2 mL/min, and 0.5 mL/min study, respectively. Rate constants associated with heat-activated persulfate treatment are 55% and 105% greater than for dissolution of residual TCE under a traditional pump and treat scenario.

The calculated rate constant for the 0.5 mL/min study is larger than that of the 0.2 mL/min study, despite a longer contact time and higher degree of activation. This is likely a result of faster dissolution associated with increased advective flow through the system when pumping at 0.5 mL/min versus 0.2 mL/min. When rate constants are converted to equivalent constants in inverse pore volumes (PV), in effect scaling for differences in pore volume size and average flowrate, the rate constants are 0.011, 0.042 and 0.020 PV⁻¹ for the control, 0.2 mL/min, and 0.5 mL/min study, respectively. It follows that under the same flow conditions, the higher level of persulfate activation in the 0.2 mL/min study would yield a higher rate for the degradation of TCE.

Figure 13 a-c: Modeled pseudo-first order dissolution for three TCE transport studies, (a) 0.2 mL/min (39.5% activated) persulfate, $k = 0.063 \text{ hr}^{-1}$ and $R^2=0.8594$, (b) 0.5 mL/min (24.6% activated) persulfate, $k = 0.083 \text{ hr}^{-1}$ and $R^2=0.6863$, and (c) Accusand control study, $k = 0.044 \text{ hr}^{-1}$ and $R^2=0.7917$.

The effects of enhanced activation of persulfate upon contact with residual TCE are illustrated in Figure 14. Specifically, the concentration of persulfate and sulfate ion in solution measured at the effluent of the heated reservoir as compared to the concentrations of the same species in the column effluent indicate marked changes occur in the concentrations of sulfate species before and after contact with residual trichloroethylene.

Figure 14a-c: Concentration of persulfate and sulfate as measured at the effluent of the heated reservoir ("Reservoir") and in the column effluent ("Effluent") as compared to measured concentration of initial persulfate stock concentration ("Initial PS") for remediation studies at (a) 0.2 mL/min (39.5% activated) persulfate (18.7% residual TCE) and (b) 0.5 mL/min (24.6% activated) persulfate (17.9% residual TCE) and for (c) persulfate-only transport study, 60°C PS-3 (9.1% activated).

It may be of interest to note that persulfate and sulfate ion concentrations measured from samples taken directly from the heated reservoir before and after the injection period during the remediation **studies** indicate no changes in reservoir concentration during experimentation. The distinct difference in sulfate-species concentrations pre- and post-injection into the column is seen only in the remediation studies, not the persulfate transport study where no TCE was present (see Figure 14 and Table 9).

Table 9: Activation gains observed after persulfate has left the heated reservoir in transport and remediation studies

Study	Percent Activation, Heated Reservoir	Percent Activation, Column Effluent	TCE Residual Saturation	Percent Increase	Percent Change, PS Concentration ¹
PS Transport, 20°C	0.0%	0.5%	--	--	0.5%
PS Transport, 60°C	9.1%	10.0%	--	9.9%	1.0%
PS Transport, 90°C	91.1%	91.2%	--	0.2%	2.5%
0.5 mL/min remediation, 60°C	9.0%	24.6%	17.9%	174.7%	17.2%
0.2 mL/min remediation, 60°C	26.8%	39.5%	18.7%	47.2%	17.3%

(1) Percent difference in measured persulfate concentration post-reservoir and measured persulfate concentration at column effluent.

This experimental evidence suggests a direct interaction between residual trichloroethylene and persulfate. The apparent increase in mass loss of persulfate ion in solution measured in these remediation studies is likely due to unactivated persulfate reacting with the high concentrations of trichloroethylene present in the system, following the persulfate reaction shown in Table 2, as previously discussed. Unactivated persulfate at ambient temperature has been used as a treatment technology on its own (e.g., [26], [68], [69], [81]). For example, one batch study reports unactivated persulfate reacting with low concentration (60 mg/L) trichloroethylene at 20°C with a half-life of 86.6 hours in an unbuffered aqueous system [81].

5 Future Work and Conclusions

Persulfate/activated persulfate was shown to be a viable remediation technique for residual (pure phase) trichloroethylene in this initial proof of concept work. More complete degradation of trichloroethylene is reasonably expected with optimization of this system going forward, along with a better understanding of the mechanisms involved in degradation. Future work will have several focuses: replicates, modeling, and a broadening of scope. Now that a system has been developed for the study of dynamic persulfate/activated persulfate behavior (e.g., the temperature-controlled, flow-through injection system plus delivery of persulfate/activated persulfate under steady-state flow conditions), work further characterizing this system can be done. For example, replicate work (i.e., reproducibility studies) needs to be completed on the trichloroethylene remediation studies. Experiments aimed to differentiate between the effects of contact time, flowrate, and persulfate activation on the degradation/dissolution of residual trichloroethylene in a natural sandy material should be conducted. Furthermore, following additional characterization of this one-dimensional, flow-through system, experiments replicating/comparing the overall transport behavior and application of a heat-activated persulfate ISCO system under two-dimensional flow should be completed. Ideally, these additional studies on persulfate/activated persulfate ISCO in both the one- and two-dimensional flow-through systems will also track for potential byproducts of trichloroethylene degradation, particularly chloride ion. This will allow for a mechanistic study of persulfate/activated persulfate ISCO for the remediation of TCE. Modeling work

is also planned prior to further publication of this work, both on transport of persulfate at different activating temperatures and the persulfate/trichloroethylene system.

This future work will continue to build on the encouraging results found in this work, furthering understanding of the behavior and mechanisms of persulfate ISCO systems. The work in this study give promising indications that a heat-activated persulfate system can be effectively scaled from the laboratory to the field scale, for several reasons. Regardless of activation temperature, persulfate shows near ideal transport behavior under steady-state flow through natural porous media. As an alternative subsurface remediation technology, these results suggest that persulfate/activated persulfate may be effectively delivered to target zones for *in-situ* chemical oxidation and, as such, should not require advanced design techniques associated with non-ideal flow conditions on application. Both column and supporting batch work indicate that any interactions between persulfate and the natural sandy material are negligible, and a full mass balance on sulfate ion species in solution was achieved. Results also indicate persulfate/activated persulfate degraded approximately 33% of the residual mass of TCE over the course of treatment while effectively decreasing the time necessary for complete dissolution of TCE residual source zone. With increasing dependence on groundwater sources for a wide range of uses, developing effective systems for addressing subsurface contamination is vital. A variety of approaches will be needed, and this research, along with others, illustrates how promising persulfate oxidation systems are for meeting that need.

References

- [1] USGS, "Freshwater - The Water Cycle," *USGS Water-Science School*. [Online]. Available: <http://water.usgs.gov/edu/watercyclefreshstorage.html>. [Accessed: 14-Jul-2015].
- [2] British Geological Survey and United Nations Environment Programme. Division of Early Warning and Assessment, *Groundwater and its susceptibility to degradation : a global assessment of the problem and options for management*. Nairobi, Kenya: Nairobi, Kenya : UNEP, 2003.
- [3] S. Siebert, J. Burke, J. M. Faures, K. Frenken, J. Hoogeveen, P. Döll, and F. T. Portmann, "Groundwater use for irrigation – a global inventory," *Hydrol. Earth Syst. Sci.*, vol. 14, no. 10, pp. 1863–1880, Oct. 2010.
- [4] NGWA, "Facts about Global Groundwater Usage," Mar-2015. [Online]. Available: <http://www.ngwa.org/Fundamentals/use/Documents/global-groundwater-use-fact-sheet.pdf>. [Accessed: 14-Jul-2015].
- [5] ATSDR (Agency for Toxic Substances and Disease Registry), "Priority List of Toxic Substances," 2013.
- [6] L. A. Desimone, P. B. McMahon, and M. R. Rosen, "The quality of our nation's waters; water quality in principal aquifers of the United States, 1991-2010," 2015.
- [7] R. Boulding, *Practical handbook of soil, vadose zone, and ground-water contamination: assessment, prevention, and remediation*. Boca Raton: Lewis Publishers, 1995.
- [8] S. G. Huling and B. E. Pivetz, "In-Situ Chemical Oxidation," 2006.
- [9] A. Tsitonaki, B. Petri, M. Crimi, H. Mosbæk, R. L. Siegrist, and P. L. Bjerg, "In Situ Chemical Oxidation of Contaminated Soil and Groundwater Using Persulfate: A Review," *Crit. Rev. Environ. Sci. Technol.*, vol. 40, no. 1, pp. 55–91, Jan. 2010.
- [10] United States. Environmental Protection Agency. Office of Solid Waste and Emergency Response, *A citizen's guide to pump and treat*. Washington, D.C.: Washington, D.C. : E.P.A., Office of Solid Waste and Emergency Response, 2001.

- [11] United States. Environmental Protection Agency. Office of Solid Waste and Emergency Response, *Cleaning up the nation's waste sites markets and technology trends*. Washington, D.C.]: Washington, D.C. : U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, 2004.
- [12] K.-C. Huang, Z. Zhao, G. E. Hoag, A. Dahmani, and P. A. Block, "Degradation of volatile organic compounds with thermally activated persulfate oxidation," *Chemosphere*, vol. 61, no. 4, pp. 551–560, Oct. 2005.
- [13] S. Ko, M. Crimi, B. K. Marvin, V. Holmes, and S. G. Huling, "Comparative study on oxidative treatments of NAPL containing chlorinated ethanes and ethenes using hydrogen peroxide and persulfate in soils," *J. Environ. Manage.*, vol. 108, pp. 42–48, Oct. 2012.
- [14] J. Liu, X. Gong, S. Song, F. Zhang, and C. Lu, "Heat-Activated Persulfate Oxidation of Chlorinated Solvents in Sandy Soil," *J. Spectrosc.*, vol. 2014, pp. 1–5, 2014.
- [15] R. H. Waldemer, P. G. Tratnyek, R. L. Johnson, and J. T. Nurmi, "Oxidation of Chlorinated Ethenes by Heat-Activated Persulfate: Kinetics and Products," *Environ. Sci. Technol.*, vol. 41, no. 3, pp. 1010–1015, Feb. 2007.
- [16] C. Liang, C. J. Bruell, M. C. Marley, and K. L. Sperry, "Thermally Activated Persulfate Oxidation of Trichloroethylene (TCE) and 1,1,1-Trichloroethane (TCA) in Aqueous Systems and Soil Slurries," *Soil Sediment Contam.*, vol. 12, no. 2, pp. 207–228, Mar. 2003.
- [17] J. Costanza, G. Otaño, J. Callaghan, and K. D. Pennell, "PCE Oxidation by Sodium Persulfate in the Presence of Solids," *Environ. Sci. Technol.*, vol. 44, no. 24, pp. 9445–9450, Dec. 2010.
- [18] C.-F. Chen, N. T. Binh, C.-W. Chen, and C.-D. Dong, "Removal of polycyclic aromatic hydrocarbons from sediments using sodium persulfate activated by temperature and nanoscale zero-valent iron," *J. Air Waste Manag. Assoc.*, vol. 65, no. 4, pp. 375–383, Apr. 2015.
- [19] X. Liao, D. Zhao, X. Yan, and S. G. Huling, "Identification of persulfate oxidation products of polycyclic aromatic hydrocarbon during remediation of contaminated soil," *J. Hazard. Mater.*, vol. 276, pp. 26–34, Jul. 2014.

- [20] W. R. Haag and C. C. D. Yao, "Rate constants for reaction of hydroxyl radicals with several drinking water contaminants," *Environ. Sci. Technol.*, vol. 26, no. 5, pp. 1005–1013, May 1992.
- [21] Y. Ji, C. Dong, D. Kong, and J. Lu, "New insights into atrazine degradation by cobalt catalyzed peroxymonosulfate oxidation: Kinetics, reaction products and transformation mechanisms," *J. Hazard. Mater.*, vol. 285, pp. 491–500, Mar. 2015.
- [22] A. Ghauch, A. M. Tuqan, and N. Kibbi, "Ibuprofen removal by heated persulfate in aqueous solution: A kinetics study," *Chem. Eng. J.*, vol. 197, pp. 483–492, Jul. 2012.
- [23] S. Rodriguez, A. Santos, A. Romero, and F. Vicente, "Kinetic of oxidation and mineralization of priority and emerging pollutants by activated persulfate," *Chem. Eng. J.*, vol. 213, pp. 225–234, Dec. 2012.
- [24] Y. Ji, C. Ferronato, A. Salvador, X. Yang, and J.-M. Chovelon, "Degradation of ciprofloxacin and sulfamethoxazole by ferrous-activated persulfate: Implications for remediation of groundwater contaminated by antibiotics," *Sci. Total Environ.*, vol. 472, pp. 800–808, Feb. 2014.
- [25] C. Liang and I.-L. Lee, "In situ iron activated persulfate oxidative fluid sparging treatment of TCE contamination — A proof of concept study," *J. Contam. Hydrol.*, vol. 100, no. 3–4, pp. 91–100, Sep. 2008.
- [26] C. Liang, I.-L. Lee, I.-Y. Hsu, C.-P. Liang, and Y.-L. Lin, "Persulfate oxidation of trichloroethylene with and without iron activation in porous media," *Chemosphere*, vol. 70, no. 3, pp. 426–435, Jan. 2008.
- [27] E. R. McKenzie, R. L. Siegrist, J. E. McCray, and C. P. Higgins, "Effects of Chemical Oxidants on Perfluoroalkyl Acid Transport in One-Dimensional Porous Media Columns," *Environ. Sci. Technol.*, vol. 49, no. 3, pp. 1681–1689, Feb. 2015.
- [28] C. E. Schaefer, R. M. Towne, D. Root, and J. E. McCray, "Assessment of Chemical Oxidation for Treatment of DNAPL in Fractured Sandstone Blocks," *J. Environ. Eng.*, vol. 138, no. 1, pp. 1–7, Jan. 2012.
- [29] S. US EPA, "Ground Water Cleanup at Superfund Sites." [Online]. Available: <http://www.epa.gov/superfund/health/conmedia/gwdocs/brochure.htm>. [Accessed: 15-Jul-2015].

- [30] R. L. Siegrist, Ed., *Principles and practices of in situ chemical oxidation using permanganate*. Columbus, Ohio: Battelle Press, 2001.
- [31] United States Environmental Protection Agency, "National Primary Drinking Water Regulations." May-2009.
- [32] R. Baciocchi, "Principles, Developments and Design Criteria of In Situ Chemical Oxidation," *Water. Air. Soil Pollut.*, vol. 224, no. 12, Dec. 2013.
- [33] G. P. Anipsitakis and D. D. Dionysiou, "Radical Generation by the Interaction of Transition Metals with Common Oxidants," *Environ. Sci. Technol.*, vol. 38, no. 13, pp. 3705–3712, Jul. 2004.
- [34] ITRC, "Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition," 2005.
- [35] A. M. Struse, R. L. Siegrist, H. E. Dawson, and M. A. Urynowicz, "Diffusive Transport of Permanganate during In Situ Oxidation," *J. Environ. Eng.*, vol. 128, no. 4, pp. 327–334, Apr. 2002.
- [36] X. D. Li, "DNAPL mass transfer and permeability reduction during in situ chemical oxidation with permanganate," *Geophys. Res. Lett.*, vol. 31, no. 6, 2004.
- [37] Venny, S. Gan, and H. K. Ng, "Current status and prospects of Fenton oxidation for the decontamination of persistent organic pollutants (POPs) in soils," *Chem. Eng. J.*, vol. 213, pp. 295–317, Dec. 2012.
- [38] E. Lipczynska-Kochany, G. Sprah, and S. Harms, "Influence of some groundwater and surface waters constituents on the degradation of 4-chlorophenol by the Fenton reaction," *Chemosphere*, vol. 30, no. 1, pp. 9–20, Jan. 1995.
- [39] G. Buxton, Q. Mulazzani, and A. Ross, "Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms, and hydroxyl radicals in aqueous solution," *J Phys Chem Ref Data*, vol. 24, no. 3, pp. 1055–1349, 1995.
- [40] Thermoretec Consulting Corp., Mission, KS, "Technology Status Review In Situ Oxidation," 1999.
- [41] H. Choi, H.-N. Lim, J. Kim, T.-M. Hwang, and J.-W. Kang, "Transport characteristics of gas phase ozone in unsaturated porous media for in-situ chemical oxidation," *J. Contam. Hydrol.*, vol. 57, no. 1–2, pp. 81–98, Jul. 2002.

- [42] W. J. Braida and S. K. Ong, "Air sparging effectiveness: laboratory characterization of air-channel mass transfer zone for VOC volatilization," *J. Hazard. Mater.*, vol. 87, no. 1–3, pp. 241–258, Oct. 2001.
- [43] Ozone Solutions, "Ozone Compatible Materials." [Online]. Available: <http://www.ozonesolutions.com/info/ozone-compatible-materials>. [Accessed: 25-Jul-2015].
- [44] B.-T. Zhang, Y. Zhang, Y. Teng, and M. Fan, "Sulfate Radical and Its Application in Decontamination Technologies," *Crit. Rev. Environ. Sci. Technol.*, vol. 45, no. 16, pp. 1756–1800, Aug. 2015.
- [45] FMC, "Persulfates, Technical Information," 2001. [Online]. Available: http://www.peroxychem.com/media/90826/AOD_Brochure_Persulfate.pdf. [Accessed: 16-Jul-2015].
- [46] United States Environmental Protection Agency, "Sodium in Drinking Water , Contaminant Candidate List," 3/6/2012. [Online]. Available: <http://water.epa.gov/scitech/drinkingwater/dws/ccl/sodium.cfm>. [Accessed: 16-Jul-2015].
- [47] United States Environmental Protection Agency, "Sulfate in Drinking Water, Unregulated," 06-Mar-2012. [Online]. Available: <http://water.epa.gov/drink/contaminants/unregulated/sulfate.cfm>. [Accessed: 16-Jul-2015].
- [48] R. L. Johnson, P. G. Tratnyek, and R. O. Johnson, "Persulfate Persistence under Thermal Activation Conditions," *Environ. Sci. Technol.*, vol. 42, no. 24, pp. 9350–9356, Dec. 2008.
- [49] D. Zhao, X. Liao, X. Yan, S. G. Huling, T. Chai, and H. Tao, "Effect and mechanism of persulfate activated by different methods for PAHs removal in soil," *J. Hazard. Mater.*, vol. 254–255, pp. 228–235, Jun. 2013.
- [50] K.-C. Huang, R. A. Couttenye, and G. E. Hoag, "Kinetics of heat-assisted persulfate oxidation of methyl tert-butyl ether (MTBE)," *Chemosphere*, vol. 49, no. 4, pp. 413–420, Oct. 2002.
- [51] V. C. Mora, J. A. Rosso, D. O. Mártire, and M. C. Gonzalez, "Phenol depletion by thermally activated peroxydisulfate at 70°C," *Chemosphere*, vol. 84, no. 9, pp. 1270–1275, Aug. 2011.

- [52] D. A. House, "Kinetics and Mechanism of Oxidations by Peroxydisulfate.," *Chem. Rev.*, vol. 62, no. 3, pp. 185–203, Jun. 1962.
- [53] L. R. Bennedsen, J. Muff, and E. G. Søgaaard, "Influence of chloride and carbonates on the reactivity of activated persulfate," *Chemosphere*, vol. 86, no. 11, pp. 1092–1097, Mar. 2012.
- [54] C. Liang and Y. Guo, "Mass Transfer and Chemical Oxidation of Naphthalene Particles with Zerovalent Iron Activated Persulfate," *Environ. Sci. Technol.*, vol. 44, no. 21, pp. 8203–8208, Nov. 2010.
- [55] J. Yan, L. Han, W. Gao, S. Xue, and M. Chen, "Biochar supported nanoscale zerovalent iron composite used as persulfate activator for removing trichloroethylene," *Bioresour. Technol.*, vol. 175, pp. 269–274, Jan. 2015.
- [56] S.-Y. Oh, H.-W. Kim, J.-M. Park, H.-S. Park, and C. Yoon, "Oxidation of polyvinyl alcohol by persulfate activated with heat, Fe²⁺, and zero-valent iron," *J. Hazard. Mater.*, vol. 168, no. 1, pp. 346–351, Aug. 2009.
- [57] M. Ahmad, A. L. Teel, and R. J. Watts, "Persulfate activation by subsurface minerals," *J. Contam. Hydrol.*, vol. 115, no. 1–4, pp. 34–45, Jun. 2010.
- [58] A. L. Teel, M. Ahmad, and R. J. Watts, "Persulfate activation by naturally occurring trace minerals," *J. Hazard. Mater.*, vol. 196, pp. 153–159, Nov. 2011.
- [59] H. Zhong, M. L. Brusseau, Y. Wang, N. Yan, L. Quig, and G. R. Johnson, "In-situ activation of persulfate by iron filings and degradation of 1,4-dioxane," *Water Res.*, vol. 83, pp. 104–111, Oct. 2015.
- [60] O. S. Furman, A. L. Teel, and R. J. Watts, "Mechanism of Base Activation of Persulfate," *Environ. Sci. Technol.*, vol. 44, no. 16, pp. 6423–6428, Aug. 2010.
- [61] JAG Consulting Group, LLC, "Case Study: Treatment of Shallow Soil Contamination Using High pH Activation of Sodium Persulfate, Industrial Site, Illinois," 2013. [Online]. Available: http://www.peroxychem.com/media/19391/FMC_Klozur_Case_Study_-_PCE-_TCE-_TEX_-_IL_-_JAG.pdf. [Accessed: 25-Jul-2015].

- [62] XDD, LLC, "Site Closure with Multi-Level Treatment Approach at a Former MGP Site: Central Illinois." [Online]. Available: <http://www.peroxychem.com/media/116782/klozur-aap-xdd-isco-case-study-mattoon-il.pdf>. [Accessed: 25-Jul-2015].
- [63] T. T. Tsai, C. M. Kao, and A. Hong, "Treatment of tetrachloroethylene-contaminated groundwater by surfactant-enhanced persulfate/BOF slag oxidation—A laboratory feasibility study," *J. Hazard. Mater.*, vol. 171, no. 1–3, pp. 571–576, Nov. 2009.
- [64] X. Gu, S. Lu, L. Li, Z. Qiu, Q. Sui, K. Lin, and Q. Luo, "Oxidation of 1,1,1-Trichloroethane Stimulated by Thermally Activated Persulfate," *Ind. Eng. Chem. Res.*, vol. 50, no. 19, pp. 11029–11036, Oct. 2011.
- [65] D. Deng, L. Peng, M. Guan, and Y. Kang, "Impact of activation methods on persulfate oxidation of methyl tert-butyl ether," *J. Hazard. Mater.*, vol. 264, pp. 521–528, Jan. 2014.
- [66] C. Liang, C.-F. Huang, and Y.-J. Chen, "Potential for activated persulfate degradation of BTEX contamination," *Water Res.*, vol. 42, no. 15, pp. 4091–4100, Sep. 2008.
- [67] J. Zhao, Y. Zhang, X. Quan, and S. Chen, "Enhanced oxidation of 4-chlorophenol using sulfate radicals generated from zero-valent iron and peroxydisulfate at ambient temperature," *Sep. Purif. Technol.*, vol. 71, no. 3, pp. 302–307, Mar. 2010.
- [68] K. S. Sra, N. R. Thomson, and J. F. Barker, "Persulfate injection into a gasoline source zone," *J. Contam. Hydrol.*, vol. 150, pp. 35–44, Jul. 2013.
- [69] V. Sohrabi, M. S. Ross, J. W. Martin, and J. F. Barker, "Potential for in situ chemical oxidation of acid extractable organics in oil sands process affected groundwater," *Chemosphere*, vol. 93, no. 11, pp. 2698–2703, Nov. 2013.
- [70] F. J. Benitez, J. L. Acero, F. J. Real, G. Roldán, and E. Rodríguez, "The Effectiveness of Single Oxidants and AOPs in the Degradation of Emerging Contaminants in Waters: A Comparison Study," *Ozone Sci. Eng.*, vol. 35, no. 4, pp. 263–272, Jul. 2013.
- [71] L. Hou, H. Zhang, and X. Xue, "Ultrasound enhanced heterogeneous activation of peroxydisulfate by magnetite catalyst for the degradation of tetracycline in water," *Sep. Purif. Technol.*, vol. 84, pp. 147–152, Jan. 2012.

- [72] A. Ghauch, G. Ayoub, and S. Naim, "Degradation of sulfamethoxazole by persulfate assisted micrometric FeO in aqueous solution," *Chem. Eng. J.*, vol. 228, pp. 1168–1181, Jul. 2013.
- [73] B. Darsinou, Z. Frontistis, M. Antonopoulou, I. Konstantinou, and D. Mantzavinos, "Sono-activated persulfate oxidation of bisphenol A: Kinetics, pathways and the controversial role of temperature," *Chem. Eng. J.*, vol. 280, pp. 623–633, Nov. 2015.
- [74] Y.-C. Lee, S.-L. Lo, P.-T. Chiueh, and D.-G. Chang, "Efficient decomposition of perfluorocarboxylic acids in aqueous solution using microwave-induced persulfate," *Water Res.*, vol. 43, no. 11, pp. 2811–2816, Jun. 2009.
- [75] Y.-C. Lee, S.-L. Lo, P.-T. Chiueh, Y.-H. Liou, and M.-L. Chen, "Microwave-hydrothermal decomposition of perfluorooctanoic acid in water by iron-activated persulfate oxidation," *Water Res.*, vol. 44, no. 3, pp. 886–892, Feb. 2010.
- [76] Y.-C. Lee, S.-L. Lo, J. Kuo, and C.-P. Huang, "Promoted degradation of perfluorooctanoic acid by persulfate when adding activated carbon," *J. Hazard. Mater.*, vol. 261, pp. 463–469, Oct. 2013.
- [77] Y. Deng and C. M. Ezyske, "Sulfate radical-advanced oxidation process (SR-AOP) for simultaneous removal of refractory organic contaminants and ammonia in landfill leachate," *Water Res.*, vol. 45, no. 18, pp. 6189–6194, Nov. 2011.
- [78] L. W. Pan, R. L. Siegrist, and M. Crimi, "Effects of In Situ Remediation Using Oxidants or Surfactants on Subsurface Organic Matter and Sorption of Trichloroethene," *Ground Water Monit. Remediat.*, vol. 32, no. 2, pp. 96–105, May 2012.
- [79] C. Liang and C.-W. Wang, "Assessing acute toxicity potential of persulfate ISCO treated water," *Chemosphere*, vol. 93, no. 11, pp. 2711–2716, Nov. 2013.
- [80] C. Liang, C.-F. Huang, N. Mohanty, and R. M. Kurakalva, "A rapid spectrophotometric determination of persulfate anion in ISCO," *Chemosphere*, vol. 73, no. 9, pp. 1540–1543, Nov. 2008.
- [81] C. Liang, Z.-S. Wang, and C. J. Bruell, "Influence of pH on persulfate oxidation of TCE at ambient temperatures," *Chemosphere*, vol. 66, no. 1, pp. 106–113, Jan. 2007.

Appendix A – Temperature Controller Design

A temperature controller was designed to keep the heated reservoir at a steady temperature throughout experimentation. The system consists of a RKC REX-C100 proportional-integral-derivative (PID) temperature controller, 25 amp solid state relay, and K-type thermocouple. A terminal block was also used because of the number of junctions. The PID controller essentially uses the SSR to throttle the voltage being sent to the heating apparatus attached to the system, which in turn maintains a steady temperature. The auto-tuning function built into the PID optimized the relay between the PID, SSR, and heating apparatus, and was recalibrated for both 60°C and 90°C. In all cases after an initial heating period, temperature stayed constant within $\pm 1^\circ\text{C}$. A simple wall outlet was wired to the system instead of directly wiring the heating element to the controller. This allowed the same controller to be connected to any heating apparatus that requires standard 15 amp/120 V power supply. Over the course of this study, a Glascol heating jacket as well as a standard hot plate were both controlled with this apparatus to great success. Thermocouples were also very easy to replace as they became worn from usage. A wiring diagram of the system is include in Figure 15

69

- Power to PID
- Control Lines, SSR to heating element
- ==== Signal Lines, PID to SSR
- ==== Lines in/out of system

Figure 15: Wiring diagram for temperature controller used in flow-through heat injection system

Appendix B - Experimental Set-up

Figure 16: Experimental set-up for heat-activation, flowthrough system.

- (a) Unactivated persulfate reservoir
- (b) HPLC Pump #1, delivers unactivated persulfate to heated reservoir
- (c) Heated reservoir, 250-mL flask, capped with rubber stopper containing magnetic stir-bar. Placed in heating mantle, and on top of magnetic stir plate.
- (d) HPLC Pump #2, pulls activated persulfate from the reservoir, delivers persulfate to column
- (e) Pump effluent/column influent tubing
- (f) PID Temperature controller
- (g) Thermocouple

Appendix C – Experimental Data

Table 10: Non-reactive Tracer Data - NRT 1A

Performed for Persulfate Temperature Transport Studies

Column: A

Darcy Velocity: 0.38 cm/min

Tracer: 499.6 mg/L PFBA

Electrolyte: 0.01 N CaCl₂

Data results for PFBA non-reactive transport, study NRT 1A; samples 1-25

Sample	Pore Volume (mL)	UV-Vis Abs	Dilution	C/C ₀
1	0.00	0.016	3.0	0.004
2	0.17	0.021	3.0	0.006
3	0.38	0.014	3.0	0.003
4	0.59	0.012	3.0	0.002
5	0.80	0.254	3.0	0.099
6	1.00	1.693	3.0	0.670
7	1.21	2.244	3.0	0.894
8	1.41	2.409	3.0	0.962
9	1.61	2.444	3.0	0.976
10	1.81	2.482	3.0	0.990
11	2.02	2.482	3.0	0.989
12	2.22	2.482	3.0	0.996
13	2.45	2.495	3.0	0.997
14	2.67	2.495	3.0	0.997
15	2.97	2.495	3.0	0.996
16	3.37	2.509	3.0	1.000
17	3.76	2.523	3.0	1.005
18	4.16	2.523	3.0	1.009
19	4.55	2.537	3.0	1.013
20	4.85	2.537	3.0	1.008
21	5.71	2.523	3.0	1.007
22	6.56	2.523	3.0	1.016
23	7.44	2.523	3.0	1.009
24	8.29	2.509	3.0	1.004
25	8.95	2.523	3.0	1.008

Table 10 (Continued) Non-reactive Tracer Data – NRT 1A

Data results for PFBA non-reactive transport, study NRT 1A; samples 26-54

Sample	Pore Volume (mL)	UV-Vis Abs	Dilution	C/C ₀	
26	9.83	2.523	3.0	1.007	
27	10.72	2.523	3.0	1.010	
28	10.93	2.523	3.0	1.009	Elution
29	11.13	2.523	3.0	1.010	
30	11.33	2.523	3.0	1.008	
31	11.53	2.495	3.0	0.997	
32	11.74	2.444	3.0	0.975	
33	11.94	1.269	1.0	0.506	
34	12.14	0.340	1.0	0.133	
35	12.34	0.296	1.0	0.036	
36	12.54	0.101	1.0	0.011	
37	12.74	0.054	1.0	0.005	
38	12.95	0.037	1.0	0.002	
39	13.25	0.028	1.0	0.001	LDL
40	13.65	0.020	1.0	0.000	LDL
41	14.10	0.016	1.0	0.000	LDL
42	14.57	0.013	1.0	-0.001	LDL
43	14.99	0.017	1.0	0.000	LDL
44	15.39	0.014	1.0	-0.001	LDL
45	15.79	0.019	1.0	0.000	LDL
46	16.10	0.020	1.0	0.000	LDL
47	16.94	0.029	1.0	0.001	LDL
48	17.84	0.027	1.0	0.001	LDL
49	18.69	0.013	1.0	-0.001	LDL
50	19.55	0.019	1.0	0.000	LDL
51	20.41	0.015	1.0	-0.001	LDL
52	21.25	0.015	1.0	-0.001	LDL
53	22.16	0.017	1.0	0.000	LDL
54	23.11	0.017	1.0	0.000	LDL

Table 11: Non-reactive Tracer Data - NRT 2A

Performed for Persulfate Temperature Transport Studies

Column: A

Darcy Velocity: 0.38 cm/min

Tracer: 504.4 mg/L PFBA

Electrolyte: 0.01 N CaCl₂

Data results for PFBA non-reactive transport, study NRT 2A; samples 1-26

Sample	Pore Volume (mL)	UV-Vis Abs	Dilution	C/C ₀	
1	0.00	0.005	1.0	0.000	LDL
2	0.15	0.001	1.0	0.000	LDL
3	0.36	0.051	1.0	0.006	
4	0.57	0.015	1.0	0.001	LDL
5	0.78	0.226	1.0	0.027	
6	0.98	0.899	4.0	0.474	
7	1.20	1.364	4.1	0.740	
8	1.43	1.745	4.0	0.923	
9	1.68	1.827	4.0	0.962	
10	1.91	1.867	4.0	0.987	
11	2.12	1.893	4.0	1.002	
12	2.33	1.845	4.0	0.976	
13	2.53	1.854	4.0	0.981	
14	2.74	1.857	4.0	0.988	
15	3.04	1.887	4.0	0.989	
16	3.44	1.873	4.0	0.991	
17	3.86	1.891	4.0	0.987	
18	4.33	1.886	4.0	0.990	
19	4.78	1.873	4.0	0.978	
20	5.18	1.876	4.0	0.981	
21	5.58	1.863	4.0	0.983	
22	5.88	1.886	4.0	0.996	
23	6.74	1.886	4.0	0.998	
24	7.64	1.883	4.1	1.003	
25	8.52	1.876	4.0	0.992	
26	9.45	1.893	4.0	1.002	

Table 11 (Continued): Non-reactive Tracer Data – NRT 2A

Data results for PFBA non-reactive transport, study NRT 2A; samples 27-58

Sample	Pore Volume (mL)	UV-Vis Abs	Dilution	C/C ₀	
27	10.39	1.854	4.1	0.989	
28	11.35	1.928	4.0	1.017	
29	12.34	1.889	4.0	0.993	
30	13.39	1.905	4.0	1.008	
31	13.60	1.863	4.1	0.997	Elution
32	13.81	1.827	4.1	0.991	
33	14.01	1.813	4.1	0.969	
34	14.21	1.824	4.1	0.973	
35	14.42	1.798	4.0	0.945	
36	14.63	0.746	4.0	0.390	
37	14.84	0.208	3.0	0.101	
38	15.06	0.076	1.0	0.025	
39	15.33	0.044	1.0	0.009	
40	15.68	0.035	1.0	0.005	
41	16.08	0.057	1.0	0.004	
42	16.48	0.022	1.0	0.007	
43	16.87	0.020	1.0	0.002	
44	17.38	0.018	1.0	0.002	
45	17.92	0.018	1.0	0.002	LDL
46	18.34	0.010	1.0	0.002	LDL
47	18.68	0.009	1.0	0.001	LDL
48	19.76	0.008	1.0	0.001	LDL
49	20.69	0.006	1.0	0.001	LDL
50	21.78	0.006	1.0	0.000	LDL
51	22.71	0.013	1.0	0.000	LDL
52	23.56	0.007	1.0	0.001	LDL
53	24.41	0.004	1.0	0.000	LDL
54	25.35	0.003	1.0	0.000	LDL
55	26.40	0.006	1.0	0.000	LDL
56	27.37	0.004	1.0	0.000	LDL
57	28.52	0.004	1.0	0.000	LDL
58	29.64	0.000	1.0	0.000	LDL

Table 12: Non-reactive Tracer Data - NRT 3A

Performed for Persulfate Temperature Transport Studies

Column: A

Darcy Velocity: 0.38 cm/min

Tracer: 493.9 mg/L PFBA

Electrolyte: 0.01 N CaCl₂

Data results for PFBA non-reactive transport, study NRT 3A; samples 1-26

Sample	Pore Volume (mL)	UV-Vis Abs	Dilution	C/C ₀	
1	-0.07	0.000	0.0	-0.002	LDL
2	0.12	0.000	0.0	-0.002	LDL
3	0.33	0.000	0.0	-0.002	LDL
4	0.54	0.000	0.0	-0.002	LDL
5	0.74	0.115	0.0	0.014	
6	0.96	1.533	2.3	0.465	
7	1.18	2.131	3.1	0.898	
8	1.41	2.328	3.1	0.976	
9	1.64	2.387	3.1	0.982	
10	1.83	2.328	3.1	0.982	
11	2.02	2.328	3.1	0.980	
12	2.21	2.357	3.1	0.995	
13	2.40	2.357	3.1	0.994	
14	2.60	2.357	3.1	0.992	
15	2.91	2.387	3.1	1.006	
16	3.31	2.357	3.2	0.998	
17	3.70	2.357	3.2	0.998	
18	4.10	2.357	3.2	0.996	
19	4.48	2.357	3.1	0.995	
20	4.86	2.357	3.2	0.997	
21	5.29	2.357	3.2	0.997	
22	6.41	2.377	3.2	1.005	
23	7.36	2.357	3.1	0.994	
24	8.31	2.377	3.1	1.002	
25	9.28	2.377	3.1	1.000	
26	10.18	2.377	3.1	0.998	

Table 12 (Continued): Non-reactive Tracer Data NRT 3A

Data results for PFBA no-reactive transport, study NRT 3A; samples 27-50

Sample	Pore Volume (mL)	UV-Vis Abs	Dilution	C/C ₀	
27	10.39	2.377	3.	0.999	Elution
28	10.61	2.377	3.1	1.002	
29	10.83	2.377	3.1	1.001	
30	11.03	2.377	3.2	1.005	
31	11.24	2.102	3.1	0.885	
32	11.45	1.119	1.9	0.284	
33	11.66	0.420	1.0	0.057	
34	11.88	0.176	1.0	0.022	
35	12.08	0.135	1.0	0.017	
36	12.29	0.100	1.0	0.012	
37	12.49	0.064	1.0	0.007	
38	12.70	0.040	1.0	0.003	
39	12.90	0.028	1.0	0.002	LDL
40	13.18	0.012	1.0	-0.001	LDL
41	13.57	0.007	1.0	-0.001	LDL
42	14.03	0.007	1.0	-0.001	LDL
43	14.52	0.008	1.0	-0.001	LDL
44	14.12	0.001	1.0	-0.002	LDL
45	15.39	0.001	1.0	-0.002	LDL
46	16.37	0.001	1.0	-0.002	LDL
47	17.41	0.001	1.0	-0.002	LDL
48	18.48	0.002	1.0	-0.002	LDL
49	19.44	0.001	1.0	-0.002	LDL
50	20.33	0.002	1.0	-0.002	LDL

Table 13: Non-reactive Tracer Data - NRT 1B

Performed for Persulfate/TCE Remediation Studies

Column: A

Darcy Velocity: 0.39 cm/min

Tracer: 504.9 mg/L PFBA

Electrolyte: 0.01 N CaCl₂

Data results for PFBA non-reactive transport, study NRT 1B; samples 1-26

Sample	Pore Volume (mL)	UV-Vis Abs	Dilution	C/C ₀	
1	0.00	0.004	1.0	0.000	LDL
2	0.14	0.004	1.0	0.000	LDL
3	0.38	0.001	1.0	0.000	LDL
4	0.60	0.028	1.0	0.003	
5	0.83	1.854	1.0	0.244	
6	1.10	1.889	3.0	0.760	
7	1.38	2.301	3.0	0.920	
8	1.61	2.420	3.0	0.968	
9	1.84	2.444	3.0	0.976	
10	2.06	2.468	3.0	0.986	
11	2.28	2.468	3.0	0.985	
12	2.51	2.509	3.0	1.003	
13	2.76	2.509	3.0	1.002	
14	3.01	2.509	3.0	1.001	
15	3.35	2.509	3.0	1.002	
16	3.83	2.523	3.0	1.007	
17	4.43	2.495	3.0	0.999	
18	5.00	2.482	3.0	1.004	
19	5.50	2.523	3.0	1.011	
20	6.01	2.495	3.0	1.000	
21	7.18	2.523	3.0	1.005	
22	8.18	2.523	3.0	1.007	
23	9.19	2.523	3.0	1.007	
24	10.27	2.509	3.0	1.003	
25	11.19	2.509	3.0	1.001	
26	12.05	2.495	3.0	1.001	

Table 13 (Continued): Non-reactive Tracer Data – NRT 1B

Data results for PFBA non-reactive transport, study NRT 1B; samples 27-54

Sample	Pore Volume (mL)	UV-Vis Abs	Dilution	C/C ₀	
27	12.73	2.523	3.0	1.007	Elution
28	13.00	2.509	3.0	1.003	
29	13.21	2.495	3.0	0.998	
30	13.43	2.495	3.0	0.996	
31	13.69	2.523	3.0	1.008	
32	13.96	1.857	3.0	0.739	
33	14.20	1.896	1.0	0.249	
34	14.43	0.653	1.0	0.083	
35	14.65	0.229	1.0	0.026	
36	14.89	0.109	1.0	0.012	
37	15.14	0.069	1.0	0.008	LDL
38	15.38	0.054	1.0	0.006	
39	15.62	0.051	1.0	0.006	
40	15.91	0.042	1.0	0.004	
41	16.29	0.036	1.0	0.004	
42	16.71	0.029	1.0	0.003	
43	17.17	0.026	1.0	0.003	
44	17.63	0.024	1.0	0.002	
45	18.14	0.025	1.0	0.003	
46	18.70	0.022	1.0	0.002	
47	19.82	0.013	1.0	0.001	
48	21.50	0.015	1.0	0.001	
49	22.24	0.015	1.0	0.001	
50	23.92	0.014	1.0	0.001	
51	24.97	0.013	1.0	0.001	
52	26.00	0.010	1.0	0.001	
53	27.31	0.007	1.0	0.000	
54	28.49	0.002	1.0	0.000	

Table 14: Persulfate Transport Data, 20°C Activation, Study: 20°C PS-1

Performed for Heat-activated Persulfate Transport Study

Column: A

Darcy Velocity: 0.38 cm/min

Concentration, C_0 : 2427.0 mg/L $\text{Na}_2\text{S}_2\text{O}_8$

Electrolyte: 0.01 N CaCl_2

Data results for activated PS transport, 20°C PS-1; samples 1-29

Sample	Pore Volume (mL)	UV-Vis Abs (avg.)	Dilution	C/ C_0	
1	-0.08	0.076	20.0	0.023	
2	0.05	0.007	19.8	0.003	LDL
3	0.18	0.002	19.9	0.001	LDL
4	0.32	0.001	19.9	0.001	LDL
5	0.46	0.002	61.9	0.005	LDL
6	0.60	0.002	62.2	0.004	LDL
7	0.73	0.012	61.6	0.014	LDL
8	0.88	0.274	62.2	0.250	
9	1.02	0.479	102.7	0.735	
10	1.16	0.586	102.0	0.899	
11	1.30	0.620	103.0	0.961	
12	1.44	0.630	103.1	0.979	
13	1.57	0.637	103.8	0.996	
14	1.71	0.672	102.9	1.043	
15	1.85	0.651	103.2	1.013	
16	2.11	0.641	103.2	0.997	
17	2.52	0.651	101.9	1.000	
18	2.92	0.647	102.6	1.001	
19	3.33	0.646	102.9	1.001	
20	3.74	0.644	103.8	1.008	
21	4.72	0.651	103.0	1.011	
22	5.57	0.647	103.3	1.006	
23	6.46	0.648	102.9	1.004	
24	7.37	0.646	103.3	1.006	
25	8.28	0.644	103.0	1.001	
26	9.17	0.648	102.8	1.004	
27	10.05	0.652	102.6	1.009	
28	10.92	0.643	103.7	1.005	
29	11.77	0.655	103.2	1.019	

**Table 14 (Continued): Persulfate Transport Data, 20°C Activation,
Study: 20°C PS-1**

Data results for activated PS transport, 20°C PS-1; samples 30-55

Sample	Pore Volume (mL)	UV-Vis Abs (avg.)	Dilution	C/C ₀	
30	12.63	0.656	103.5	1.023	Elution
31	12.83	0.634	103.8	0.992	
32	12.96	0.646	103.1	1.003	
33	13.10	0.652	102.8	1.011	
34	13.24	0.649	103.1	1.009	
35	13.38	0.651	102.8	1.009	
36	13.52	0.651	103.0	1.011	
37	13.68	0.628	103.3	0.976	
38	13.84	0.365	102.5	0.555	
39	13.99	0.127	104.7	0.200	
40	14.13	0.281	20.2	0.083	LDL
41	14.41	0.091	19.8	0.027	
42	14.81	0.018	19.8	0.006	
43	15.21	0.008	19.8	0.003	
44	15.60	0.005	20.3	0.002	
45	16.01	0.002	19.9	0.001	
46	16.42	0.001	19.8	0.001	
47	17.40	0.001	19.8	0.001	
48	18.27	-0.001	19.8	0.001	
49	19.13	-0.001	6.7	0.000	
50	20.03	-0.001	19.9	0.001	
51	20.88	0.000	19.8	0.001	
52	21.75	-0.001	19.8	0.001	
53	22.61	-0.002	19.9	0.000	
54	23.45	0.000	20.0	0.001	
55	24.38	-0.001	19.9	0.001	

Table 15: Persulfate Transport Data, 20°C Activation, Study: 20°C PS-2

Performed for Heat-activated Persulfate Transport Study

Column: A

Darcy Velocity: 0.38 cm/min

Concentration, C_0 : 2410.6 mg/L $\text{Na}_2\text{S}_2\text{O}_8$

Electrolyte: 0.01 N CaCl_2

Data results for activated PS transport, 20°C PS-2; samples 1-30

Sample	Pore Volume (mL)	UV-Vis Abs (avg.)	Dilution	C/C_0	
1	0.00	0.000	20.3	-0.001	LDL
2	0.05	0.001	20.1	0.000	LDL
3	0.21	0.001	20.3	0.000	LDL
4	0.39	0.001	20.3	0.000	LDL
5	0.57	0.001	20.2	0.000	LDL
6	0.72	0.002	20.2	0.000	LDL
7	0.86	0.161	20.1	0.048	
8	0.99	0.200	100.9	0.299	
9	1.14	0.427	102.5	0.649	
10	1.28	0.559	101.7	0.851	
11	1.42	0.616	101.0	0.934	
12	1.56	0.629	102.3	0.968	
13	1.69	0.639	102.2	0.982	
14	1.82	0.636	103.2	0.987	
15	1.96	0.643	102.7	0.992	
16	2.25	0.636	103.4	0.989	
17	2.63	0.650	101.8	0.995	
18	3.00	0.645	102.4	0.993	
19	3.38	0.646	102.1	0.992	
20	3.76	0.636	104.1	0.996	
21	4.19	0.645	102.7	0.996	
22	4.63	0.643	103.2	0.997	
23	4.95	0.643	102.9	0.996	
24	5.85	0.637	104.0	0.996	
25	6.75	0.645	103.1	1.000	
26	7.64	0.639	103.7	0.997	
27	8.57	0.648	102.3	0.997	
28	9.46	0.650	102.2	0.999	
29	10.30	0.650	102.2	0.999	
30	11.16	0.645	102.7	0.996	

Table 15 (Continued): Persulfate Transport Data, 20°C Activation, Study: 20°C PS-2

Data results for activated PS transport, 20°C PS-2; samples 31-57

Sample	Pore Volume (mL)	UV-Vis Abs (avg.)	Dilution	C/C ₀	
31	11.35	0.644	102.2	0.989	Elution
32	11.49	0.658	101.4	1.005	
33	11.62	0.657	101.8	1.006	
34	11.76	0.658	101.8	1.008	
35	11.90	0.651	102.7	1.005	
36	12.03	0.661	101.1	1.005	
37	12.17	0.658	101.3	1.003	
38	12.31	0.603	101.9	0.922	
39	12.46	0.377	102.6	0.569	
40	12.60	0.845	20.2	0.258	
41	12.74	0.379	20.2	0.113	LDL
42	12.88	0.184	20.2	0.055	
43	13.01	0.094	20.2	0.028	
44	13.14	0.048	20.1	0.014	
45	13.35	0.015	20.1	0.004	
46	13.80	0.014	20.2	0.003	
47	14.32	0.004	20.2	0.001	
48	14.72	0.003	20.2	0.000	
49	15.11	0.002	20.2	0.000	
50	15.40	0.001	20.2	0.000	
51	16.39	0.000	20.2	-0.001	
52	17.42	0.000	20.1	-0.001	
53	18.26	0.000	20.1	-0.001	
54	19.09	0.000	20.1	-0.001	
55	19.97	-0.001	20.3	-0.001	
56	20.96	0.000	20.4	-0.001	
57	21.85	-0.001	20.4	-0.001	

Table 16: Persulfate Transport Data, 60°C Activation, Study: 60°C PS-1

Performed for Heat-activated Persulfate Transport Study

Column: A

Darcy Velocity: 0.38 cm/min

Concentration, C_0 : 2357.6 mg/L $\text{Na}_2\text{S}_2\text{O}_8$

Electrolyte: 0.01 N CaCl_2

Data results for activated PS transport, 60°C PS-1; samples E-1 - 19

Sample	Pore Volume (mL)	UV-Vis (avg.)	Dilution	C/C_0	
E-1	-22.08	0.985	59.8	0.906	Equilibration
E-2	-21.69	0.985	59.9	0.907	
E-3	-20.48	0.983	60.0	0.906	
E-4	-18.76	0.977	60.3	0.906	
E-5	-15.83	0.970	60.6	0.904	
E-6	-13.75	0.975	60.4	0.906	
E-7	-11.85	0.986	59.8	0.907	
E-8	-9.68	0.981	60.0	0.905	
E-9	-7.37	0.976	60.2	0.904	
1	-0.07	0.012	19.9	0.000	LDL/Injection
2	0.07	0.012	19.9	0.000	LDL
3	0.21	0.011	19.9	0.000	LDL
4	0.37	0.013	19.8	0.001	LDL
5	0.52	0.012	20.0	0.000	LDL
6	0.66	0.015	19.8	0.001	LDL
7	0.80	0.385	19.9	0.114	
8	0.94	1.263	19.9	0.390	
9	1.10	0.933	39.8	0.570	
10	1.28	0.958	60.1	0.884	
11	1.44	0.959	59.8	0.881	
12	1.59	0.959	60.0	0.884	
13	1.72	0.969	60.4	0.900	
14	1.87	0.975	60.2	0.902	
15	2.02	0.967	59.9	0.890	
16	2.17	0.972	61.2	0.913	
17	2.34	0.969	60.1	0.895	
18	2.53	0.968	60.4	0.899	
19	2.81	0.970	60.2	0.897	

Table 16 (Continued): Persulfate Transport Data, 60°C Activation, Study: 60°C PS-1

Data results for activated PS transport, 60°C PS-1; samples 20-53

Sample	Pore Volume (mL)	UV-Vis (avg.)	Dilution	C/C ₀	
20	3.19	0.969	60.3	0.897	
21	3.59	0.968	60.4	0.898	
22	3.99	0.964	60.2	0.892	
23	4.40	0.964	60.6	0.897	
24	4.83	0.964	60.6	0.898	
25	5.79	0.968	60.3	0.896	
26	6.71	0.970	60.1	0.895	
27	8.03	0.969	60.0	0.894	
28	9.26	0.969	59.8	0.891	
29	10.57	0.974	60.0	0.897	
30	12.93	0.961	60.4	0.892	
31	14.40	0.959	61.0	0.899	
32	14.63	0.947	61.5	0.895	Elution
33	14.85	0.961	60.7	0.896	
34	15.08	0.966	60.4	0.896	
35	15.27	0.976	60.0	0.901	
36	15.39	1.407	40.0	0.875	
37	15.58	1.044	39.8	0.641	
38	15.70	0.688	19.9	0.207	
39	15.85	0.261	20.0	0.077	
40	16.03	0.133	19.9	0.038	
41	16.15	0.089	20.0	0.024	
42	16.33	0.063	19.9	0.016	
43	16.47	0.040	19.9	0.009	
44	16.62	0.028	20.4	0.005	LDL
45	16.78	0.024	19.9	0.004	LDL
46	16.96	0.022	20.0	0.003	LDL
47	17.30	0.018	19.8	0.002	LDL
48	17.77	0.016	19.9	0.002	LDL
49	18.25	0.017	20.0	0.002	LDL
50	18.65	0.017	19.9	0.002	LDL
51	19.00	0.015	20.0	0.001	LDL
52	19.56	0.016	20.0	0.002	LDL
53	20.02	0.015	20.0	0.001	LDL

Table 16 (Continued): Persulfate Transport Data, 60°C Activation, Study: 60°C PS-1

Data results for activated PS transport, 60°C PS-1; samples 54-57

Sample	Pore Volume (mL)	UV-Vis (avg.)	Dilution	C/C ₀	
54	20.37	0.014	20.1	0.001	LDL
55	21.23	0.013	19.8	0.001	LDL
56	22.08	0.013	20.0	0.001	LDL
57	23.07	0.013	19.9	0.001	LDL

Table 17: Persulfate Transport Data, 60°C Activation, Study: 60°C PS-2

Performed for Heat-activated Persulfate Transport Study

Column: A

Darcy Velocity: 0.38 cm/min

Concentration, C_0 : 2330.9 mg/L $\text{Na}_2\text{S}_2\text{O}_8$

Electrolyte: 0.01 N CaCl_2

Data results for activated PS transport, 60°C PS-2; samples E-1 - 12

Sample	Pore Volume (mL)	UV- Vis (avg.)	Dilution	C/Co	
E-1	-27.10	0.979	60.6	0.910	Equilibration
E-2	-25.32	0.885	67.2	0.909	
E-3	-23.25	0.982	60.3	0.908	
E-4	-21.31	0.970	61.1	0.908	
E-5	-20.66	0.995	59.5	0.908	
E-6	-18.02	0.974	60.7	0.907	
E-7	-14.29	0.971	60.8	0.904	
E-8	-10.65	0.975	60.6	0.906	
E-9	-8.62	0.960	61.5	0.904	
E-10	-6.78	0.964	61.2	0.903	
E-11	-5.37	0.967	61.0	0.903	
E-12	-3.71	0.966	60.8	0.901	
E-13	-1.76	0.968	60.7	0.900	
E-14	-0.23	0.970	60.7	0.902	
E-15	0.15	0.965	60.8	0.900	
1	-0.07	0.012	20.2	0.000	LDL
2	0.07	0.012	20.2	0.000	LDL
3	0.20	0.013	20.0	0.000	LDL
4	0.35	0.013	20.2	0.000	LDL
5	0.50	0.011	20.2	0.000	LDL
6	0.63	0.013	20.1	0.000	LDL
7	0.76	0.057	19.9	0.014	
8	0.90	0.462	40.2	0.273	
9	1.05	1.150	40.5	0.718	
10	1.22	0.922	60.1	0.849	
11	1.40	0.946	60.5	0.876	
12	1.54	0.951	60.4	0.880	

Table 17 (Continued): Persulfate Transport Data, 60°C Activation, Study: 60°C PS-2

Data results for activated PS transport, 60°C PS-2; samples 13-46

Sample	Pore Volume (mL)	UV- Vis (avg.)	Dilution	C/Co	
13	1.71	0.945	60.7	0.878	
14	1.90	0.949	60.6	0.881	
15	2.08	0.954	60.5	0.884	
16	2.29	0.965	60.0	0.887	
17	2.50	0.970	59.8	0.890	
18	2.72	0.961	60.4	0.889	
19	3.06	0.960	60.4	0.888	
20	3.46	0.967	60.2	0.893	
21	3.85	0.954	61.0	0.891	
22	4.25	0.966	60.2	0.891	
23	4.66	0.966	60.2	0.892	
24	5.08	0.959	60.5	0.888	
25	5.50	0.961	60.4	0.890	
26	6.51	0.955	60.9	0.891	
27	7.59	0.957	60.7	0.889	
28	8.45	0.968	59.9	0.889	
29	9.44	0.963	60.2	0.889	
30	10.39	0.956	60.6	0.889	
31	10.57	0.960	60.4	0.082	Elution
32	10.71	0.959	60.5	0.889	
33	10.86	0.957	60.8	0.892	
34	11.04	0.971	59.8	0.890	
35	11.23	0.964	60.4	0.892	
36	11.39	0.955	60.6	0.888	
37	11.54	1.043	51.5	0.826	
38	11.72	1.395	20.0	0.433	
39	11.89	0.507	20.0	0.150	
40	12.04	0.211	20.0	0.061	
41	12.21	0.105	20.0	0.029	
42	12.40	0.077	20.0	0.020	
43	12.56	0.056	19.9	0.014	
44	12.70	0.046	20.0	0.011	
45	12.86	0.035	20.0	0.007	LDL
46	13.14	0.024	19.9	0.004	LDL

Table 17 (Continued): Persulfate Transport Data, 60°C Activation, Study: 60°C PS-2

Data results for activated PS transport, 60°C PS-2; samples 47-57

Sam1ple	Pore Volume (mL)	UV-Vis (avg.)	Dilution	C/Co	
47	13.55	0.021	20.1	0.003	LDL
48	14.00	0.017	20.0	0.002	LDL
49	14.43	0.018	20.1	0.002	LDL
50	14.85	0.017	20.0	0.002	LDL
51	16.05	0.017	20.0	0.002	LDL
52	17.01	0.017	19.8	0.002	LDL
53	17.92	0.017	20.0	0.002	LDL
54	18.97	0.017	19.9	0.002	LDL
55	19.87	0.016	20.0	0.001	LDL
56	20.74	0.015	20.1	0.001	LDL
57	21.81	0.014	19.9	0.001	LDL

Table 18: Persulfate Transport Data, 60°C Activation, Study: 60°C PS-3

Performed for Heat-activated Persulfate Transport Study, Sulfate Species Mass Balance

Column: A

Darcy Velocity: 0.38 cm/min

Concentration, C_0 : 2320.4 mg/L $\text{Na}_2\text{S}_2\text{O}_8$

Electrolyte: 0.01 N CaCl_2

Data results for activated PS transport, 60°C PS-3; samples E-1 - 16

Sample	Pore Volume (mL)	UV-Vis (avg., PS)	Dilution (PS)	C/C_0 (PS)	C/C_0 (SO_4)	
E-1	-18.98	0.980	0.0	0.925		Equilibr.
E-2	-17.78	0.956	0.0	0.902		
E-3	-16.10	0.963	0.0	0.919		
E-4	-14.70	0.970	0.0	0.919		
E-5	-12.62	0.962	0.0	0.919		
E-6	-11.41	0.969	0.0	0.921		
E-7	-9.90	0.963	0.0	0.919		
E-8	-7.63	0.962	0.0	0.918	0.126	
E-9	-6.47	0.957	0.0	0.908	0.120	
E-10	-4.15	0.969	0.0	0.916	0.139	
E-11	-2.54	0.968	0.0	0.918	0.136	
E-12	-0.73	0.966	0.0	0.922	0.135	
E-13	-0.29	0.978	0.0	0.927	0.141	
1	0.00	0.017	20.0	0.003	0.010	LDL/Inj.
2	0.12	0.026	20.0	0.006	0.010	LDL
3	0.31	0.011	20.0	0.001	0.008	LDL
4	0.49	0.011	20.0	0.001	0.016	LDL
5	0.67	0.020	60.6	0.011	0.007	LDL
6	0.87	0.110	60.5	0.096	0.032	
7	1.06	0.821	59.7	0.769	0.090	
8	1.25	0.934	60.3	0.889	0.110	
9	1.43	0.969	60.0	0.919	0.122	
10	1.61	1.010	57.0	0.912	0.128	
11	1.83	0.954	60.1	0.906	0.106	
12	2.08	0.962	60.3	0.917	0.124	
13	2.30	0.962	59.8	0.909	0.123	
14	2.49	0.913	60.0	0.865	0.121	
15	2.71	0.955	63.1	0.951	0.119	
16	2.93	0.967	60.1	0.918	0.119	

Table 18 (Continued): Persulfate Transport Data, 60°C Activation, Study: 60°C PS-3

Data results for activated PS transport, 60°C PS-3; samples 17-53

Sample	Pore Volume (mL)	UV-Vis Abs (avg.)	Dilution	C/C ₀ (PS)	C/C ₀ (SO ₄)	
17	3.12	0.966	59.8	0.913	0.122	
18	3.35	0.961	60.1	0.913	0.129	
19	3.68	0.962	60.0	0.912	0.138	
20	4.03	0.955	60.5	0.911	0.128	
21	4.39	0.961	60.2	0.914	0.138	
22	4.76	0.965	60.1	0.917	0.134	
23	5.14	0.962	60.0	0.912	0.139	
24	6.13	0.955	60.3	0.909	0.129	
25	7.14	0.951	61.1	0.917	0.133	
26	8.30	0.963	60.3	0.917	0.139	
27	9.20	0.972	59.9	0.920	0.135	
28	10.25	0.965	59.8	0.912	0.134	
29	10.60	0.959	60.3	0.141	0.140	Elution
30	10.88	0.944	61.5	0.420	0.134	
31	11.12	0.953	60.5	0.662	0.137	
32	11.33	0.960	60.3	0.915	0.140	
33	11.53	1.177	40.1	0.751	0.115	
34	11.72	0.310	39.9	0.186	0.055	
35	11.92	0.201	19.9	0.060	0.023	
36	12.12	0.076	19.9	0.021	0.029	
37	12.30	0.058	20.0	0.016	0.026	
38	12.50	0.047	20.1	0.012	0.014	
39	12.74	0.035	20.0	0.008	0.016	LDL
40	12.95	0.023	20.0	0.005	0.018	LDL
41	13.16	0.021	20.0	0.004	0.018	LDL
42	13.36	0.015	20.0	0.002		LDL
43	13.55	0.016	19.9	0.002	0.022	LDL
44	13.74	0.016	19.9	0.002		LDL
45	14.02	0.014	19.9	0.002		LDL
46	14.41	0.013	20.0	0.002	0.008	LDL
47	14.78	0.013	19.9	0.002		LDL
48	15.15	0.012	20.1	0.001		LDL
49	15.97	0.012	20.0	0.001	0.016	LDL
50	16.78	0.014	20.0	0.002		LDL
51	17.62	0.013	20.0	0.002		LDL
52	18.47	0.012	19.9	0.001	0.010	LDL
53	19.41	0.012	19.9	0.001		LDL

Table 19: Persulfate Transport Data, 60°C Activation, Study: 90°C PS-1

Performed for Heat-activated Persulfate Transport Study

Column: A

Darcy Velocity: 0.38 cm/min

Concentration, C_0 : 2479.9 mg/L $\text{Na}_2\text{S}_2\text{O}_8$ Electrolyte: 0.01 N CaCl_2

Data results for activated PS transport, 90°C PS-1; samples E-2 – 18

Sample	Pore Volume (mL)	UV-Vis Abs (avg.)	Dilution	C/ C_0	
E-2	-14.24	0.299	19.9	0.085	
E-3	-12.60	0.297	19.9	0.084	
E-4	-10.69	0.295	21.2	0.089	
E-5	-8.44	0.294	19.9	0.084	
E-6	-6.99	0.296	19.9	0.084	
E-7	-5.69	0.299	19.8	0.084	
E-8	-4.16	0.305	19.8	0.086	
E-9	-2.65	0.295	19.9	0.084	
E-10	-0.81	0.295	19.9	0.084	
1	-0.71	0.012	19.8	0.000	LDL
2	-0.52	0.010	20.2	0.000	LDL
3	-0.33	0.011	19.9	0.000	LDL
4	-0.14	0.014	20.0	0.001	LDL
5	0.07	0.010	20.0	0.000	LDL
6	0.26	0.010	19.9	0.000	LDL
7	0.43	0.011	19.9	0.000	LDL
8	0.61	0.013	20.0	0.001	LDL
9	0.80	0.070	19.9	0.018	
10	1.00	0.196	19.9	0.056	
11	1.18	0.258	19.9	0.074	
12	1.35	0.272	19.9	0.078	
13	1.52	0.279	19.8	0.079	
14	1.69	0.282	19.9	0.080	
15	1.88	0.285	19.9	0.081	
16	2.07	0.286	19.9	0.081	
17	2.25	0.288	19.9	0.081	
18	2.42	0.287	19.9	0.081	

Table 19 (Continued): Persulfate Transport Data, 90°C Activation, Study: 90°C PS-1

Data results for activated PS transport, 90°C PS-1; samples 19-52

Sample	Pore Volume (mL)	UV-Vis Abs (avg.)	Dilution	C/C ₀	
19	2.58	0.290	19.9	0.082	
20	2.76	0.290	19.8	0.082	
21	2.95	0.288	20.0	0.082	
22	3.23	0.288	19.9	0.082	
23	3.64	0.289	19.9	0.082	
24	4.05	0.289	19.9	0.082	
25	4.49	0.291	19.9	0.082	
26	4.93	0.289	20.0	0.082	
27	5.35	0.290	19.9	0.082	
28	5.68	0.292	19.9	0.082	
29	6.57	0.288	19.9	0.081	
30	7.54	0.291	19.9	0.082	
31	8.44	0.291	19.9	0.082	
32	9.39	0.290	19.8	0.082	
33	10.37	0.291	19.8	0.082	
34	12.25	0.288	19.9	0.082	
35	14.43	0.289	19.8	0.082	
36	17.13	0.292	19.9	0.083	
37	17.32	0.290	19.9	0.082	
38	17.54	0.291	19.9	0.082	
39	17.78	0.291	19.9	0.082	
40	18.00	0.292	19.8	0.082	
41	18.19	0.295	19.7	0.083	
42	18.38	0.292	19.8	0.082	
43	18.63	0.290	19.9	0.082	
44	18.84	0.265	19.9	0.076	
45	19.05	0.124	19.9	0.034	
46	19.24	0.042	19.9	0.009	
47	19.41	0.024	20.0	0.004	LDL
48	19.59	0.020	19.9	0.003	LDL
49	19.78	0.016	20.0	0.001	LDL
50	19.95	0.014	20.0	0.001	LDL
51	20.14	0.015	20.0	0.001	LDL
52	20.34	0.014	20.0	0.001	LDL

Table 19 (Continued): Persulfate Transport Data, 90°C Activation, Study: 90°C PS-1

Data results for activated PS transport, 90°C PS-1; samples 53-62

Sample	Pore Volume (mL)	UV-Vis Abs (avg.)	Dilution	C/C _o	
53	20.66	0.012	19.9	0.000	LDL
54	21.08	0.012	20.0	0.000	LDL
55	21.45	0.011	19.9	0.000	LDL
56	21.85	0.012	19.8	0.000	LDL
57	22.27	0.011	20.0	0.000	LDL
58	23.30	0.011	19.9	0.000	LDL
59	24.23	0.011	19.0	0.000	LDL
60	25.37	0.011	19.8	0.000	LDL
61	26.83	0.011	19.9	0.000	LDL
62	28.19	0.012	19.9	0.000	LDL

Table 20: Persulfate Transport Data, 90°C Activation, Study: 90°C PS-2

Performed for Heat-activated Persulfate Transport Study

Column: A

Darcy Velocity: 0.38 cm/min

Concentration, C_0 : 2407.4 mg/L $\text{Na}_2\text{S}_2\text{O}_8$

Electrolyte: 0.01 N CaCl_2

Data results for activated PS transport, 90°C PS-1; samples E-1 – 14

Sample	Pore Volume (mL)	UV-Vis Abs (avg.)	Dilution	C/C_0	
E-1	-17.98	0.315	19.7	0.089	Equilibrium
E-2	-15.00	0.333	20.0	0.095	
E-3	-12.41	0.333	19.9	0.095	
E-4	-10.89	0.334	19.9	0.095	
E-5	-9.94	0.334	19.9	0.095	
E-6	-8.86	0.335	19.9	0.095	
E-7	-7.48	0.337	19.8	0.096	
E-8	-6.37	0.335	19.9	0.096	
E-9	-4.87	0.335	19.9	0.095	
E-10	-3.48	0.336	19.9	0.096	
E-11	-2.61	0.334	19.9	0.095	
E-12	-1.48	0.338	19.8	0.096	
E-13	-0.16	0.332	19.9	0.095	
1	-0.07	0.015	20.0	0.001	LDL/Injection
2	0.08	0.017	19.9	0.002	LDL
3	0.23	0.017	19.9	0.002	LDL
4	0.37	0.018	19.9	0.002	LDL
5	0.51	0.013	19.9	0.000	LDL
6	0.68	0.017	20.0	0.002	LDL
7	0.85	0.078	19.9	0.020	
8	1.01	0.171	20.0	0.071	
9	1.15	0.307	19.9	0.088	
10	1.29	0.315	19.9	0.088	
11	1.43	0.318	19.9	0.091	
12	1.58	0.315	20.0	0.090	
13	1.73	0.316	19.9	0.090	
14	1.89	0.315	19.9	0.090	

Table 20 (Continued): Persulfate Transport Data, 90°C Activation, Study: 90°C PS-2

Data results for activated PS transport, 90°C PS-1; samples 15-49

Sample	Pore Volume (mL)	UV-Vis Abs (avg.)	Dilution	C/C ₀	
15	2.06	0.317	19.8	0.090	
16	2.22	0.316	20.1	0.091	
17	2.37	0.316	20.0	0.090	
18	2.52	0.318	20.0	0.091	
19	2.68	0.323	19.9	0.092	
20	2.85	0.321	19.9	0.092	
21	3.19	0.325	19.8	0.093	
22	3.68	0.324	19.9	0.092	
23	4.09	0.324	19.9	0.092	
24	4.52	0.328	19.9	0.093	
25	5.04	0.327	19.9	0.093	
26	6.13	0.329	19.9	0.094	
27	7.23	0.328	19.9	0.094	
28	8.19	0.330	20.0	0.094	
29	9.41	0.330	20.0	0.095	
30	10.62	0.328	20.0	0.094	
31	11.50	0.327	20.1	0.094	
32	11.76	0.330	19.8	0.095	Elution
33	12.00	0.333	19.9	0.095	
34	12.18	0.333	20.0	0.095	
35	12.35	0.332	19.9	0.092	
36	12.53	0.321	20.0	0.053	
37	12.70	0.191	20.0	0.016	
38	12.86	0.065	19.9	0.006	
39	13.01	0.030	20.0	0.004	LDL
40	13.14	0.023	20.0	0.003	LDL
41	13.27	0.020	20.0	0.003	LDL
42	13.41	0.020	19.9	0.002	LDL
43	13.56	0.019	20.0	0.002	LDL
44	13.73	0.017	20.1	0.001	LDL
45	13.92	0.015	20.0	0.001	LDL
46	14.11	0.015	20.0	0.000	LDL
47	14.27	0.013	19.9	0.001	LDL
48	14.46	0.014	19.9	0.001	LDL
49	14.76	0.016	19.9	0.001	LDL

Table 20 (Continued): Persulfate Transport Data, 90°C Activation, Study: 90°C PS-2

Data results for activated PS transport, 90°C PS-1; samples 50-59

Sample	Pore Volume (mL)	UV-Vis Abs (avg.)	Dilution	C/C ₀	
50	15.17	0.015	19.7	0.001	LDL
51	15.54	0.015	19.9	0.001	LDL
52	15.97	0.014	21.1	0.001	LDL
53	16.49	0.014	19.9	0.001	LDL
54	17.60	0.014	20.0	0.001	LDL
55	19.30	0.014	19.9	0.001	LDL
56	20.42	0.015	19.9	0.001	LDL
57	21.41	0.015	19.9	0.001	LDL
58	22.41	0.014	20.0	0.001	LDL
59	23.35	0.015	19.9	0.000	LDL

Table 21: 0.5 mL/min Remediation Data, 60°C Activation

Performed for Heat-activated Persulfate Remediation of Residual, Proof of Concept

Column: A

Darcy Velocity: 0.38 cm/min

Concentrations, C₀: 2427.4 mg/L Na₂S₂O₈, 1259 mg/L TCE

Electrolyte: 0.01 N CaCl₂

Data results for 0.5 mL/min Remediation Data, 60°C Activation; samples 1-16

Sample	Pore Volume (mL)	UV-Vis Abs (avg.) TCE	TCE C/C ₀ (UV)	GC-FID Area, TCE	TCE C/C ₀ (GC-FID)	UV-Vis Abs (avg.) PS	Dilution PS	PS C/C ₀	UV-Vis Abs (avg.) SO ₄	Dilution SO ₄	SO ₄ C/C ₀
1	-9.31			370396.80	1.03						
2	-8.68										
3	-8.01										
4	-7.33			430522.40	1.19						
5	-1.50										
6	-0.77										
7	0.19	1.186	1.11								
8	0.72			401073.10	1.11	0.043	20.4	0.007			
9	1.13					0.475	40.6	0.552	0.147	11.5	0.189
10	1.41					0.402	62.2	0.708	0.352	9.6	0.286
12	1.72					0.417	62.0	0.734	0.060	10.1	0.331
13	2.25	1.532	1.00	468548.70	1.29	0.440	62.3	0.781	0.398	8.6	0.283
14	3.16	1.592	1.06								
15	4.01	1.543	1.01			0.443	61.7	0.779	0.334	9.3	0.268
16	4.88	1.551	1.02			0.463	59.5	0.788	0.671	5.8	0.294

Table 21 (Continued): 0.5 mL/min Remediation Data, 60°C Activation

Data results for 0.5 mL/min Remediation Data, 60°C Activation; samples 17-36

Sample	Pore Volume (mL)	UV-Vis Abs (avg.) TCE	TCE C/C ₀ (UV)	GC-FID Area, TCE	TCE C/C ₀ (GC-FID)	UV-Vis Abs (avg.) PS	Dilution PS	PS C/C ₀	UV-Vis Abs (avg.) SO ₄	Dilution SO ₄	SO ₄ C/C ₀
17	5.85	1.546	1.01			0.441	61.7	0.775	0.375	9.0	0.281
18	6.59										
19	7.28	1.593	1.06			0.443	61.8	0.781	0.580	7.0	0.312
20	8.18	1.532	1.00				62.5				
21	9.04	1.508	0.98			0.444	61.7	0.780	0.511	6.9	0.278
22	9.86	1.560	1.03								
23	10.50	1.576	1.04								
24	11.52	1.561	1.03	331315.70	0.92	0.461	59.8	0.787			
25	12.92	1.526	1.00								
26	13.81	1.473	0.95								
27	16.44	1.533	1.00	378864.20	1.05	0.403	62.2	0.711	0.907	7.1	0.234
28	17.52	1.524	0.99								
29	18.27	1.546	1.02								
30	19.24	1.527	1.00			0.409	62.0	0.720			
31	20.34	1.532	1.00	401196.70	1.11						
32	21.21	1.483	0.96								
33	22.20	1.540	1.01			0.382	62.1	0.670			
34	23.05	1.503	0.98								
35	23.88	1.471	0.95								
36	24.74	1.521	0.99			0.382	62.4	0.674			

Table 21 (Continued): 0.5 mL/min Remediation Data, 60°C Activation

Data results for 0.5 mL/min Remediation Data, 60°C Activation; samples 37-56

66

Sample	Pore Volume (mL)	UV-Vis Abs (avg.) TCE	TCE C/C ₀ (UV)	GC-FID Area, TCE	TCE C/C ₀ (GC-FID)	UV-Vis Abs (avg.) PS	Dilution PS	PS C/C ₀	UV-Vis Abs (avg.) SO ₄	Dilution SO ₄	SO ₄ C/C ₀
37	25.60	1.510	0.98								
38	26.50	1.508	0.98								
39	27.40	1.521	0.99								
40	28.44	1.502	0.97								
41	29.40	1.563	1.03			0.832	62.5	0.758	0.626	10.0	0.238
42	30.28	1.505	0.98								
43	33.09	1.397	0.88								
44	35.38	1.537	1.01								
45	37.56	1.581	1.05								
46	39.57	1.484	0.96								
47	41.77	1.458	0.94								
48	44.28	1.480	0.96								
49	46.65	1.530	1.00								
50	49.51	1.574	1.04								
51	51.73	1.534	1.00			0.777	62.3	0.704	0.788	8.0	0.232
52	54.18	1.542	1.01								
53	57.72	1.509	0.98								
54	61.33	1.577	1.04								
55	65.01										
56	68.75	1.331	0.82								

Table 21 (Continued): 0.5 mL/min Remediation Data, 60°C Activation

Data results for 0.5 mL/min Remediation Data, 60°C Activation; samples 57-76

Sample	Pore Volume (mL)	UV-Vis Abs (avg.) TCE	TCE C/C ₀ (UV)	GC-FID Area, TCE	TCE C/C ₀ (GC-FID)	UV-Vis Abs (avg.) PS	Dilution PS	PS C/C ₀	UV-Vis Abs (avg.) SO ₄	Dilution SO ₄	SO ₄ C/C ₀
100	57	74.19	1.380	0.86							
	58	80.95	1.349	0.84							
	59	85.29	1.556	1.02							
	60	89.76	1.512	0.98							
	61	93.36	1.443	0.92		0.841	62.2	0.763	0.627	9.9	0.236
	62	97.59	1.439	0.92							
	63	100.49	1.493	0.97							
	64	102.73	1.493	0.97							
	65	105.07	1.503	0.98							
	66	105.91	1.496	0.97		0.833	62.6	0.760	0.545	10.1	0.214
	67	110.98	1.404	0.89							
	68	115.87									
	69	116.61	1.416	0.90							
	70	118.80			340886.90	0.95					
	71	119.69	1.390	0.87		0.851	62.5	0.775	0.571	9.9	0.218
	72	122.49			309734.60	0.86					
	73	123.31	1.319	0.81							
	74	125.36			335331.40	0.93					
	75	126.29	1.364	0.85							
	76	128.32			338774.80	0.94					

Table 21 (Continued): 0.5 mL/min Remediation Data, 60°C Activation

Data results for 0.5 mL/min Remediation Data, 60°C Activation; samples 77-96

Sample	Pore Volume (mL)	UV-Vis Abs (avg.) TCE	TCE C/C ₀ (UV)	GC-FID Area, TCE	TCE C/C ₀ (GC-FID)	UV-Vis Abs (avg.) PS	Dilution PS	PS C/C ₀	UV-Vis Abs (avg.) SO ₄	Dilution SO ₄	SO ₄ C/C ₀
77	129.30	1.261	0.76			0.822	62.7	0.751	0.481	10.0	0.191
78	132.11			297839.30	0.83						
79	132.90	1.254	0.75								
80	133.46			307290.70	0.86						
81	134.19	1.238	0.73								
82	134.75			285746.50	0.80						
83	135.41	1.217	0.72	268783.60	0.75	0.412	62.3	0.729	0.978	7.1	0.252
84	136.21	1.214	0.71								
85	136.72			254453.60	0.71						
86	137.36	1.241	0.74	259547.90	0.73						
87	138.22	1.211	0.71								
88	138.86			254000.70	0.71						
89	139.58	1.211	0.71	27116.80	0.10	0.802	62.4	0.728	0.625	10.9	0.259
90	141.08	1.168	0.67	188156.50	0.53						
91	141.85	1.095	0.61								
92	142.44			234486.90	0.66						
93	143.14	1.135	0.64	211390.00	0.60						
94	144.69	1.095	0.61								
95	145.17			222418.10	0.63						
96	145.81	1.074	0.59	218928.90	0.62	0.823	62.4	0.748	0.563	10.4	0.226

Table 21 (Continued): 0.5 mL/min Remediation Data, 60°C Activation

Data results for 0.5 mL/min Remediation Data, 60°C Activation; samples 97-116

Sample	Pore Volume (mL)	UV-Vis Abs (avg.) TCE	TCE C/C ₀ (UV)	GC-FID Area, TCE	TCE C/C ₀ (GC-FID)	UV-Vis Abs (avg.) PS	Dilution PS	PS C/C ₀	UV-Vis Abs (avg.) SO ₄	Dilution SO ₄	SO ₄ C/C ₀
97	147.56	1.041	0.56								
98	148.19			216692.30	0.61						
99	149.00	1.019	0.54	197062.60	0.56	0.833	62.5	0.759	0.545	10.0	0.213
100	151.91	0.990	0.51	136192.30	0.39						
101	154.52	0.974	0.50	138790.80	0.40						
102	156.34			157817.50	0.45						
103	190.65										
104	191.24	0.517	0.07	19411.30	0.08	0.853	62.6	0.778	0.604	9.9	0.229
105	192.36	0.496	0.05	16027.80	0.07						
106	207.15			13599.60	0.06						
107	212.43			13033.40	0.06						
108	219.24	0.467	0.01	10406.00	0.04						
109	223.79	0.461	0.00	11406.70	0.05	0.865	63.0	0.794	0.532	9.9	0.206
110	231.20	0.467	0.01	10532.20	0.04						
111	232.04	0.465	0.01	8783.50	0.04						
112	232.92	0.468	0.01	11040.80	0.05						
113	237.22			11001.70	0.04						
114	252.15	0.467	0.01	8669.80	0.04						
115	252.97	0.475	0.02	8940.00	0.04						
116	253.96	0.470	0.01	8949.30	0.04						

Table 21 (Continued): 0.5 mL/min Remediation Data, 60°C Activation

Data results for 0.5 mL/min Remediation Data, 60°C Activation; samples 117-132

Sample	Pore Volume (mL)	UV-Vis Abs (avg.) TCE	TCE C/C ₀ (UV)	GC-FID Area, TCE	TCE C/C ₀ (GC-FID)	UV-Vis Abs (avg.) PS	Dilution PS	PS C/C ₀	UV-Vis Abs (avg.) SO ₄	Dilution SO ₄	SO ₄ C/C ₀
117	256.27			9091.10	0.04						
118	289.31	0.474	0.02	7412.50	0.03						
119	290.25	0.468	0.01	7574.80	0.03						
120	291.18	0.473	0.02	7180.50	0.03	0.856	62.4	0.779	0.624	9.9	0.236
121	294.15			8104.70	0.03						
122	294.76			2710.00	0.01						
123	313.88			8271.00	0.03						
124	315.54			8280.89	0.03						
125	353.40			5434.95	0.02						
126	354.06			5459.99	0.02						
127	389.62			5473.51	0.02						
129	390.56			3899.43	0.02						
130	400.99			4152.09	0.02						
131	401.71	0.470	0.01	4541.10	0.02	0.854	62.4	0.777	0.530	10.9	0.226
132	403.24			4767.55	0.02						

Table 22: 0.2 mL/min Remediation Data, 60°C Activation

Performed for Heat-activated Persulfate Remediation of Residual, Proof of Concept

Column: A

Darcy Velocity: 0.15 cm/min

Concentrations, C₀: 2469.3 mg/L Na₂S₂O₈, 1127 mg/L TCE

Electrolyte: 0.01 N CaCl₂

Data results for 0.2 mL/min Remediation Data, 60°C Activation; samples 1-15

	Sample	Pore Volume (mL)	UV-Vis Abs (avg.) TCE	TCE C/C ₀ (UV)	GC-FID Area, TCE	TCE C/C ₀ (GC-FID)	UV-Vis Abs (avg.) PS	Dilution PS	PS C/C ₀	UV-Vis Abs (avg.) SO ₄	Dilution SO ₄	SO ₄ C/C ₀
104	1	-9.00	1.085	1.00	4986804.20	1.09						
	2	-8.41	1.134	1.04	5014374.60	1.09						
	3	-7.21	1.270	1.16	5160150.30	1.12						
	4	-6.01	1.276	1.17	5043743.10	1.10						
	5	-4.76	1.245	1.14	4999481.50	1.09						
	6	-3.50	1.286	1.17	4799184.00	1.05						
	7	-2.21	1.280	1.17	4596609.20	1.00						
	8	-0.75	1.258	1.15	4387494.20	0.96						
	9	-0.29			3996191.60	0.88						
	10	0.26	1.288	1.18	4797878.60	1.05	0.018	19.7	0.001	0.001	28.0	0.058
	11	0.81	1.303	1.19	4584135.50	1.00	0.227	39.3	0.123	0.052	13.0	0.052
	12	1.22					0.970	39.8	0.574	0.842	10.0	0.333
	13	1.46					1.020	39.4	0.599	0.873	10.1	0.346
	14	1.71					1.028	39.1	0.598	0.912	10.0	0.359
	15	2.15	1.608	1.06	1548284.00	0.35	1.029	39.4	0.604	1.041	10.0	0.407

Table 22 (Continued): 0.2 mL/min Remediation Data, 60°C Activation

Data results for 0.2 mL/min Remediation Data, 60°C Activation; samples 16-35

Sample	Pore Volume (mL)	UV-Vis Abs (avg.) TCE	TCE C/C ₀ (UV)	GC-FID Area, TCE	TCE C/C ₀ (GC-FID)	UV-Vis Abs (avg.) PS	Dilution PS	PS C/C ₀	UV-Vis Abs (avg.) SO ₄	Dilution SO ₄	SO ₄ C/C ₀
16	16.76	1.611	1.06	4410717.80	0.96	1.033	39.6	0.610	1.016	10.0	0.398
17	17.46	1.611	1.06	4507571.10	0.98						
18	18.96	1.607	1.06	4214450.70	0.92						
19	20.38	1.588	1.04	4668265.50	1.02	1.013	39.4	0.594	0.775	13.1	0.403
20	22.14	1.594	1.05	4653399.70	1.02						
21	23.56	1.599	1.05	4346928.00	0.95						
22	25.15	1.575	1.03	3981579.00	0.87	1.031	39.6	0.608	1.005	10.1	0.395
23	26.73	1.583	1.04	1970226.70	0.44						
24	27.44	1.610	1.06	4398824.90	0.96						
25	28.90	1.600	1.05	2085157.60	0.47						
26	30.42	1.621	1.07	4386213.10	0.96	1.068	38.4	0.611	0.668	15.3	0.410
27	31.95	1.619	1.07	4625493.50	1.01						
28	33.76	1.634	1.08	4646483.80	1.01						
29	34.48	1.627	1.07	4705225.40	1.03	1.064	39.1	0.620	0.953	10.1	0.375
30	50.54	1.568	1.02	4518251.30	0.99	1.033	39.8	0.613	1.197	10.1	0.467
31	51.26	1.597	1.05	4541567.50	0.99						
32	51.94	1.614	1.06	4297044.20	0.94						
33	53.89	1.612	1.06	4860216.30	1.06						
34	55.71	1.607	1.06	4725661.70	1.03	1.028	39.5	0.604	0.844	11.1	0.370
35	57.43	1.593	1.04	3861692.50	0.85						

Table 22 (Continued): 0.2 mL/min Remediation Data, 60°C Activation

Data results for 0.2 mL/min Remediation Data, 60°C Activation; samples 36-55

Sample	Pore Volume (mL)	UV-Vis Abs (avg.) TCE	TCE C/C ₀ (UV)	GC-FID Area, TCE	TCE C/C ₀ (GC-FID)	UV-Vis Abs (avg.) PS	Dilution PS	PS C/C ₀	UV-Vis Abs (avg.) SO ₄	Dilution SO ₄	SO ₄ C/C ₀
36	59.48	1.590	1.04	4466385.90	0.98						
37	61.42	1.592	1.04	4760999.20	1.04	1.039	39.8	0.617	0.865	11.2	0.380
38	63.29	1.556	1.01	4455591.30	0.97						
39	64.01	1.598	1.05	4336308.20	0.95						
40	66.16	1.566	1.02	4553757.80	0.99	1.050	39.5	0.617	0.875	11.2	0.386
41	68.28	1.594	1.05	4693638.30	1.02						
42	68.93	1.592	1.04	4689361.60	1.02	1.056	39.4	0.619	0.757	12.5	0.377
43	82.77	1.575	1.03	4470175.50	0.98	1.035	39.1	0.603	0.353	25.7	0.388
44	84.47	1.584	1.04	4593173.10	1.00						
45	85.87	1.579	1.03	4299743.20	0.94						
46	87.34	1.583	1.04	4200562.80	0.92	1.057	39.2	0.617	0.762	12.5	0.379
47	88.58	1.558	1.01	3920691.10	0.86						
48	90.81	1.534	0.99	4612756.20	1.01						
49	91.57	1.563	1.02	4139845.40	0.91						
50	92.35	1.540	1.00	4517089.00	0.99	0.985	39.7	0.581	0.899	12.6	0.443
51	94.50	1.531	0.99	4369239.30	0.96						
52	95.24	1.532	0.99	4241302.50	0.93						
53	96.73	1.548	1.00	4504848.80	0.98	1.064	39.3	0.624	0.700	13.9	0.387
54	98.24	1.481	0.95	4461709.90	0.97						
55	99.00	1.552	1.01	4373616.10	0.96						

Table 22 (Continued): 0.2 mL/min Remediation Data, 60°C Activation

Data results for 0.2 mL/min Remediation Data, 60°C Activation; samples 56-75

Sample	Pore Volume (mL)	UV-Vis Abs (avg.) TCE	TCE C/C ₀ (UV)	GC-FID Area, TCE	TCE C/C ₀ (GC-FID)	UV-Vis Abs (avg.) PS	Dilution PS	PS C/C ₀	UV-Vis Abs (avg.) SO ₄	Dilution SO ₄	SO ₄ C/C ₀
56	101.24	1.535	0.99	4720028.80	1.03	1.030	39.7	0.610	0.700	12.7	0.355
57	102.63	1.552	1.01	4303349.10	0.94						
58	104.38	1.530	0.99	4297712.70	0.94	1.035	39.7	0.611	0.671	14.1	0.377
59	104.86			4087075.00	0.89						
60	117.07	1.321	0.80	3617399.20	0.79						
61	117.59			3777636.90	0.83						
62	118.27	1.352	0.83	2969916.20	0.66	1.027	39.2	0.600	0.540	17.4	0.383
63	120.10	1.296	0.78	2827745.20	0.63						
64	120.81	1.241	0.73	2814566.50	0.62	1.012	39.3	0.592	0.845	12.4	0.413
65	121.53	1.213	0.71	2037283.50	0.46	1.024	39.7	0.606	0.593	15.8	0.378
66	122.27	1.212	0.71	2640213.80	0.59						
67	123.04	1.149	0.65	2468140.80	0.55						
68	123.75	1.152	0.65	2241140.40	0.50						
69	124.44	1.149	0.65	2386297.50	0.53						
70	125.83	1.080	0.59	2152847.60	0.48	1.041	39.8	0.618	0.737	12.4	0.365
71	126.57	1.026	0.54	2349481.60	0.52						
72	127.27	0.992	0.51	1760173.00	0.40						
73	127.98	1.019	0.54	2013562.20	0.45						
74	129.00	1.001	0.52	1922265.00	0.43						
75	131.23	0.980	0.50	1125546.40	0.26	1.039	39.7	0.614	0.626	14.6	0.368

Table 22 (Continued): 0.2 mL/min Remediation Data, 60°C Activation

Data results for 0.2 mL/min Remediation Data, 60°C Activation; samples 76-95

Sample	Pore Volume (mL)	UV-Vis Abs (avg.) TCE	TCE C/C ₀ (UV)	GC-FID Area, TCE	TCE C/C ₀ (GC-FID)	UV-Vis Abs (avg.) PS	Dilution PS	PS C/C ₀	UV-Vis Abs (avg.) SO ₄	Dilution SO ₄	SO ₄ C/C ₀
76	131.95	0.965	0.49	2055075.80	0.46						
77	132.65	0.952	0.48	1992533.50	0.45						
78	133.43	0.940	0.47	1721907.90	0.39						
79	134.15	0.920	0.45	1889466.80	0.42						
80	134.88	0.926	0.45	1720046.80	0.39	1.038	39.8	0.616	0.752	12.7	0.378
81	135.94	0.923	0.45	1598867.20	0.36						
82	136.82	0.878	0.41	1716469.00	0.39						
83	138.73	0.913	0.44	1713711.20	0.39						
84	139.47	0.913	0.39	572712.00	0.14	1.039	38.8	0.601	0.777	12.6	0.386
85	140.34	0.918	0.39	1553778.30	0.35						
86	141.10	0.903	0.38	1514767.10	0.34						
87	141.81	0.910	0.39	1453085.60	0.33						
88	142.46			1363152.90	0.31						
89	153.33	0.856	0.34	1253967.20	0.29	1.022	39.4	0.600	0.819	12.5	0.405
90	154.04	0.850	0.33	1209701.60	0.28						
91	160.51	0.841	0.32	1135687.00	0.26	1.004	39.6	0.591	0.840	12.6	0.418
92	161.21	0.864	0.34	947542.00	0.22						
93	161.97	0.842	0.33	961000.20	0.23						
94	169.47	0.782	0.27	876558.00	0.21						
95	170.21	0.795	0.28	740909.90	0.18						

Table 22: 0.2 mL/min Remediation Data, 60°C Activation

Data results for 0.2 mL/min Remediation Data, 60°C Activation; samples 95-119

Sample	Pore Volume (mL)	UV-Vis Abs (avg.) TCE	TCE C/C ₀ (UV)	GC-FID Area, TCE	TCE C/C ₀ (GC-FID)	UV-Vis Abs (avg.) PS	Dilution PS	PS C/C ₀	UV-Vis Abs (avg.) SO ₄	Dilution SO ₄	SO ₄ C/C ₀
96	171.02	0.785	0.27	321224.60	0.09						
97	172.16	0.757	0.25	617123.20	0.15						
98	174.01	0.796	0.28	775193.00	0.19	0.997	39.8	0.590	0.818	12.5	0.403
99	174.78	0.738	0.23	797034.60	0.19						
100	189.69	0.653	0.16	439368.80	0.11	1.012	39.5	0.596	0.851	12.5	0.419
101	190.40	0.666	0.17	522119.90	0.13						
102	192.26	0.667	0.17	445513.80	0.12						
103	193.02	0.659	0.16	433464.20	0.11						
104	194.56	0.644	0.15	462905.30	0.12	1.013	39.2	0.591	0.832	12.5	0.409
105	196.18	0.642	0.15	427430.80	0.11						
106	197.67	0.640	0.15	419524.70	0.11						
107	199.34	0.622	0.13	369053.10	0.10	1.022	39.3	0.599	0.807	12.6	0.403
108	202.80	0.611	0.12	327355.60	0.09						
109	203.59	0.603	0.11	223165.50	0.07						
110	205.71	0.571	0.09	314830.20	0.09	1.020	39.7	0.603	0.827	12.5	0.407
111	206.21			285211.20	0.08						
112	224.47	0.564	0.08	29806.30	0.01	1.018	39.6	0.601	0.823	12.5	0.406
113	225.17	0.558	0.07	50281.00	0.02						
114	242.66	0.529	0.05	3888.60	0.00						

Table 22 (Continued): 0.2 mL/min Remediation Data, 60°C Activation

Data results for 0.2 mL/min Remediation Data, 60°C Activation; samples 115-125

110	Sample	Pore Volume (mL)	UV-Vis Abs (avg.) TCE	TCE C/C ₀ (UV)	GC-FID Area, TCE	TCE C/C ₀ (GC-FID)	UV-Vis Abs (avg.) PS	Dilution PS	PS C/C ₀	UV-Vis Abs (avg.) SO ₄	Dilution SO ₄	SO ₄ C/C ₀
	115	243.56	0.617	0.13	3126.20	0.00	1.004	39.7	0.593	0.680	14.9	0.404
	116	244.70	0.544	0.06	4743.00	0.00						
	117	260.16	0.649	0.15	3306.20	0.00	1.012	39.8	0.599	0.869	12.5	0.429
	118	260.99	0.464		3877.60	0.00						
	119	279.10	0.480	0.00	3712.10	0.00	1.025	39.5	0.603	0.807	12.5	0.399
	120	279.81	0.642	0.15	3552.40	0.00						
	121	296.51	0.864	0.34	2875.90	0.00						
	122	297.44	0.752	0.25	3609.50	0.00						
	123	299.59	0.521	0.04	2785.90	0.00	1.027	39.9	0.610	0.804	12.5	0.399
	124	304.88	0.557	0.07	3137.20	0.00						
	125	309.17					1.032	39.8	0.611	0.631	12.5	0.317

Table 23: 100 mM Batch Studies

Performed for control of persulfate interaction with Accusand, sampling containers, other mass loss effects

Asterisk (*) indicates sample done without Accusand.

111	Solution	Sample	Weight Day 1 (g)	Weight Day 9 (g)	% Wt. Change	Conc. Day 1 PS (mg/L)	Conc. Day 9 PS (mg/L)	Normalized Conc.: C/Co	Wt. Loss Corrected Conc. PS (mg/L)	Corrected Norm. Conc.
	DI	A	35.1425	34.7543	-1.10%	23554	23805	1.01	23542	1.00
	DI	B	35.2352	35.2212	-0.04%	23554	23755	1.01	23745	1.01
	DI	C	35.7305	34.7255	-2.81%	23554	23781	1.01	23112	0.98
	DI	D	35.0989	34.8578	-0.69%	23554	24015	1.02	23851	1.01
	DI	E	35.8416	35.8373	-0.01%	23554	23676	1.01	23673	1.01
	DI	F*	25.088	24.7579	-1.32%	23554	24083	1.02	23766	1.01
	DI	G*	25.2251	24.8972	-1.30%	23554	24006	1.02	23694	1.01
	CaCl ₂	H	35.3849	35.3846	0.00%	26061	26293	1.01	26293	1.01
	CaCl ₂	I	35.2779	35.195	-0.23%	26061	26379	1.01	26317	1.01
	CaCl ₂	J	35.1602	35.1598	0.00%	26061	26308	1.01	26307	1.01
	CaCl ₂	K	35.3102	34.9589	-0.99%	26061	26340	1.01	26078	1.00
	CaCl ₂	L	35.0817	34.7322	-1.00%	26061	26192	1.01	25931	0.99
	CaCl ₂	M*	25.2957	25.0049	-1.15%	26061	26079	1.00	25779	0.99
	CaCl ₂	N*	25.1561	25.0953	-0.24%	26061	26398	1.01	26335	1.01

Table 24: 10 mM Batch Studies

Performed for control of persulfate interaction with Accusand, sampling containers, other mass loss effects

Asterisk (*) indicates sample done without Accusand.

112	Solution	Sample	Weight Day 1 (g)	Weight Day 9 (g)	% Wt. Change	Conc. Day 1 PS (mg/L)	Conc. Day 9 PS (mg/L)	Normalized Conc.: C/Co	Wt. Loss Corrected Conc. PS (mg/L)	Corrected Norm. Conc.
	DI	A	35.1213	34.9605	-0.46%	2217	2289	1.03	2279	1.03
	DI	B	35.3488	35.2964	-0.15%	2217	2276	1.03	2273	1.02
	DI	C	35.6916	35.4641	-0.64%	2217	2304	1.04	2289	1.03
	DI	D	35.863	35.6398	-0.62%	2217	2291	1.03	2277	1.03
	DI	E	35.1442	35.0503	-0.27%	2217	2289	1.03	2283	1.03
	DI	F*	25.5138	25.2646	-0.98%	2217	2352	1.06	2329	1.05
	DI	G*	25.5294	25.5302	0.00%	2217	2323	1.05	2323	1.05
	CaCl2	A'	35.1933	35.1392	-0.15%	2657	2628	0.99	2624	0.99
	CaCl2	B'	35.8661	35.8652	0.00%	2657	2608	0.98	2608	0.98
	CaCl2	C'	35.2082	35.2076	0.00%	2657	2619	0.99	2619	0.99
	CaCl2	D'	35.3804	35.1783	-0.57%	2657	2650	1.00	2635	0.99
	CaCl2	E'	35.6896	35.4536	-0.66%	2657	2639	0.99	2622	0.99
	CaCl2	F*	25.186	25.1843	-0.01%	2657	2705	1.02	2705	1.02
CaCl2	G*	25.0721	24.9199	-0.61%	2657	2681	1.01	2665	1.00	

Table 25: 60°C Batch Activation Study

Performed for Heat-activation of persulfate kinetics

Concentrations, C_0 : 2393.6 mg/L $\text{Na}_2\text{S}_2\text{O}_8$

Electrolyte: 0.01 N CaCl_2

Data results for 60°C Batch Activation of persulfate; samples 1-11

113	Sample	Time (hr)	Dilution	UV-Vis Abs. (Avg.), PS	C/ C_0 , PS	
	1	0.0	104.9	0.618	0.975	
	2	12.9	104.5	0.325	0.498	
	3	24.7	103.2	0.150	0.213	
	4	36.8	62.4	0.121	0.101	
	5	48.8	61.9	0.065	0.047	
	6	60.8	62.0	0.036	0.019	
	7	73.0	61.7	0.023	0.006	
	8	86.8	20.0	0.041	0.008	
	9	95.3	20.1	0.022	0.007	
	10	99.5	20.1	0.018	0.001	LDL
	11	111.2	20.0	0.007	-0.003	LDL

Table 26: 90°C Batch Activation Study

Performed for Heat-activation of persulfate kinetics, and sulfate species mass balance

Concentrations, C_0 : 2375.8 mg/L $\text{Na}_2\text{S}_2\text{O}_8$

Electrolyte: 0.01 N CaCl_2

Data results for 90°C Batch Activation of persulfate; samples 1-17

	Sample	Elapsed Time	Dilution, PS	UV-Vis Abs. (avg.), PS	C/ C_0 , PS	Dilution, SO_4	UV-Vis Abs. (avg.), SO_4	C/ C_0 , SO_4
114	1	0.13	59.8	1.103	0.999	13.7	0.020	0.020
	2	0.23	59.4	1.099	0.988	11.7	0.038	0.030
	3	0.33	59.4	0.971	0.870	19.8	0.163	0.142
	4	0.50	60.0	0.662	0.592	19.8	0.598	0.429
	5	0.69	59.1	0.459	0.398	19.7	0.877	0.611
	6	0.86	39.4	0.529	0.308	29.9	0.523	0.717
	7	1.03	19.7	0.833	0.246	29.7	0.596	0.785
	8	1.19	19.7	0.662	0.195	29.5	0.653	0.836
	9	1.36	19.7	0.530	0.154	29.7	0.683	0.870
	10	1.61	19.7	0.375	0.107	29.9	0.726	0.920
	11	1.86	19.8	0.272	0.076	29.6	0.783	0.967
	12	2.11	19.7	0.196	0.052	29.7	0.750	0.937
	13	2.37	19.7	0.141	0.035	31.8	0.738	0.981
	14	2.71	19.7	0.091	0.020	31.7	0.734	0.973
	15	3.03	19.7	0.062	0.015	31.8	0.730	0.972
	16	3.37	19.7	0.041	0.009	33.5	0.708	0.992
	17	3.74	19.6	0.031	0.006	33.5	0.707	0.990
	18	4.14	19.7	0.021	0.003	33.5	0.720	1.006
	19	4.49	19.9	0.017	0.002	33.6	0.716	1.003
	20	5.00	19.7	0.016	0.001	33.8	0.712	1.005
	21	6.56	19.8	0.016	0.001	33.4	0.719	1.002