

2006-08-23

Slurry Test Evaluation for In-Situ Remediation of TCE Contaminated Aquifer

Sachin Sharma
Worcester Polytechnic Institute

Follow this and additional works at: <https://digitalcommons.wpi.edu/etd-theses>

Repository Citation

Sharma, Sachin, "Slurry Test Evaluation for In-Situ Remediation of TCE Contaminated Aquifer" (2006). *Masters Theses (All Theses, All Years)*. 960.

<https://digitalcommons.wpi.edu/etd-theses/960>

This thesis is brought to you for free and open access by [Digital WPI](#). It has been accepted for inclusion in Masters Theses (All Theses, All Years) by an authorized administrator of Digital WPI. For more information, please contact wpi-etd@wpi.edu.

Slurry Test Evaluation for In-Situ Remediation of TCE Contaminated Aquifer

By

Sachin Sharma

A Thesis

Submitted to the Faculty

of the

WORCESTER POLYTECHNIC INSTITUTE

In partial fulfillment of the requirement for the

Degree of Master of Science

In

Environmental Engineering

By

August 23, 2006

APPROVED:

Professor John Bergendahl, Major Advisor

Professor James C. O'Shaughnessy, Co-Advisor

Professor Frederick Hart, Head of Department

Acknowledgments

I would like to thank Professor John Bergendahl for his help and for having the patience to answer enthusiastically to all my questions. I would like to thank Professor James C.O' Shaughnessy for his continuous support and suggestions during this work.

I would like to thank Mr. Don Pelligrino for his help in lab work and ordering supplies. I would like to thank Amanda Kohler for her help in conducting experiments in a timely fashion. I would like to thank Agata Lajoie for her cooperation in carrying out all the necessary paper work required for this work. I would like to thank Jyoti for her assistance in conducting experiments in safe manner.

Table of Contents

CHAPTER 1 INTRODUCTION	1
CHAPTER 2 BACKGROUND	4
2.1 Trichloroethylene	4
2.1.1 Health Aspect	7
2.1.2 Current Treatment Methods	8
2.2 Oxidation via Fenton's Reagent	10
2.3 Persulfate Oxidation	12
Chapter 3 Materials and Methods	16
3.1 Materials	16
3.2 Methods	17
3.3 Equipment	18
3.3.1 Programming the Gas Chromatograph	18
3.3.2 Headspace sampling	19
3.4 Equipment	20
CHAPTER 4 Procedures	21
4.1 Producing standard curves	21
4.2 Soil slurries for ferrous activated peroxide oxidation	27
4.3 Slurries for persulfate oxidation activated by ferrous, ozone and ZVI	29
Chapter 5 Results and Discussion	30
5.1 Oxidation using Hydrogen peroxide in Soil Slurries using MAE	30
5.2 Aqueous oxidation of TCE using Sodium Persulfate	32
5.3 Aqueous oxidation of TCE using Sodium Persulfate and Ozone	43
5.4 Zero Valent Iron and Ozone Activated Persulfate Oxidation of TCE	46
CHAPTER 6 Conclusions	48
Chapter 7 Future Work	49
CHAPTER 8 Works Cited	50
Appendix A: Control and oxidation data	54

List of Figures

<i>Fig 2-1: Chemical structure of TCE</i>	7
<i>Fig 3-1: Samples for slurry test</i>	20
<i>Figure 3-2: Headspace Method Diagram</i>	22
<i>Figure 4-1: Standard curve for Trichloroethylene (TCE) showing peak area as a function of TCE concentration</i>	25
<i>Figure 4-2: Standard curve for trans-1,2-dichloroethene (DCE) showing the concentration of trans-1,2-DCE as a function of the peak area</i>	26
<i>Figure 4-3: Standard curve for cis-1,2-dichloroethene (DCE) showing the concentration of cis-1,2-DCE as a function of the peak area</i>	27
<i>Figure 4-4: Standard curve for 1,1-dichloroethene (DCE) showing the concentration of 1,1-DCE as a function of the peak area</i>	28
<i>Figure 5-1: Average Percent of TCE removed from the soil for the different hydrogen peroxide/soil sample size variation</i>	33
<i>Fig 5-2: Picture shows the 40 ml batch reactor for slurry testing with and without foil</i>	35
<i>Figure 5-3: controls for TCE degradation</i>	37
<i>Fig 5-4: Adsorption control for TCE on various media. Error bar shows the standard deviation for controls</i>	38
<i>Fig 5-5: % Destruction of TCE at Persulfate/Iron/TCE molar ratio of 20/1/1 and 20/0/1</i>	38
<i>Fig 5-6: Destruction of TCE after 24 hrs for various molar ratios</i>	39
<i>Fig 5-7: Effect on the pH at 0 hr as the molar dose was changed at room temperature of 25⁰C</i>	40
<i>Fig 5-8: Effect on the pH at 24 hrs as the molar dose was changed at room temperature of 25⁰C</i>	41
<i>Fig5-9: Reaction Kinetics at Persulfate/Iron/TCE molar ratio of 10/1/1 and 10/0/1</i>	42
<i>Fig 5-10: % TCE remaining at 10/1/1 molar ratio of Persulfate/Iron/TCE</i>	43
<i>Fig 5-11: % TCE remaining at 10/0/1 molar ratio of Persulfate/Iron/TCE</i>	44

<i>Fig 5-12: pH variation with increased media loading</i>	47
<i>Fig 5-13: Reaction Kinetics at Persulfate/Iron/TCE molar ratio of 10/0/1 with ozone saturated water</i>	48
<i>Fig 5-14: First order reaction kinetics for methanol quenched ozone activated persulfate oxidation of TCE</i>	49

Abstract

Trichloroethylene (TCE) is the most commonly found groundwater pollutant. The focus of this research was to determine the effectiveness of chemical oxidation for in-situ remediation of TCE contaminated aquifers. Analytical techniques were developed to measure the concentration of TCE and its degradation products in soil and in solution. Slurry tests were conducted to emulate in situ conditions. Various media used for the slurry tests included sand, silica and glass beads. In-situ chemical oxidation of the TCE was performed using sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), Fenton's reagent, Ozone and sodium persulfate activated by iron, ozone and zero valent iron.

Persulfate oxidation was shown to be effective for TCE oxidation in the presence of all the media tested in slurry tests for various molar ratios of oxidant and catalyst (Fe). Approximately 75% of TCE destruction takes place in the first 5 minutes of the slurry test and 90% destruction within 24 hours. Fenton's oxidation was tried with varying concentration of H_2O_2 and slurry volume. Percent removal of TCE decreased from a hydrogen peroxide concentration of 3.34% to 5% (w/v). It was found that persulfate oxidation activated by zero valent iron removed TCE more effectively than persulfate oxidation activated by ferrous iron. For persulfate oxidation activated by ozone it was found that 95% of TCE was destroyed at persulfate/TCE molar concentration of 10/1 with an initial rate constant of 0.2854/min. It was also found that increasing the amount of solids in the slurry test decreased the effectiveness of chemical oxidation.

CHAPTER 1 INTRODUCTION

TCE or Trichloroethylene is a colorless or blue organic liquid with a chloroform-like odor. TCE is a DNAPL (dense non aqueous phase liquid); since it's heavier than water it sinks down in an aquifer. TCE is mainly used to remove grease from fabricated metal parts, in dry cleaning, paint removers, printing inks and adhesives. TCE does not occur naturally and is only produced by two companies in the United States ("Chemical Profile", 2002). The demand for TCE in industry is growing; from 2000 to 2005 demand grew from 187 million pounds to an estimated 267 million pounds. Use as a hydrofluorocarbon intermediate accounts for 67% of TCE consumption and metal degreasing accounts for 30%. Historically, the main use for TCE was as a metal degreaser, however stricter state and local regulations have caused a decline in its use ("Chemical Profile", 2002). The United States Environmental Protection Agency (EPA) set a maximum contaminant level at 5 µg/L of trichloroethylene (TCE) for drinking water.

Production of TCE has increased from just over 260,000 lbs. in 1981 to 320 million lbs. in 1991. Major environmental releases of trichloroethylene are due to air emissions from metal degreasing plants. Wastewater from metal finishing, paint and ink formulation, electrical/electronic components, and rubber processing industries also may contain trichloroethylene. From 1987 to 1993, according to the Toxics Release Inventory, trichloroethylene releases to water and land totaled over 291,000 lbs. These releases were primarily from steel pipe and tube manufacturing industries. While it has been estimated that 60% of total TCE produced in the United States is lost to the atmosphere, with

negligible discharge into water bodies (Cohen and Ryan, 1985). The largest releases occurred in Pennsylvania and Illinois. The largest direct releases to water occurred in West Virginia (EPA, 2005).

The regulation for trichloroethylene became effective in 1989. Between 1993 and 1995, EPA required water suppliers to collect water samples every 3 months for one year and analyze them to find out if TCE was present above 0.5 ppb. If it was present above this level, the system was required to monitor this contaminant until the system took immediate steps to remediate the problem or the State has determined that the contaminant would remain reliably and consistently below the MCL.

TCE contaminated soil can be difficult to treat since the TCE is a DNAPL. Most of the remedial methods for groundwater remediation at contaminated sites involve some type of pump and treat system. Typically the groundwater is extracted by wells, followed by surface treatment of the water by sorption and aqueous chemical oxidation before disposal. Although this type of treatment method is accepted by government environmental agencies, however it was not very successful (Mackay and Cherry, 1989; Travis and Doty, 1990; Bartow and Davenport, 1995). Practical problems such as the presence of chlorinated solvent pools in the saturated zone and complexities relating to surface gradient, varying longitudinal and vertical subsurface profile, migration of contaminants to inaccessible low permeability regions, creation of vadose zone and processes such as retardation of the pollutants by sorption of contaminants onto solids

greatly extend the time required to effectively remove the refractory contaminants. These problems are major obstacles to conventional pump and treat remedial techniques (Mackay and Cherry, 1989; NRC, 1994). Even if TCE can be treated by pump and treat system, which can take long times and still has the potential risk to exposing to public as it quite volatile. The unsatisfactory results from conventional pump and treat processes have indicate the need for innovative alternatives to conventional pump and treat remedial techniques. Among such alternatives are the various in situ techniques where removal of the contaminant from the saturated zone is not required, but instead the contaminants are destroyed in place. Other mean of treating the contaminated soil it to dig it and treat offsite, which can be costly and has the potential danger of volatilizing the TCE into air. In situ oxidation of a aquifer involve injection of fluids which can have some problem such as displacement of the contaminant due to the very nature of plug flow, and thus having problems in efficient mixing (Gates and Siegrist, 1995). This project evaluated the feasibility of in-situ remediation of TCE contaminated soil using chemical oxidation. In-situ remediation unlike other method is quite safe to work with and does not pose the threat of inhalation of TCE. In-situ remediation of TCE contaminated aquifer can be done by injecting the combination of oxidizing agents to mineralize the TCE.

CHAPTER 2 BACKGROUND

2.1 Trichloroethylene

TCE is a halogenated, aliphatic organic compound. In pure phase, it is a colorless liquid with a slightly sweet smell. TCE has unique properties and solvent effects, so it has widely been used as an ingredient in industrial cleaning solutions and as a “universal” degreasing agent. TCE was replaced with tetrachloroethylene in the dry cleaning industry. TCE has also been discontinued for the following uses: fumigants, extractant for decaffeinating coffee, in cosmetics and drug products (EPA, 2001). The molecular formula for TCE is C_2HCl_3 and its chemical structure is shown in Figure 2-1. TCE has several trade names and synonyms listed below (EPA, consumer fact sheet, 2005).

- 1,1,2-Trichloroethylene
- Acetylene trichloroethylene Algylen
- Anameth
- Benzinol
- Chlorilen
- CirCosolv
- Germalgene
- Lethurin
- Perm-a-chlor
- Petzinol
- Philex
- TRI-Plus M
- Vitran

Trichloroethylene released to soil will either evaporate or leach into ground water. If released to surface water, it will also quickly evaporate. Solubility of TCE in water at 20°C and 1 atm is 1000 ppm (Russell et al, 1992; EPA, 2001). It has only a moderate potential to accumulate in aquatic life. In the gas phase, it is relatively stable in air, but unstable in light or moisture. The reactivity of TCE in aqueous solution varies with

conditions. It is incompatible with strong caustics or alkalis. It is chemically active with metals such as barium, lithium, titanium and beryllium (EPA, 2001). Several of its properties can be seen in Table 2-1.

Table 2-1: Properties of TCE (Russell et al., 1992; EPA, 2001)

Density, g/ml	1.46
Solubility,mg/L@20 ⁰ C	1000
Henry' Law Constant,atm-m ³ /mol@20 ⁰ C	0.00892
Molecular Weight ,g	131.4
Boiling Point	86.7 ⁰ C
Melting Point	-73 ⁰ C
Vapor Pressure@0 ⁰ C,mmHg	19.9
Vapor Pressure@20 ⁰ C,mmHg	57.8
Log Octanol-Water Partition Coefficient	2.42

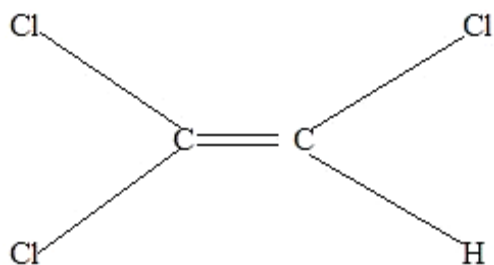


Fig 2-1: Chemical structure of TCE

The chemical structure of TCE indicates its chemical reactivity. Three chlorine atoms attached to the carbon-carbon double bond make TCE a highly oxidized compound. TCE

is highly oxidized, thus resists further oxidation but is readily reduced (Russell *et al.*, 1992). It is however possible to oxidize TCE using chemicals such as potassium ferrate. Delucca *et al.* (1983) determined that 30 ppm potassium ferrate would completely oxidize 100 ppb TCE in less than fifty minutes at 20⁰ C and at a pH of 8.3. Size of the three carbon atom surrounding the double bond in the TCE is responsible for steric hindrances (Russell *et al.*, 1992). This lowers the rate at which large nucleophile groups can approach or react with the carbon-carbon double bond.

During a rainfall, chemicals can easily percolate from the unsaturated zone to the water table. If the chemical is an immiscible liquid such as petroleum based solvent, an additional phase may be created. This could be a water immiscible phase which is called non aqueous phase liquid (NAPL). TCE is dense non aqueous phase liquid (DNAPL). So when TCE is present in pure phase, it sinks through the water and migrates along the natural gradient of the surface with the flow of water. TCE can easily spread in an aquifer through dissolution, advection and dispersion depending upon the velocity and turbulence in the channel or ground water. The low K_{oc} value of 2.42 for TCE indicates little retardation by soil or aquifer organic materials.

Henry's coefficient describes the relative tendency of a compound to volatilize from liquid to air. The Henry's coefficient for TCE is 0.00892 (unit less) which is high enough, when combined with its low solubility in water and high vapor pressure, so it can efficiently transfer to the atmosphere. Since the TCE is quite volatile, exposure is mainly through inhalation, ingestion and dermal absorption. Transformation and degradation

processes of TCE in environment are very slow. TCE does not absorb ultraviolet light at wavelengths less than 290 nanometers, so it does not photolyze in the atmosphere or in water naturally (Wendelin *et.al*, 1993).

2.1.1 Health Aspect

Trichloroethylene is not carcinogenic; it is thought to become a human health hazard only after processing in the human liver (Bartseh et al, 1979; EPA, 1992). Epoxidation by liver oxidase enzymes confers a suspected carcinogenic nature (Apfeldorf and Infante, 1981; Tu et al., 1985). The symptoms of exposure to TCE are manifested in central nervous system problems (WHO, 1985). They include headache, drowsiness, hypohydrosis, and tachycardia. Psychomotor impairment was noticed after inhalation exposure to 5,400 mg/m³ (1000 ppm) for 2 hours in work place conditions (WHO, 1985). TCE vapors can cause eye irritation. High oral doses; 200 ml to 300 ml can be toxic to the liver and kidneys. TCE dose of 7,000 mg/kg body weight can be lethal to an adult (WHO, 1985). Reductive dehalogenation of TCE leads to production of vinyl chloride which in contrast to TCE is known carcinogen [Fed. Regist. 1984, 49:114, 24334(11)].

2.1.2 Current Treatment Methods

- Wastewater and municipal water supply treatment processes which use coagulation, sedimentation, precipitation, softening, filtration and chlorination are ineffective for reducing the concentration of TCE to non hazardous levels (Robeck and Love, 1983). In wastewater treatment ozone is also used to remove organic material. In this case reaction of ozone with the carbon –carbon (Glaze and Kang (1988) and Francis (1987)) double bond takes place or nucleophilic substitution by hydroxyl radicals takes place. Hydroxyl radicals are generated by the decomposition of ozone. Their results indicate that direct ozonation of TCE is a slow process under alkaline conditions in ground water. To increase the production of hydroxyl radicals or to increase the oxidation potential of ozone Glaze and Kang (1988) have suggested four ways.

- Variation in pH
- Addition of Hydrogen Peroxide
- Addition of Ultra Violet radiation
- Addition of a combination of Ultra Violet radiation and Peroxide

Air stripping also is used to remove TCE from contaminated water. It requires a constant stream of air to expel TCE out from solution into air, taking advantage of low Henry's coefficient and water solubility. A typical air stripper is designed in a manner to allow the percolation of large volumes of air through contaminated water. The main limitation of

this method is large volumes of air are required. This process only shifts the contaminant from water to air which is not environmental friendly and is of concern.

Granular activated carbon (GAC) is also used to adsorb TCE from water. However GAC has certain limitations.

- High dissolved organic carbon and other contaminants can compete with TCE for binding sites, thus saturating the column earlier than required. A concentration of 10 ppm natural organic matter in river water has been shown to reduce TCE adsorption by 70% (Amy *et.al.*, 1987).
- A sorbent has a finite capacity for a specific contaminant. With fixed bed adsorbents, when the sorption limit is reached the contaminant can breakthrough. It is necessary to regenerate the GAC media or replace it after breakthrough occurs. At a concentration of 1 ppm TCE at a neutral pH and 20°C, the capacity of TCE on a GAC was found to be approximately 28 mg/g (Hugh et al., 1992).

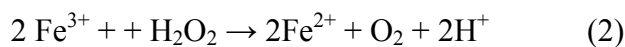
Combined air stripping and granular activated carbon (GAC) adsorption is also one of the popular technologies to remove TCE. Air stripping can not lower the concentration of TCE in water to acceptable drinking water standard without high air flow rates. So the effluent from the air stripper can be sent to GAC column with reduced influent levels to finally get the most desirable effluent quality.

TCE is susceptible to chemical reduction. Transition metals play a vital role in abiotic reductions. Major reductive components can be electrons or reducing equivalents produced from biological reactor or molecular hydrogen (Barbash and Roberts, 1986). Reduction of TCE is possible by any compound that has low oxidation potential (or high reduction potential) for efficient hydrogen transfer under ambient conditions. Natural dehalohydrolysis of TCE occurs with byproduct alcohol. Half lives of this reaction are on the order of days to centuries (Barbash and Roberts, 1986). Removal of chlorine atom from one carbon coincides with removal of hydrogen from the adjacent carbon. However natural dehalohydrolysis is not considered to be a significant mechanism for degradation.

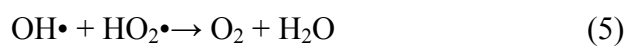
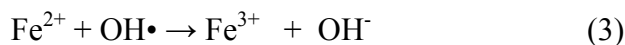
2.2 Oxidation via Fenton's Reagent

Advanced oxidation processes involves the generation of hydroxyl free radicals ($\text{OH}\cdot$). Hydroxyl radicals are one of the strongest oxidants known after fluorine. Hydroxyl radicals react with dissolved constituents through a series of complex reactions until the constituents are completely mineralized. Hydroxyl radicals once generated, can attack organic molecules by radical addition, hydrogen abstraction, electron transfer and radical combination (SES, 1994). Today there are many technologies present to produce $\text{OH}\cdot$ in aqueous phase. Fenton's reagent is a mixture of hydrogen peroxide and ferrous iron. During Fenton's oxidation, iron cycles between the +II and +III oxidation states yielding hydroxyl radicals ($\text{OH}\cdot$) as shown in equation 1. The ferric iron (+III) can react with hydrogen peroxide to return to the +II oxidation state, as shown in equation 2. Fenton's

oxidation is best under acidic conditions because at higher pH iron has a lower solubility (Huling *et al.*, 2000; Teel *et al.*, 2001).

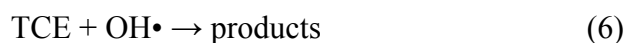


Other reactions may take place during Fenton's oxidation (Teel *et al.*, 2001).



The hydroperoxyl radical ($\text{HO}_2\cdot$) is an oxidant, but not as strong an oxidant as the hydroxyl radical. The hydroxyl radical is considered responsible for oxidizing organic contaminants in water (Chen *et al.*, 2001).

Advanced oxidation of TCE occurs with the following reaction:



Hydroxyl radicals may also react with organics to produce another radical by hydrogen abstraction:



Where RH is an organic compound. These radicals can convert Fe^{3+} back to Fe^{2+} :



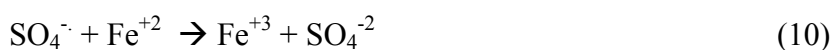
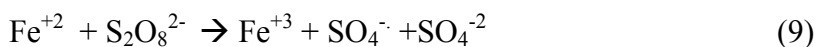
Research has been conducted on the effectiveness of Fenton's reagent for treating chlorinated organics. In general the reaction of hydroxyl radicals with organic material, to completion will produce water, carbon dioxide and salts. Teel *et al.* (2001) found that in classical Fenton's oxidation of TCE, 78% of the initial TCE was degraded. 2.5 moles of

H₂O₂ were consumed per mole of TCE. During this reaction, 1.9 moles of chloride were released per mole of TCE, thus not all of the chlorine was displaced from the TCE (Teel *et al.*, 2001).

Bergendahl and Thies successfully applied “Fe⁰/H₂O₂” advanced oxidation of MTBE (Bergendahl and Thies, 2004). The oxidation reactions were able to destroy over 99% of the MTBE within 10 min, and showed significant generation, and subsequent degradation of acetone. Second-order rate constants for MTBE degradation were 1.9*10⁸ M⁻¹S⁻¹ at pH 7.0 and 4.4*10⁸ M⁻¹S⁻¹ at pH 4.0. In this project the Zero -Valent iron was added in the form of powder.

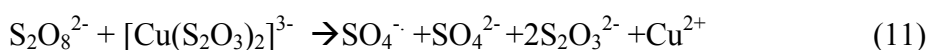
2.3 Persulfate Oxidation

The persulfate anion is a strong oxidant with a redox potential of 2.01 V (Latimer, 1952). Persulfate anions can be easily generated from sodium persulfate (Na₂S₂O₈) by adding water. At ambient temperature (~20⁰C), the persulfate anions can be decomposed by transition metal activators (e.g. Fe⁺²) to sulfate free radicals (SO₄^{·-}) which have a redox potential of 2.6 V (Ebersson, 1987). Sulfate free radicals are a powerful oxidant which can potentially destroy organic contaminants. The overall stoichiometric reaction between persulfate and ferrous ion is shown in the following equations (Kolthoff *et al.*, 1951).



The persulfate –ferrous reactions result in rapid production of sulfate free radicals. A free radical half life of 4 seconds was reported at a persulfate ferrous ion concentration of 10^{-3} M and a temperature of 40°C (Banerjee and Konar, 1984). Sulfate free radicals convert ferrous ion to ferric ion through Eq (3). The reaction coefficient (at diffusion controlled rate) for Eq (3) has been reported to be $1 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$ (Heckel et al., 1966). There are many other activators found in the literature include ions of copper, silver (House, 1962), manganese (House, 1962; Lenka and Dash, 1963; Kislenco *et.al.*, 1997), cerium (House, 1962; Skarzewski, 1984), and cobalt (Lenka and Dash, 1983). Sodium persulfate can also be thermally activated to form sulfate free radicals ($\text{SO}_4^{\cdot-}$) (Liang et al., 2003). Persulfate oxidation can be promoted by the addition of a reducing agent such as sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) to form a persulfate –thiosulfate redox system (Morgan, 1946; Riggs and Rodrigues, 1967; Narain et al, 1981; Sarac, 1999).

The set of reactions between persulfate and copper thiosulfate complex anion ($[\text{Cu}(\text{S}_2\text{O}_3)_2]^{3-}$) has been reported as (Prölss and Patat, 1968):



Persulfate reaction can also be activated by ferrous ion in similar way to that obtained with copper by King and Steinbach (1930) and Morgan (1946). The reactions with iron to produce sulfate free radical are as follows:



Comparison of various chelating agents to hold Fe^{+2} in soil slurries was done by Liang *et.al* (2004) found that citric acid is the most effective chelating agent. Various others chelating agents used were ethylenediaminetetraacetic acid (EDTA), sodium triphosphate (STPP) and 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). TCE degradation was achieved both in soil slurries and aqueous systems and degradations results were plotted for 24 hr at a $\text{S}_2\text{O}_8^{2-}$ /chelate/ Fe^{+2} /TCE molar ratio of 20/25/5/1. TCE degradation up to 34%, 73% and 41% were observed in aqueous systems when EDTA- Fe^{+2} , STPP- Fe^{+2} , and HEDPA- Fe^{+2} were used respectively whereas in soil slurries 33%, 67% and 54% were observed respectively. For the same molar ratio using citric acid as chelating agent TCE degradation was approximately 90% in aqueous phase and approximately 80% in soil slurries after 1 hr and nearly 100% destruction was achieved in both systems for 24 hr period.

2.4 Hypothesis and Objective

There are two hypothesis formulated

- TCE can be effectively destroyed in-situ using various oxidizing agents such as persulfate, ozone, hydrogen peroxide.
- Presence of solids (media) reduces the effectiveness of in-situ remediation.

To test these hypothesis, the **objectives** of this research were:

- To conduct slurry tests using various oxidizing agents such as persulfate, ozone and hydrogen peroxide in varying molar doses.
- To conduct slurry tests with varying amount of solids or media
- To measure the extent and rate at which TCE is removed from the slurry.

Chapter 3 Materials and Methods

3.1 Materials

All chemicals were A.C.S grade from Fisher Scientific. The TCE and Methanol were an assay of 99.9%, Anhydrous Citric acid ($C_6H_8O_7$ assay 100.5%), Ferrous sulfate ($FeSO_4 \cdot 7H_2O$ assay 101.0%), Sodium persulfate ($Na_2S_2O_8$ assay 98.0%), Sodium Hydroxide (NaOH 50% w/w) and 30% Hydrogen peroxide. Glass beads (unwashed, 425-600 μm) used in the experiments were from Sigma. Silica (fine granular, 40-100 mesh) was from Fisher Scientific. Sand used in the experiment was Massachusetts native soil and sieved through sieve no.30 (0.0234). Zero-valent iron used was carbonyl iron micro powder supplied from ISP technologies. The water was from an RO pure ST reverse osmosis system, followed by an E-pure system supplied by Barnstead/ThermoLyne (Dubuque, Iowa). The cis-dichloroethylene (DCE) (5,000 $\mu g/mL$), trans-dichloroethylene (DCE) (5,000 $\mu g/mL$), 1,1-DCE (1,000 $\mu g/mL$) and Vinyl Chloride (VC) (100 $\mu g/mL$) standards, all diluted in methanol, were from Ultra Scientific (N.Kingstown, Rhode Island).

3.2 Methods

All glassware was washed with Alconox detergent. The glassware was rinsed four times in tap water and once in E-pure water. Stock solutions were kept in a 4°C refrigerator until use. The 2.25% (by weight) of Fe^{+2} solutions were prepared by adding solid $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to E-Pure water. Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) was added to the 2.25% Fe^{+2} solution of 1:1 molar ratio (citric acid: Fe^{+2}) solution. Finally the pH of Citric acid: Fe^{+2} (1:1) solution was adjusted to 6 with 30% sodium hydroxide (NaOH). Persulfate solution was made by adding Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$ assay 98.0%) powder to E-pure water. Hydrogen peroxide was diluted from 30% to 20 % and 10% with E-pure water for use in lab. All the media namely sand, glass beads and silica were muffle furnaced at a temperature of 550°C for 24 hours to ensure minimum organic content. Iron content of the sand was measured by atomic adsorption.



Fig 3-1: Samples for slurry test

3.3 Equipment

3.3.1 Programming the Gas Chromatograph

An Agilent 6890 gas chromatograph (GC) with HP GC ChemStation software was used to determine the concentrations of contaminants. An Agilent 7683 auto-sampler was attached to the GC to aid in quick analyses. Ultra high purity nitrogen gas from ABCO welding supplies (Waterford,CT) was used as the carrier gas. The injector was equipped with a 100 μL syringe that was used to inject 50 μL of gas from the headspace in the

sample vials into the GC. The sample was injected into a split-less inlet with initial temperature of 50°C and pressure of 8.06 psi. A 250°C ECD detector was used. A Restek Rtx-5SILMS column had a nominal length of 30.0 m, nominal diameter of 320 µm and a nominal film thickness of 0.5 µm. The column was housed in the oven with an initial temperature of 28°C. After 7 minutes the temperature in the oven raised 10°C/minute until a temperature of 200°C was reached. The output from the ECD detector was read and the software calculates peak area using the following constraints: initial slope sensitivity of 120, initial peak width of 0.8, and initial area and height rejects of 0.5.

3.3.2 Headspace sampling

Headspace sampling method for the gas chromatograph was chosen because of its simplicity and ability to be rapidly conducted. For this sampling method, 440 mg of sodium chloride was added to a gas chromatograph sample vial; the salt helps to volatilize compounds in solution. Then 1 ml of the liquid to be sampled was added to the vial. The remaining area in the vial was the headspace. After tightly capping the vial it was hand agitated for about a minute then placed on the shaker table allowing time for volatilization of the chemicals from the liquid. After being taken off the orbit shaker, the vial was placed in the auto-sampler for analysis. The sample taken by the GC was taken from the headspace as seen in Figure 3-2.

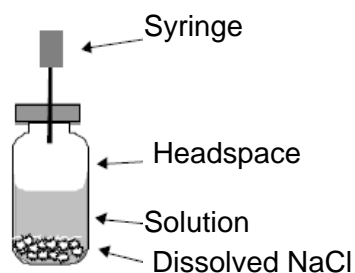


Figure 3-2: Headspace Method Diagram.

3.4 Equipment

The pH measurement was done using an Orion model 420A pH meter equipped with an Orion915600 pH probe. The meter was calibrated each time before use with buffer solutions of pH 4.00, pH 7.00 and pH 10.00 (Fisher Scientific, Airlawn, NJ). Ozone was generated using a Labzone ozone generator from Ozonology Inc (Northbrook, IL). Feed gas for ozone generation was compressed pure oxygen with feed gas inlet pressure of 25 psi and 6 SCFH (Standard cubic feet per hour). The orbit shaker was from Labline Instruments Inc. (Melrose Park, ILL) and used at 100 rpm for all experiment. The Muffle furnace was from Thermolyne. Micro stir bars covered with Teflon PTFE fluoropolymer were used in the GC vials for complete mixing were from Fisher Scientific (NJ). Diameter of the micro stir bar was 2 mm and length was 7 mm. A convection microwave from Sharp Carousal was used for microwave extractions. Atomic adsorption AAnalyst 300 with a flame atomizer was used for iron analysis of sand (Perklin Elmer Instruments).

CHAPTER 4 Procedures

4.1 Producing standard curves

The first phase of the experiments was to develop standard curves for the different compounds of interest and determine the retention times for each compound on the gas chromatograph using the headspace sampling method. Standard curves were produced for TCE, 1,1-DCE, cis-1,2-DCE, trans-1,2-DCE. Stock solutions that were prepared in the lab were diluted with purified water directly in a GC vial containing 440 mg of sodium chloride. It was found that mixing the smaller volumes directly in the GC vials minimized the loss of the contaminant through volatilization. A stock solution of 500 ppm of TCE was prepared in lab by adding 155 μL of 99.9% pure TCE to 199.845 ml of e-pure water. This solution was allowed to mix overnight to produce a homogenous solution. Dilutions for TCE were created in 10, 25, 50, 100, 200 and 300 ppm concentration by mixing the volumes of 500 ppm TCE and water as given in Table 1. These dilutions were allowed to mix on the shaker table for 2 hours at 100 rpm before being run through the gas chromatograph.

Cis- and trans-1, 2-DCE stock solutions of 500 ppm were purchased from Ultra Scientific (N.Kingstown, Rhode Island). From this stock solution 100, 200, 300, and 400 ppm dilutions were produced. To obtain lower readings, a stock solution of 100 ppm was prepared in lab by adding 40 μL of 5000 ppm of the 1,2-DCE solution to 1.96 mL of water. This stock solution was allowed to mix overnight. Dilutions of 10, 25, and 50 ppm

where prepared from the 100 ppm stock solution All dilutions where allowed to mix on the shaker table for 24 hour before running on the gas chromatograph.

For 1,1-DCE a stock solution of 1000 ppm was purchased from Ultra Scientific (N.Kingstown, Rhode Island). Final concentrations used for the standard curve were 20, 50, 100, and 200 ppm. These dilutions were allowed to mix on the shaker table for 24 hours before being run through the gas chromatograph. The vinyl chloride stock solution of 100 ppm was purchased from Ultra Scientific (N.Kingstown, Rhode Island). Dilutions where prepared at 5, 10, 25 and 50 ppm. These dilutions were placed on the shaker table for 24 hours before running on the gas chromatograph.

While running the dilution series it was noted that for each contaminant, peaks were eluting from the GC at specific times. These retention times are shown in Table 4.1. For the cis-1,2-DCE two peaks were present, however, only the peak at 4.1 minutes, which was larger, was used in creating the standard curve.

Table 4.1: Retention time for each contaminant on an Agilent 6890 GC system

Contaminant	Retention time
Trichloroethylene	6.9 minutes
1,1 Dichloroethene	2.7 minutes
1,2 cis-dichloroethene	4.1 & 5.5 minutes
1,2 trans-dichloroethene	3.3 minutes
Vinyl Chloride	2.1 minutes

The points used to create the standard curves were the known concentrations in the GC vial and the corresponding output peak areas from the GC. The peak area was plotted along the x-axis because this is the known value in later experiment runs, the units varied

depending on the size of the peak areas formed by the different contaminants. The concentration of the contaminant was plotted along the y-axis and is expressed in mg/L or parts per million (ppm). A linear regression was performed on the plotted data to find the best fit line. A good fit was found if the variation (r^2 -value) was close to 1.

The TCE standard curve is seen in Figure 2. Dilutions of TCE were created from a minimum of 1 ppm up to a maximum of 500 ppm. GC was not able to accurate results the TCE at higher concentration due to degenerations of peaks.

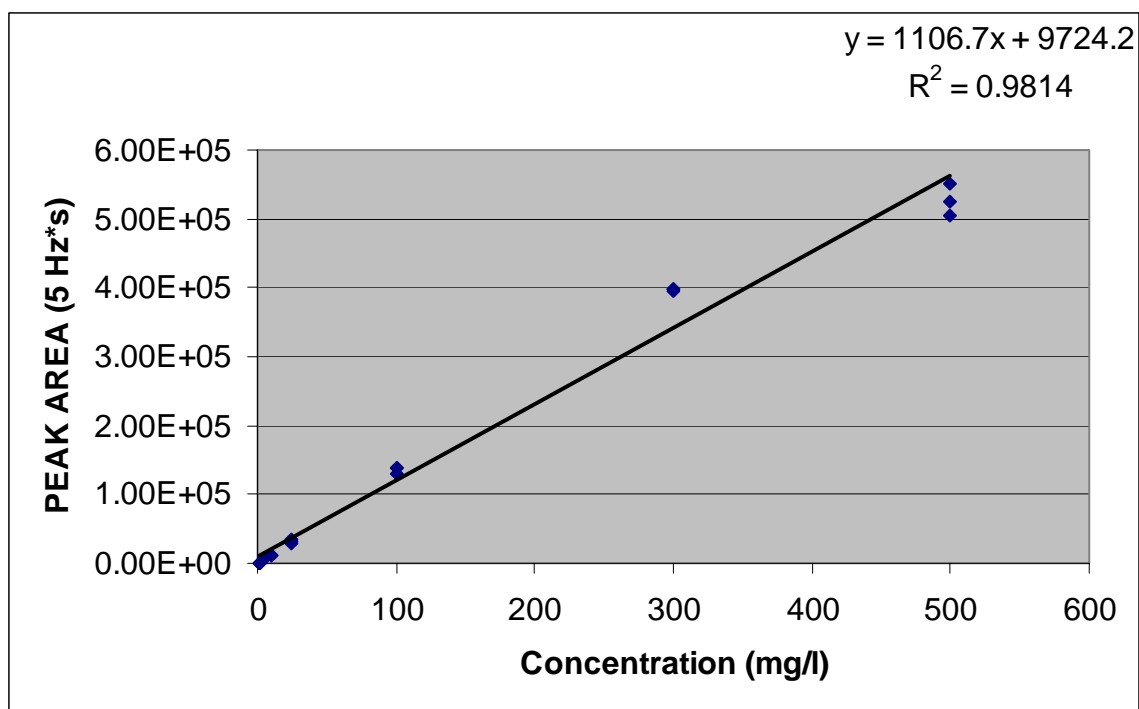


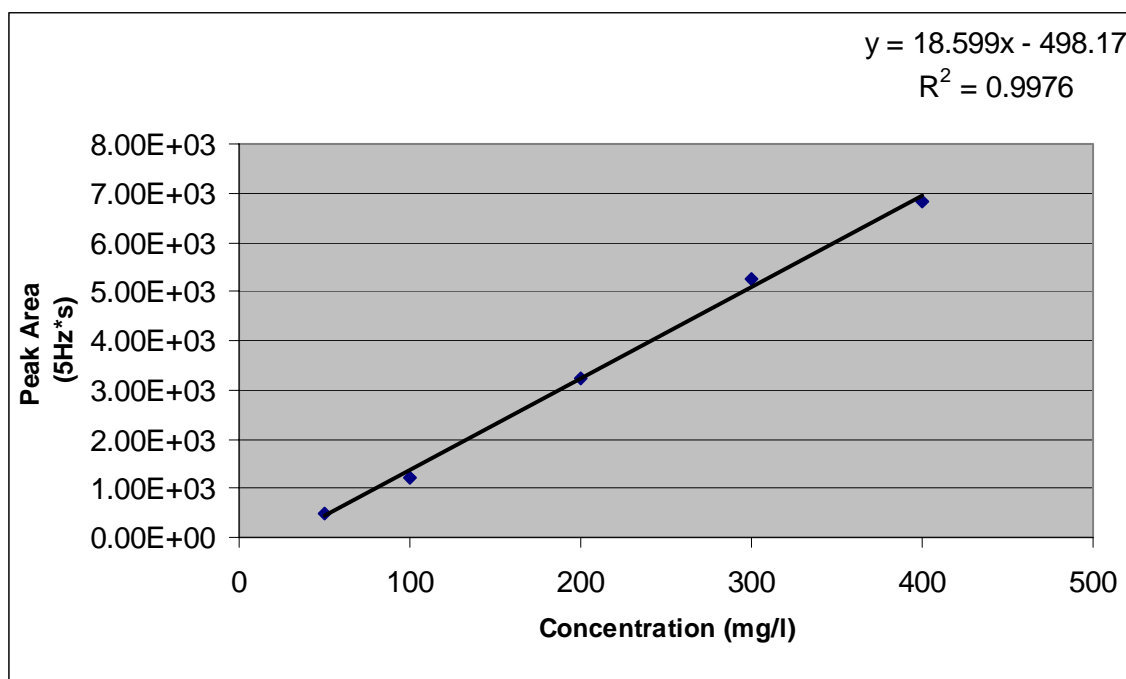
Figure 4-1: Standard curve for Trichloroethylene (TCE) showing peak area(5Hz*s) as a function of TCE concentration.

For TCE, the peak areas ranged from approximately 1.045×10^3 to almost 5.26×10^5 this correlates into concentrations of TCE from 1 ppm to 500 ppm. The best fit line was

found to give the concentration of TCE (C_{TCE}) in terms of the peak area (PA). The equation and its r^2 -value of the line are:

$$C_{TCE} = 9.04 \times 10^{-4} * PA - 8.79 \quad ; \quad r^2 = 0.9814$$

The trans-1,2-DCE standard curve is seen in Figure 4-2. While dilutions of trans-1,2-DCE were created from a minimum of 10ppm up to a maximum of 500 ppm, only concentrations between 50 and 400ppm formed peaks detected by the software in the linear range.



*Figure 4-2: Standard curve for trans-1,2-dichloroethene (DCE) showing the concentration of trans-1,2-DCE as a function of the peak area (5Hz*s).*

The peak areas range from approximately 500 to almost 7,000 (7x1000) this correlates into concentrations of trans-1, 2-DCE from 50 to 400ppm. The best fit line gives the

concentration of trans-1, 2-DCE (C_{trans}) in terms of the peak area (PA) through the following equation, also given is the variation:

$$C_{trans}=53.64*PA+27.22; \quad r^2=0.9976.$$

The cis-1,2-DCE standard curve is seen in Figure 4-3. While dilutions of cis-1,2-DCE were created from a minimum of 10 ppm up to a maximum of 500 ppm, only concentrations between 25 and 400 ppm formed peaks detected by the software in the linear range.

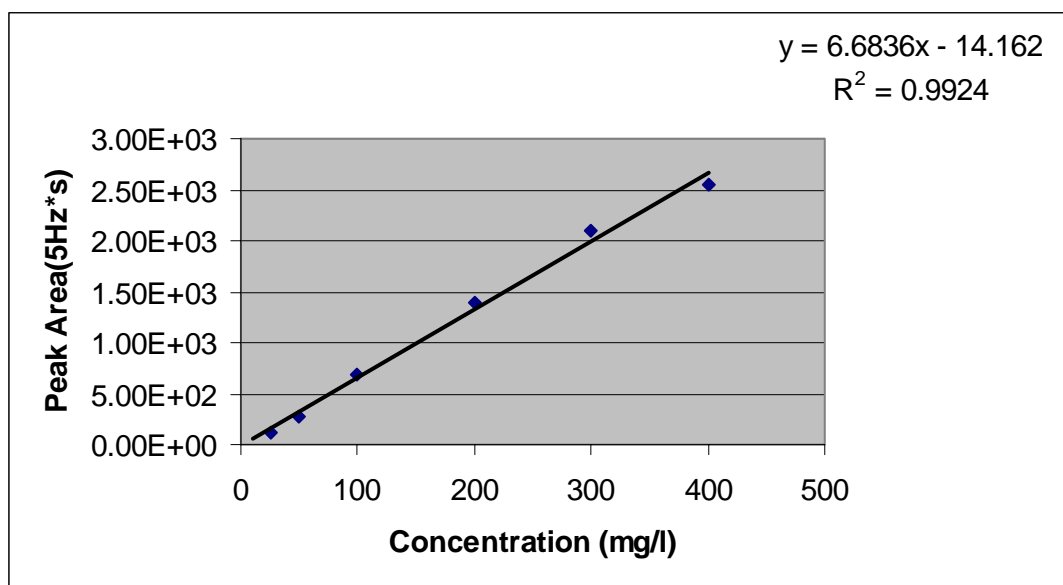


Figure 4-3: Standard curve for cis-1,2-dichloroethene (DCE) showing the concentration of cis-1,2-DCE as a function of the peak area(5Hz*s).

The peak areas range from approximately 100 to just over 2,500 (25x100 on graph) this correlates into concentrations of cis-1,2-DCE from 25 to 400 ppm. The best fit line gives the concentration of TCE (C_{cis}) in terms of the peak area (PA) through the following equation, also given is the variation:**Error! No table of figures entries found.**

$$C_{cis}=14.85*PA+3.46 \quad ; \quad r^2=0.9924.$$

The 1,1-DCE standard curve is seen in Figure 4-4. While dilutions of 1, 1-DCE were created from a minimum of 20 ppm up to a maximum of 300 ppm, only concentrations between 20 and 200ppm formed peaks detected as linear by the software.

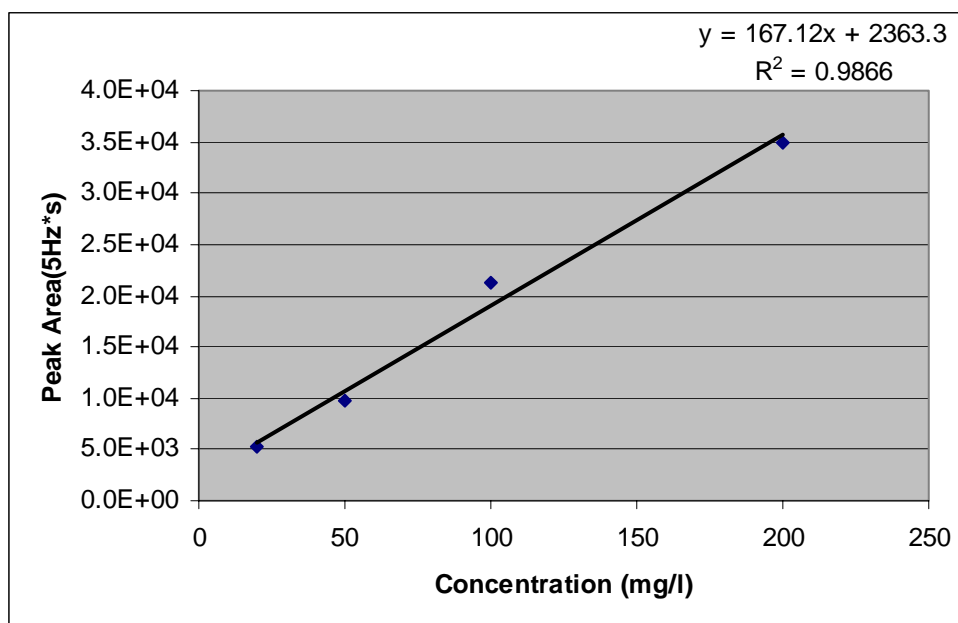


Figure 4-4: Standard curve for 1,1-dichloroethene (DCE) showing the concentration of 1,1-DCE as a function of the peak area(5Hz*s).

The peak areas range from approximately 500 to approximately 3,500 (2.5x1000 on graph) this correlates into concentrations of 1,1-DCE from 20 to 200 ppm. The best fit line gives the concentration of 1,1-DCE ($C_{1,1}$) in terms of the peak area (PA) through the following equation, also given is the variation:

$$C_{1,1} = 59.04 * PA + 12.71 \quad ; \quad r^2 = 0.9866.$$

No standard curve is available for vinyl chloride. The concentrations used in the dilution series created peaks that were too small to be measured by the software. Peaks were visually noted as present and this was how the retention time was determined.

4.2 Soil slurries for ferrous activated peroxide oxidation

Soil slurries were conducted on soil that had been contaminated with pure TCE; this was completed by first measuring a pre-determined mass of soil into a capped container then pure TCE is poured over the soil so that the soil is completely covered. Weighing the container at this point indicates the amount of TCE that was added. This mixture was allowed to mix on the shaker table for at least an hour after being vigorously shaken for about a minute. After mixing, the excess TCE was drained off the soil and is again weighed. The change in mass is attributed to the excess TCE. The difference between the starting TCE mass and excess TCE mass is the amount of TCE that was associated with the soil; these masses can be used to determine the concentration of TCE on the soil.

A microwave assisted extraction process was used to estimate the amount of TCE in the soil. This process was performed by adding 0.5 g of contaminated soil to 200 mL of e-pure water, shaking by hand for about 1 minute, and then placing in the microwave for 90 sec at 20% power. During the microwaving process, the solvent (water) absorbs the microwave energy and then detaches the contaminant from the soil. The advantages of using this extraction process is that water, which is environmentally-friendly and

inexpensive, can be used as a solvent and the process requires little time and effort. After being microwave, 1 mL of solution is taken and placed in a GC vial containing NaCl (Figure 1 above).

After the soil is contaminated, a predetermined mass was transferred to a screw cap vial. Then 13.33 mL of a 1:1 citric acid and Fe^{+2} solution was added to the vial. The citric acid and Fe^{+2} solution was prepared by first preparing a 2.25% Fe^{+2} solution (adding 22.40 grams of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to a 200 mL volumetric flask and then filling the flask); the next step was to add 15.48 grams of citric acid to the 200mL solution; finally, the pH is adjusted to 6 with sodium hydroxide (NaOH,30%). After adding the citric acid/ Fe^{+2} solution, 6.67 mL of hydrogen peroxide was added to the vials. The concentration of hydrogen peroxide depended on the experiment being run; care should be taken that the hydrogen peroxide concentration is low enough that the resulting reaction remains inside the vial.

After allowing the reaction to slow vials were loosely capped and securely placed on the shaker table at 100 rpm and let react for approximately 24 hours. After the 24 hours had elapsed, 1 mL of the solution above the soil was placed in a GC vial according to the headspace sampling method to determine what products have been placed in solution. Microwave extraction was performed on the soil from the slurry by adding 0.75 g of soil to 200 mL of water. This mixture was shaken for approximately 30 seconds to suspend smaller particles and the placed in the microwave for 90 seconds at 20% power. After

removing from the microwave 1 mL of solution was withdrawn and placed in a GC vial containing NaCl.

4.3 Slurries for persulfate oxidation activated by ferrous, ozone and ZVI.

Slurries were made using sand, silica and glass beads. All the media was muffle furnace at 550⁰ C for 24 hrs to burn off the organics and the 40 ml batch reactor was foil wrapped. First of all the 10 gm of the media was added to the 40 ml reactor and then 13.33 ml of ferrous iron: citric (1/1 molar) acid solution was added. A stock solution of TCE was prepared for 750 mg/l and 20 ml of it was added to the slurry to make up the desired molar ratio of TCE/iron of 1/1 and 1/0. In the end the 6.67 ml of sodium persulfate was added to the slurry to make up persulfate/TCE molar ratio of 10/1, 5/1, 10/0 and 5/0. For ozone activated persulfate oxidation 13.33 ml of ozone saturated water was used instead of ferrous: citric solution. For zero valent iron ½ gm of ZVI powder was added to the system before the addition of oxidant. Slurry bottles were immediately capped tightly and kept on the orbit shaker for 24 hrs at 100 rpm.

Chapter 5 Results and Discussion

5.1 Oxidation using Hydrogen peroxide in Soil Slurries using MAE

Samples of both the slurry solution and the MAE (Microwave assisted extraction) soil run show the presence of only TCE. The absence of the TCE degradation products may be attributed to the complete mineralization of TCE and all byproducts. Mass transfer of TCE from soil to solution can also be limiting. Once in solution TCE is degraded by the radicals there; the daughter products will then start out in solution where they are rapidly degraded if TCE does not desorb rapidly enough to also be acted on. To test this theory, the slurry test was run using aqueous TCE and it was found that complete degradation of TCE occurred without any daughter products. Another plausible reason for the absence of daughter products is that they are created and destroyed in a shorter or longer time than being monitored. To test this, slurry tests should be run for different lengths of time. An additional benefit is that TCE degradation can then be monitored with respect to time.

Figure 5-1 shows the average percent TCE removal from soil based on the initial hydrogen peroxide concentration. The slurry tests were run using 5, 10 and 20 grams of soil. One noticeable trend is that for the slurries containing less contaminated soil, the percent TCE removed is greater. This may be due to the fact that despite the initial concentration of TCE in the slurry the same amount is being degrading during the process. So for equal amounts of TCE removed will have a larger impact on smaller initial concentrations of TCE.

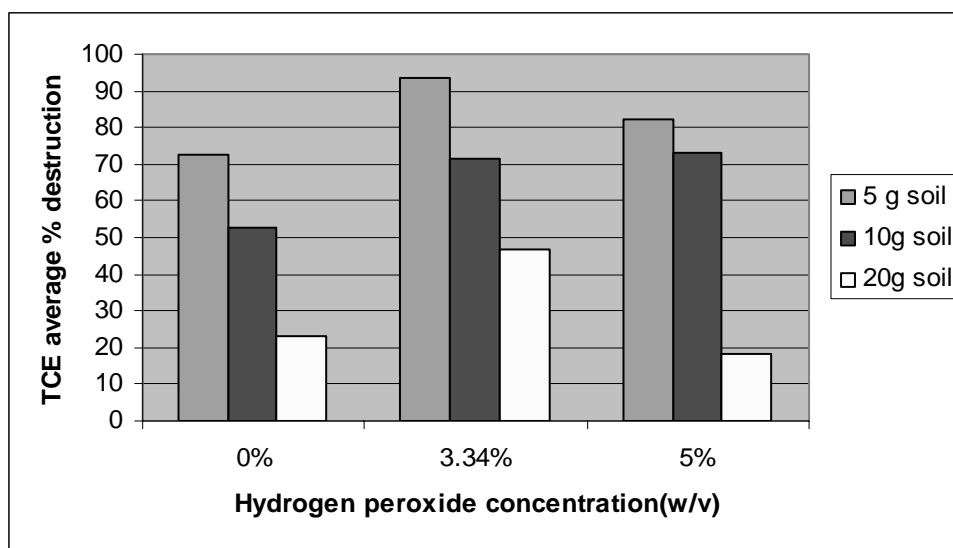


Figure 5-1: Average Percent of TCE removed from the soil for the different hydrogen peroxide/soil sample size variations.

For all the slurries run at a 0% hydrogen peroxide concentration there was evidence of TCE removal from the soil. This can be explained by the fact that the TCE is moving from the soil and into the slurry solution. To determine how much TCE is actually being destroyed the results for the slurry solutions must be quantifiable. Then the amount destroyed can be calculated by the amount originally present minus the sum of the amount present in soil and in solution. Another possible explanation of TCE removal at 0% hydrogen peroxide is that some TCE may be volatilizing into the slurry vial headspace. To test this hypothesis samples should be run with minimal amounts of headspace and these results compared with results obtained using the current method.

For the slurries using 5 and 20 grams of contaminated soil, the percent removal decreases from a hydrogen peroxide concentration of 3.34% to 5%. This is due to the competitive reaction chemistry involved with hydroxyl radical as shown below.



So as the hydroxyl generation increases it eats up the hydrogen peroxide thus decreasing further production of hydroxyl radical. Another explanation is that while measuring out the soil for MAE, the soil may have been in contact with the air for a longer period of time at the 3.34% concentration. Running more samples from each of the slurry test should reduce these impacts. An additional explanation may be that there is a shortage of the ferrous ion to catalyze the hydrogen peroxide. Adjusting the concentration of ferrous ion will test this hypothesis. Mohanty and Wei achieved complete removal of 2,4-Dinitrotoluene (DNT) in aqueous solution using Fenton's oxidation with a H_2O_2 :DNT: Fe^{2+} molar ratio of 20:1:2.5.

5.2 Aqueous oxidation of TCE using Sodium Persulfate

Aqueous oxidation of TCE was done in all the four medias (sand, silica, glass beads and water). Controls were run in aqueous medium with citric acid, Fe^{+2} solution (1:1 molar ratio) and persulfate solution individually and degradation of TCE was recorded after 24

hr. All the controls were done with and without aluminum foil wrap to detect the UV degradation of TCE in solution.

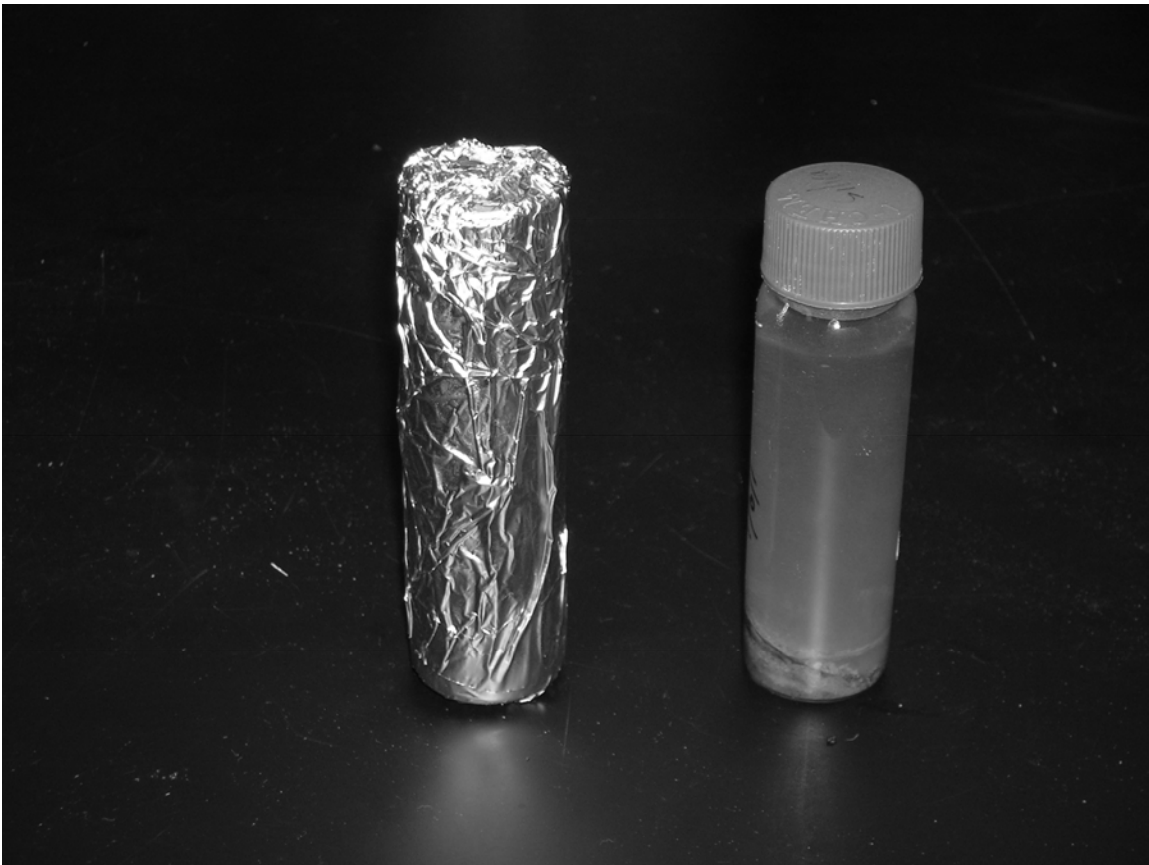


Fig 5-2: Picture shows the 40 ml batch reactor for slurry testing with and without foil.

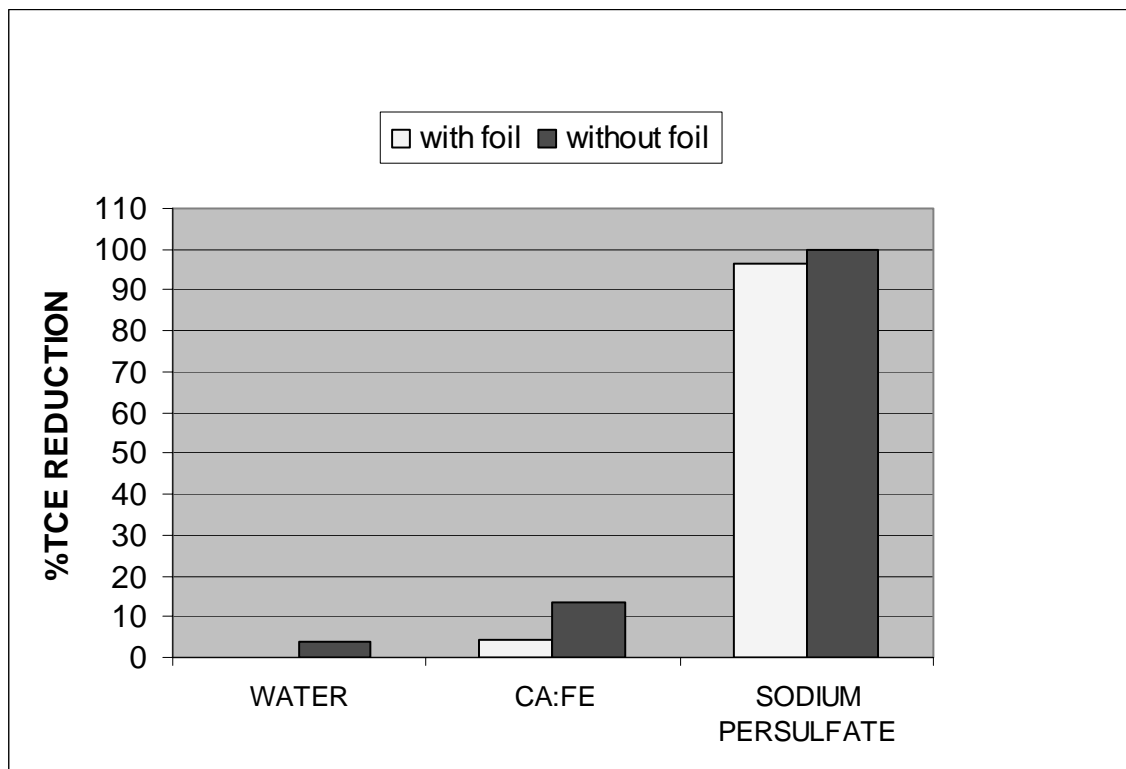


Figure 5-3: controls for TCE degradation

Control Medium	% TCE reacted (With foil)	%TCE reacted (Without foil)
WATER	0	3.82
CA:FE	4.41	13.42
SODIUM PERSULFATE	96.30	100

It was found that UV rays naturally present in the ambient light degraded the TCE in aqueous phase approximately 5%. Controls were also done to detect the amount of adsorption of TCE on to media. All the media were muffle furnaceed at 550⁰ C to burn off all the organics present in them and then the controls were run with TCE at 500 ppm.

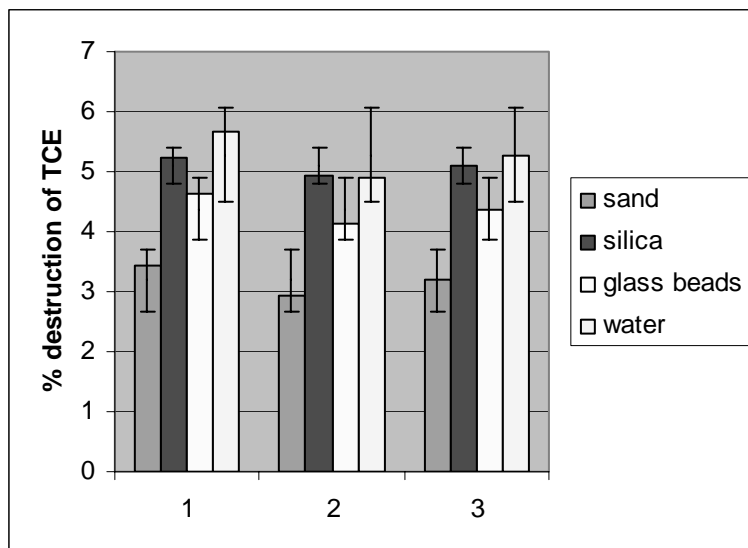


Fig 5-4: Adsorption control for TCE on various media. Error bar shows the standard deviation for controls.

After the controls were run persulfate oxidation was tried to test the % destruction of TCE. Experiments were done at persulfate/Iron/ TCE molar ratios of 20/1/1 and 20/0/1. Figure 5-5 below shows the results from the experiments.

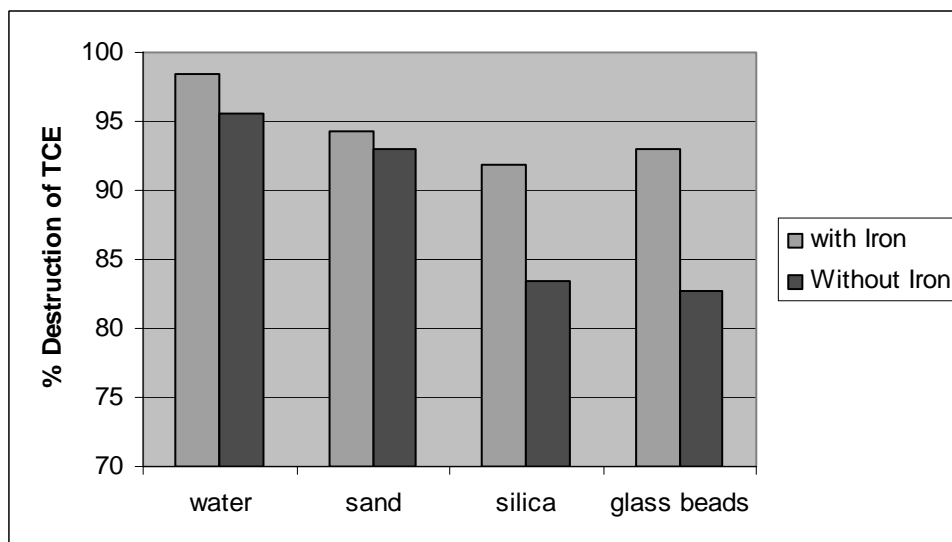


Fig 5-5: % Destruction of TCE at Persulfate/Iron/TCE molar ratio of 20/1/1 and 20/0/1

Percent destruction at molar ratios of 20/1/1 and 20/0/1 was found to be greater than 95%, so experiment were conducted at various molar ratios as indicated in figure below. All the samples were foil wrapped to prevent degradation from UV.

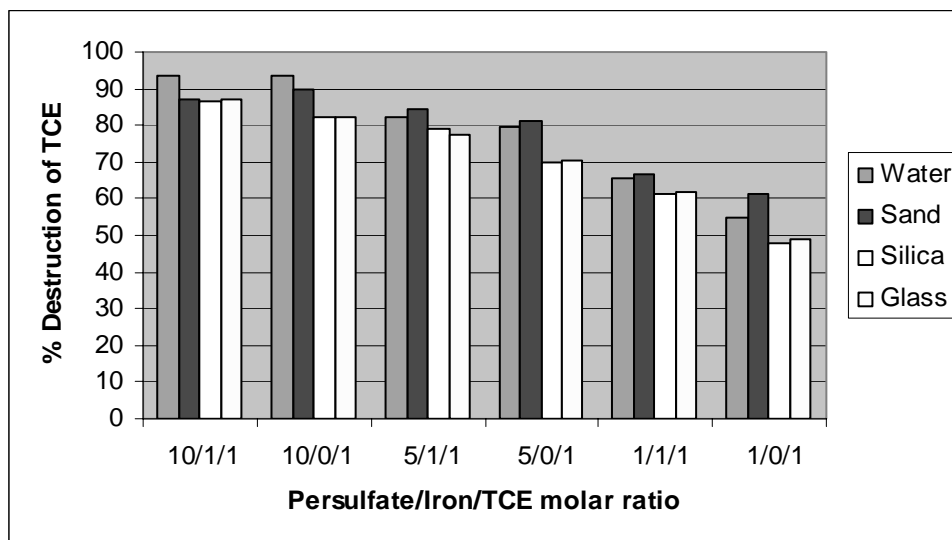


Fig 5-6: Destruction of TCE after 24 hrs for various molar ratios

From Figure 5-6 it is clear that ferrous iron catalysis the persulfate reactions and thus helps in more effective degradation of TCE. Liang *et.al* (2004) found that when ferrous ion was added sequentially in small increments to the reaction, it helped in destroying TCE. After 5 successive additions of Fe^{2+} equivalent to initial $\text{Fe}^{2+}/\text{TCE}$ molar ratios of 1/1, 2/1 and 5/1, the final $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}/\text{TCE}$ molar ratios reached were 20/5/1, 20/10/1, and 20/25/1 and the overall TCE removals were 73%, 84% and 95%, respectively. As compared to the experiment when all Fe^{+2} was added at once for the same final $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}/\text{TCE}$ molar ratios, sequential addition of Fe^{2+} improved the TCE removal by

26%, 27%, and 31% for $S_2O_8^{2-}/Fe^{2+}/TCE$ molar ratios of 20/5/1, 20/10/1, and 20/25/1, respectively. Higher degradation of TCE in this research can be attributed to way of making slurries which can affect the final % TCE remaining. Soil with high organic content can also lead to high oxidant demand and lower the TCE degradation efficiency. None of the Liang *et.al* soil samples were subjected to muffle furnace leading to f_{oc} of 0.316%. Linag *et.al* also found that maximum degradation of TCE occurred at near neutral pH. Linag *et.al* found that lowering the system pH would increase the degradation of TCE. Figure 5-7 and 5-8 show the variation of pH at 0 hr and 24 hr respectively for all the media in the experiment data shown in Fig 5-6. As the molar ratio of persulfate/iron/TCE was decreased from 10/1/1 to 1/0/1 the pH of the system increased which in turn increased the degradation of TCE. Although due to the lack of oxidant at near neutral pH in the Figure 5-7 and 5-8 show that complete mineralization was not achieved.

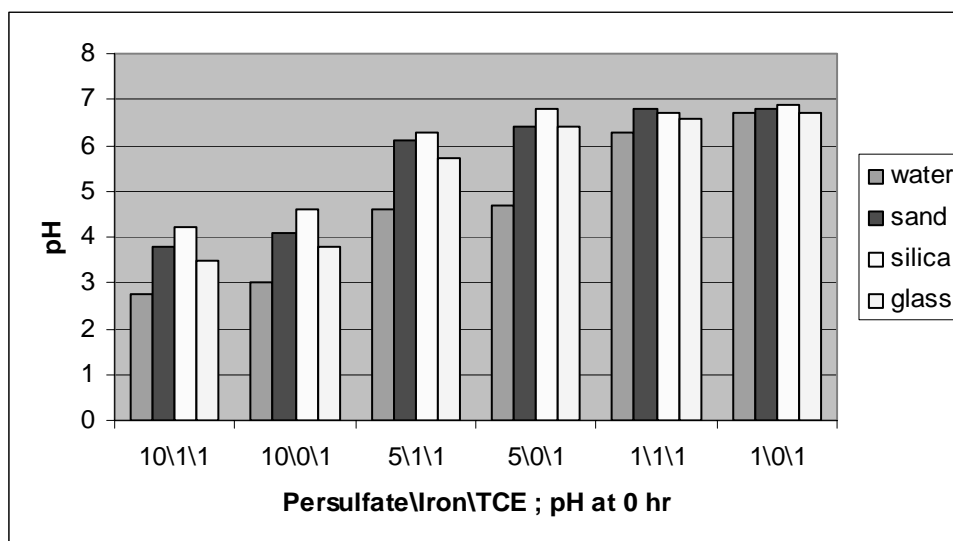
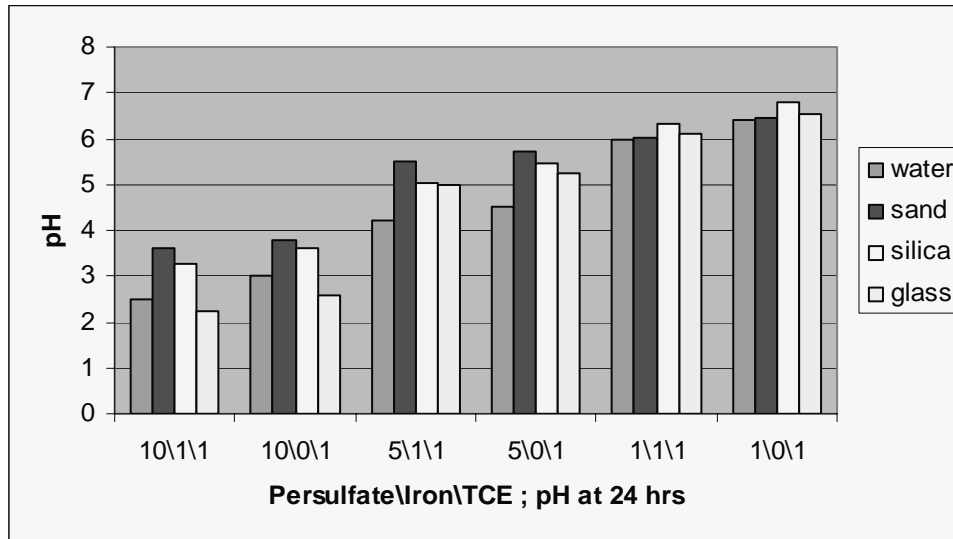


Fig 5-7: Effect on the pH at 0 hr as the molar dose was changed at room temperature of $25^{\circ}C$



5-8: Effect on the pH at 24 hrs as the molar dose was changed at room temperature of 25°C

Ferrous iron activated persulfate oxidation of TCE was carried out for 24 hr period and the results were plotted in Figure 5-6. Since the degradation efficiency of persulfate was found to be higher than 90 percent at molar ratio of 10/1/1 and 10/0/1(persulfate/Iron/TCE). So the reaction kinetics were studied for this molar ratio for all the media. Results are shown in the figure below.

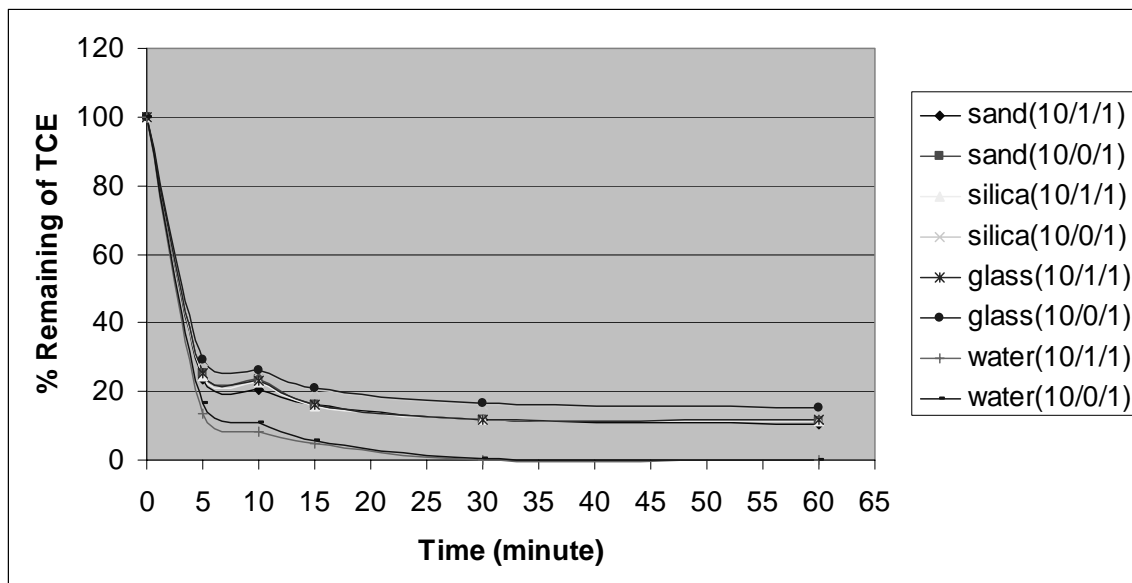


Fig5-9: Reaction Kinetics at Persulfate/Iron/TCE molar ratio of 10/1/1 and 10/0/1

For all the samples it was found that most of the degradation was rapid and took place within the first five minutes. From Figure 5-9 it can be seen that approximately 80% of the TCE is oxidized in the first 5 minutes and the rate of destruction is much slower after five minutes. Liang *et.al* (2004) studied the influence of chelate/ Fe^{+2} molar ratios on the kinetics of aqueous oxidation of TCE by ferrous activated persulfate. Liang *et.al* (2004) found that all persulfate/chelate (citric acid)/ferrous/TCE molar ratios greater than 20/1/10/1 resulted in nearly 100% TCE destruction after 20 min reaction period. In an experiment with persulfate/chelate/ferrous/TCE molar ratio of 20/2/20/1 exhibited lack of ability to maintain the enough chelated iron in the solution and therefore TCE degradation and persulfate decomposition stalled after 20 min. Liang *et.al* concluded that higher initial Fe^{+2} content at persulfate/chelate/ferrous/TCE molar ratio of 20/2/20/1, showed less effective TCE degradation and more persulfate decomposition. So the excess unchelated ferrous iron would compete for sulfate free radicals and finally result in

lowering of the TCE degradation efficiency. Liang *et.al* (2004) also found that at persulfate/chelate (citric acid)/Fe⁺²/TCE molar ratio of 10/2/10/1, 96% of the TCE degradation took place within 1 hr. Liang *et.al* (2004) also studied the effect of varying the persulfate concentration. It was found that at persulfate/chelate (citric acid)/ferrous/TCE molar ratio of 5/0.2/1/1 and 10/0.2/1/1 resulted in 17% and 13% of TCE remaining and 52 % and 74 % of persulfate remaining after 24 hr period respectively.

Since persulfate oxidation worked quite efficiently for the above mentioned molar ratios, for 10 gm of the media. Since the amount of solids added was expected to play a vital part in the process, the amount of media added was varied to investigate effect on the efficiency. Additional media led to more oxidant demand since the surface media (sand, silica, glass beads) may react with oxidants. Figure 5-10 and 5-11 shows the effect of increased solids in the system for sand, silica and glass beads.

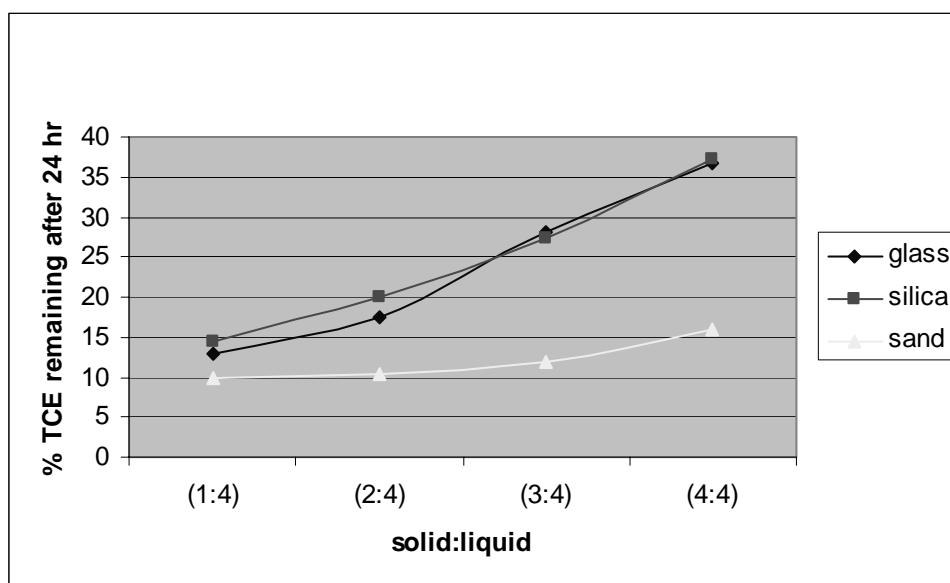


Fig 5-10: % TCE remaining at 10/1/1 molar ratio of Persulfate/Iron/TCE

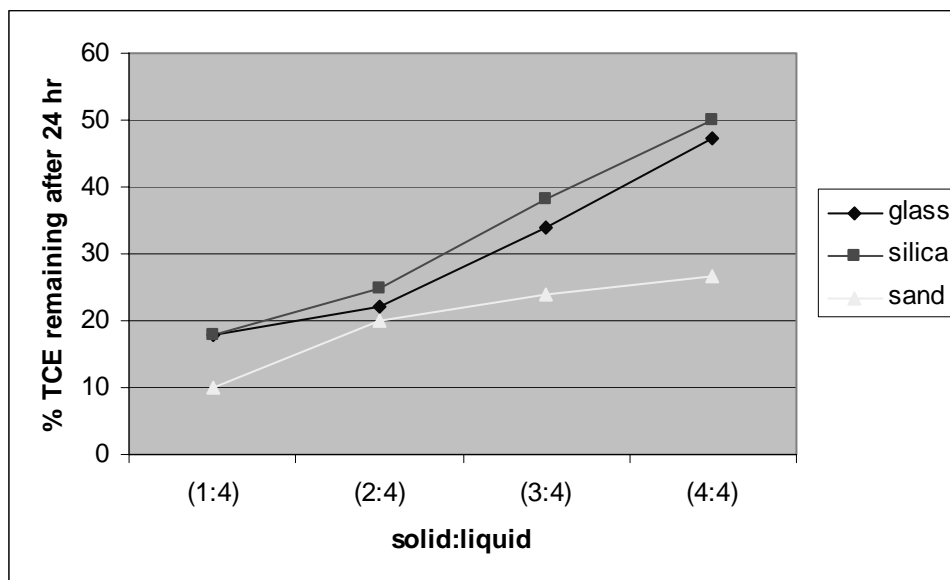


Fig 5-11: % TCE remaining at 10/0/1 molar ratio of Persulfate/Iron/TCE

From the above figures it can be easily seen that extent of oxidation of TCE is reduced with increased media loadings as the minerals in the soils and the surface of the glass and silica consume the persulfate. pH data was also recorded for all the experiments and shown in Figure 5-12. The addition of media can also affect the pH of the system which in turn affects the degradation efficiency of the persulfate oxidation. Watts *et.al* (2004) studied the effect of varying slurry volume for mineralization of benzo[a]pyrene (BaP; group A; confirmed carcinogen) on two soils using catalyzed hydrogen peroxide. Watts *et.al* found that the interactive effects of H₂O₂ concentration and iron (II) amendment were significantly higher than the effect of slurry volume. Watts *et.al* found that excess slurry volume (containing H₂O₂ that is not in contact with the sorbed or NAPL-phase BaP) consumes H₂O₂ while not degrading the sorbed or NAPL contaminant. Watts studied the BaP mineralization by % ¹⁴C-CO₂ recovery. Based on statistical analysis of

the experimental data, BaP oxidation in the silica sand was described by following relationship:

$$\begin{aligned}
 &^{14}\text{C-CO}_2 \text{ Recovery (\%)} \\
 &= 40.7 + 1.47 * 10^{-3}(\text{H}_2\text{O}_2) - 3.40(\text{Slurry volume}) - 2.33(\text{Iron}) + 1.07 * 10^{-7}(\text{H}_2\text{O}_2)^2 \\
 &+ 3.0 * 10^{-2}(\text{Slurry volume})^2 + 4.58 * 10^{-1}(\text{Slurry volume}) * (\text{Iron}),
 \end{aligned}$$

BaP oxidation in the Palouse loess soil was described by following relationship:

$$\begin{aligned}
 &^{14}\text{C-CO}_2 \text{ Recovery (\%)} \\
 &= 53.1 + 1.13 * 10^{-3}(\text{H}_2\text{O}_2) - 5.79(\text{pH}) - 0.122(\text{Slurry volume})^2 - 0.360(\text{pH})^2 \\
 &+ 0.838(\text{Slurry volume}) * (\text{pH}),
 \end{aligned}$$

Where H_2O_2 is the hydrogen peroxide concentration (mM), slurry volume for silica sand is the slurry volume (x 0.31 ml/g, the silica sand field capacity) and slurry volume for Palouse loess soil is slurry volume (x 0.42 ml/g, the silica and sand field capacity), (Iron) is the iron(II) amendment concentration (mM). Watts *et.al* (2004) data indicated that the most efficient systems are those in which the slurry volume was low, i.e., the results suggest that the close proximity of the reactive species to the sorbed or NAPL-phase BaP is an important factor in promoting a stoichiometrically efficient reaction that enhances its desorption/dissolution and mineralization. Excess H_2O_2 that decomposed to reactive species away from the soil was probably not effective in degrading and mineralizing sorbed or NAPL-phase BaP. Watts and Stanton (1993) obtained similar results for oxidation of ^{14}C -hexadecane; they found that the degradation of hexadecane required

relatively high concentrations of H_2O_2 and that the most efficient stoichiometry was at low slurry volumes.

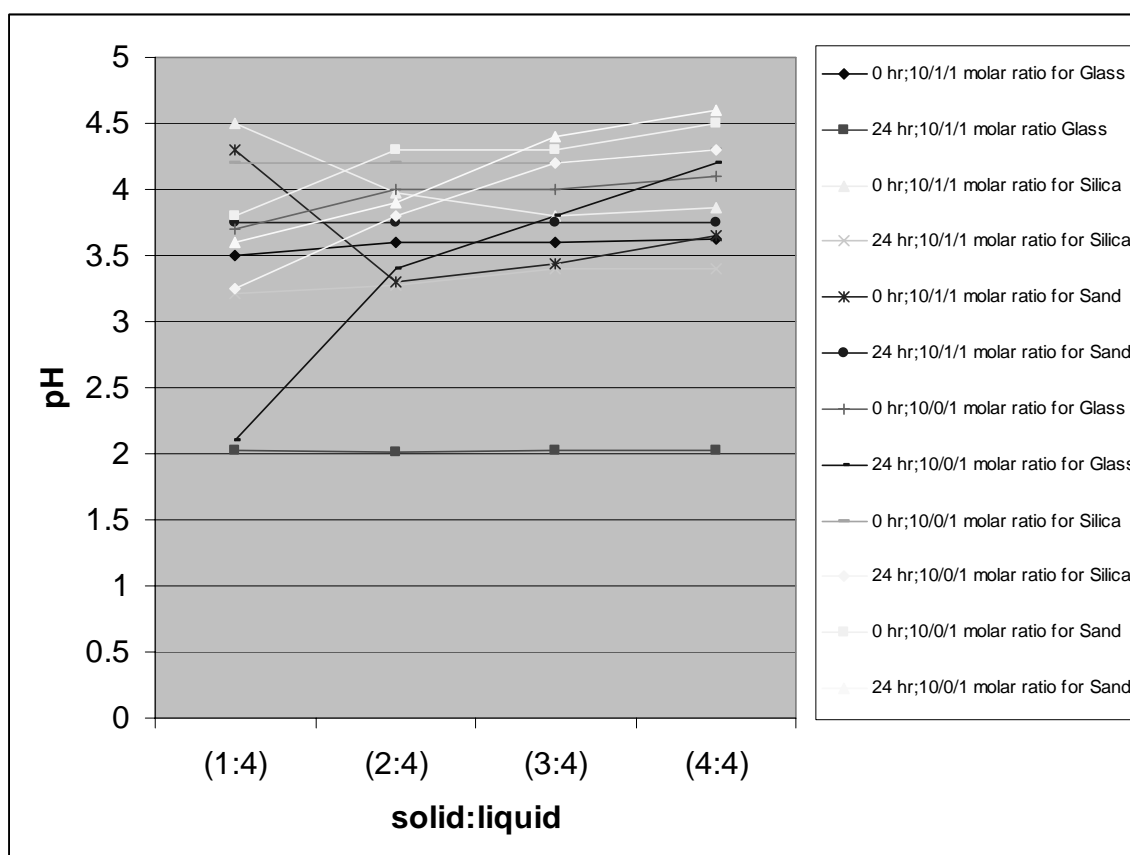


Fig 5-12: pH variation with increased media loading.

5.3 Aqueous oxidation of TCE using Sodium Persulfate and Ozone

Ozone is an unstable gas produced when oxygen molecules dissociate into atomic oxygen. Since ozone decomposes to oxygen very rapidly after generation thus it must be generated onsite. In these experiments the ozone was generated using “Ozongenerator” using high purity oxygen and high voltage is applied across gap of narrowly spaced

electrodes. The high energy corona created by this arrangement dissociates one oxygen molecule, which re-forms with two other oxygen molecules to create two ozone molecules. Ozone was then bubbled through a stone into the water for immediate consumption.

Ozonated water was used with persulfate solution for the destruction of TCE. 10 gm of media was mixed with 13.33 ml of ozone saturated water and 6.67 ml of persulfate solution and finally 20 ml of TCE was added to make up Persulfate/Iron/TCE molar ratio of 10/0/1 and the reaction was recorded over time and it was quenched with 3.65 gm of methanol to make persulfate/methanol molar ratio of 1/100. Result for these set of reactions were recorded at a times of 0, 1, 5, 10, 30, 60, 120 and 180 minutes and the data was plotted to determine the rate of reaction. Results are plotted in figure 5-13.

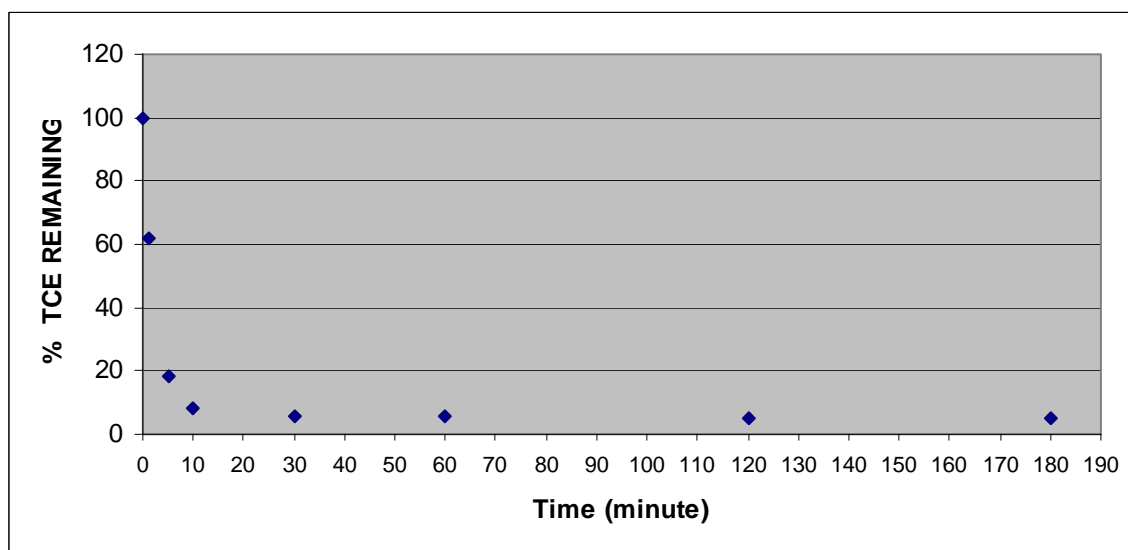


Fig 5-13: Reaction Kinetics at Persulfate/Iron/TCE molar ratio of 10/0/1 with ozone saturated water.

To calculate the rate constant the results (≤ 10 min) were plotted again and the first order rate constant was calculated. Results are shown in Fig 5-14.

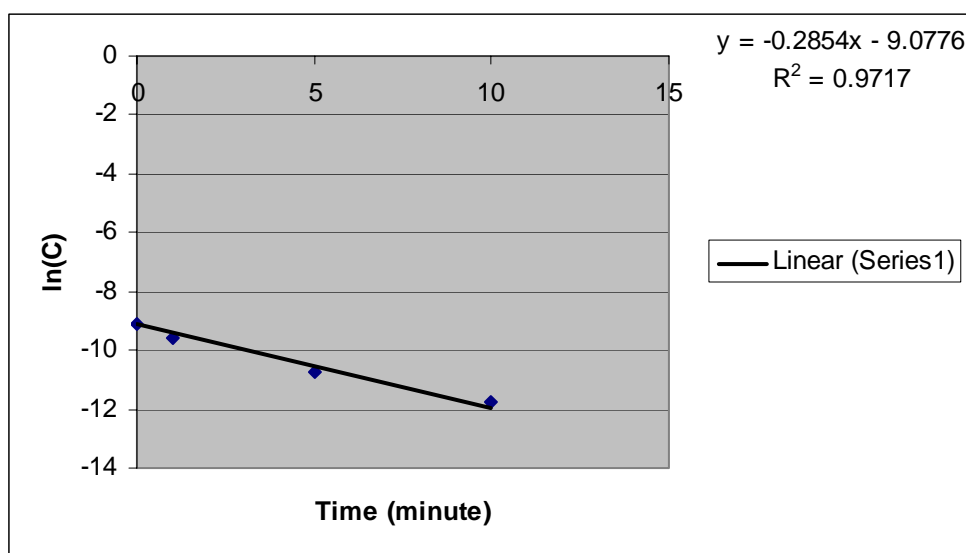


Fig 5-14: First order reaction kinetics for methanol quenched ozone activated persulfate oxidation of TCE.

From Figure 5-14, the equation of the line can be compared to the logarithmic equation of a first order reaction.

$$C = C_0 \exp^{-kt}$$

$$\ln C = \ln C_0 - kt \quad (17)$$

$$Y = -0.2854X - 9.0776 \quad (18)$$

Comparing (17) and (18) the rate constant is 0.2854/min or 0.00476/sec. The rate constant was calculated at constant temperature and pressure conditions of 25⁰ C and 1 atm respectively. An empirical kinetic rate law (neutral pH, aerobic) has been determined

for the aqueous oxidation of TCE by Knauss *et.al* (1998). Measurement of both the rate of disappearance of TCE and the rate of appearance of CO₂ and Cl⁻ were the basis for their mass balance. Buffer solutions were used to fix pH and stoichiometrically sufficient amounts of dissolved O₂ were used to make the reactions pseudo zero-order in O₂. A standard chemical kinetic approach was used, two orders-of-magnitude in initial TCE concentrations were spanned and the resulting double-log plot (log concentration vs. log initial rate) was used to determine the rate constant ($k=5.77\pm 1.06 \times 10^{-7} \text{ s}^{-1}$) and reaction order ($n_c=0.8520.03$) for the rate law. By determining rate constants over the temperature interval 343±373 K, the Arrhenius activation energy (E_a) for the reaction was determined to be 108.024.5 kJ/mol.

5.4 Zero Valent Iron and Ozone Activated Persulfate Oxidation of TCE.

Zero valent iron (ZVI) activated persulfate oxidation of TCE using 13.33 ml of ozone saturated water was most effective in destroying TCE when the persulfate /TCE molar ratio was 10/1. Complete (100%) TCE destruction took place when ½ gm of the ZVI powder was added to the slurry test. Bergendahl and Thies found that 99% destruction of MTBE (methyl *tert*-butyl ether) took place when H₂O₂: MTBE molar ratio was 440:1. The oxidation byproduct acetone was also destroyed at that dosage. Total organic carbon was also reduced by 86% when H₂O₂: MTBE molar ratio of 220:1 and above was used. Doong and Chang (1998) studied the effect of Fe⁰ and Fe²⁺ as catalysts in the photo-assisted degradation of organophosphorous pesticides (methamidophos, malathion,

diazinon, phorate, and EPN) in a UV/H₂O₂ system. Near complete removal of the pesticides occurred with either Fe⁰ or Fe²⁺ added as a catalyst to the UV/H₂O₂ system with little difference in degradation rate constants when Fe⁰ was used instead of Fe²⁺. It was hypothesized by Doong and Chang (1998) that the Fe⁰ was oxidized to Fe²⁺ and then Fe³⁺. Doong and Chang (1998) investigated the rate of degradation of pesticides in a UV/H₂O₂ system supplemented with Fe⁰ and Fe²⁺. They found that an Fe⁰:H₂O₂ molar ratio of 25:1 was sufficient to degrade 10 mg/L of pesticides in approximately 200 min. Bergendahl and Thies (2003) found that an a much lower Fe⁰:H₂O₂ molar ratio of 1.8:1 and without UV radiation was sufficient to degrade 1 mg/L of MTBE. For this project ZVI worked much better than ferrous iron in terms of TCE degradation efficiency even when only ½ a gram of ZVI powder was added to slurry test.

CHAPTER 6 Conclusions

In this work a slurry test was developed to evaluate various oxidants for in-situ remediation of TCE contaminated aquifer. This project presented a feasible alternative to current treatment technologies which consist of pump and treat system, air stripping and digging of soil followed by treatment. There were two hypothesis formed at the beginning of this project. First one was that TCE can be destroyed in-situ using various oxidizing agents such as hydrogen peroxide, sodium persulfate and ozone. The second hypothesis was the presence of solids (media) reduces the effectiveness of in-situ oxidation.

It was found that:

- TCE was degraded rapidly by all the oxidizing agents used in these experiments. Activated persulfate oxidation was shown to be effective for TCE oxidation in the presence of all the media tested in slurry tests for various molar ratios of oxidants.
- With increased solids the TCE removal efficiency was lowered as the solids may play role in the process.
- With Ozone activated persulfate oxidation, 90% of the TCE removal takes place in first 10 minutes indicating a feasible option for in-situ treatment
- Zero valent iron seems to enhance the ozone activated persulfate oxidation. For same molar dose of persulfate, zero valent iron appeared to work better than ferrous iron.
- The solid media plays a vital part in oxidation as it can change the pH of the system and can further increase or decrease the removal of TCE from system.

Chapter 7 Future Work

- Experimentation should be conducted using different chelating agents to keep iron in solution available for catalyzing the reactions. In this project the chelating agent used was citric acid. Liang *et.al* (2003) used various chelating agent for ferrous activated persulfate oxidation and found that citric acid was more effective than ethylenediamintetraacetic acid (EDTA), sodium triphosphate (STPP) and 1-hydroxyehtane-1, 1-diphosphonic acid (HEDPA). A similar study should be carried out for ozone and iron activated persulfate oxidation.
- From this project it was found that variation in solids loading affects the final % remaining TCE. An in depth study of media surface behavior under various molar doses of oxidant and catalyst should be studied, so as to gain better understanding of the in-situ remediation process.
- This project evaluated the rate constant for ozone activated persulfate oxidation at fixed temperature, pressure and pH conditions. Further study should be done at varying temperature, pressure and pH conditions.

CHAPTER 8 Works Cited

- Amy, G.L., R.M. Narbaitz and W.J. Cooper. 1987. Removing VOC's from Groundwater Containing Humic Substances by Means of Coupled Air Stripping and Adsorption. *Journ. AWWA* 49:54.
- Apfeldorf, R. and R.F. Infante. 1981. Review of Epidemiology Study Results of Vinyl Chloride-Related Compounds *Environ. Health Perspective*. 41:221-226.
- Banerjee, M. and Konar, R.S., 1984. Comment on the paper "Polymerization of acrylonitrile initiated by $K_2S_2O_8$ -Fe(II) redox system". *J. Polym. Sci.: Polym. Chem.* 22: 1193-1195.
- Bartseh, H., C. Malaveille, A. Barbin and G. Planche. 1979. Mutagenic and Alkylating Metabolism of Haloethylenes, Chlorobutadienes and Dichlorobutenes produced by Rodent or Human Liver Tissues. Evidence for Oxirane Formation by Cytochrome P-450 Linked Microsomal Monooxygenases *Arch. Toxicol.* 41:249-278.
- Bergendahl J .A. and Thies T.P, Fenton's oxidation of MTBE with zero-valent iron. 2004. *Water Research*, 38(2) 327-334.
- Chemical Profile: Trichloroethylene. *Chemical Market Reporter* 262.3 (2002): 31.
- Chen, Ge; Hoag, George, E.; Chedda, Pradeep; Nadim, Farhad, Woody, Bernard A. Dobbs, Gregory M. The Mechanism and Applicability of In Situ Oxidation of Trichloroethylene with Fenton's Reagent. *Journal of Hazardous Materials*. 2001, 87 (1), 171-186.
- Cohen, Y. and P.A. Ryan. 1985. Multimedia Modeling of Environmental Transport: Trichloroethylene Test Case. *Environ. Sci. Tech.* 19:412-417.
- Dilling, W.L. 1975. Interphase Transfer Processes. II. Evaporation Rates of Chloromethanes, Ethanes, Ethylenes, Propanes and Propylenes from Dilute Aqueous Solutions, Comparisons with Theoretical Predictions. *Environ. Sci. Tech.* 11:405-409.
- Doong R, Chang W. 1998. Photoassisted iron compound catalytic degradation of organophosphorous pesticides with hydrogen peroxide. *Chemosphere* 37(13): 2563-72.

- Ebersson, L., 1987. *Electron Transfer Reactions in Organic Chemistry*. , Springer-Verlag, Berlin.
- Environmental Protection Agency (EPA). 2001. Sources, Emission and Exposure for Trichloroethylene (TCE) and Related Chemicals. EPA/600/R-00/099. March, National Center for Environmental Assessment-Washington Office.
- EPA. CERCLIS Database. 1 July 2005. 27 July 2005.
<<http://cfpub.epa.gov/supercpad/cursites/srchrslt.cfm>>.
- EPA. Consumer Factsheet on: TRICHLOROETHYLENE. 14 Feb. 2005.
<<http://www.epa.gov/safewater/dwh/c-voc/trichlor.html>>
- Gates, D.D., Siegrist, R.L., 1995. In-situ chemical oxidation of trichloroethylene using hydrogen peroxide. *J. Environ. Engin.* 121: 639-644.
- Glaze, W.H. and J. Kang. 1988. Advanced Oxidation of trichloroethylene using hydrogen peroxide. *J. Environ. Engin.* 121: 639-644.
- Glaze, W.H. and J. Kang. 1988. Advanced Oxidation. Processes for Treating Groundwater Contaminated with TCE and PCE: Laboratory Studies. *Journ. AWWA* 57:63.
- Hara, J. et al. 2005. Kinetics of trichloroethene dechlorination with iron powder. *Water Research* .39: 1165-1173.
- Heckel, H., Henglein, A. and Beck, G., 1966. Pulsradiolytische Untersuchung des Radikalanions $\text{SO}_4^{\cdot-}$. *Ber. Bunsenges. Phys. Chem.* 70: 149-154.
- House, D.A., 1962. Kinetics and mechanism of oxidations by peroxydisulfate. *Chem. Rev.* 62: 185-203.
- Hugh, Russell, H.; Matthews, John, E.; Sewell, Guy, W. 1992. EPA Ground Water Issue: TCE Removal from Contaminated Soil and Ground Water. EPA/540/S-92/002.
- Huling, Scott G.; Arnold, Robert G.; Sierka, Raymond A.; Jones, Patrick K.; Fine, Dennis D. 2000. Contaminant Adsorption and Oxidation via Fenton Reaction. *Journal of Environmental Engineering.* 126 (7), 595-600.
- Kevin G. Knauss, Michael J. Dibley, Roald N. Leif, Daniel A. Mew, Roge D. Aines. 1998. Aqueous oxidation of trichloroethene (TCE): a kinetic analysis. *Applied Geochemistry.* 14 : 531-541.

- King, C.V. and Steinbach, O.F., 1930. Kinetics of the reaction between persulfate and thiosulfate ions in dilute aqueous solution. *J. Am.Chem. Soc.* 52: 4779–4795.
- Latimer, M., 1952. *Oxidation Potentials.* , Prentice-Hall, Inc., Englewood Cliffs, NJ.
- Lenka, S. and Dash, S.B., 1983. Polymerization of acrylonitrile initiated by potassium persulfate–cobalt (II) and potassium persulfate–manganese (II) redox system. *J. Macromol. Sci.-Chem.* A 20 3: 397–407.
- Liang, C., C.J. Bruell, Marley, M.C., Sperry, K.L. 2004. Persulfate Oxidation for In Situ Remediation of TCE: I. Activated by Ferrous Ion with and without a Persulfate-Thiosulfate Redox Couple. *Chemosphere* 55:1213-1223.
- Liang, C., C.J. Bruell, Marley, M.C., Sperry, K.L. 2004. Persulfate oxidation for in situ remediation of TCE. II. Activated by chelated ferrous ion. *Chemosphere* 55 (2004): 1225-1233.
- Liang C. , Wang Z. S., Bruell C. J, 2006. Influence of pH on persulfate oxidation of TCE at ambient temperatures. *Chemosphere* xxx (2006) xxx–xxx (Article in press).
- Mohanty NR, Wei IW. 1993. Oxidation of 2,4-dinitrotoluene using Fenton’s reagent: reaction mechanisms and their practical applications. *Hazardous Waste Hazardous Mater.* 10(2):171–83.
- Mackay, D.M., Cherry, J.A., 1989. Groundwater contamination: Pump-and-treat remediation. *Environ. Sci. Technol.* 23: 630-636.
- Morgan, L.B., 1946. Transient molecular species occurring in persulphate oxidations. *Trans. Faraday Soc.* 42: 169–183.
- Narain, H., Jagadale, S.M. and Ghatge, N.D., 1981. Studies of redox polymerization. I. Aqueous polymerization of acrylamide by an ascorbic acid–peroxydisulfate system. *J. Polym. Sci.* 19: 1225–1238.
- Neta, P., Huie, R.E. and Ross, A.B., 1988. Rate constants for reactions of inorganic radicals in aqueous solution. *J. Phys. Chem. Ref. Data* 17 3:1027–1084.
- Prölss, V.H. and Patat, F., 1968. Effect of heavy metal traces on the kinetics of acrylonitrile polymerization in the aqueous phase initiated with the peroxydisulfate–thiosulfate redox system. *Makromol. Chem.* 114: 11–30.

- Richard J. Watts, Patrick C. Stanton, Jimmy Howsawkung, Amy L. Teel, 2002. Mineralization of a sorbed polycyclic aromatic hydrocarbon in two soils using catalyzed hydrogen peroxide. *Water Research* 36: 4283–4292.
- Riggs, J.P., and Rodrigues, F., 1967. Polymerization of acrylamide initiated by the persulfate–thiosulfate redox couple. *J. Polym. Sci.: Part A-1* 5: 3167–3181.
- Robeck, G.G. and O.T. Love. 1983. Removal of Volatile Organic Contaminants from Groundwater. *Environ. Micro.* 53:949-954.
- Sarac, A.S., 1999. Redox polymerization. *Prog. Polym. Sci.* 24: 1149–1204.
- Skarzewski, J., 1984. Cerium catalyzed persulfate oxidation of polycyclic aromatic hydrocarbons to quinines. *Tetrahedron* 40 23: 4997–5000.
- Teel, A. L., Warberg, C. R.; Atkinson, D. A.; Watts, R. J. 2001. Comparison of Mineral and Soluble Iron Fenton’s Catalysts for the Treatment of Trichloroethylene. *Water Research.* 35 (4), 977-984.
- Watts RJ, Stanton PC. 1999. Mineralization of sorbed and NAPL-phase hexadecane by catalyzed hydrogen peroxide. *Water Research* 33:1405–14.
- Wendelin M. R. and Crews P. C. 1993 .Influence of Shade Depth on the Effectiveness of Selected Ultraviolet Absorbers in Reducing Fading”. *Textile Research Journal.*
- World health Organization (WHO). *Environmental Health Criteria* 50: Trichloroethylene. Geneva, 1985.

Appendix A: Control and oxidation data.

Standard curve data for TCE.

CONC(ppm)	PEAK AREA (5Hz*s)
500	5.26E+05
500	5.50E+05
500	5.06E+05
300	3.99E+05
300	3.98E+05
300	3.94E+05
100	1.38E+05
100	1.31E+05
100	1.37E+05
25	3.07E+04
25	3.36E+04
25	3.01E+04
10	1.09E+04
10	1.10E+04
10	1.09E+04
5	7.08E+03
5	6.06E+03
5	5.49E+03
1	1219.993
1	1075.51
1	1045.9

Standard curve data for 1,1-DCE

Concentration (ppm)	Peak Area (5Hz*s)
20	5259.5
50	9734.2
100	21355.6
200	34937.5
300	32190.6

Standard curve data for Trans 1,2-DCE

Conc.	Peak Area(5Hz*s)
50	489.3
100	1230.6
200	3225
300	5266.4
400	6826.4

Standard curve data for Cis 1,2-DCE

Conc.	Peak Area (5Hz*s)
10	
25	111.1
50	269.3
100	679.9
200	1393.5
300	2106.3
400	2539.8

Data for adsorption control on all the media with foil wrapped samples.

Media	%loss of TCE	%loss of TCE	%loss of TCE
sand	3.45	2.93	3.19
silica	5.25	4.94	5.1
glass beads	4.63	4.12	4.38
water	5.67	4.89	5.28

Data for catalyzing effect of iron.

% DESTRUCTION OF TCE		
Media	with Fe	without Fe
water	98.42	95.52
sand	94.29	93.01
silica	91.84	83.46
glass beads	93.06	82.66

Oxidation for TCE for all the media at various molar ratios.

sand10/1/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	48
final total volume(ml)	40
final total <i>ug</i> of TCE	1920
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.46164E-05
% destruction of TCE	87.2
sand10/0/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	122.9
final total volume(ml)	40
final total <i>ug</i> of TCE	4916
MW of TCE <i>ug</i>	131359000
final total moles of TCE	3.74242E-05
% destruction of TCE	67.22666667
sand 5/1/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	90
final total volume(ml)	40
final total <i>ug</i> of TCE	3600

MW of TCE <i>ug</i>	131359000
final total moles of TCE	2.74058E-05
% destruction of TCE	76
sand 5/0/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	94
final total volume(ml)	40
final total <i>ug</i> of TCE	3760
MW of TCE <i>ug</i>	131359000
final total moles of TCE	2.86238E-05
% destruction of TCE	74.93333333
Silica 10/0/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	48
final total volume(ml)	40
final total <i>ug</i> of TCE	1920
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.46164E-05
% destruction of TCE	87.2
Silica 5/1/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	59
final total volume(ml)	40
final total <i>ug</i> of TCE	2360

MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.7966E-05
% destruction of TCE	84.26666667
Silica 10/1/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	50.6
final total volume(ml)	40
final total <i>ug</i> of TCE	2024
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.54082E-05
% destruction of TCE	86.50666667
Silica 5/0/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	112
final total volume(ml)	40
final total <i>ug</i> of TCE	4480
MW of TCE <i>ug</i>	131359000
final total moles of TCE	3.4105E-05
% destruction of TCE	70.13333333
Glass 10/0/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	32.5

final total volume(ml)	40
final total <i>ug</i> of TCE	1300
MW of TCE <i>ug</i>	131359000
final total moles of TCE	9.89654E-06
% destruction of TCE	91.33333333
Glass 10/1/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	49
final total volume(ml)	40
final total <i>ug</i> of TCE	1960
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.49209E-05
% destruction of TCE	86.93333333
Glass 5/1/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	45.5
final total volume(ml)	40
final total <i>ug</i> of TCE	1820
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.38552E-05
% destruction of TCE	87.86666667
Glass 5/0/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	110

final total volume(ml)	40
final total <i>ug</i> of TCE	4400
MW of TCE <i>ug</i>	131359000
final total moles of TCE	3.3496E-05
% destruction of TCE	70.66666667
water 5/1/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	31.3
final total volume(ml)	40
final total <i>ug</i> of TCE	1252
MW of TCE <i>ug</i>	131359000
final total moles of TCE	9.53113E-06
% destruction of TCE	91.65333333
water 10/1/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	23.6
final total volume(ml)	40
final total <i>ug</i> of TCE	944
MW of TCE <i>ug</i>	131359000
final total moles of TCE	7.18641E-06
% destruction of TCE	93.70666667
water 5/1/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	31.3

final total volume(ml)	40
final total <i>ug</i> of TCE	1252
MW of TCE <i>ug</i>	131359000
final total moles of TCE	9.53113E-06
% destruction of TCE	91.65333333
water 5/0/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	76.2
final total volume(ml)	40
final total <i>ug</i> of TCE	3048
MW of TCE <i>ug</i>	131359000
final total moles of TCE	2.32036E-05
% destruction of TCE	79.68

sand 1/1/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	125
final total volume(ml)	40
final total <i>ug</i> of TCE	5000
MW of TCE <i>ug</i>	131359000
final total moles of TCE	3.80636E-05
% destruction of TCE	66.66666667
sand 1/0/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000

MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191

final (mg/l))	145
final total volume(ml)	40
final total <i>ug</i> of TCE	5800
MW of TCE <i>ug</i>	131359000
final total moles of TCE	4.41538E-05
% destruction of TCE	61.33333333
glass 1/1/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	143
final total volume(ml)	40
final total <i>ug</i> of TCE	5720
MW of TCE <i>ug</i>	131359000
final total moles of TCE	4.35448E-05
% destruction of TCE	61.86666667
glass 1/0/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	191
final total volume(ml)	40
final total <i>ug</i> of TCE	7640
MW of TCE <i>ug</i>	131359000
final total moles of TCE	5.81612E-05
% destruction of TCE	49.06666667
silica 1/1/1	
initial (mg/l))	375
initial total volume(ml)	40

initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	145
final total volume(ml)	40
final total <i>ug</i> of TCE	5800
MW of TCE <i>ug</i>	131359000
final total moles of TCE	4.41538E-05
% destruction of TCE	61.33333333
silica 1/0/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	195
final total volume(ml)	40
final total <i>ug</i> of TCE	7800
MW of TCE <i>ug</i>	131359000
final total moles of TCE	5.93793E-05
% destruction of TCE	48
water 1/1/1	
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	125.57
final total volume(ml)	40
final total <i>ug</i> of TCE	5022.8
MW of TCE <i>ug</i>	131359000
final total moles of TCE	3.82372E-05
% destruction of TCE	66.51466667
water 1/0/1	
initial (mg/l))	375
initial total volume(ml)	40

initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	170
final total volume(ml)	40
final total <i>ug</i> of TCE	6800
MW of TCE <i>ug</i>	131359000
final total moles of TCE	5.17665E-05
% destruction of TCE	54.66666667

Kinetics for TCE oxidation

sand10/1/1	15 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	60.6
final total volume(ml)	40
final total <i>ug</i> of TCE	2424
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.84532E-05
%TCE REMAINING	16.16
sand10/1/1	30 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	43.4
final total volume(ml)	40
final total <i>ug</i> of TCE	1736
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.32157E-05

%TCE REMAINING	11.57333333
sand10/0/1	15 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	60.2
final total volume(ml)	40
final total <i>ug</i> of TCE	2408
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.83314E-05
%TCE REMAINING	16.05333333
sand10/0/1	30 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	43.6
final total volume(ml)	40
final total <i>ug</i> of TCE	1744
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.32766E-05
%TCE REMAINING	11.62666667
silica10/1/1	15 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	59.6
final total volume(ml)	40
final total <i>ug</i> of TCE	2384
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.81487E-05

%TCE REMAINING	15.89333333
silica10/1/1	30 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	43.6
final total volume(ml)	40
final total <i>ug</i> of TCE	1744
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.32766E-05
%TCE REMAINING	11.62666667
silica10/0/1	15 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	76.2
final total volume(ml)	40
final total <i>ug</i> of TCE	3048
MW of TCE <i>ug</i>	131359000
final total moles of TCE	2.32036E-05
%TCE REMAINING	20.32
silica10/0/1	30 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	60
final total volume(ml)	40
final total <i>ug</i> of TCE	2400
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.82705E-05

%TCE REMAINING	16
glass10/1/1	15 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	60
final total volume(ml)	40
final total <i>ug</i> of TCE	2400
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.82705E-05
%TCE REMAINING	16
glass10/1/1	30 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	45
final total volume(ml)	40
final total <i>ug</i> of TCE	1800
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.37029E-05
%TCE REMAINING	12
glass10/0/1	15 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	78
final total volume(ml)	40
final total <i>ug</i> of TCE	3120
MW of TCE <i>ug</i>	131359000

final total moles of TCE	2.37517E-05
%TCE REMAINING	20.8
glass10/0/1	30 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	63
final total volume(ml)	40
final total <i>ug</i> of TCE	2520
MW of TCE <i>ug</i>	131359000
final total moles of TCE	1.91841E-05
%TCE REMAINING	16.8
water10/1/1	15 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	18.8
final total volume(ml)	40
final total <i>ug</i> of TCE	752
MW of TCE <i>ug</i>	131359000
final total moles of TCE	5.72477E-06
%TCE REMAINING	5.013333333
water10/1/1	30 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	1
final total volume(ml)	40
final total <i>ug</i> of TCE	40
MW of TCE <i>ug</i>	131359000

final total moles of TCE	3.04509E-07
%TCE REMAINING	0.266666667
water10/0/1	15 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	21.5
final total volume(ml)	40
final total <i>ug</i> of TCE	860
MW of TCE <i>ug</i>	131359000
final total moles of TCE	6.54694E-06
%TCE REMAINING	5.733333333
water10/0/1	30 MIN
initial (mg/l))	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total moles of TCE	0.000114191
final (mg/l))	1.7
final total volume(ml)	40
final total <i>ug</i> of TCE	68
MW of TCE <i>ug</i>	131359000
final total moles of TCE	5.17665E-07
%TCE REMAINING	0.453333333