DEGRADATION OF TETRACHLOROETHYLENE AND TRICHLOROETHYLENE UNDER THERMAL REMEDIATION CONDITIONS

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DEGRADATION OF TETRACHLOROETHYLENE AND TRICHLOROETHYLENE UNDER THERMAL REMEDIATION CONDITIONS

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LIST OF ABBREVIATIONS AND SYMBOLS

Cl^-	Chloride Ion
CO	Carbon Monoxide
CO_2	Carbon Dioxide
$COCl_2$	Phosgene
DCA	Dichloroacetylene
DCAA	Dichloroacetic acid
1,1-DCE	1,1-dichloroethylene
cis-DCE	cis-1,2-dichloroethylene
^oC	Degrees Celsius
DNAPL	Dense Non-Aqueous Phase Liquid
Fe_2S	Pyrite
GC/ECD	Gas chromatograph with electron capture detector
GC/FID	Gas chromatograph with flame ionization detector
GC/MS	Gas chromatograph with mass spectrometer
$HCCl_3$	Chloroform
HCl	Hydrochloric acid
HNO_3	Nitric acid
IC	Ion Chromatography
k	Reaction rate coefficient
NaOH	Sodium Hydroxide
NAPL	Non-Aqueous Phase Liquid
PbS	Galena
PCE	Tetrachloroethylene
TCAA	Trichloroacetic acid
TCE	Trichloroethylene

SUMMARY

Thermal remediation involves heating subsurface environments and collecting fluids in order to recover contaminants such as tetrachloroethylene (PCE) and trichloroethylene (TCE). While increasing subsurface temperature can lead to changes in the distribution of contaminants between the solid, liquid, and gas phases, there is also an increased potential for PCE and TCE to degrade. This work was performed to determine the rate of PCE and TCE degradation and products formed in laboratory-scale experiments designed to simulate thermal remediation conditions.

The conditions during transport of gas-phase TCE were simulated using a series of iso-thermal flow-through experiments in the temperature range from 60 to 800^{o}C. Degradation of TCE was not evident at temperatures of less than 240^{o}C; however, chloroacetic acids, which comprised less than 0.1% of the influent TCE on a carbon basis, were detected. At temperatures greater than 300^{o}C, TCE readily degraded where the identities of the degradation products were a function of oxygen and water content. With oxygen present, TCE degraded to form CO, phosgene, and CO_2 with minor amounts of hexachloroethane, PCE, and carbon tetrachloride. Without oxygen, TCE degraded to form minor amounts of pentachlorobutadiene and hexachlorobenzene. Increasing the amount of water vapor was found to decrease the amount of TCE degraded as evidenced by an increase in TCE recovery and a decrease in the amount of degradation products formed. However, unwanted chlorinated carbon degradation products were detected in an atmosphere of gas saturated with boiling water, the maximum water content expected during thermal remediation. Although the vapor recovery system used during thermal remediation is anticipated to capture these TCE degradation products, the amount of missing carbon (~17%) in experiments completed at 800^{o}C makes the prospect of recovering all TCE degradation products doubtful.

Experiments were conducted using hermetically sealed ampules to simulate heating dissolved phase PCE and TCE over periods of up to 75 days. At 120^{o}C, the first-order TCE degradation half-life was 330 days and the degradation products included CO and CO_2, glycolate, formate, and chloride. The rate of TCE disappearance was increased

with the addition of 1% (wt.) goethite, which suggests that the presence of iron bearing soil minerals can increase rates of TCE degradation during thermal remediation. In contaminated field samples, TCE was found to degrade to form cis-1,2-dichloroethylene at 95^{o}C coincident with the formation of hydrogen gas. Degradation of PCE was not evident in field samples or in deionized water and is not expected to degrade during thermal remediation at temperatures below 95^{o}C.

CHAPTER 1

INTRODUCTION

Chlorinated organic solvents, such as tetrachloroethylene (PCE) and trichloroethylene (TCE), are common pollutants at military and industrial facilities worldwide. Improper disposal or release of these organic liquids into the subsurface typically results in the formation of a contaminated source zone that consists of dense non-aqueous phase liquid (DNAPL) existing as entrapped ganglia and potentially high-saturation pools residing above layers of low permeability media. Due to the combination of low aqueous solubility and mass transfer limitations, DNAPL-contaminated aquifers often serve as long-term sources of groundwater contamination that may persist for decades or even centuries. Many remedial techniques are available to recover DNAPL mass from source zones including thermal treatment, air sparging, co-solvent flushing, and surfactant flushing. Of these technologies, thermal treatment provides two distinct advantages in that no chemical agents are introduced into the subsurface and heat can cross the heterogeneous and low permeability porous media regions that are bypassed by injected treatment fluids. The term "thermal treatment" includes a number of technologies designed to deliver heat to the subsurface such as hot water injection, steam flushing, conductive heating, resistive heating, and electromagnetic heating (Davis, 1997). In situ thermal treatments are usually combined with groundwater and vapor extraction systems to facilitate contaminant mass recovery from the subsurface and together comprise a thermal remediation system (Udell, 1997). The resulting increase in subsurface temperature can lead to substantial changes in the distribution of chlorinated

solvents between the solid, liquid, and gas phases. For example, the vapor pressure, Henry's Law constant, and aqueous solubility of TCE and PCE increase with increasing temperature (Horvath, 1982; Knauss et al., 2000a; Heron et al., 1998a), while the sorption coefficient of PCE decreased by 40% when the temperature was raised from 22 to 92^{o}C (Sleep and McClure, 2001). In addition, the mass transfer rate coefficient for the dissolution of residual TCE-NAPL into flowing water increased by a factor of 2 when the temperature was increased from 5 to 40^{o}C, and was proportional to the corresponding increase in the molecular diffusion coefficient of TCE in water (Imhoff et al., 1997).

Thermal remediation of contaminated subsurface environments consists of two distinct processes: one involves recovering *gas* phase contaminants and the other involves prolonged heating to drive the volatile chlorinated solvents from the *dissolved* phase to the gas phase. Thus, gas-phase chlorinated solvents are exposed to soil heated to elevated temperatures while flowing toward extraction wells during the recovery process and dissolved-phase chlorinated solvents are maintained at elevated temperatures for extended periods of time before being transferred to the gas phase.

The in-situ degradation of TCE into carbon dioxide and chloride has been claimed to occur during thermal conductive heating at temperatures ranging from 500 to 700^{o}C (Baker and Kuhlman, 2001). There have been many experimental studies that show TCE can be readily transformed into compounds with greater toxicity, however, these studies used conditions found in combustion systems with relatively short residence time (i.e., seconds). The residence time during in situ thermal conductive heating is thought to be greater, on the order of minutes, hours, or days, based on the large volume of subsurface that has to be treated and the comparatively limited capacity of compressors employed to

recover subsurface vapors. Therefore, one goal of this work was to determine the products formed after passing gas-phase TCE through a laboratory-scale apparatus heated from 60 to 800^{o}C with residence time representative of in situ thermal remediation conditions.

Although thermal treatment technologies are capable of removing large quantities of DNAPLs from the subsurface (U.S. EPA, 2004), it is likely that not all of the contaminant mass will be recovered. In fact, dissolved-phase contaminant concentrations may increase following thermal treatment due to enhancements in aqueous solubility, mass transfer, and organic liquid mobility at elevated temperature and pressure (Davis, 1997). Optimization techniques, such as depressurizing the subsurface during steam flooding, have been employed to reduce the amount of dissolved-phase contaminant mass remaining after thermal treatment (Udell and Itamura, 1998). However, depressurization involves increasing the rate of vapor extraction and leads to an increase in the ex-situ volume of contaminated water that must be contained and treated thus an increase in remediation costs. Another approach, referred to as Hydrous Pyrolysis/Oxidation (HPO), is based on the premise that chlorinated solvents undergo complete oxidation to form carbon dioxide (CO_2) and chloride (Cl^-) in oxygenated water at elevated temperatures (Knauss et al., 2000b; Betts, 1998). Experimental evidence to support aqueous phase oxidation of chlorinated solvents during thermal treatment is based primarily on the results of one laboratory study in which the concentration of TCE was monitored in a completely water-filled, gold-walled reactor operated at temperatures between 70 to 100^{o}C (Knauss et al., 1999). For experiments conducted at 90^{o}C, the average first-order half-life for TCE disappearance was 2.1 days, with only carbon dioxide and chloride

detected as reaction products (Knauss et al., 1999). This means that dissolved phase TCE, which remains after recovering most of the DNAPL mass from the heated source zone, would rapidly degrade by a heat induced reaction with the oxygen that was dissolved in water. For example, a source zone with TCE concentrations near its water solubility limit of 1,000 mg/L would be reduced to drinking water standards (0.005 mg/L) within 35 days in a subsurface heated to 90^{o}C. Given that it takes several months for sites to cool to ambient temperatures after thermal treatment, this rate of TCE degradation implies that TCE can be destroyed in situ without the need to perform costly optimization techniques.

Earlier studies of dissolved-phase TCE stability were conducted in 0.3 mL flame-sealed glass tubes maintained at temperatures ranging from 70 and 140^{o}C (Jeffers et al., 1989; Jeffers and Wolfe, 1996). Based on rate parameters reported for neutral conditions, the first-order half-life for TCE disappearance was estimated to be 49 years at 90^{o}C (Jeffers and Wolfe, 1996). At this rate, it would take 861 years for the TCE to degrade from 1,000 mg/L down to drinking water standards.

These results illustrate the relatively large variability of published TCE degradation rates at elevated temperatures, and the apparent sensitivity of thermally-induced TCE degradation to experimental conditions. These differences have important implications regarding the operation of a thermal treatment system. If the rate determined by Knauss et al. (1999) is used, then a remediation engineer would recommend turning off the costly groundwater and vapor extraction systems after TCE-NAPL mass recovery had ceased by reasoning that any residual TCE would degrade in the hot subsurface before the site has cooled to ambient conditions. However, if the rate determined by Jeffers et al. (1996) is assumed valid, then a remediation engineer would recommend

recovery optimization techniques during the site cool down phase to ensure that site groundwater can meet drinking water requirements. Optimization techniques involve pumping large volumes of vapor and water from the subsurface in effort to reduce in situ contaminant concentrations. The recovered fluids then have to be treated before being released to surface water bodies. Therefore, the difference between recommending that a site be allowed to cool without undergoing optimization procedures and recommending implementation of optimization techniques involves the decision of whether or not to process large volumes of fluids, which in turn directly effects remediation cost and duration. Thus, another goal of the work described herein was to measure the rate of degradation for dissolved phase TCE and PCE.

Additional factors may impact laboratory-scale thermal degradation studies, including the presence of solids, incubation time, reactor materials, and solution conditions. Subsurface solids (i.e., soils, sediments, and aquifer materials) consist of minerals and organic matter, which could facilitate abiotic degradation of chlorinated solvents at elevated temperatures and potentially lead to the formation of products other than those observed in single-phase (e.g., aqueous or gas) systems. Reductive dechlorination of dissolved-phase chloroethylenes such as TCE, has been widely reported in the presence of zero-valent metals at room temperature (e.g., Miehr et al., 2004; Gilham and O'Hannesin, 1994). In addition, Ferry et al. (2004) observed abiotic degradation of cis-dichloroethylene (cis-DCE) and 1,1-DCE in an aquifer material that contained magnetite. In contrast, no changes in aqueous-phase concentrations of TCE were observed in 1 mL glass bulbs containing either galena (PbS), pyrite (Fe_2S), or subsurface materials from Waterloo, Canada and Columbus, Ohio that were incubated at

106 ^{o}C for 72 hours (Jeffers et al., 1994). However, in situ thermal remediation typically involves heating the contaminated subsurface for extended periods of time, up to several months in field-scale applications completed to date (U.S. EPA, 2004).

Degradation products that could potentially form during thermal treatment of *dissolved* phase chlorinated solvents are not limited to carbon dioxide and chloride, but also include acutely toxic compounds such as dichloroacetyl chloride ($CHCl_2COCl$) and phosgene ($COCl_2$), which have been detected during photocatalytic treatment of TCE contaminated water (Haag et al., 1996, Amama et al., 2001).

The three primary goals of this work were:

1. Determine the degradation products formed when subjecting *gas*-phase TCE to temperatures in the range from 60 to 800^{o}C.
2. Determine the rate of *dissolved*-phase TCE and PCE degradation in the temperature range from 22 to 120^{o}C.
3. Identify *dissolved*-phase TCE and PCE degradation products in experimental systems containing gas, water, and solids heated for greater than one month in duration.

The first goal was met by passing gas-phase TCE through a laboratory scale apparatus heated at set temperatures in the range from 60 to 800^{o}C with the residence time fixed at approximately 4.3 minutes. The recovery of TCE and degradation products formed were determined by passing the gas phase effluent leaving the heated apparatus through liquid filled containers (i.e, liquid traps) or through containers maintained at

-10°C and -78°C (i.e, cold traps). Additionally, the gas effluent leaving the traps was collected in a Tedlar bag to determine the degradation products not retained in the traps. The compounds present in the traps and Tedlar bag were determined using gas chromatography (GC) techniques. Specific experiments were conducted to investigate the effects of temperature, water vapor content, solids (Ottawa sand), and oxygen content on TCE degradation and product formation. The water vapor content ranged from carrier gas saturated with water at 25°C to gas saturated with boiling water (100°C). Separate experimental series were completed using air (i.e., 21% O_2) and nitrogen (i.e., 0% O_2) as the carrier gas. Limited experiments were completed with solids due to unfavorable solids-apparatus interactions that resulted in frequent equipment failure. These conditions cover the range of temperatures, water and oxygen contents anticipated for gas-phase recovery of TCE during thermal remediation.

The second and third goals were met by determining the change in TCE and PCE content, along with the products formed, in hermetically sealed glass ampules that were incubated between the temperatures of 22 and 120°C for up to 75 days. Degradation products were identified in the gas, aqueous, and solid phases using GC and ion chromatography (IC) analytical techniques. The rate of degradation and products formed were determined as a function of ampule oxygen and solids content. The solids used included Ottawa sand and Ottawa sand amended with 1% (wt.) goethite for experiments with TCE and PCE contaminated field soils from West Fargo, ND.

CHAPTER 2

BACKGROUND INFORMATION

The following sections describe relevant physical and chemical properties of TCE and PCE and the temperature dependent partitioning of TCE and PCE between water and gas phases, and the operational conditions associated with commonly used in-situ thermal treatment technologies. This background information is provided as basis for the conditions employed in the experiments described in Chapter 3: Flow-Through Experiments and Chapter 4: Ampule Experiments.

2.1 Trichloroethylene and Tetrachloroethylene Physical Properties

TCE and PCE are important solvents used for cleaning textiles (dry cleaning), metal parts, and electrical components with their primary use as the raw materials for the manufacture of hydrofluorocarbon refrigerants (HSIA, 2001 and HSIA, 1999). TCE consists of two carbon atoms connected by a double bond (i.e., ethylene) to which are bonded three chlorine atoms and a hydrogen atom (Figure 2.1a) while PCE has four chorine atoms bonded to the ethylene molecule (Figure 2.1b). TCE and PCE are colorless, sweet smelling, volatile liquids that are acutely toxic to humans when ingested (Mertens, 1999; Hickman, 1999). Even though TCE is referred to as a non-flammable liquid, it should be kept away from open flames and metal surfaces with temperatures greater than 176^{o}C due to the flammability of its vapors (Mertens, 1999). If TCE is exposed to a temperature greater than 420^{o}C when oxygen is present, it will spontaneously ignite (Mallinckrodt and Baker, 2003a). PCE is the most stable chlorinated

solvent with no flash point, however, at temperatures greater than 300°C, it breaks down to form the poisonous gas phosgene along with hydrogen chloride (ASTDR, 1997a).

Figure 2.1: Conceptual structure of trichloroethylene (TCE) and tetrachloroethylene (PCE).

Table 2.1: Select Properties of PCE and TCE			
Properties (at 20°C)	**TCE** (McNeill, 1978)	**PCE** (Keil, 1978)	**Water** (Gebhart et al., 1988)
Molecular Weight (g/mol)	131.39	165.83	18.02
Melting Point (°C)	-87.1	-22.7	0
Boiling Point (°C)	86.7	121.2	100
Critical Temperature (°C)	271.0	347.1	374
Critical Pressure (MPa)	5.02	9.74	22.35
Explosive Limit in Air (Vol%)	8 to 10.5	*no data*	*no data*
Liquid Viscosity (cP)	0.58	0.84	0.99
Liquid Density (g/mL)	1.465	1.623	0.998
Solubility in Water (mg/L)	1,068	150	--
Vapor Pressure (MPa)	0.008	0.002	0.002
Henry's Coefficient ($H = C_g/C_l$)[a]	0.314	0.533	--
MPa = 1.00 bar = 1.02 atm cP = 100 × g/cm s [a] Staudinger and Roberts, 2001			

Even though TCE and PCE are sparingly soluble in water (Table 2.1), they are some of the most commonly found groundwater contaminants in the United States and with TCE at 316 and PCE at 209 of the 1,604 National Priority List (NPL) sites (U.S. EPA, 2005). While the long-term health effects of drinking water contaminated with

small amounts of TCE or PCE are not yet known, the U.S. EPA has set the maximum contaminant level (MCL) for drinking water at 5 μg/L (ATSDR, 1997a and 1997b). If TCE or PCE are found in groundwater at concentrations greater than 5 μg/L, then treatment or control of the groundwater is usually required.

2.2 TCE- and PCE-Water Phase Behavior

The purpose of heating subsurface regions contaminated with chlorinated solvents is to drive the solvent into the vapor phase where is can be recovered with a vapor extraction system. The following sections describe the changes in the partitioning of TCE and PCE between water and gas phases with increasing temperature. There are at least two potential solvent/water mixture scenarios: one is a source zone that contains TCE- and/or PCE-NAPL with water (two immiscible fluids, Section 2.2.1) and the second is when TCE and/or PCE are dissolved in water (Section 2.2.2). In both scenarios, the composition of the vapor above a water/solvent mixture will be enriched in either TCE or PCE, whichever is present, because the vapor pressure of TCE and PCE are both greater than that of water with increasing temperature. This enriching of the vapor phase is the physical basis for thermal treatment.

2.2.1 Boiling of Immiscible Fluid Mixtures

When the temperature of a water and TCE-NAPL mixture is increased, boiling is estimated to occur at 73.0^{o}C, which is below the boiling point of either water (100^{o}C) or TCE-NAPL (86.7^{o}C). By definition, boiling occurs when the vapor pressure of a liquid mixture exceeds the surrounding gas phase pressure. For a mixture consisting of two immiscible liquids, such as water and TCE-NAPL, the total vapor pressure is equal to the

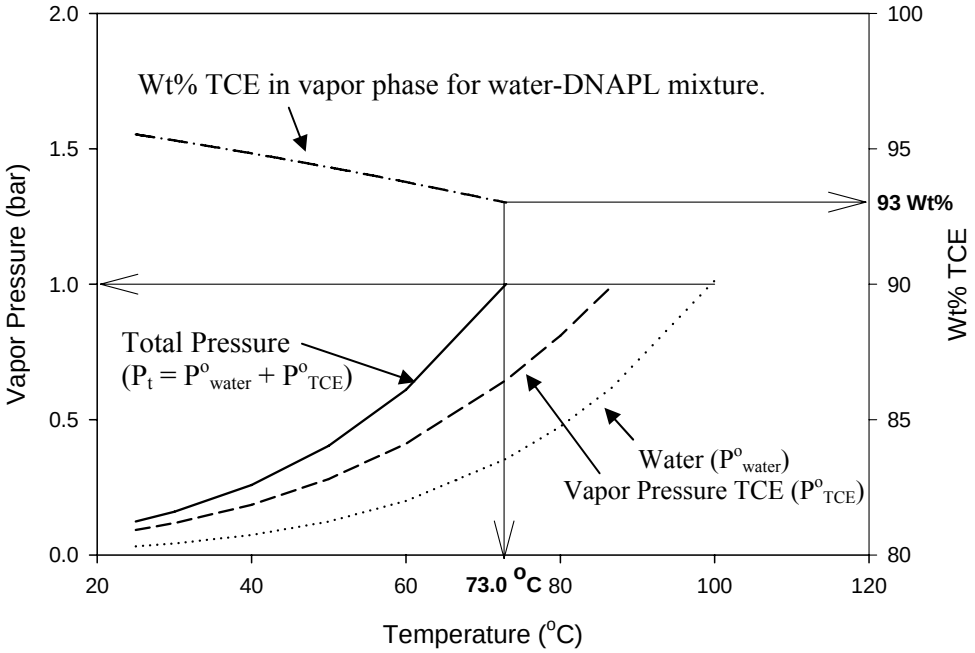

Figure 2.2: Water and TCE-NAPL vapor pressure as a function of solution temperature at 1 bar or 1.02 atm of total gas phase pressure.

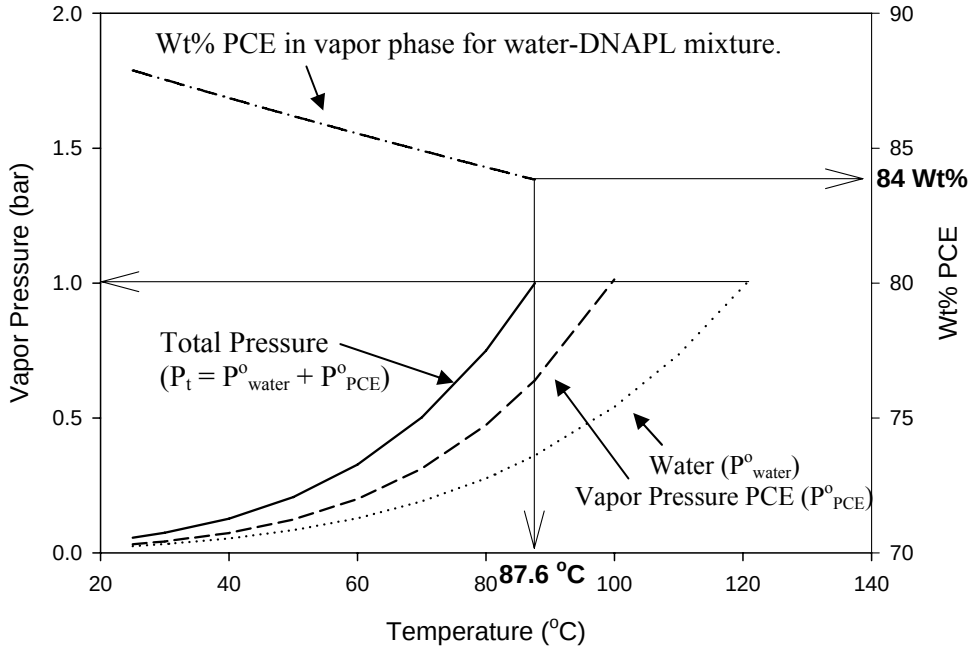

Figure 2.3: Water and PCE-NAPL vapor pressure as a function of solution temperature at 1 bar or 1.02 atm of total gas phase pressure.

sum of the vapor pressures of each pure constituent (Dalton's Law: $P_t = P^o_{water} + P^o_{TCE}$), and the mixture will boil when the total vapor pressure is equal to the local gas phase pressure ($P_t = P_{atm}$) (Atkins, 1998). As long as TCE-NAPL is present, the mixture will boil at the lower temperature (73.0°C), and since TCE-NAPL has a greater vapor pressure than water, the composition of the boiling vapor is 93% TCE and 7% water by weight (Horvath, 1982). This phenomenon serves as the basis for steam distillation, in which TCE is separated from water at temperatures below its normal (pure) boiling point and is also referred to as azeotropic boiling since the temperature and vapor composition at the boiling point are fixed as long as liquid TCE-NAPL is present (U.S. EPA, 2004).

The diagram in Figure 2.2 shows the pure phase vapor pressures calculated using the Antoine equation [$P^o = 10^{(A-(B/(T+C))}$] and parameters measured for TCE-NAPL (McDonald, 1944) and water (Bridgeman and Aldrich, 1964) along with the total vapor pressure which is the sum of the pure phase vapor-pressures. Figure 2.2 also contains the weight percent of TCE based on the fraction of TCE vapor pressure relative to the total vapor pressure. Boiling of the TCE-NAPL and water mixture would occur at 73.0 °C, assuming that the surrounding gas phase pressure was at 1 bar, with 93% of the vapor consisting of TCE by weight. The corresponding parameters for PCE-NAPL and water are shown in Figure 2.3 with the boiling point for a water and PCE-NAPL mixture at 87.6°C, well below the PCE-NAPL boiling point of 121.2°C.

The initial goal of in situ thermal treatment is to heat the chlorinated solvent source zone to at least the azeotropic boiling point temperature (e.g., 87.6°C for PCE-NAPL) and capture the enriched vapor for above ground treatment and disposal. As the NAPL is removed and the amount of solvent in the recovered vapor decreases, what is

left behind is water saturated in the solvent. At that point, remediation of a site involves removing dissolved phase contaminantion from water which is described by Henry's law.

2.2.2 Thermal Enhanced Stripping of Dissolved Phase Chlorinated Solvents

Once the pure phase NAPL has been removed through the azeotropic boiling process described above, chlorinated solvents remain dissolved in water at or near their water saturation points. The removal of this so called residual contaminant mass is accomplished by removing additional volumes of vapor while the subsurface remains at elevated temperature.

Mackay at al. (1979) performed isothermal stripping experiments by passing air through a stagnant column of water contaminated with organic solvents and found that the removal of organics from the water could be described using a first order decay expression:

$$\ln[C_w] = \ln[C_w^0] - \frac{HG}{V_l}t \tag{2.1}$$

where G was the gas flow rate through the stagnant water of volume V_l with the concentration of the organic solvent (C_w) decreasing from its initial concentration (C_w^0) with time (t). Increasing the temperature leads to an increase in the rate of removal of a dissolved phase solvent due to an increase in the temperature dependent Henry's coefficient (H), which relates the concentration of a sparingly soluble solvent in the water phase to that in the gas phase (air-water equilibrium). The temperature dependence of the Henry's coefficient has been described using the van't Hoff correlation (Staudinger and Roberts, 2001):

$$\log(H) = A - \frac{B}{T} \tag{2.2}$$

where *A* and *B* are coefficients determined by fitting experimental data and *T* is the absolute temperature in Kelvins. Figure 2.4 shows the Henry's coefficient for TCE and PCE as a function of temperature using the correlations reported in Staudinger and Roberts (2001), which were based on results of 12 experiments completed over the temperature range from 1 to 50°C.

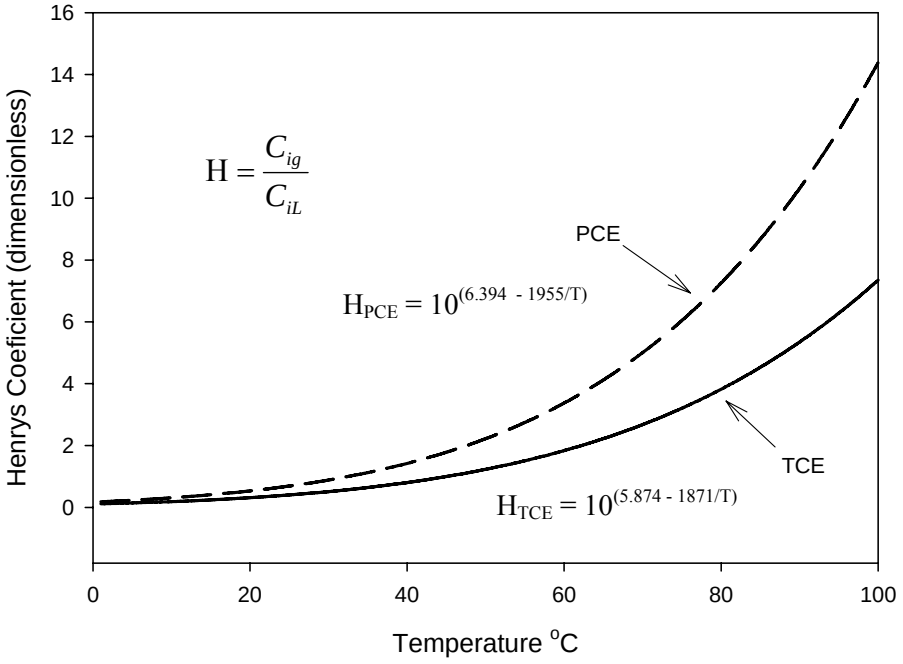

Figure 2.4: Henry's coefficient with increasing temperature for TCE and PCE dissolved in water using correlation parameters reported in Staudinger and Roberts (2001).

The effect of increasing temperature on the rate of dissolved-phase TCE removal from a bubble column is shown with a plot of Equation 2.1 in Figure 2.5. Increasing the temperature from 20 to 90°C results in a decrease from 5.2 hours to 19 minutes in the time required to reduce TCE concentrations from 100 mg/L to the drinking water standard of 0.005 mg/L.

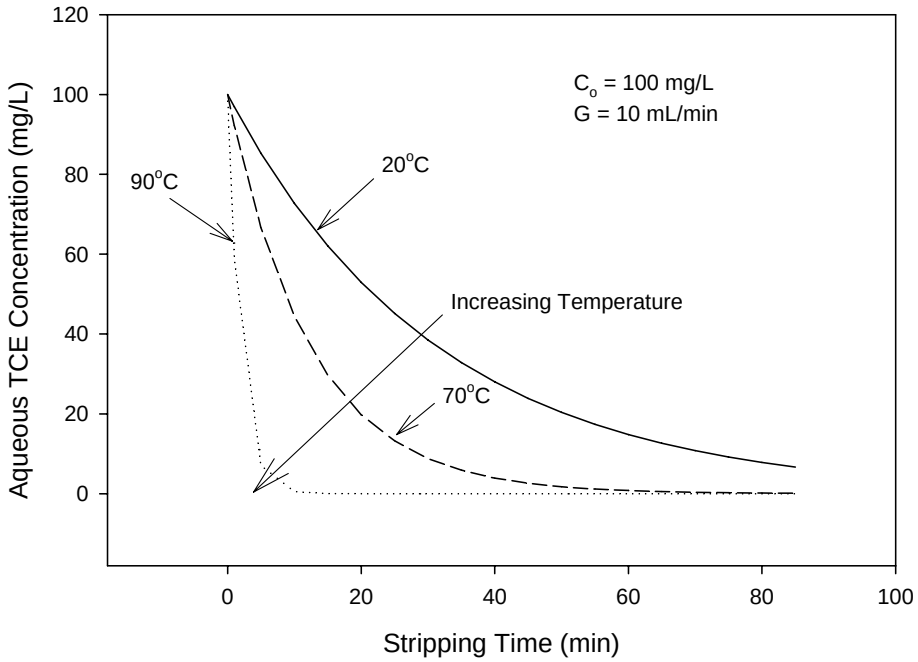

Figure 2.5: Rate of TCE removal from a bubble column as a function of system temperature with an initial aqueous concentration of 100 mg/L and gas flow rate of 10 mL/min using the temperature dependent Henry's correlation of Staudinger and Roberts (2001).

Increasing the amount of solvent in the gas phase by increasing temperature does not mean that aqueous phase TCE concentrations will magically decrease to drinking water levels. Gas flow is needed to strip TCE from the water as described by Equation 2.1 and also to provide volumes of fresh gas into which TCE can partition. Equation 2.1 is a simple first-order decay model that assumes the concentration of TCE is uniform throughout the aqueous phase (perfect mixing) and that the TCE in the gas phase is in equilibrium with the aqueous phase (long column). Accepting these assumptions, Equation 2.1 demonstrates that the rate of TCE removal is also sensitive to the rate of gas flow (G) in addition to system temperature. Figure 2.6 shows that decreasing the rate of gas flow (G) leads to a decrease in the rate of TCE removal. In fact, if G is set to a value

of zero in Equation 2.1, then no TCE will be removed from the system. From this analysis, there has to be gas flow in order to remove TCE; heat alone won't help.

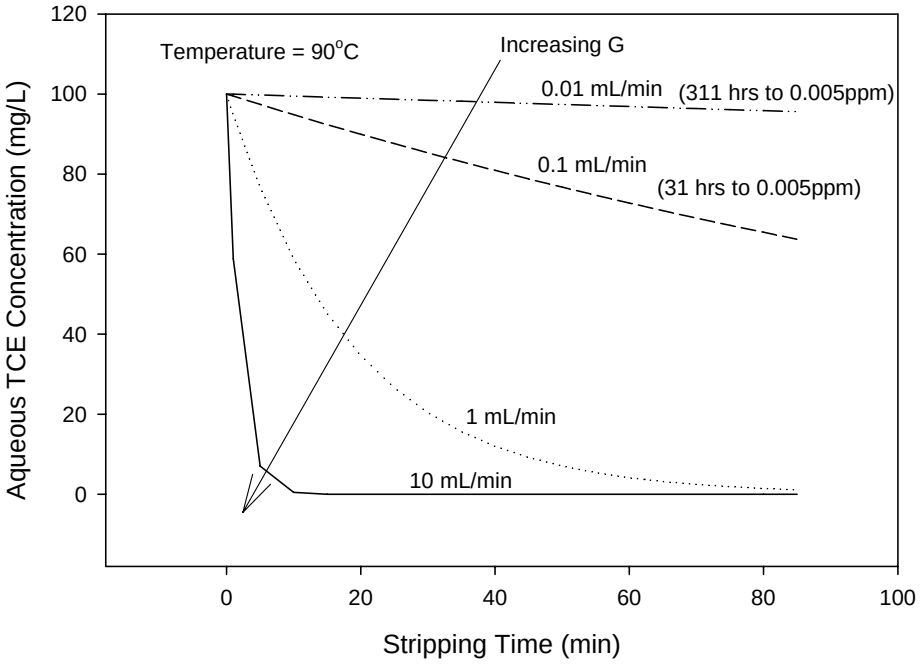

Figure 2.6: Rate of TCE removal from a bubble column as a function of gas flow rate (G) for fixed temperature of 90°C and initial TCE concentration of 100 mg/L.

Itamura and Udell (1995) derived an equation which they used to describe the change in chlorinated solvent concentration as water is evaporated due to an increase in temperature and/or decrease in pressure. They suggest that decreasing subsurface pressure will cause an increase in the rate of water evaporation thus dewatering the subsurface. Since both TCE and PCE preferentially partition from the water into the gas phase, they predicted that a large reduction in the aqueous phase concentration would result after removing a comparatively small amount of water (e.g., 1 wt%). This finding served as the basis for thermal remediation optimization methods such as pressure cycling that are used to enhance the recovery of dissolved phase chlorinated solvents.

2.3 Operational Conditions of In Situ Thermal Treatment Technologies

Steam flushing, electrical resistive heating, and thermal conductive heating are the three thermal remediation techniques commonly used to treat aquifers contaminated with chlorinated solvents (U.S. EPA, 2004). The main difference between each technology is in how heat is delivered to the subsurface: steam flushing uses the latent heat in steam injected into the subsurface, electrical resistive heating uses the heat dissipated by passing electrical current through water saturated and electrically-conductive soil, and thermal conductive heating relies on heated steel rods to conduct heat through soil (Table 2.2). The type of heat delivery in turn fixes the maximum temperature for each technology. Steam flushing and electrical resistive heating achieve peak temperatures in the 70 to 140^{o}C range since heat is translated primarily by water vapor whereas thermal conductive heating achieves higher temperatures after removing water near the heat source.

Table 2.2: Commonly Employed In Situ Thermal Treatment Technologies

Technology	Heat Delivery	Maximum Temperature Range (^{o}C)	Number of Sites Treated (EPA Database*)
Steam Flushing	Latent heat of steam	70 to 140	36
Electrical Resistive Heating	Resistance to electrical current	70 to 200	30
Thermal Conductive Heating	Conduction of heat	500 to 800	15

*In-Situ Thermal Treatment Site Profile Database, US Environmental Protection Agency, Office of Solid Waste and Emergency Response, Technology Innovation Program**,** Washington, D. C. (www.cluin.org/products/thermal/)

One feature common to all three thermal remediation techniques is the time to reach the average operating temperature (usually between 60 and 100^{o}C) and the time required for the site to cool to ambient temperature. These rates are controlled more by

the rate of heat dissipation at a particular site rather than the type of technology used. While there is little publicly available documentation of these heat-up and cool-down times, the heat-up time is reported to be between one and two weeks, and the time required for the site to cool to ambient temperatures may be up to one year (Friis et al., 2005). Another common theme for in-situ thermal remediation systems is the need to pump large volumes of water and vapor from the subsurface; otherwise, the volatilized solvents will simply flow to a lower temperature location and condense, potentially spreading the contaminants over a greater subsurface volume. During the Savannah River Site steam flushing application in Aiken, SC, 45 million pounds of steam were injected and 176 million cubic feet of vapor was extracted over a 12 month period in effort to recover 30,000 kg (18,500 L) of PCE (U.S. EPA, 2004).

The purpose of the following sections is to describe the range of subsurface conditions that have been noted during previous applications of each technology. This review is in effort to select experimental conditions that are anticipated to represent subsurface conditions (e.g., temperature, residence time) to which TCE and PCE might be exposed during thermal treatment.

2.3.1 Steam Flushing

Injecting steam into the subsurface through wells has been shown to be effective for mobilizing fluids, heating the subsurface, and removing TCE and PCE from source zones (Udell, 1997). The steam drive process occurs in two stages, with the initial stage involving the displacement of condensed fluids from the subsurface to recovery wells. The second stage occurs after a subsurface channel of steam forms to connect the injection and extraction wells, commonly referred to as steam breakthrough. During the

initial displacement stage, the subsurface temperature is increased to at least the boiling point of the system (e.g., water and TCE-NAPL = 73.0^{o}C at 1 atm), which results in the formation of a vapor phase that is enriched in the volatile contaminant (Udell, 1997). The contaminant rich vapor phase will then condense at low temperature surfaces to form mobile banks of NAPL that must be captured for a steam drive to successfully recover the target contaminant. The generation of mobile NAPL banks is no longer encouraged due to the potential for uncontrolled migration (Kaslusky and Udell, 2002). The injection of air along with steam during the initial displacement stage is now promoted as a means to recover chlorinated solvents in the more easily controlled vapor phase. Thus NAPL contaminants present in the gas phase will be exposed to soil at elevated temperatures along with oxygen and steam as they migrate toward vacuum extraction wells.

Steam has been injected at pressures from as low as 3 psig at the A.G. Communications Systems Site located in Northlake, IL and up to 60 psig at the Savannah River Site 321-M Solvent Storage Tank Area located in Aiken, SC (U.S. EPA, 2004). Steam injection pressures are limited so that steam will not breakthrough to the ground surface. For example, the lower steam injection pressure at A.G. Communications was due to the shallow injection depth of 40 feet below ground surface (bgs) while higher steam injection pressures could be used at Savannah River where the injection depth was 143 feet bgs. Specifying the steam pressure also fixes the steam temperature where the injection pressure of 3 psig (17.7 psia) fixes the steam temperature at 105.3^{o}C and a steam pressure of 60 psig (74.7 psia) corresponds to a steam temperature of 153.0^{o}C according to saturated steam correlations (Harvey et al., 1996).

The subsurface at the Savannah River Site was heated to an average temperature of 87^{o}C for a period of 12 months while the temperatures ranged from 20 to 74^{o}C at the A.G. Communications Site over a period of 5 years (U.S. EPA, 2004). An average temperature of 60^{o}C with a maximum temperature of 140^{o}C was observed after 5 months of injecting steam into the subsurface at the Visalia Superfund Site located in Visalia, CA (U.S. DOE, 2000). Other steam drive demonstrations have resulted in maximum temperatures of 100^{o}C within the most permeable soil layers (Udell, 1997).

The residence time of gas-phase contaminants in the heated subsurface is difficult to anticipate since each steam flushing application is tailored to specific subsurface conditions. The residence time at the Visalia Superfund Site was determined by measuring the time to recover xenon and helium gas tracers. The initial displacement stage residence time was 10 hours between an injection and extraction well that were 24 meters apart based on the xenon tracer (Newmark et al., 1998). A vapor phase residence time of 10 hours was measured for the same wells after steam breakthrough had occurred using the helium tracer. In-situ thermal destruction of the resident contaminants was claimed to have occurred during both the initial and second tracer experiments.

In summary, the maximum anticipated subsurface temperatures during steam flushing ranges between 74 and 140^{o}C, with a residence time ranging from hours during the initial displacement stage, to days and months during the second long-term stage. For most steam flushing applications, the residence time of gas-phase contaminants flowing through heated soil during transport to vapor recovery wells is expected to be less than one day.

2.3.2 Electrical Resistive Heating

Passing electrical current through the subsurface results in the ohmic heating of electrically conductive soil layers (Carrigan and Nitao, 2000). The electrical current is delivered through steel rods (electrodes) installed into the contaminated soil and requires that water be injected into the annular space between the soil and electrodes during electrical resistive heating to prevent the soil adjacent to the electrodes from drying out. The temperature of the electrically conductive soil lenses can theoretically approach 200^{o}C (Carrigan and Nitao, 2000) with the goal of maintaining the overall subsurface temperature near the boiling point of the contaminant and water mixture (e.g., water and TCE-NAPL = 73.0^{o}C at 1 atm). Volatile organic compounds and water within the heated or electrically conductive soil lenses would be transferred into adjacent cooler soil lenses through electro-osmosis for recovery by vacuum extraction wells located in unsaturated soil overlying the heated region. For example, a TCE-contaminated aquifer was heated to a temperature of 73^{o}C for 3 months using electrical resistive heating (Beyke, 2002). Approximately 4,500 kg (3,000 L) of TCE was recovered through vapor extraction wells located above the heated aquifer formation. Heron et al. (1998b) demonstrated electrical resistive heating in a controlled laboratory-scale box filled with TCE-contaminated water. An average temperature of 90^{o}C was maintained within the box for a period of 25 days, and a single centrally-located extraction well was used to recover gas-phase TCE.

In summary, electrical resistive heating will result in the exposure of contaminants to temperatures ranging from 70 to 200^{o}C for a period of time greater than one day. The residence time of gas phase contaminants that pass through heated soil during transport to vapor recovery wells is expected to be less than one day.

2.3.3 Thermal Conductive Heating

Steel wells can be used to heat subsurface regions contaminated with chlorinated solvents via thermal conduction with recovery of the volatilized solvents accomplished by applying vacuum extraction through the heated steel well screens. Vinegar et al. (1999) reported using heater well temperatures between 745 and 900^{o}C to remediate a site located in Portland, IN that was contaminated with TCE and PCE. The heater wells were located every 7.5 feet resulting in one heater well every 50 square feet with the soil temperatures between heater wells ranging from 100 up to 250^{o}C after heating for 5 months.

In conductive heating remedial systems, gas from uncontaminated subsurface regions flows into the contaminated treatment zone that have been heated to temperatures between 100 to 250^{o}C, and becomes saturated with the volatile contaminants (e.g., TCE). The uncontaminated gas entering the heated treatment zone may be atmospheric air with 21% oxygen or may come from other subsurface regions and have low oxygen content due to microbiologic consumption. The contaminant-saturated gas then travels through a high temperature region located adjacent to each heater/vacuum extraction well. Baker and Kuhlman (2002) suggest that TCE degradation occurs as vapors migrate through the soil region adjacent to the heater/vacuum well, which may reach temperatures of 500 to 700^{o}C. This high temperature zone is claimed to function as a "packed-bed reactor that is hot enough to accomplish rapid decomposition by either pyrolysis, if oxygen is deficient, or by oxidation, if oxygen is available" (Baker and Kuhlman, 2002, p. 4).

Stegemeier and Vinegar (2001) speculate that the high temperature soil region (500 to 700^{o}C) extends approximately 1 foot radially from each heater well. The

residence time of TCE within this 1-foot region is controlled by the rate of gas extraction. A single 1,800 cfm blower was used to extract gas from 130 heater/vacuum wells at the Portland, IN site (Stegemeier and Vinegar, 2001). The treatment zone area was 7,500 square feet to a depth of 18 feet, which represents a treatment volume of approximately 40,500 cubic feet, assuming a gas filled porosity of 0.3. Using the reported blower capacity and the estimated treatment volume, yields an estimate for the overall gas residence time of 22.5 minutes (40,500 ft^3 ÷ 1,800 ft^3/min = 22.5 min). A first-cut estimate of the gas residence time within the 1-foot high-temperature zone that is adjacent to each heater well is 0.5 minutes according to:

$$\frac{\pi\ 1^2\ ft^2 \mid 18\ ft \mid 130\ wells \mid 0.3\ ft^3\ void \mid min}{\qquad\qquad\quad\ \ \mid\ \ \mid\ \ \mid\ ft^3\ soil \mid 4{,}669\ ft^3} = 0.5\ min \qquad (2.3)$$

which represents the circular area around the well, the length of well screen, the number of wells, and the porosity of soil divided by flow rate. Here, the gas flow rate was corrected to 500°C using the ideal gas law according to:

$$\frac{1{,}800\ ft^3}{min} \left| \frac{773\ K}{298\ K} \right. = 4{,}669\ ft^3/min\ at\ 500^oC \qquad (2.4)$$

A second application of thermal conductive heating used a 3,000 cfm blower to extract gas from 761 heater/vacuum wells at a TCE-contaminated site in Eugene, OR (Stegemeier and Vinegar, 2001). The estimated residence time in the 1-foot high temperature zone for this case was 1.1 minutes, calculated following the approach described above. These residence time estimates assume that gas is uniformly removed from each well and that no preferential flow channels exist. In reality, the gas flow through each 1-foot high temperature zone could range from seconds to days depending on the soil gas permeability and pressure distribution within the vacuum manifold

system. According to data presented by Baker and Kuhlman (2002), the destruction of 99% of the TCE entering the 500 to 700°C region would require a residence time of approximately 7 days at 500°C and 7 seconds at 700°C. The thought is that TCE enters into the high temperature zone at 500°C and is transformed into intermediate products. The intermediate products formed from TCE degradation at 500°C then undergo further transformations as they encounter temperatures near 700°C closer to the heater/vacuum wells.

Based on the examples discussed above, thermal conductive heating may result in gas phase TCE being exposed to temperatures ranging from 100 to 250°C for a period of time greater than a month, and to temperatures ranging from 500 to 700°C for a period from days to seconds.

2.3.4 Hybrid Thermal Technologies

The three technologies discussed above, steam flushing, electrical resistive heating, and thermal conductive heating, may be implemented simultaneously. For example, the thermal treatment design for the Young-Rainey Science, Technology, and Research (STAR) Center located in Largo, FL involved a combination of electrical resistance to initially heat surrounding and underlying soils, followed by steam drive to flush contaminants from soils within the preheated region to extraction wells (U.S. DOE, 2003). The overall site temperatures were at or greater than 100°C for a period of 70 days with maximum temperatures of 120°C. In practice, this would mean potentially exposing chlorinated solvents to temperatures approaching 200°C before driving them toward high permeability soils where they could be recovered via steam flushing at temperatures less than 120°C.

2.4 Selected Experiments on the Stability of TCE and PCE

The following sections provide information on the methods and results of past laboratory experiments performed to investigate the thermal stability of TCE. The first four sections (2.4.1 through 2.4.4) focus on the stability of TCE-NAPL and the products formed after exposing TCE to oxygen and water. The subsequent two sections (2.4.5 and 2.4.6) address the stability of gas-phase TCE and the products formed after introducing TCE into heated quartz tubes along with the importance of the chlorine to hydrogen ratio on the distribution of degradation products.

2.4.1 TCE- and PCE-NAPL Degradation by Oxygen

The stability of TCE-NAPL in industrial process equipment has been a research topic since at least 1932. Experiments were initially performed to determine the conditions that caused the degradation of TCE and the formation of corrosive degradation products, which could damage industrial equipment. Carlisle and Levine (1932) studied TCE degradation by placing TCE-NAPL and pure oxygen, or air, into 85 mL glass vials and heating the sealed vials to a temperature between 24 and 130^{o}C. The vials were opened after 24 hours and 25 mL of the NAPL contents were equilibrated with 25 mL of water to determine the amount of chloride that had formed along with the amount of free acid formed. No analysis of gas-phase constituents present in the head space of glass vials was performed. In the presence of pure oxygen, the amount of TCE degraded increased with increasing temperature as indicated by the increase free acid. The minimum amount of TCE degraded in 24 hours was 0.001% (mole basis) at 24^{o}C, while the maximum of 2.52% (mole basis) occurred at a temperature of 130^{o}C. The maximum first-order half-life for the disappearance of TCE with pure oxygen present was 475 years

at 24°C, and 99 days at 130°C based on the %TCE degraded in 24 hours. A lower TCE degradation rate was observed with air present, presumably due to the decrease in oxygen content.

Mugdan and Wimmer (1934) quantified the degradation products in the gas phase and NAPL after passing oxygen gas through TCE-NAPL that was heated to temperatures between 50 and 70°C. The gas-phase products included hydrochloric acid (HCl), carbon monoxide (CO), and phosgene ($COCl_2$), while the only product found in the NAPL was dichloroacetyl chloride (Cl_2HC_2OCl). After passing oxygen gas through TCE-NAPL heated to 60°C, Kirkbride (1942) observed the formation of additional products in the NAPL, including TCE epoxide ($Cl_2COCHCl$) and hexachlorobutene ($C_4H_2Cl_6$).

McKinney et al. (1955) found that TCE-NAPL was completely degraded to 15% gas-phase products and 85% NAPL products, on a molar basis, after passing oxygen through TCE-NAPL at 70°C. The gas-phase products included HCl, CO, and phosgene ($COCl_2$), while the NAPL reaction product was water-soluble, had a density of 1.545 g/mL at 20°C, and was found to be a nearly equal mixture of dichloroacetyl chloride (Cl_2HC_2OCl) and TCE epoxide ($Cl_2COCHCl$) (Table 2.3). McKinney et al. (1955) completed experiments using 1) TCE stabilized with triethylamine, 2) unstabilized TCE, and 3) TCE that had been used for extracting oil from soybeans. The triethylamine stabilizer was removed from TCE-NAPL by the soybean oil extraction process meaning that this used, or waste TCE, which was historically released into the environment, was no longer stabilized against reacting with oxygen. The complete degradation of TCE-NAPL was reported after 193 hours of bubbling oxygen through TCE-NAPL at 70°C. However, the reaction rate was determined after addition of benzoyl peroxide to TCE,

where benzoyl peroxide is known to generate peroxyl radical initiator compounds above 70^{o}C (Fossey et al., 1995). McKinney et al. (1955) also found that partially-oxidized TCE influenced the rate of TCE degradation.

Table 2.3: Gas- and Liquid-Phase TCE-NAPL Oxidation Products (McKinney et al., 1955)

Reaction Product	Phase	Approximate Amount (% mole basis)
hydrochloric acid (HCl)	gas	5
carbon monoxide (CO)	gas	5
phosgene ($COCl_2$)	gas	5
dichloroacetyl chloride (Cl_2HC_2OCl)	NAPL	47
TCE epoxide ($Cl_2COCHCl$)	NAPL	38

The reaction between oxygen and TCE-NAPL is thought to involve a radical chain reaction mechanism (Kaberdin and Potkin, 1994). Kucher et al. (1990) used azo-bis-isobutyronitrile, a known temperature induced radical chain initiator, to study the oxidation of TCE in acetonitrile at 75^{o}C. The reaction products included TCE epoxide ($Cl_2COCHCl$) and dichloroacetyl chloride (Cl_2HC_2OCl) in a ratio of 3:1 after 1 hour of reaction time.

PCE-NAPL is also thought to react with oxygen via a radical chain mechanism (Kucher et al., 1987) to yield products similar to that of TCE, with trichloroacetyl chloride and PCE epoxide as the main reaction intermediates (Keil, 1978)

In summary, exposing TCE- and PCE-NAPL to oxygen in the temperature range from 50 to 75^{o}C, in the absence of water, resulted in the formation of gas-phase and NAPL reaction products that were thought to result from a radical chain reaction mechanism. The next section covers past experiments performed to examine the

compounds formed after exposing the TCE- and PCE-NAPL and oxygen degradation products to water.

2.4.2 Hydrolysis of TCE- and PCE-NAPL Degradation Products

Placing the TCE-NAPL degradation products dichloroacetyl chloride and TCE epoxide in water at 27 and 75°C resulted in the formation of gas- and aqueous-phase products (Table 2.4). The gas-phase products included CO and CO_2, and the aqueous-

Table 2.4: Hydrolysis of TCE-NAPL Degradation Products
(McKinney et al., 1955)

Reactor Temperature (°C)		27	75
Reaction Product	Phase	moles formed per 147.4 g of liquid reaction products	
carbon monoxide (CO)	gas	0.087	0.100
carbon dioxide (CO_2)	gas	0.005	na
chloride ion (Cl^-)	aqueous	1.410	1.200
dichloroacetic acid (HCl_2C_2OOH)	aqueous	0.740	0.850
oxoacetic acid (HOC_2OOH)	aqueous	0.180	0.057
formic acid (HCOOH)	aqueous	0.033	0.060

na – not analyzed.

phase products included chloride ions, dicholoroacetic acid (HCl_2C_2OOH) along with oxoacetic (HOC_2OOH) and formic acid (HCOOH). The temperature of the reaction (27 or 75°C) appeared to have little effect on the distribution of hydrolysis products. Similar reaction product distributions were also noted in water that contained NaOH at 10 and 30°C. McKinney et al. (1955) speculated that dichloroacetic acid (DCAA) was the hydrolysis product of dichloroacetyl chloride, while the non-chlorinate organic acids were formed from the hydrolysis of TCE epoxide. The degradation of TCE epoxide was

determined in a separate experiment by Kline et al. (1978) that involved injecting TCE epoxide into a solution of acetone (0.2 mL) which contained 1.5 mL of 0.5 M sodium phosphate buffer. Dichloroacetic acid (DCAA) was the only reported degradation product after 4 minutes at 37^{o}C. Cai and Guengerich (1999) prepared TCE epoxide from TCE using m-chloroperbenzoic acid, a known radical initiator compound, and then placed TCE epoxide in water at 0^{o}C, and the degradation products were measured as a function of pH. The products formed included CO in the gas phase, formic acid, oxoacetic acid, and DCAA in the aqueous phase over a pH range from 0 to 14. The amount of CO and formic acid formed increased with pH, the amount of oxoacetic acid decreased with pH, and the amount of DCAA formed was independent of pH. In a similar experiment, Yoshioka et al. (2002) prepared PCE epoxide by exposing PCE-NAPL to a mercury arc lamp while bubbling oxygen through the reactor. They mixed PCE epoxide with an aqueous solution at 0^{o}C and found that PCE epoxide formed CO and CO_2 in the gas phase and oxalic acid ($HOOC_2OOH$) in the aqueous phase along with approximately 1.2 mole% of trichloroacetic acid (Cl_3C_2OOH).

Based on the work described above, TCE can be transformed into dichloroacetyl chloride and TCE epoxide after exposure to oxygen with TCE epoxide, and potentially dichloroacetyl chloride, being transformed into DCAA upon exposure to water where trichloroacetic acid (TCAA) was found as one of the aqueous-phase PCE degradation product. Thus DCAA and TCAA are two of the degradation products anticipated to form during the thermal treatment of TCE or PCE contaminated subsurface environments. DCAA is a colorless liquid at room temperature (25^{o}C) with a density of 1.57 g/mL, a melting point of between 9 and 11^{o}C, and a boiling point of 197^{o}C (Mallinckrodt and

Baker, 2003b). TCAA, in pure form at 25°C, appears as white, hydroscopic crystals with a melting point of 58°C (Mallinckrodt and Baker, 2004). DCAA and TCAA have been classified as probable human carcinogens with the maximum contaminant level goal of zero mg/L for DCAA and 0.3 mg/L for TCAA (U.S. EPA, 1998). DCAA and TCAA are soluble in water with a practical drinking water treatment level of 0.06 mg/L.

Haag et al. (1996) measured the rate of DCAA disappearance from water heated to between 88 and 180°C as a function of NaOH concentration. The authors obtained a half-life of 1.71 days for the hydrolysis of DCAA at 103°C and pH 7, and a half-life of 1.27 hours with 0.96 M of NaOH present. Prager et al. (2001) showed that DCAA was hydrolyzed to chloride and oxoacetic acid in heated water and that a temperature of 180°C was required to achieve complete degradation of DCAA in 8 minutes.

Table 2.5: Rate of Dichloroacetic Acid (DCAA) Disappearance from Heated Water (Prager et al., 2001)

Temperature (°C)	First Order Disappearance Rate (1/day)	Half-Life (day)
60	9.3×10^{-4}	742
70	4.8×10^{-3}	143
80	2.3×10^{-2}	30.5
90	9.8×10^{-2}	7.0
100	39.3×10^{-2}	1.8
120	5.1	0.14

The expected half-life for DCAA in water at pH 7 calculated from the Arrhenius parameters determined by Prager et al. (2001) are given in Table 2.5. TCAA degrades more rapidly than DCAA to form CO_2 and chloroform ($HCCl_3$) in heated water (Prager et al., 2001). Thus DCAA is expected to accumulate in water during the degradation of TCE

at temperatures less that 70°C while DCAA is expected to be degraded into oxoacetic acid within a few days at temperatures greater than 90°C based on the half-lives given in Table 2.5. TCAA is expected to degrade into CO_2 and chloroform during thermal treatment.

2.4.3 Degradation of TCE and PCE Dissolved in Water at Elevated Temperatures

Carlisle and Levine (1932) placed approximately 25 mL of TCE-NAPL and 25 mL of water into 80 mL glass vials with nitrogen in the gas headspace to determine if TCE was degraded by water at elevated temperatures. The vials were sealed and heated to fixed temperatures between 50 and 150°C for 24 hours. After cooling the vials to room temperature, the acid content of the water, an indicator of TCE degradation via the formation of acidic compounds, was determined. Less than 0.35% by weight of the TCE-NAPL was lost based on the amount of acid formed, which led Carlisle and Levine (1932) to conclude that TCE does not readily hydrolyze in water up to a temperature of 150°C.

Dilling et al. (1975) completed a year-long experiment at ambient conditions to measure the persistence of TCE and PCE dissolved in water. Oxygen-saturated water (8 mg/L O_2) containing 1.0 mg/L each of TCE, PCE, and chloroform was loaded into three ice-cooled Pyrex tubes so that approximately one-half of the tube volume was filled with solution (i.e., gas phase was present) and then the tubes were flame sealed. The sealed tubes were placed in a dark container and stored at approximately 25°C. One tube was destructively sampled after 6 months (182 days), and the remaining two tubes were destructively sampled after one year (365 days). Only aqueous samples were collected and they were only analyzed for TCE, PCE, and chloroform content.

Table 2.6: Rate of Dissolved Phase TCE, PCE, and Chloroform Disappearance at 25°C from Sealed Ampules (Dilling et al., 1975)			
Kinetic Parameters	TCE	PCE	Chloroform
First-order disappearance rate (1/day)×1000	2.1	2.6	1.5
Half-life (days)	320	263	462

The reported first-order disappearance rate for dissolved phase TCE was 2.1×10^{-3} day^{-1}, corresponding to a first-order half-life of 326 days at 25°C (Table 2.6). PCE disappeared at a slightly faster rate with a half-life of 263 days while chloroform was more recalcitrant with a half-life of 462 days. In a separate experiment, Pearson and McConnell (1975) measured the persistence of TCE and PCE in water using sealed glass bottles and reported a half-life of 2.5 years (912 days) for the disappearance of TCE from water at 25°C and 6 year half-life for PCE.

Jeffers and Wolfe (1996) studied the disappearance of chlorinated solvents dissolved in water by placing approximately 0.3 mL of contaminated water in glass tubes and flame sealing both ends to create a sealed bulb with approximately 0.02 mL of gas-phase headspace. The contaminated water was prepared by mixing water with NAPL for 2 minutes at room temperature to yield an initial concentration estimated to be 10% of the solubility limit for each solvent (i.e., 110 mg/L for TCE, 15 mg/L for PCE) (Jeffers et al., 1989). Experiments were completed in water with 0.01 M of HCl at pH 7 (Jeffers and Wolfe, 1996) and in alkaline water containing from 0.1 to 0.001 M of NaOH (Jeffers, et al., 1989; Jeffers and Wolfe, 1996). The water used was deionized, distilled, and boiled prior to use, which probably resulted in low dissolved oxygen content, however, no dissolved oxygen measurements were reported. The bulbs were heated to temperatures between 60 and 190°C for an unspecified period of time. The bulbs were then cooled to

room temperature and the liquid content was analyzed by gas chromatography for parent compound content only. The only data reported were the activation energy and pre-exponential factor for the Arrhenius equation [$k = A \times \exp(-E_a/RT)$] which was used to estimate a first-order rate constant at 25°C for each compound. The estimated half-life for the disappearance of TCE and PCE from water at 25°C was greater than 100,000 years, which was significantly greater than estimated by Dilling et al. (1975) or Pearson and McConnell (1975). The calculated first-order rate constant at 90°C for TCE was 3.9×10^{-5} (1/day) with a half-life of approximately 49 years based on the Arrhenius parameters reported by Jeffers and Wolfe (1996). The calculated first-order rate constant at 90°C for PCE was 1.4×10^{-8} (1/day) with a half-life of approximately 131,000 years based on the Arrhenius parameters reported by Jeffers et al. (1989).

Gu and Siegrist (1997) increased the rate of TCE disappearance from water by adding sodium hydroxide (NaOH). They reported the complete disappearance of TCE after 300 minutes from an aqueous solution that had an initial TCE concentration of 630 mg/L after amending with 2 M of NaOH and heating to greater than 60°C. The primary reaction products included chloride and glycolic acid ($HOCH_2COOH$), with intermediate products including DCAA and monochloroacetic acid (H_2ClC_2OOH). Nearly all the chlorine atoms originally present as TCE were recovered as chloride in the reactor effluent at 80°C, however, only 60% of the carbon atoms introduced were recovered as organic acids. Gu and Siegrist (1997) suggested that the unaccounted for carbon may have been lost to gas phase degradation products (i.e., CO_2) that were not captured for analysis.

Atwater et al. (1996) demonstrated the removal of TCE from water using a flow-through reactor that contained ruthenium and platinum on activated carbon granular solids heated to between 90 and 120^{o}C. The water contained TCE at 15 mg/L and dissolved oxygen in stoichiometric excess. When operated at 120^{o}C, the reactor was capable of removing 91% of the influent TCE with a residence time of 12 seconds. However, the appearance of chloroform ($HCCl_3$) in the reactor effluent led Atwater et al. (1996) to increase the residence time to 5 minutes in order to achieve the complete degradation of TCE without forming the unwanted chloroform degradation product.

In summary, TCE and PCE dissolved in water are degraded with half-lives ranging from approximately 1 year (Dilling et al., 1975) to greater than 100,000 years (Jeffers et al., 1989) at room temperature (25^{o}C). The rate of TCE and PCE degradation can be increased by heating with the half-lives reduced to 49 and 131,000 years, respectively at 90^{o}C based on results by Jeffers et al. (1989). The rate of TCE degradation can be further increased by adding sodium hydroxide or solid catalysts with the completed degradation of TCE after 300 minutes at 60^{o}C when amended with 2 M NaOH and after 5 minutes at 120^{o}C with the ruthenium catalyst.

2.4.4 In-Situ Thermal TCE Degradation Experiment

Knauss et al. (1999) measured the disappearance of TCE from a water-filled reactor in an effort to demonstrate that dissolved-phase TCE could be degraded in-situ during thermal treatment of TCE contaminated aquifers. The reactor consisted of a gold-walled cylinder with a wall thickness of 0.01 inch and an outside diameter of 1.75 inches by 7 inches long for a total volume of approximately 250 mL (Seyfried et al., 1979). The gold cylinder was sealed with a titanium head piece that contained a single gold capillary

tube for sample collection. The gold cylinder and titanium seal were held within a steel housing that was pressurized so that all reactants and products remained dissolved in water.

Table 2.7: Summary of Knauss et al. (1999) Experimental Results

Experiment	duration (days)	Temperature (^{o}C)	Initial TCE (mg/L)	Final Cl^- (mM)	Cl found/ Cl feed (%)	Final CO_2 (mM)	CO_2 found/ CO_2 feed (%)
TCE-35	6.11	100	5.96	0.151	111	0.157	173
TCE-37	19.2	81	5.87	0.114	100	0.116	152
TCE-39	11.1	90	21.30	0.400	92	0.310	107
TCE-40	43.3	70	5.50	0.145	118	0.182	224
TCE-41	4.24	90	1.45	0.035	105	0.070	315
TCE-42	7.28	90	2.87	0.016	244	N/A	N/A
TCE-43	2.23	90	1.62	0.049	143	0.056	246
TCE-51	7.2	90	6.09	5.563*	4012	0.120	130
TCE-53	3.31	90	5.15	3.809*	3517	0.104	144

*Data presented by Knauss et al. (1999) Table 1, but appears to be incorrectly reported.
Reported analytical detection limits: TCE = 0.0002 mM, Cl^- = 0.003 mM, CO_2 = 0.068 mM.

Knauss et al. (1999) reported results obtained for nine separate experimental runs (Table 2.7). Each experiment was completed with air-saturated water (8 mg/L O_2) that contained 150 mg/L of phosphate buffer (pH 7.2). Water solutions with initial TCE concentrations between 0.3 and 21 mg/L were placed into the gold-walled reactor with no headspace and heated to a fixed temperature between 70 and 100^{o}C at a constant pressure of 1 MPa (10 bar) for an extended time period. Aqueous samples were collected from the reactor periodically through the gold capillary tube into 1 mL gas tight syringes. Analysis for inorganic ions, including chloride, was completed using a HPLC (HP 1090) connected to a conductivity detector. The aqueous phase TCE content was determined

using purge and trap separation with analysis by a gas chromatograph connected to a flame ionization detector.

Knauss et al. (1999) reported that chloride, hydronium ions (H^+), and dissolved CO_2 were the only degradation products detected during preliminary experiments designed to look for intermediates. However, no analysis of the experimental results was provided to demonstrate that the initial amount of TCE in the reactor was accounted for by the degradation products detected at the end of the experiment (i.e., mass balance). Based on the data presented by Knauss et al. (1999) for the amount of chloride and CO_2 detected, the carbon and chloride mass balances were calculated and are provided in Table 2.7. The final amount of chloride was within 11% of the initial amount introduced as TCE (moles Cl^- = 3 × moles TCE) for experiments TCE-35 through -41 but was greater than the initial amount for experiments TCE-42 through -53. For example, the amount of chloride reported in experiment TCE-42 was 244% of the initial amount of TCE present in the reactor. The amount of chlorine formed during experiments TCE-51 and -53 may have been reported incorrectly since these values are orders-of-magnitude in excess of the amount of chlorine initially present in the reactor as TCE or may indicate that the reactor was not adequately cleaned between runs.

There was greater variability in the carbon mass balance shown in Table 2.7 as compared to the chloride balance, which may have been due to the difficulty in measuring dissolved phase CO_2 at these low concentrations. Knauss et al. (1999) determined the amount of dissolved total CO_2 formed, stated as the sum of carbonic acid (H_2CO_3), carbonate (HCO_3^-), and bicarbonate (CO_3^{-2}), using direct infrared (IR) spectroscopy. No description of the IR analysis method (e.g., sorption bands used or scan

time) was provided, although the reported detection limit was 0.068 mM. Falk and Miller (1992) studied fourier-transform infrared (FTIR) spectroscopy as an analytical method for determining the aqueous phase concentration of total CO_2 using the co-added signals from 400 interferograms (5-minute scan time) with 4 cm^{-1} band resolution. Falk and Miller (1992) concluded that this was not a feasible analysis technique for HCO_3^- or CO_3^{-2} because the adsorption bands (1385 and 1360 cm^{-1}, respectively) overlapped and were within the water vapor region. Analysis of dissolved CO_2 was found to be feasible at the 2342.9 cm^{-1} adsorption band, with an estimated detection limit of 0.4 mM. Falk and Miller (1992) stated that increasing the scan time could have decreased the detection limit. Burt and Rau (1994) reported a dissolved CO_2 detection limit of 0.24 mM. Hence, the detection limit reported by Knauss et al. (1999) is 3.5 to 6 times lower than those reported by Burt and Rau (1994) and Falk and Miller (1992). The ratio of the CO_2 found to CO_2 (as TCE) in the feed, as reported in Table 2.7, was consistently greater than 100% which may indicate that the IR analysis method employed by Knauss et al. (1999) was not sensitive to the low CO_2 concentrations because the signal to noise ratio was too small to accurately resolve the 2342.9 cm^{-1} adsorption band.

Knauss et al. (1999) provided the following expression for the rate of TCE disappearance based on the experiments completed at 90°C when dissolved oxygen was in excess:

$$\frac{dC_{TCE}}{dt} = -5.77 \pm 1.06x10^{-7}\, s^{-1} C_o^{0.85\pm0.03} \tag{2.5}$$

where C_o is the initial TCE concentration (mol/kg ~ molality). Although Equation 2.5 fit the experimental data, analyzing the data reported by Knauss et al. (1999) using traditional kinetic reaction modeling techniques provides additional detail regarding the

mechanism of TCE disappearance. Figure 2.7 contains the concentration of TCE with time, as measured by Knauss et al. (1999), for four of the experiments completed at 90°C. Also shown in Figure 2.7 is the predicted TCE concentration with time assuming a zero-order reaction model described by:

$$\frac{dC_{TCE}}{dt} = -k_0 \quad \text{or} \quad C_{TCE} = C_{TCE}^{initial} - k_0 t \tag{2.6}$$

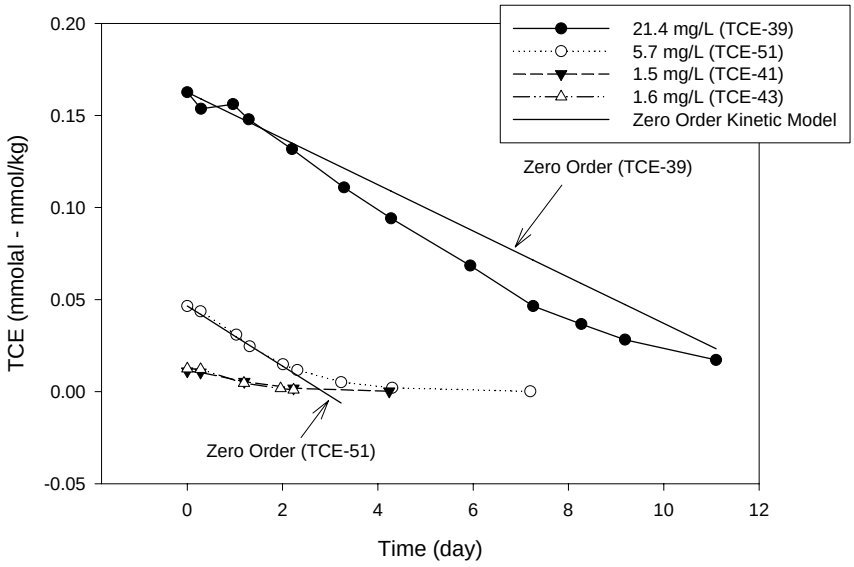

Figure 2.7: Measured concentration of TCE vs. incubation time along with a zero-order reaction model fit.

The disappearance of TCE appears to follow the zero-order reaction model over the initial two days, however, the rate of TCE disappearance increased relative to the zero-order rate after two days for Experiment TCE-39 and decreased relative to the zero-order rate for Experiments TCE-51, -41, and -43.

Figure 2.8 contains the same data shown in Figure 2.7 plotted as the natural log of the TCE concentration normalized by the initial TCE concentration. Also shown in Figure 2.8, is the change in normalized TCE concentration as predicted according to a first-order reaction model described by:

$$\frac{dC_{TCE}}{dt} = -k_1 C_{TCE} \quad \text{or} \quad \ln\left(\frac{C_{TCE}}{C_{TCE}^{initial}}\right) = -k_1 t \tag{2.7}$$

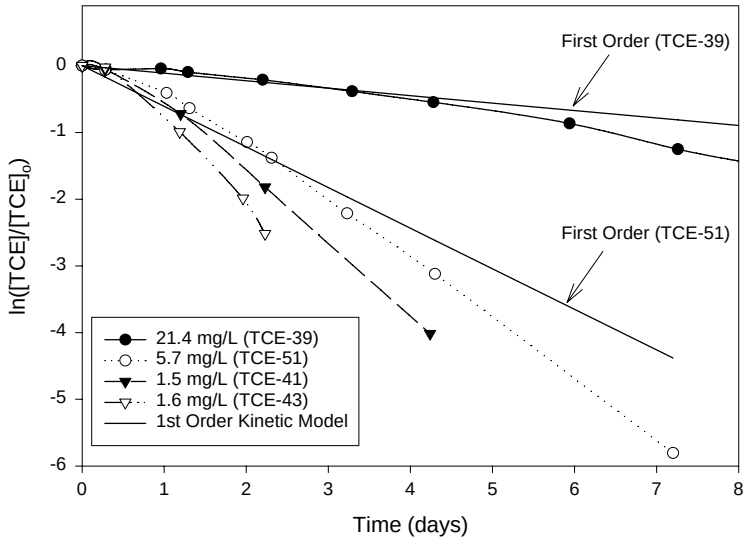

Figure 2.8: Natural log of the measured TCE concentration normalized by the initial TCE concentration vs. incubation time along with the first-order reaction model fit.

The disappearance of TCE from the gold-walled reactor did not follow the first-order reaction model in that the rate of TCE disappearance was less than predicted by the first-order model during the initial two days of each experiment followed by an increase in the rate of TCE disappearance relative to that predicted by the first-order model. The rate of TCE disappearance also appears to depend on the initial concentration of TCE with a

decrease in the rate of TCE disappearance corresponding to an increase in the initial TCE concentration (Figure 2.8).

Figure 2.9 contains the same data shown in Figures 2.7 and 2.8 but plotted as the reciprocal of the TCE concentration vs. time, consistent with a second-order reaction model describe by:

$$\frac{dC_{TCE}}{dt} = -k_2 C_{TCE}^2 \quad \text{or} \quad \frac{1}{C_{TCE}} = \frac{1}{C_{TCE}^{initial}} + k_2 t \tag{2.8}$$

The disappearance of TCE during Experiment TCE-39 appears to follow the second-order reaction model (Equation 2.8) over a period of four days but then the rate of TCE disappearance deviates from that predicted by the second-order model.

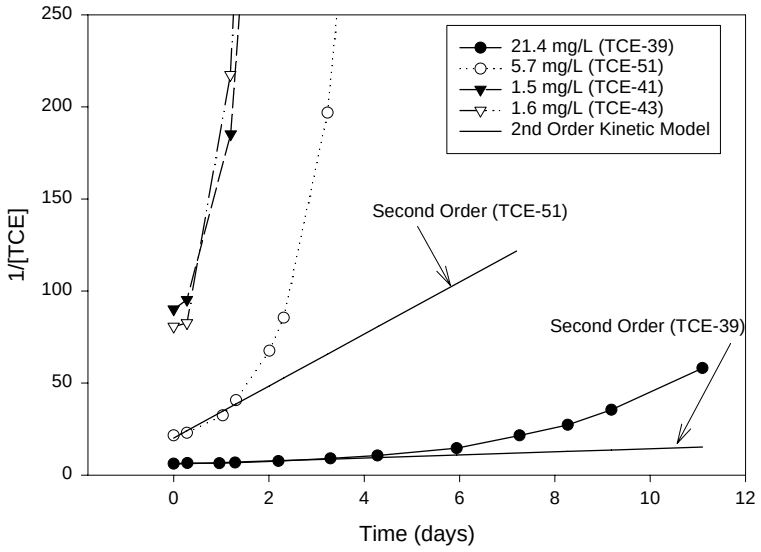

Figure 2.9: Reciprocal of the measured concentration of TCE vs. incubation time along with the second-order reaction model fit.

While the disappearance of TCE from the gold-walled reactor operated at 90°C followed the zero-order reaction model over the initial two days of each experiment (Figure 2.7), the disappearance of TCE was not described by the zero-, first-, or second-order reaction models over the entire experimental period. An alternative reaction model involves a radical chain reaction mechanism which incorporates the following reaction steps:

Initiation: $TCE + M \xrightarrow{k_1^*} TCE^*$ (2.9)

Peroxyl Radical: $TCE^* + O_2 \xrightarrow{k_2^*} TCE\text{-}O_2^*$ (2.10)

Propagation: $TCE + TCE\text{-}O_2^* \xrightarrow{k_3^*}$ TCE epoxide + dichloroacetyl chloride (2.11)

The symbol M represents some radical initiator such as the gold or titanium surface within the reactor or chlorine radicals which transfer a single electron to TCE and results in the formation of the TCE radical species (TCE*). This three step TCE disappearance mechanism was based on work by Kucher et al. (1990) and was used to fit the results for the Knauss et al. (1999) experiment completed at 70°C (TCE-40). The 70°C experiment was chosen because the rate of TCE disappearance was slower as compared to the 90°C experiments and thus the features that indicate a radical chain mechanism, including a delayed reaction rate during the initial three days (reactor heat-up was less than one day) as the concentration of the peroxyl radicals increased followed by an increase in the TCE disappearance rate between day 10 and 40 (Figure 2.10), were more pronounced.

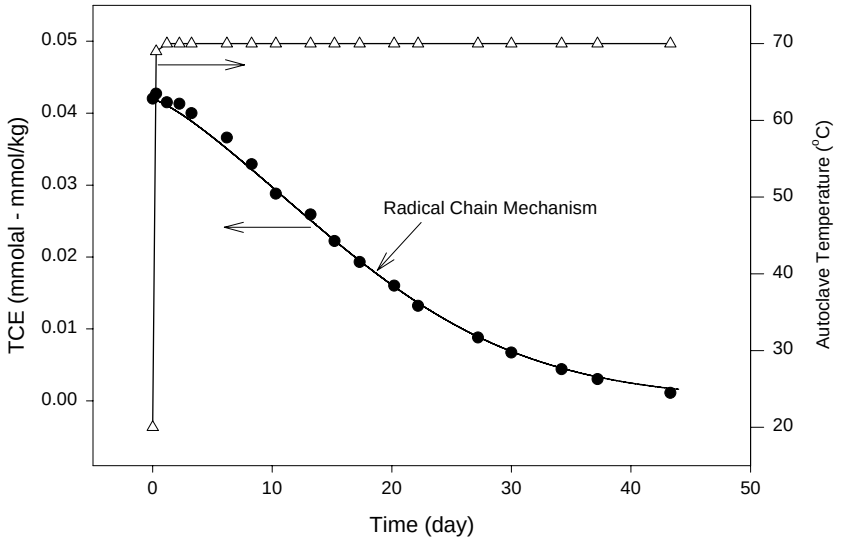

Figure 2.10: Measured concentration of TCE vs. incubation time for Experiment TCE-40 along with a radical chain reaction model fit.

Figure 2.10 shows the concentration of TCE vs. time data as reported by Knauss et al. (1999) along with the best fit using the reaction model described by Equations 2.9 through 2.11 determined using finite difference analysis with time steps of 0.1 days. The disappearance of TCE followed the radical chain model over the 43 day experimental period with the reaction rate coefficients for the initiation and peroxyl radical formation (k_1* and k_2*) equal to 1.62 and 1.80 mmolal^{-1} day^{-1} respectively, while the rate coefficient for the peroxyl radical attack on TCE (k_3*) was equal to 132.6 mmolal^{-1} day^{-1}.

The good agreement between the radical chain model and the measured TCE disappearance for Experiment TCE-40 does not necessarily validate this model. However, the radical chain model is consistent with two of the key observations made by Knauss et al. (1999), namely that the rate of TCE disappearance was dependent on the

initial TCE concentration and that the rate of TCE disappearance was independent of the dissolved oxygen concentration as long as it was in excess of the initial amount of TCE present. The dependence on the initial TCE concentration is due to the slow rate of radical initiation (k_1* and k_2*) compared to the fast rate of the peroxyl-radical TCE reaction (k_3*). That is, the formation of peroxyl radicals is the rate limiting step (k_2*/k_3* = 0.01).

Knauss et al. (1999) found that dissolved-phase TCE could be degraded in a heated reactor with CO_2 and chloride as the only detected degradation products. The time for one-half of the initial amount of TCE to be degraded at 90^{o}C ranged from approximately 1 to 5 days depending on the initial TCE concentration (Figure 2.7). Knauss et al. (1999) reported that the rate of TCE disappearance from the heated reactor was best described using a pseudo first-order reaction model (Equation 2.5). Analysis of the Knauss et al. (1999) data provided herein suggests that a radical chain reaction mechanism provided the best fit for the disappearance of TCE over the entire experimental period.

The radical initiated reaction of TCE may have been due to a lack of reactor conditioning prior to each experiment. Seyfried et al. (1987), who developed the gold-walled reactor system, recommended rinsing the titanium head with dilute HCl solution followed by concentrated HNO_3 solution to remove any potential sources of contamination. They also recommended heat treating the titanium head at 300^{o}C in air to develop an inert surface oxide layer. For example, McCollom and Seewald (2003) reported heating their titanium fittings in air for 24 hours at 400^{o}C prior to use in

experiments on the hydrothermal stability of formic acid. Knauss et al. (1999) did not discuss procedures used to prepare their reactor.

2.4.5 Degradation of Gas-Phase TCE and PCE within Heated Quartz Tubes with Oxygen Present (Oxic)

One method of treating unwanted chlorinated solvents is by feeding the waste into incinerators operated at temperatures greater than 1,000^{o}C. The degradation of chlorinated solvents and the products formed during the incineration process have been studied by passing gas-phase solvents through heated quartz tubes, trapping the effluent leaving the quartz tubes, and analyzing the traps to determine the degradation products formed. The following section provides details of past quartz tube experimental results with the goal of anticipating the degradation products that might form during the high-temperature treatment of subsurface environments contaminated with TCE and PCE.

Graham et al. (1986) measured the amount of TCE degraded after injecting TCE-NAPL into a heated quartz tube (2 second residence time) as a function of quartz tube temperature and oxygen concentration (Table 2.8). The amount of TCE degraded increased with quartz tube temperature and oxygen content. TCE degradation was initiated at 600^{o}C when the amount of oxygen present was equal to the stoichiometric amount required for the complete combustion of TCE (2.5 moles of O_2 per mole TCE) and decreased to 500^{o}C when the amount of oxygen present was in excess to the stoichiometric amount. Temperatures greater than 800^{o}C were required to degrade 99% of the TCE introduced into the quartz tube, independent of oxygen content. Similar results were reported for PCE with the temperatures in excess of 800^{o}C required to degrade 99% of PCE introduced into a quartz tube with air as the carrier gas (Dellinger et

al., 1984). Graham et al. (1986) detected the greatest number of TCE degradation products at 750°C with some products detected at 1000°C after 99.9% of the parent TCE had been degraded, however, the exact identity and distribution of products was not reported.

Table 2.8: Amount of TCE Degraded after Passing Through a Heated Quartz Tube
Residence Time of 2 Seconds
(Graham et al., 1986)

Quartz Tube Temperature (°C)	500	600	650	700	800
Oxygen Content	Amount TCE degraded (Wt%)				
Stoichiometric	nm	0	nm	85	98.5
Excess	0	20	70	90	98.5

nm – not measured.

Increasing the residence time within a quartz tube has been shown to decrease the temperature at which TCE degradation is initiated. Yasuhara and Morita (1990) passed air (80% N_2 and 20% O_2) at 50 mL/min through chilled TCE and into a quartz tube that was maintained at a temperature between 300 and 800°C. The amount of oxygen present, approximately 1.6 moles O_2 per mole TCE, was less than the stoichiometric amount required for complete combustion. The residence time within the quartz tube ranged from 23 to 43 seconds (Table 2.9), and the degradation of TCE was initiated at a temperature of less than 300°C with approximately 99% of the TCE degraded at 500°C. Therefore, an increase in the quartz tube residence time to greater than 20 seconds resulted in 200 and 300°C reduction in the temperature required for the initiation of TCE degradation and for 99% destruction of TCE, respectively. Zhang and Kennedy (2002) found that TCE degradation within a surface boundary layer with residence time of approximately 0.04 seconds did not occur until the temperature reached 1000°C.

Table 2.9: Selected Degradation Products after Passing TCE through a Quartz Tube (Yasuhara and Morita, 1990)						
Quartz Tube Temperature (^oC)	300	400	500	600	700	800
Residence Time (seconds)	43	36	32	28	25	23
Selected Reaction Products	Amount present in liquid trap after 1 hour (% of Carbon in Feed)					
trichloroethylene (C_2HCl_3)	65.51	31.02	0.17	0.00	0.00	0.00
tetrachloroethylene (C_2Cl_4)	0.30	6.95	11.78	13.92	4.68	0.03
carbon tetrachloride (CCl_4)	0.02	0.76	3.58	6.81	4.48	2.87
hexachloroethane (C_2Cl_6)	0.18	1.94	0.27	0.06	0.04	0.00
hexachlorobutadiene (C_4Cl_6)	0.21	0.94	0.91	0.18	0.00	0.00
hexachlorobenzene (C_6Cl_6)	0.00	0.24	0.43	0.09	0.01	0.00
Total	66.21	41.84	17.13	21.06	9.21	2.90

Yasuhara and Morita (1990) also quantified condensable TCE degradation products by passing the effluent gas stream leaving the quartz tube through a dichloromethane (CH_2Cl_2) filled trap. The greatest number of reaction products (23 compounds) was identified in the dichloromethane trap fluid after 1 hour of feeding TCE into a quartz tube maintained at 400^{o}C. The most prevalent compounds found at 400^{o}C included TCE, tetrachloroethylene (C_2Cl_4), carbon tetrachloride (CCl_4), hexachloroethane (C_2Cl_6), hexachlorobutadiene (C_4Cl_6), and hexachlorobenzene (C_6Cl_6). TCE was not present (i.e., > 99% destruction) in the dichloromethane trap fluid when the quartz tube was maintained at temperatures greater than 600^{o}C, while tetrachloroethylene (C_2Cl_4) and carbon tetrachloride (CCl_4) were detected at all temperatures between 300 and 800^{o}C (Table 2.9).

Yashuara (1993) completed a similar experiment by passing air (80% N_2 and 20% O_2) at 100 mL/min through a PCE reservoir and into a quartz tube that was maintained at a temperature between 310 and 940^{o}C. The amount of oxygen present, approximately

12.4 moles O_2 per mole TCE, was greater than the stoichiometric amount required for complete combustion. The residence time in these experiments ranged from 5 to 10 seconds with PCE degradation products detected at 310^{o}C and 99% of the PCE degraded at 810^{o}C. The primary PCE degradation products were phosgene ($COCl_2$) and hydrogen chloride with minor amounts of methyl trichloroacetate, hexachloroethane, dichlorocyclopentane among the 15 identified degradation products. The source of hydrogen for HCl was attributed the water dissolved in the PCE-NAPL that was fed into the quartz tube.

In summary, passing gas-phase TCE through quartz tubes heated between 300 and 800^{o}C resulted in the formation of a wide variety of chlorinated compounds from carbon tetrachloride (CCl_4) and tetrachloroethylene (C_2Cl_4) to hexachlorobenzene (C_6Cl_6). The main products after passing PCE through a quartz tube heated to between 310 and 940^{o}C was phosgene and hydrogen chloride. Thus these compounds are anticipated to form during the in-situ thermal treatment of regions contaminated with TCE or PCE where temperatures exceed 300^{o}C.

The experiments described above were completed with oxygen present. Another series of experiments were completed under oxygen starved conditions to simulate conditions during which incinerators operate in a fuel lean mode. The following section describes the degradation of TCE and PCE along with the products formed in the absence of oxygen.

2.4.6 Degradation of Gas-Phase TCE and PCE within Heated Quartz Tubes without Oxygen Present (Anoxic)

Mulholland et al. (1992) determined the condensed-phase products formed after passing TCE and nitrogen (no oxygen present) through a heated quartz tube (1.5 second residence time) at temperatures ranging from 800 and 1200^{o}C. The solids produced by the degradation of TCE were collected on a filter, which was subsequently rinsed with dichloromethane (CH_2Cl_2) to determine the tar and soot fractions, where soot was defined as the fraction that is insoluble in dichloromethane. Approximately 10% (wt.) of the TCE that passed through the quartz tube heated to 800^{o}C was converted into tar demonstrating that oxygen plays an important role in achieving the complete destruction of TCE in these heated quartz tube experiments since 99% of TCE was degraded at 500^{o}C with oxygen present in the experiments of Yasuhara and Morita (1990). The chemical species present in the tar fraction were identified using mass spectrometry (MS), liquid chromatography, and IR analysis. Hexachlorobenzene (C_6Cl_6), hexachlorophenylacetylene (C_8Cl_6), octachlorostyrene (C_8Cl_8), and octachloronaphthalene ($C_{10}Cl_8$) were the most abundant compounds found in the tar based on MS response.

Tirey et al. (1990) completed quartz tube experiments by passing PCE and helium through a quartz tube heated to between the temperatures of 500 and 1,050^{o}C with residence times from 0.5 to 5 seconds. At 800^{o}C, 24.6% of the influent PCE was degraded after passing through the heated quartz tube, significantly less that the 99% degradation reported by Yasuhara (1993) with oxygen present at 810^{o}C. Chlorine gas (Cl_2) was the primary PCE degradation product found by Tirey et al. (1990) with the

primary carbon products consisting of deposits within the reactor. The identity of the carbon compounds was not determined.

Oxygen plays an important role in degrading TCE and PCE in heated quartz tubes. Oxygen is expected to be present in the subsurface during in-situ thermal treatment as surface air is drawn into the heated treatment zone by the vacuum extraction system. However, oxygen limited conditions could exist in subsurface environments where oxygen has been depleted by microbial activity or where reducing conditions are present.

2.4.7 TCE Degradation Products as a Function of the Cl/H Ratio

Reducing the amount of chlorinated degradation products and increasing the non-chlorinated products is thought to be dependent on the amount of chlorine and hydrogen in the high-temperature region. Mulholland et al. (1992) suggested that the ratio of the chlorine to hydrogen (Cl/H) present in the quartz tube would affect the type of degradation products formed. With a Cl/H ratio of less than one (Cl/H<1), chlorine would preferentially react with hydrogen to form HCl, and with a Cl/H ratio of greater than 1 (Cl/H>1), chlorine was predicted to react with carbon to form chlorinated hydrocarbons. This section provides details on experiments performed that determined the changes in TCE and PCE degradation product distribution as a function of the chlorine to hydrogen ratio.

The experiments completed by Mulholland et al. (1992), Yasuhara and Morita (1990) represent results for TCE degradation with a Cl/H ratio of 3, thus the observed chlorinated hydrocarbons were the expected TCE degradation products. In contrast, Werner and Cool (2000) measured the products formed during combustion of TCE using a chlorine to hydrogen ratio of less than 1 (Table 2.10). TCE was introduced into a

methane flame that consisted of 17% CH_4, 35% O_2, 46% Ar, and 2% TCE by volume for a Cl/H ratio of approximately 0.09. The final combustion products included (in order of abundance) H_2O, CO_2, CO, HCl, methane (CH_4), and O_2. Intermediates identified in the flame adjacent to the burner surface (200 to 1000°C) included dichloroethylene ($C_2H_2Cl_2$), vinyl chloride (C_2H_3Cl), ethylene (C_2H_4), dichloroethenol (Cl_2C_2HOH), dichloroketene (Cl_2C_2O), chloroketene (C_2HClO), and ketene (C_2H_2O), indicating that the oxidation state of the TCE carbon atoms was being reduced within the flame with Cl/H ratio of less than one. The observation that the TCE carbons were reduced in low

Table 2.10: Selected Compounds Detected after Passing TCE through a Flame with Cl/H Ratio of 0.09
(Werner and Cool, 2000)

Species in Flame	Initial Flame (200-1000°C) (% mole basis)	Final Flame (1500°C) (% mole basis)
carbon monoxide (CO)	6.00	6
carbon dioxide (CO_2)	3.00	11
hydrochloric acid gas (HCl)	2.50	2.5
water (H_2O)	17.00	19
methane (CH_4)*	3.00	0.5
oxygen (O_2)*	12.00	0.5
dichloroehtylene ($C_2H_2Cl_2$)	0.50	nd
ethylene (C_2H_4)	0.40	nd
vinyl chloride (C_2H_3Cl)	0.07	nd
ketene	0.05	nd
dichloroethanol	0.01	nd
dichloroketene	0.01	nd
chloroketene	0.01	nd

Maximum measured values estimated from graphs found in Werner and Cool (2002).
*Present in feed.
nd – below analysis detection limit.

Cl/H ratio flames is also supported by the results of Yang and Kennedy (1993) who found acetylene, ethylene, and ethane were the primary intermediates after introducing TCE into a methane flame with Cl/H ratio of 0.14.

In subsurface environments, water is expected to be the major source of hydrogen affecting the chlorine to hydrogen ratio. Chuang and Bozzelli (1986) performed an experiment using hydrogen gas (H_2) and water as the hydrogen sources for the transformation of chloroform ($CHCl_3$) to HCl within a heated quartz tube operated over a temperature range of 550 to 1000^{o}C. The residence times were between 0.02 and 2 seconds, and the Cl/H ratio was approximately 0.14. Several intermediate products were formed in the presence of hydrogen gas, including dichloromethane, monochloromethane, and methane, which indicated that the chloroform carbon oxidation state had been reduced. The products formed when water was used as the hydrogen source at temperatures below 950^{o}C included tetrachloroethylene (C_2Cl_4) and TCE indicating an increase in the number of chlorine atoms per carbon or that the chloroform carbon had been oxidized. Although the complete destruction of chloroform was observed using both hydrogen and water, hydrogen was able to reduce chloroform beginning at 600^{o}C, consistent with the fact that water is more stable at elevated temperatures than hydrogen.

The ratio of chlorine to hydrogen may affect the type of TCE degradation products formed. With a Cl/H ratio of greater than one, the chlorine produced from the degradation of TCE may react with the remaining TCE and TCE degradation products to form chlorinated compounds. With a Cl/H ratio of less than one the chlorine may react

with hydrogen atoms to yield HCl and prevent the formation of unwanted chlorinated hydrocarbons.

CHAPTER 3

FLOW-THROUGH EXPERIMENTS

Six flow-through experiment were completed to determine the degradation products formed by passing gas-phase TCE through a quartz tube heated to between 60 and 800^{o}C (Table 3.1). The initial four experiments were executed to develop methods and procedures in order to produce repeatable experimental results, thus experiments 1 through 4 are termed preliminary experiments. The first preliminary experiment was performed to determine the minimum temperature at which TCE degradation products could be detected with the quartz-tube partially filled with sand. The second preliminary experiment was performed to gain results for comparison with the results obtained by Yasuhara and Morita (1990) who determined the TCE degradation products using an empty quartz-tube apparatus. The third preliminary experiment focused on determining

Table 3.1: Completed Flow-Through Experiments

Flow-through experiment		Quartz Tube Contents	Temperature Range (^{o}C)	Purpose
Preliminary	1	100 grams Sand	24 to 420	Identify degradation products
	2	Empty	22 to 480	Compare with literature results
	3	100 grams Sand and Completely Sand Filled	420	Partially vs. completely sand filled quartz tube
	4	Empty	420	Evaluate effect of water
5		Empty	120 to 420	Degradation products as a function of oxygen, and water vapor content
6		Empty	120 to 800	Degradation products as function of water vapor content

the degradation products within a partially and completely sand-filled quartz-tube apparatus operated at 420^{o}C. The fourth preliminary experiment introduced water vapor into the TCE saturated carrier gas to determine the effect of water on the degradation products formed within an empty quartz-tube apparatus operated at 420^{o}C. Results from the four preliminary experiments were used to design the fifth experiment that was completed to determine the amount of each TCE degradation product formed as a function of three experimental variables including 1) quartz tube temperature, 2) oxygen content, and 3) water vapor content. The sixth experiment was performed to improve the recovery of TCE and its degradation products as a function of water vapor content with air as the carrier gas.

The quartz tube experimental apparatus along with the methods used to prepare the apparatus and trap chemical compounds in the gas-phase effluent exiting the quartz tube are presented in Section 3.1. Experimental methods and results specific to each of the initial four flow-through experiments are given in Sections 3.2 through 3.5. The methods and results for the fifth (Section 3.6) and sixth (Section 3.7) experiments are presented separately due to the expanded efforts employed to determine all the TCE degradation products formed. The final section (Section 3.8) provides a discussion of how the results of the experiments described in the previous sections apply to each of the three thermal remediation technologies

3.1 Quartz Tube Experimental System

The quartz tube experimental system consisted of a quartz-glass tube, a quartz-glass pre-mix chamber, and a quartz-glass effluent transition (Figure 3.1). The quartz tube was General Electric Type 124 fused quartz glass (Technical Glass Products,

Mentor, OH), with an outer diameter (OD) of 38 mm, wall thickness of 2 mm, and a length of 53 cm. There were two quartz tubes: one was custom made (Lillie Glassware, Marietta, GA) by installing a slotted quartz-glass shelf located at the midpoint of the quartz tube (quartz tube #1) and the other consisted of a section of quartz tube without slotted shelf (quartz tube #2). The pre-mix chamber was custom made (Lillie Glassware, Marietta, GA) to provide an approximate 70 mL volume where gas and TCE could mix before entering the quartz tube. The effluent transition was custom made (Lillie Glassware, Marietta, GA) from quartz glass to transition the gas flow from the 38 mm OD tube down to an 8 mm OD tube. The pre-mix chamber and effluent transition were

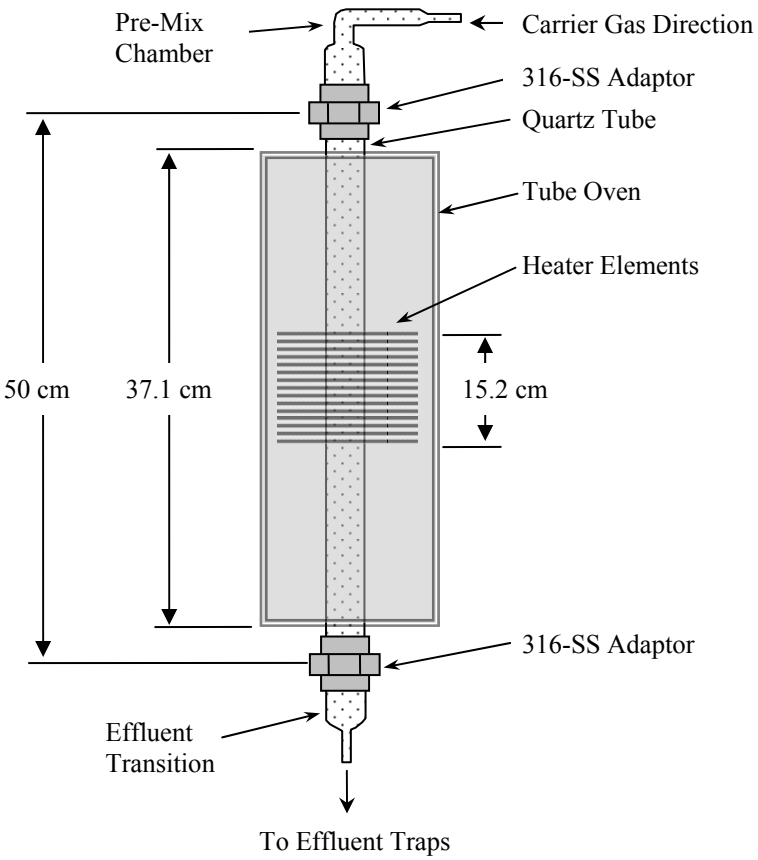

Figure 3.1: Quartz tube experimental apparatus.

connected to the quartz tube using custom made 38 mm ID, 316 grade stainless steel (316-SS) adapters (Swagelok Co., Salon, OH) fitted with viton o-rings.

The flowrate of the TCE-free carrier gas at 22^{o}C entering into the experimental apparatus was determined using a mass flow meter (Model 179A, MKS Instruments, Andover, MA). The mass flow meter was calibrated using an ADM2000 gas flow meter (J&W Scientific, Folsom, CA) that had been calibrated by California Integrated Coordinators (Placerville, CA). The pressure within the reaction system was determined using a pressure transducer (Honeywell, Freeport, IL), which was calibrated using a combination of water (0.02 to 0.05 bar) and mercury (0.07 to 0.7 bar) filled manometers. Both the mass flow meter and pressure transducer were connected to a datalogger (CR23X, Campbell Scientific, Logan UT) to automatically record the gas flow rate and pressure within the quartz tube system at one second intervals during each isothermal experiment.

3.1.1 Quartz Tube Preparation

The quartz tube and associated connectors were prepared prior to each isothermal experiment by washing in hot (45^{o}C) tap water with detergent (Versa-Clean, Fisher Scientific). The tube and connectors were then rinsed in deionized (DI) water and placed in a drying oven at 200^{o}C for a period of 2 hours. The tube and connectors were allowed to cool to room temperature and the experimental apparatus was assembled and rinsed with approximately 20 mL of dichloromethane (DCM) for a period of 5 minutes. A 2 mL sample of the DCM rinse was collected and stored at 4^{o}C until analyzed to demonstrate the organic-free initial experimental condition. After collecting the DCM rinse, the experimental apparatus was disassembled and remained in the vent hood for a period of 5

minutes to remove the residual DCM. The apparatus was then re-assembled after placing the quartz tube within a 20 inch long by 1.5 inch ID galvanized steel pipe that was located in the tube oven (Model 21100, Barnstead-Thermolyne, Dubuque, IA). The steel pipe served to protect the tube oven from damage by shards of quartz glass that formed during quartz tube failures.

3.1.2 Quartz Tube Temperature Profile

The temperature profile within the empty quartz tube from the gas inlet to outlet was measured while the tube oven was operated at 120°C (Figure 3.2). The temperature within the quartz tube was measured by inserting a certified traceable oven thermometer encased in a vermiculite filled enclosure (Fisher Scientific, Fair Lawn, NJ) into the heated quartz tube. The oven thermometer was held at a specific location within the quartz tube for 5 minutes and removed to read the temperature value. This temperature

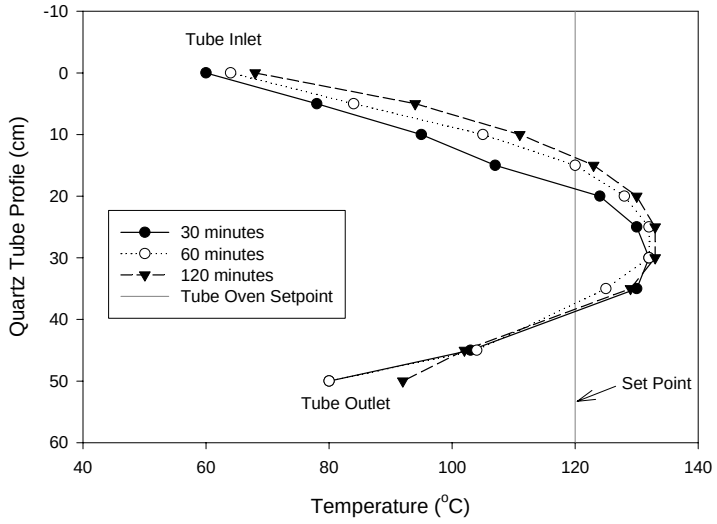

Figure 3.2: Temperature profile within the quartz tube heated to 120°C.

measurement procedure was repeated over the entire length of the quartz tube from inlet to outlet in approximately 5 cm increments. There was no gas flow during the temperature profile measurement procedure. The temperature profile in the quartz tube was determined after 30, 60, 90 and 120 minutes of heating with the temperature profiles after heating the tube for 90 and 120 minutes nearly identical.

As shown in Figure 3.2, the quartz tube is not at a uniform temperature throughout its entire length. TCE entering the quartz tube experiences increasing temperatures (temperature gradient) with the tube inlet at 70^{o}C and the maximum tube temperature (130^{o}C) located approximately 25 cm or about 10 inches from the tube inlet. This temperature gradient is similar in length to the one foot wide, 500 to 700^{o}C high-temperature zone claimed to cause the in-situ destruction of TCE during thermal conductive heating (Section 2.3.3). An attempt was made to measure the temperature profile of the quartz tube with the oven at 240^{o}C, however, the thermometer enclosure began to smoke after being inserted into the tube and the enclosure was not advanced further to avoid causing the enclosure to catch fire. No attempt was made to measure the temperature profile of the quartz tube at 420^{o}C; the high temperature profile is thought to be similar to that shown in Figure 3.2 with the region approximately 25 cm from the inlet at 420^{o}C while the tube inlet is at ambient temperature since it is located outside the oven. This temperature profile matches that provided by Barnstead-Thermolyne which shows that the maximum oven temperature is located 18.5 cm from the oven opening at the center-point within the oven. The heater elements are located within the middle 15.2 cm of the oven and there are no heating elements within 11 cm of the tube oven opening (Figure 3.1).

3.1.3 Solids Preparation and Sample Extraction

Sand from Ottawa, IL (ASTM 20-30 Sand, U.S. Silica Co., Berkeley Springs, WV) was placed into a 3 L capacity Pyrex glass drying tray and a 1 N solution of nitric acid was added to cover the sand and the sand was then allowed to soak in the nitric acid solution for 30 minutes before draining the excess liquid. The 1 N nitric acid soaking process was repeated and then the sand was rinsed in DI water, then placed into a drying oven and heated to 130^{o}C for 3 hours to remove excess moisture followed by baking the sand at 200^{o}C for 2 hours.

Post experiment sand samples (5 grams each) were collected and placed into separate 25 mL test tubes along with 2 mL of DI water. Each test tube was sealed with a Teflon lined septum affixed with an aluminum crimp and then placed in a freezer. The frozen sand samples were then processed using a hot solvent extraction method that involved incubating the 5 gram soil samples in a 1:1 (by volume) iso-octane and methanol mixture at 85^{o}C for 24 hours. Previous work performed at Georgia Tech has shown that the hot solvent extraction method, based on the work of Sawhney *et al.* (1988) and Huang and Pignatello (1990), is equivalent to Soxhlet extraction for chlorinated benzenes (Prytula, 1998).

3.1.4 TCE Used in Experiments

A 2 L volume of 99.5% American Chemical Society (ACS) reagent-grade TCE was obtained from Sigma-Aldrich, Inc. (Milwaukee, WI). The TCE was not stabilized with an anti-oxidant and was stored in a flammable storage locker at all times. TCE from this single 2 L bottle was used in all experiments and for the preparation of calibration solutions. A dedicated 40 mL vial with Teflon lined septum affixed with a screw cap was

periodically filled with TCE from the 2 L bottle and TCE for each experiment was dispensed directly from the 40 mL vial. The 40 mL vial was stored in the flammable storage locker along with the 2 L bottle.

3.1.5 DCM Effluent Trap and Analysis

The effluent end of the quartz tube was connected to a 40 mL screw-thread vial via a 10 cm long section of 1/16 inch OD poly ether-ether ketone (PEEK) tubing. The PEEK tubing was affixed to the 38 to 8 mm effluent transition by a 316-SS Swagelok (Solon, OH) union with Teflon ferules and was inserted through a pre-drilled hole in a Teflon lined septum affixed to the 40 mL vial with an open-hole screw cap. The 40 mL vial contained approximately 30 mL of dichloromethane (DCM) and was located in a 500 mL beaker filled with crushed ice. The purpose of the DCM filled 40 mL vial was to trap all compounds with greater than two carbons (e.g., tetrachloroethylene) exiting the quartz tube.

After passing the TCE saturated carrier gas through the heated quartz tube, the DCM trap was removed, sealed with a Teflon lined septum without holes, and weighed using an analytical balance (Model# AG245, Mettler-Toledo, Columbus, OH). The weight of the DCM filled trap was used to estimate the volume of DCM in the 40 mL vial assuming a DCM density of 1.325 g/mL. The concentration of TCE in the DCM trap fluid was determined by collecting three, 2 mL DCM samples and placing them into autosampler vials to which an internal standard of 1,1,1-trichloroethane was added followed by sealing the autosampler vials with Teflon lined septa affixed by crimp seal. The analysis of the DCM fluids consisted of using an automatic liquid sampler (HP6890) to inject 1 uL of DCM into a GC (HP6890) equipped with a 30 m by 0.32 mm OD DB-5

column (Agilent Technologies, Palo Alto, CA) that was connected to a Flame Ionization Detector (FID). The GC inlet was operated at 9.45 psi in the split mode (10:1) at 200^{o}C with helium as the carrier gas and a constant column flowrate of 2 mL/min. The GC oven temperature was isothermal at 50^{o}C for 8 minutes followed by at 20^{o}C/min ramp to 150^{o}C. The FID was operated at 300^{o}C with 400 mL/min of air, 30 mL/min hydrogen, and 40 mL/min of nitrogen as the makeup gas.

TCE calibration standards in the concentration range from 8,000 to 20,000 mg/L were analyzed by GC/FID to determine the amount of TCE in the DCM trap fluid. The calibration standards were prepared by first adding approximately 30 mL of DCM to 50 mL glass volumetric flasks (50±0.05mL at 20^{o}C) and then the flasks were sealed with ground-glass stoppers. The initial weight of the flasks and DCM was determined using an analytical balance (Model# AG245, Mettler-Toledo, Columbus, OH) after allowing the stoppered flasks to stand for a period of 30 minutes. Neat TCE was then injected into each flask using a gas tight syringe, the stopper inserted into each flask, and then the weight of each 50 mL flask with TCE was recorded. Each flask was then filled to the indicator mark with DCM, stoppered, and inverted several times to mix the solution. The concentration of each calibration solution was calculated using the weight of TCE added and the volume of DCM (50 mL). GC/FID analysis of an EPA 8240B/8260A Matrix Spike Mix (Sigma-Aldrich, Milwaukee, WI) spiked into DCM was performed to verify TCE retention time and concentration.

The identity of compounds associated with unidentified chromatographic peaks from the GC/FID analysis of DCM trap fluids was determined using a GC (Varian Star 3600CX) equipped with a 30 m by 0.25 mm OD CP-Sil 8 CB Low Bleed/MS capillary

column (Varian) connected to a Varian Saturn 2000 Ion Trap Mass Spectrometer (MS). Compounds were identified using software (SaturnView ver. 5.41, Varian, Inc., Palo Alto, CA) that matched their mass spectra with reference mass spectra in the NIST/EPA/NIH Mass Spectral Library (NIST98). The mass spectrometer was tuned to optimize the detector voltage (EM-Voltage) and mass axis calibrated using perflurorotributylamine (FC-43) prior to each use.

The amounts of PCE and carbon tetrachloride (CCl_4), which were identified during GC/MS analysis, were determined using GC/FID analysis. The GC/FID response was determined using calibration solutions prepared in DCM from ACS grade PCE and CCl_4 (Sigma-Aldrich, Milwaukee, WI). The amounts of hexachloroethane (HCA) and pentachloroethane (PCA) were determined using the ratio of their respective MS chromatogram peak areas to that of PCE.

3.2 TCE Degradation in a Quartz Tube with Sand Heated from 24 to 420^{o}C (First Preliminary Flow-Through Experiment)

Trichloroethylene (TCE) recovery was determined for 9 tube oven temperatures including 24, 40, 60, 120, 180, 240, 300, 360, and 420^{o}C at 1 atm of carrier gas pressure during the first experiment. This experiment was performed to determine if TCE could be degraded within the quartz tube and if the quartz tube could withstand operating in the temperature range from ambient to 600^{o}C; no attempt was made to recover all the TCE introduced into the quartz tube. This preliminary experiment involved passing dry, breathing-grade air (Airgas-South, Inc., Marietta, GA) through a gas-washing bottle (250 mL Pyrex) filled with TCE NAPL at 22^{o}C. The TCE saturated air was then passed through the quartz tube that contained 100 grams of acid washed 20-30 mesh Ottawa sand positioned on quartz-glass wool (Technical Glass Products, Mentor, OH) and held at

the midpoint of the quartz tube by a slotted quartz-glass shelf (quartz tube #1). The TCE saturated air was passed through the apparatus for a period of approximately 16 minutes, which represented about 3 pore volumes (320 mL total quartz tube pore volume assuming sand porosity of 0.3) and resulted in 450 mg, on average, of TCE being transferred into the quartz tube. The mass of TCE delivered to the tube was determined gravimetrically by measuring the weight (PG503-S, Mettler-Toledo, Inc., Columbus, OH) of the TCE filled gas-washing bottle before and after each 16 minute period. The airflow rate was approximately 60 ml/min, which resulted in a residence time of approximately 5 minutes at 25^{o}C. The effluent from the heated quartz tube passed through a vial containing dichloromethane (DCM) to trap all condensable products; no gas samples were collected. At the end of 16 minutes, the airflow was stopped and the gas pressure within the quartz tube apparatus was monitored for a period of 5 minutes to test for gas leaks. No additional volume of air was passed through the quartz tube after each 16 minute TCE introduction period meaning that at least 1 pore volume of TCE saturated air remained in the tube at the end of each 16 minute trial. The temperature of the quartz tube was increased, allowed to stabilize for 30 minutes, and the 16 minute TCE introduction period was repeated. The apparatus was not disassembled between each TCE introduction period.

The amount of TCE recovered in the DCM trap fluid at each experimental temperature, with respect to the amount of TCE delivered to the apparatus, is shown in Figure 3.3. The amount of TCE recovered in the DCM trap fluid was less than the amount delivered to the quartz tube for temperatures less than 240^{o}C, the missing mass of TCE at these temperatures was thought to be located within the apparatus since no effort

was employed to flush TCE from the apparatus after the 16 minute introduction period. PCE and carbon tetrachloride (CCl_4) were detected in the DCM trap fluid after passing TCE saturated air through the quartz tube at 300°C and the amount of PCE and CCl_4 detected continued to increase with tube temperature: no PCE or CCl_4 was introduced into the quartz tube. The experiment was terminated prior to reaching 600°C due to the significant amount of degradation products detected at 420°C.

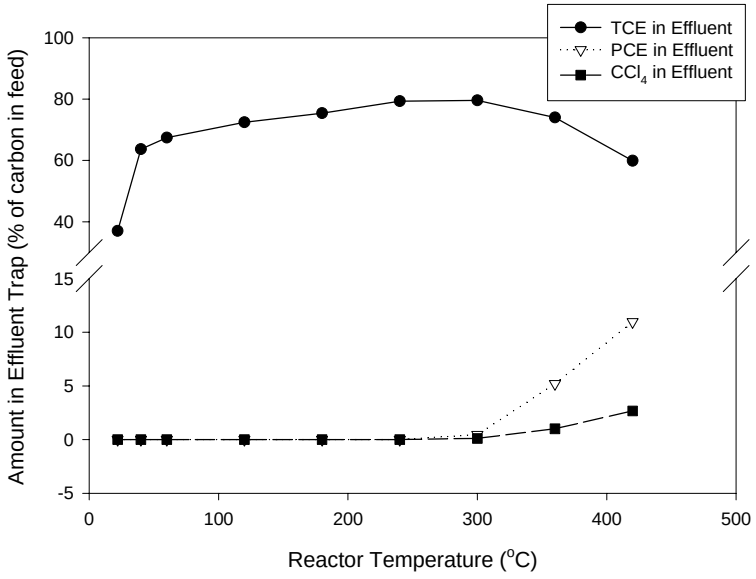

Figure 3.3: Amount of TCE, PCE, and carbon tetrachloride (CCl_4) recovered after passing gas-phase TCE in air through a quartz tube with 100 g Ottawa sand (first preliminary flow-through experiment).

Results of the first flow-through experiment demonstrated that TCE underwent thermally induced degradation while passing through the quartz tube apparatus heated to temperatures greater than 300°C. PCE and CCl_4 were the degradation products detected in the DCM trap and represent chlorinated oxidation products that were expected to form

during TCE degradation because the Cl/H ratio was equal to 3 (Section 2.4.7) as TCE was the only source of chlorine and hydrogen in these experiments.

3.3 TCE Degradation in an Empty Quartz Tube Heated Between 24 and 480°C (Second Preliminary Flow-Through Experiment)

The second preliminary experiment involved passing dry, breathing grade air that was saturated with TCE through an empty quartz tube (without sand); the same quartz tube (quartz tube #1) used in the first preliminary flow-through experiment (Section 3.2). Trichloroethylene (TCE) recovery was determined for 9 tube oven temperatures (7 temperatures with replicates at 120 and 240°C) including 24, 120, 240, 300, 360, 420, and 480°C at 1 atm of carrier gas pressure. The quartz-tube apparatus was disassembled and decontaminated between each TCE introduction period for temperatures above 300°C due to the presence of degradation products observed during the first preliminary flow-through experiment. The airflow rate was approximately 60 mL/min, which resulted in a residence time of approximately 5 minutes at 25°C. The TCE saturated air was passed through the empty apparatus for a period of 20 minutes, which represented 3 pore volumes (400 mL total quartz tube volume) and resulted in 700 mg, on average, of TCE being transferred into the quartz tube where the mass of TCE delivered to the tube was determined gravimetrically as in the first preliminary flow-through experiment.

The empty reactor experiments were performed to replicate the results produced by Yasuhara and Morita (1990) who passed TCE saturated air through an empty quartz tube in the temperature range from 300 to 800°C. The second preliminary flow-through experiment was intended to reach a maximum temperature of 600°C, however, the last experiment was completed at 480°C as the quartz tube shattered into many small pieces while heating to 540°C. The destruction of the quartz tube at 540°C was unexpected as

these tubes were rated to 1,200°C (Technical Glass Products, Mentor, OH). The amount of TCE, PCE, and CCl_4 recovered in the DCM trap fluid for each experimental temperature, with respect to the amount of TCE introduced into the apparatus, is shown in Figure 3.4 along with the results of Yasuhara and Morita (1990) for comparison.

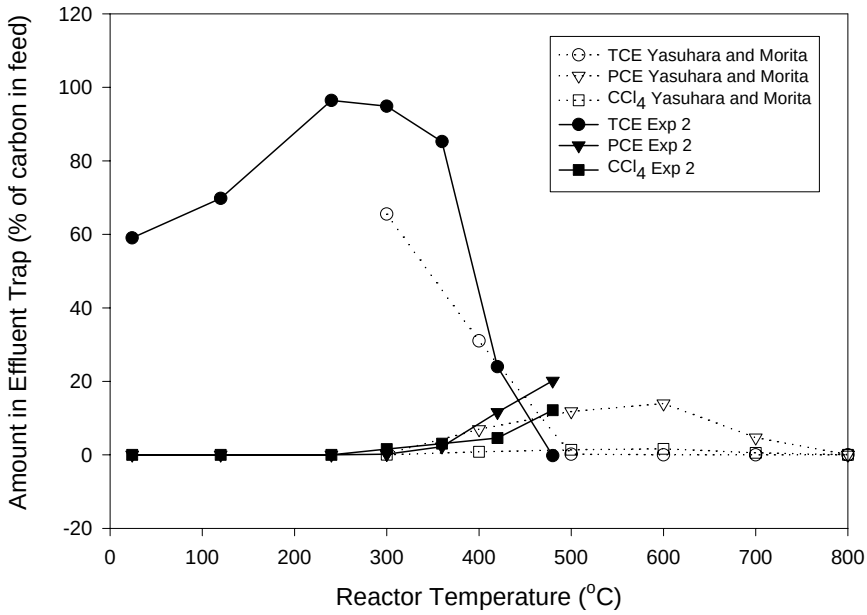

Figure 3.4: Amount of TCE, PCE, and carbon tetrachloride (CCl_4) recovered after passing gas-phase TCE in air through an empty quartz tube (second preliminary flow-through experiment).

The results from the second preliminary flow-through experiment and the results of Yasuhara and Morita (1990) follow similar trends between 300 and 500°C, and are in good agreement regarding the temperature at which TCE was no longer detected in the DCM trap (~500°C). The residence time in the Yasuhara and Morita (1990) experiments at 500°C was estimated to be 32 seconds where the residence time at 480°C in this experiment was approximately 3 minutes after correcting for the expansion of carrier gas

using the idea gas law. Dry air without TCE was passed through the quartz tube for 15 minutes after the 20 minute TCE introduction period in all experiments completed above the temperature of 240^{o}C. Consequently, the amount of TCE recovered in the DCM trap over the two trapping periods was close (~98%) to the amount of TCE introduced into the tube for the experiment completed at 240^{o}C. This level of TCE recovery was thought to demonstrate that TCE was not being degraded at temperatures of less than 240^{o}C within the experimental apparatus.

Results of the second preliminary flow-through experiment demonstrated that degradation products in addition to PCE and CCl_4 must have formed at 420^{o}C as the amount of TCE, PCE, and CCl_4 detected in the DCM trap were less than approximately 35% of the amount of TCE introduced into the quartz tube. The missing degradation products were expected to be CO and CO_2 based on the past experimental work described in Section 2.4.7.

3.4 TCE Degradation in a Quartz Tube Partially and Completely Filled with Sand at 420^{o}C (Third Preliminary Flow-Through Experiment)

The third preliminary flow-through experiment involved passing dry, breathing grade air saturated with TCE through a quartz tube that was completely filled with sand and, in addition, through a quartz tube that was partially filled with sand. The purpose of this experiment was to determine if filling the empty volume of the tube with sand had an effect on the amount of TCE degraded and the degradation products formed. Experiments were completed at 420^{o}C since this temperature was found during the second preliminary flow-through experiment to degrade a significant amount of TCE and produce detectable amounts of degradation products. The partially sand-filled quartz tube experiment was completed with 100 grams of acid treated 20-30 mesh Ottawa sand located on a quartz

shelf (quartz tube #1) and used the same flow conditions (16 minute TCE introduction period) as in the first preliminary flow-through experiment (Section 3.2).

The completely sand-filled experiment was completed with 700 grams of acid treated 20-30 mesh Ottawa sand located in the quartz without glass shelf (quartz tube #2). TCE saturated air was passed through the completely sand-filled quartz-tube operated at a temperature of 420^{o}C and 1 atm carrier gas pressure for a period of approximately 16 minutes. This time represents 5.4 tube pore volumes (177 mL pore volume assuming a sand porosity of 0.3) and resulted in 551 mg of TCE being introduced into the tube. The airflow rate was approximately 60 ml/min, which resulted in a residence time of approximately 3 minutes at 25^{o}C. At the end of 16 minutes, airflow was stopped and the system pressure was monitored for a period of 3 minutes to test for gas leaks. Hence, at least 1 pore volume of TCE saturated air remained in the apparatus at this time. A second trapping period was completed by passing dry air without TCE through the apparatus for a period of 20 minutes to flush any residual TCE vapor from the tube. After the trapping periods were complete, the tube was then capped and allowed to cool to room temperature overnight. The apparatus was disassembled the following day and 5 gram sand samples were collected from near the entrance, at the mid-way point, and exit of the sand-filled quartz tube. A sample of the glass wool located at the exit of the quartz tube was also collected. The sand and glass wool samples were handled and processed using a hot solvent extraction method (Section 3.1.3). PCE was the only compound detected in the iso-octane extracts and only from the sand sample collected at the tube exit.

The completely sand-filled tube produced more PCE and had lower TCE recovery than the tube containing 100 grams of sand and tube without sand (Figure 3.5). The sand-

filled tube also produced more pentachloroethane (C_2HCl_5) and hexachloroethane (C_2Cl_6) than the partially-filled and empty tube. Thus the effect of increasing the amount of Ottawa sand was to increase the amounts of chlorinated-carbon TCE degradation products at 420°C with air as the carrier gas.

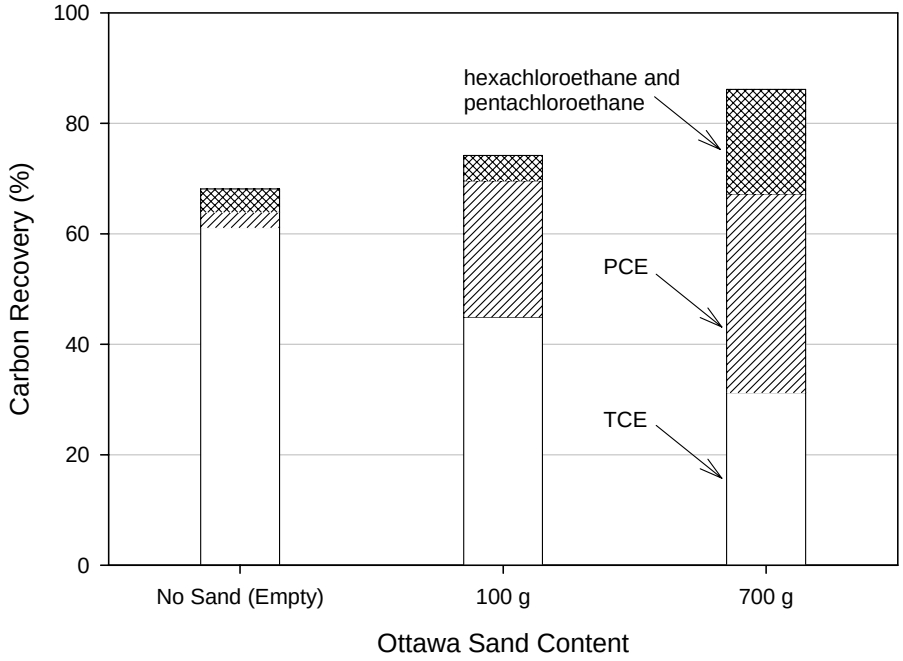

Figure 3.5: Amount of TCE, PCE, pentachloro- and hexachloroethane recovered after passing gas-phase TCE in air through an empty quartz tube, a quartz tube with 100 g Ottawa sand, and a quartz tube with 700 g of Ottawa sand (third preliminary flow-through experiment).

3.5 TCE Degradation in a Quartz Tube at 420°C with Increasing Water Vapor Content (Fourth Preliminary Flow-through experiment)

The fourth preliminary flow-through experiment involved passing humidified air and gas-phase TCE through an empty quartz tube operated at 420°C to determine if the hydrogen atoms in the water molecules would lead to a decrease in the amount of

chlorinated hydrocarbon degradation products. The experiment was completed using three different carrier gas humidity levels, including 0, 25, and 100% relative humidity (RH) at 22°C. The 25% RH experiment used a 1:3 flow-rate ratio of air that had passed through a water filled gas-washing bottle at 22°C and air saturated with TCE at 22°C. The 100% RH experiment involved passing air through a gas-washing bottle that contained an approximate 1:1 by volume mixture of TCE-NAPL and water at 22°C. A 1.6 L Tedlar bag was used to capture all the gas leaving the DCM trap and the gas within the Tedlar bag was analyzed for CO_2 content using a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD).

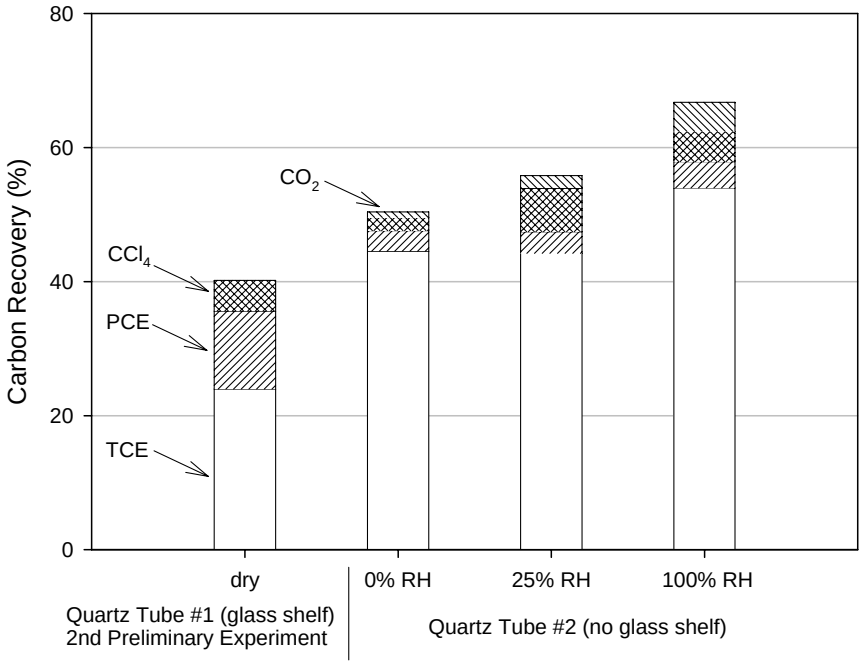

Figure 3.6: Amount of TCE, PCE, CCl_4, and CO_2 recovered after passing gas-phase TCE in humidified air through an empty quartz tube (fourth preliminary flow-through experiment).

The results from the fourth preliminary flow-through experiment demonstrated that the addition of water-vapor led to an increase in the amount of CO_2 and CCl_4 detected (Figure 3.6). However, reduced carbon compounds such as methane (CH_4) were not detected in gas samples from the Tedlar bag. The lack of reduced carbon may have occurred because there was less than a stoichiometric amount of hydrogen present in the gas entering the quartz tube or because water is not a good source of hydrogen.

The minimum ratio of chlorine to hydrogen in air entering the quartz tube was greater than one for the fourth flow-through experiment and was an insufficient amount of hydrogen to react with the chlorine present in TCE to form hydrogen chloride. This led to the suggestion that experiments with greater amounts of water vapor should be performed to determine if TCE could be degraded without forming chlorinated carbon degradation products.

The amount of CO_2 represented less than 5% of the total amount of carbon introduced into the quartz tube as TCE, thus additional degradation products had formed during the fourth flow-through experiment. This observation led to the development of a method to detect carbon monoxide (CO) in addition to CO_2 along with the use of an additional liquid filled trap to determine the amount of phosgene ($COCl_2$) formed.

3.6 TCE Degradation in a Quartz Tube Heated to 120, 240, and 420^{o}C as a Function of Oxygen, Water Vapor, and Solids Content (Fifth Flow-Through Experiment)

The fifth flow-through experiment was designed based on the results of the initial four preliminary flow-through experiments with the goal of accounting for all TCE degradation products in effort to close the mass balance. The fifth flow-through experiment was planned so that the amount of each TCE degradation product would be determined as a function of four experimental variables: 1) quartz tube temperature, 2)

oxygen content, and 3) water vapor content. The quartz tube temperatures were limited to 120, 240, and 420^{o}C to reduce the number of individual experiments in the series while staying within the temperature range relevant to thermal remediation techniques. The following sections described the methods (Section 3.6.1) used to complete and the results (Section 3.6.2) of the fifth flow-through experiments.

3.6.1 Fifth Flow-Through Experiment Methods

The residence time through the quartz tube was fixed at approximately 4.3 minutes for all steady-state temperature trials during the fifth flow-through experiment. This represented a gas flow rate of approximately 85 mL/min (at 22^{o}C) with the empty quartz tube at 120^{o}C which was the upper measurement limit of the mass flow meter and thus fixed the residence time for all subsequent experiments completed at temperatures greater than 120^{o}C. The gas flow rates to achieve a 4.3 minute residence time were calculated using the ideal gas law to correct for the gas expansion within the quartz tube at elevated temperatures. The gas flow rate used with the empty quartz tube at 240^{o}C was approximately 65 mL/min (at 22^{o}C) and approximately 48 mL/min (at 22^{o}C) with the quartz tube at 420^{o}C.

The following sections describe the method of introducing TCE into the quartz tube (Section 3.6.1.1), procedures used to vary the water vapor content of the quartz tube (Section 3.6.1.2), additional methods used to trap and analyze the compounds present in the quartz tube effluent (Section 3.6.1.3), and measures employed to collect and determine compounds that remained within the quartz tube after each experimental trail (Section 3.6.1.4).

3.6.1.1 TCE Introduction Method

In the preliminary flow-through experiments, TCE saturated carrier gas was introduced into the quartz-tube apparatus. For the fifth flow-through experiment, TCE was introduced into the pre-mix chamber, as shown in Figure 3.7, as neat liquid TCE at a

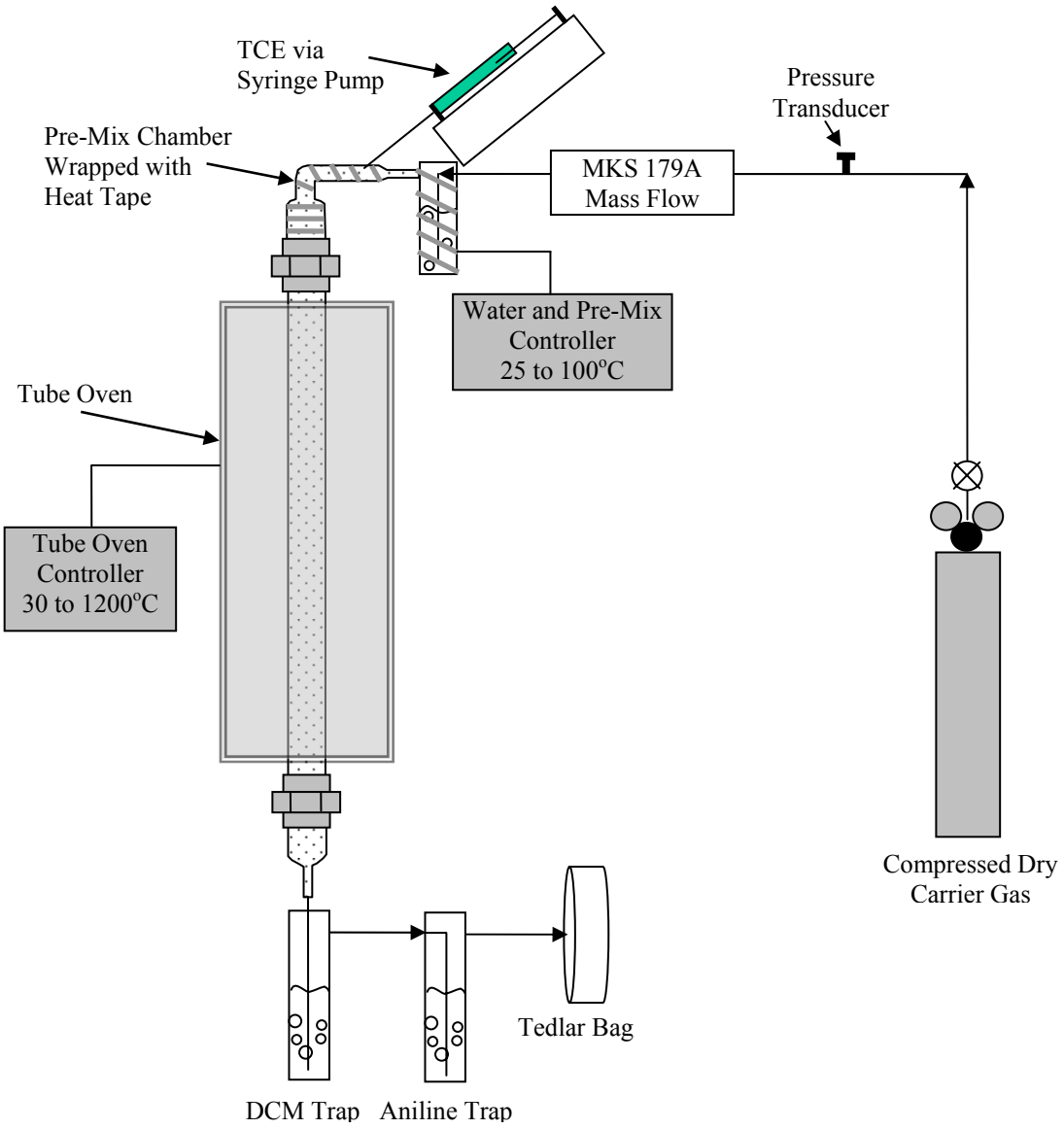

Figure 3.7: Quartz tube apparatus for the fifth flow-through experiment.

fixed rate of 0.68 mL/hr using a syringe pump (Model 11, Harvard Apparatus, Holliston, MA). This allowed the rate of TCE introduction to be fixed while adjusting the amount of water entering the quartz tube to vary the chlorine to hydrogen ratio inside the heated quartz tube. The process of introducing TCE into the pre-mix chamber consisted of initially recording the weight of a 1 mL gas-tight syringe, which contained approximately 0.34 mL (~0.5 g) of neat TCE, using an analytical balance (Model# AG245, Mettler-Toledo, Columbus, OH) with 0.001 gram readability. The analytical balance had been checked using an ASTM E617 class 2 certified traceable 20±0.0001 gram weight (Cat.# 820000.2, Denver Instruments, Denver, CO) prior to determining the syringe weight. The syringe needle was then inserted through a Teflon lined septum affixed with a crimp seal to a port located on the pre-mix chamber and TCE was injected at the slow rate of 0.68 mL/hr for a period of 30 minutes. There were no drops of neat TCE visible at the syringe needle tip, which was located inside the premix chamber, when using this TCE injection rate so that TCE entered the quartz tube in the gas phase. After the 30 minute TCE introduction period, the syringe was removed from the pre-mix chamber and the final weight recorded using the analytical balance and the amount of TCE introduced into the apparatus was determined by the difference in weight between the initial TCE-filled syringe and the final syringe weight after the 30 minute TCE injection period. The quartz tube was then flushed with TCE-free humidified carrier gas for 45 minutes after removing the syringe to recover as much of the TCE introduced into the experimental apparatus as possible.

3.6.1.2 Introduction of Water Vapor: Cl/H Ratio

The carrier gases used in the fifth flow-through experiment were ultra zero grade air (Airgas-South, Inc., Marietta, GA) or nitrogen (Airgas-South, Inc., Marietta, GA). The ultra zero grade air (UZA) was used as received while the nitrogen was passed through an oxygen trap (Alltech Associates, Inc., Deerfield, IL) before entering the quartz tube.

The carrier gas was humidified by passing through a mini-bubbler (ACE Glass, Vineland, NJ) filled with approximately 30 mL of deionized (DI) water prior to entering the quartz tube (Figure 3.5). The DI water was freshly dispensed from a Nanopure® analytical deionization system (model D4741, Barnstead International, Dubuque, IA) with a conductance of greater than 18 MΩ-cm. The amount of water vapor entering the quartz tube was adjusted by increasing the temperature of the mini-bubbler and pre-mix chamber using a resistant-wire based heat tape (McMaster-Carr, Atlanta, GA) that was wrapped around the mini-bubbler and pre-mix chamber and connected to a feedback voltage controller equipped with a K-type thermocouple. Three inlet temperatures were used including room temperature (22), 60 and 100^{o}C. The temperatures were chosen to explore a range of chloride to hydrogen (Cl/H) ratios based on the work presented in Section 2.4.7. The room temperature inlet condition had a calculated Cl/H ratio of 1 at a carrier-gas flow rate of 85 mL/min with the TCE liquid influent rate fixed at 0.68 mL/hr. The 60^{o}C inlet temperature had a calculated Cl/H ratio of 0.28 and the 100^{o}C inlet temperature had a Cl/H ratio of 0.07. The 100^{o}C inlet temperature represented a condition where the number of hydrogen atoms in water was approximately 15 times greater than the number of chlorine atoms in TCE.

3.6.1.3 Effluent Trapping Procedure and Analyses

The gas stream leaving the ice-cooled, DCM filled trap (Section 3.1.5) was collected in 1.6 L Tedlar bags to retain all single-carbon, non-condensable degradation products (e.g., carbon dioxide). Each bag was flushed three times with nitrogen gas prior to use. The Tedlar bag was removed from the quartz tube effluent stream when full and a gas sample from the bag was immediately analyzed to determine the amount of CO and CO_2 formed by the degradation of TCE in the heated quartz tube. The gas sample from the Tedlar bag was collected by pulling approximately 60 mL of the Tedlar bag contents through a 250 uL gas sample loop attached to a gas sampling valve heated to 120^{o}C and located within an insulated box on a Hewlett-Packard (HP) 6890 Gas Chromatograph (GC). The gas sample in the 250 uL sample loop was then injected into the GC inlet that was operated at 8.90 psi in the splitless mode for 0.75 minutes at 200^{o}C and was connected to a 30 m by 0.32 mm OD Carboxen-1010 column (Supelco, Bellefonte, PA) attached to a thermal conductivity detector (TCD). Helium was used as the capillary column carrier-gas at a constant flow of 2 mL/min and the GC oven was operated at 35^{o}C for 7 minutes followed by a 40^{o}C/min temperature ramp to 130^{o}C for 5 minutes. The TCD was operated at 210^{o}C with a helium reference flow of 15 mL/min and helium makeup flow at 5 mL/min. The Carboxen-1010 column is capable of separating O_2, N_2, CO, CO_2, and water. However, TCE and other organic compounds are retained within the carbon molecular sieve based column; the column was periodically conditioned at 200^{o}C to remove organic compounds. The GC/TCD was calibrated using serial dilution of an initial 100 mL volume of certified carbon dioxide (15%), carbon monoxide (7%), oxygen (5%), and nitrogen (73%) gas mixture (Scotty Specialty Gases, Plumsteadville, PA). The

serial dilution was performed in a 500 mL syringe (Model S-500, Hamilton Company, Reno, NV) with nitrogen as the dilution gas. At least three CO/CO_2 concentrations were used to calibrate the GC/TCD response. This technique had a detection limit of approximately 300 uL/L (ppmv) for CO and 500 uL/L (ppmv) CO_2.

In addition to the DCM trap, a second 40 mL vial filled with approximately 30 mL of toluene that contained 2% (wt.) aniline was added to the 420^{o}C UZA experiments to determine the amount of phosgene formed during the degradation of TCE. Any phosgene present in the effluent reacted with the aniline to form carbanilide (1,3-diphenylurea), a stable compound. The toluene/aniline traps were analyzed by first removing all the tolulene from the trap by passing nitrogen at 20 mL/min through the trap while heating the trap to 60^{o}C. The trap was taken to complete dryness and weighed to determine the mass of carbanilide formed. A 10 mL volume of acetonitrile was then added to dissolve the dry carbanilide and the concentration of carbanilide was determined by measuring the ultraviolet (UV) light absorbance at 254 nm. Calibration solutions were prepared using carbanilide (Sigma-Aldrich, Milwaukee, WI) in acetonitrile. This second trap and analysis methods was based on U.S. EPA method TO-6 (U.S. EPA, 1999).

The GC/MS analysis of the DCM trap fluids from the 420^{o}C experiments identified a number of TCE degradation products. However, the amount of chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), tetrachloroethylene (PCE), hexachloroethane (C_2Cl_6), hexachlorobutadiene (C_4Cl_6), and hexachlorobenzene (C_6Cl_6) were determined by GC/FID analysis. Master stock solutions (10,000 mg/L) for each of the previous compounds were prepared in DCM using ACS grade reagents (Sigma-Aldrich, Milwaukee, WI). Hexachlorobenzene (HCB) master stock was prepared by adding HCB

solids to iso-octane. The GC/FID response was determined for each compound using at least four calibration standards prepared by volumetric dilution of the master stock at concentrations in the expected range.

3.6.1.4 Quartz Tube Rinse Procedure and Analyses

The quartz tube was removed from the tube oven after cooling to room temperature and the interior of the sealed apparatus was rinsed with DI water and by iso-octane to determine the TCE degradation products that had formed and condensed onto the quartz glass surfaces. The apparatus was initially rinsed with approximately 30 mL of DI water for a period of 5 minutes to collect the water-soluble compounds (i.e., chloride) that formed at each experimental temperature. The second rinse used 30 mL of iso-octane for a period of 5 minutes to collect the non-polar TCE degradation products (i.e., hexachlorobenzene) from the experimental apparatus.

The chloride content of all water solutions was measured using a colorimetric method described by Bergmann and Sanik (1957). The method involved a selective chemical reaction between free chloride, mercuric thiocyanate [$Hg(SCN)_2$], and iron (III) ions from ferric ammonium disulfate [$FeNH_4(SO_4)_2$] as shown in Equation 3.1:

$$2Cl^- + Hg(SCN)_2 + FeNH_4(SO_4)_2 \rightarrow 2Fe(III)\ HgCl_2 + 2Fe(SCN)^{+2} \qquad (3.1)$$

The resulting iron-thiocyanate complex [$Fe(SCN)^{+2}$] forms a yellow color that is directly related to the amount of chloride present in water samples. The method consisted of placing 2 mL of a water sample into a 3 mL capacity Suprasil quartz cuvette (Fisher Scientific, Fair Lawn, NJ). Next, 200 uL of a 9 M nitric acid solution with 250 mM of ferric ammonium sulfate was added to the cuvette followed by 200 uL of ethanol

saturated with mercuric thiocyanate. The cuvette was capped with a Teflon lid, inverted 4 times to mix the contents, and then placed in a Varian spectrometer (Model Cary 3E). The light absorption at 460 nm was measured after 10 minutes with reference to DI water contained in a second transmission matched cuvette. Calibration solutions at concentrations of 2, 20, 50, 100, 200, 400, 600, and 1000 uM were prepared in 100 mL volumetric flasks using a certified 1,000 mg/L chloride master stock (SPEX CertiPrep, Metuchen, NJ). The detection limit for this technique was approximately 0.1 mg/L.

The haloacetic acid content of water samples was determined using procedures based on EPA method 552.2 (U.S. EPA, 1995). This procedure involved 1) pH adjustment, 2) liquid-liquid extraction, 3) derivatization, and 4) neutralization followed by GC analysis. The water-rinse samples were contained in 40 mL glass vials sealed with Teflon lined septa affixed with screw caps. The pH of each water rinse sample was adjusted to less than 0.5 by adding 1.5 mL of concentrated sulfuric acid (H_2SO_4) to convert any carboxylates present into the acid form. The pH adjustment was followed by adding 5 mL of methyl-tert butyl ether (MTBE) to the 40 mL vials which were then resealed and hand shaken for 2 minutes to extract the haloacetic acids. Approximately 3 mL of the MTBE was then transferred from each 40 mL vial to 14 mL glass vials using a Pasteur pipette. One mL of acidic methanol (10% H_2SO_4) was added to each 14 mL vial, which were sealed with a Teflon lined septa affixed with a screw cap and then placed in an oven at 50^{o}C for a period of 2 hours to convert the carboxylic acids to their derivatized, methyl ester form. After cooling the 14 mL vials to room temperature, the MTBE extract and acid methanol mixture was neutralized by adding 2 mL of saturated sodium bicarbonate solution. Two, 1 mL samples of the MTBE extracts were transferred

from the 14 mL vials into 2 mL autosampler vials and the internal standard, 1,2,3-trichloropropane, was added to each 2 mL vial, and the vials were then sealed with Teflon lined septa affixed with aluminum crimps.

The analysis of the MTBE extracts consisted of using an automatic liquid sampler (HP7683) to inject 1 uL of sample into a GC (HP6890) equipped with a 30 m by 0.32 mm OD HP-1 capillary column connected to an electron capture detector (ECD). The GC inlet was operated at 7.00 psi in the splitless mode for 0.5 minutes at 200^{o}C with helium as the column carrier gas at a constant flowrate of 2 mL/min. The GC oven was operated at 35^{o}C for 21 minutes followed by an 11^{o}C/min temperature ramp to 136^{o}C for 3 minutes, and a final temperature ramp of 20^{o}C/min to 230^{o}C for 3 minutes. The ECD was operated at 250^{o}C with a nitrogen gas makeup flow of 60 mL/min. Dichloroacetic acid calibration standards at concentrations of 12, 50, 100, and 400 ug/L were prepared from a 60 mg/L primary dilution standard made from ACS grade dichloroacetic acid (Sigma-Aldrich, Milwaukee, WI). The calibration samples were processed with each sample batch along with at least two uncontaminated water samples including freshly dispensed DI water and a storage blank.

The GC/ECD chromatograms from the analysis of the MTBE extracts collected from the 420^{o}C UZA experiments contained peaks that eluted at times different than dichloroacetic acid. A GC (HP 6890) equipped with a 30 m by 0.32 mm DB-5ms column connected to a mass select detector (MSD, HP5973) was used to identify the compounds associated with the unknown peaks. The GC operating conditions were identical to the GC/ECD method given above. Compounds were identified using software (ChemStation

ver. D.00.00.38, Agilent Technologies, Palo Alto, CA) that matched their mass spectra with reference mass spectra in the NIST/EPA/NIH Mass Spectral Library (NIST02).

The iso-octane rinse was initially analyzed using the Varian GC/MS (Section 3.1.5) to determine the identity of TCE degradation products. The amount of each degradation product was then determined using GC/FID analysis as described for the DCM trap fluid in Section 3.6.1.3.

3.6.2 Fifth Flow-Through Experiment Results

Empty quartz-tube experiments were completed for tube temperatures of 120, 240, and 420^{o}C at carrier gas pressures of 1 atm. Separate experiments were completed with the inlet at room temperature (22), 60, and 100^{o}C for each tube temperature to evaluate the effect of increasing the quartz-tube water content on TCE degradation and the degradation products formed. Separate flow-through experiments were completed with nitrogen and air (UZA) as the carrier gas to evaluate the effect of oxygen on TCE degradation (Table 3.2).

Table 3.2: Experimental Matrix used for the Fifth Flow-Through Experiment

Tube (^{o}C)	Inlet (^{o}C)	Tube Contents	Carrier Gas	Variable
120, 240, 420	22, 60, 100	Empty	Nitrogen	baseline
120, 240, 420	22, 60, 100	Empty	Air	oxygen

Water vapor was introduced into the quartz tube by passing the carrier gas (nitrogen or air) through a water filled bubbler. The amount of water vapor in the carrier gas was increased by increasing the temperature as which the bubbler was maintained, designated as inlet (^{o}C) in Table 3.2. The relative humidity at each inlet temperature is

close to 100% while the water vapor pressure, or amount of water entering the quartz tube, was increased from 0.03 atm at 22°C, to 0.20 atm at 60°C, and to 1.00 atm at 100°C. These three inlet temperatures represent chlorine to hydrogen ratios (Cl/H) of 1.00, 0.28, and 0.07, respectively.

An initial sand-filled experiment was completed for tube temperatures of 120 and 240°C, however, the sand-filled quartz tube shattered at 400°C while heating to 420°C. Based on this experience and the quartz tube failures during preliminary experiments, it was concluded that sand-filled quartz tubes are not capable of consistently withstanding temperatures greater than 400°C. Because of this limitation, the planned sand-filled experiments were not completed. The following sections address the recovery of TCE after being introduced into an empty, heated quartz-tube (Section 3.6.2.1) along with the identity and quantity of TCE degradation products detected in the DCM trap (Section 3.6.2.2), Tedlar bag (Section 3.6.2.3), water rinse (Section 3.6.2.4), and iso-octane rinse (Section 3.6.2.5). The final section provides the distribution of carbon and chlorine recovered in the traps, Tedlar bag, and quartz tube rinses (Section 3.6.2.6).

3.6.2.1 TCE Recovery

The amount of TCE detected in the DCM trap with respect to the amount introduced into the quartz tube as a function of tube temperature and carrier gas is shown in Figure 3.6. The average recovery of TCE with nitrogen as the carrier gas was greater than 94% at all the experimental temperatures. With air as the carrier gas, the average recovery of TCE was greater than 94% for tube temperatures of 120 and 240°C but dropped to approximately 53% for the tube at 420°C. The amount of TCE recovered at each tube temperature shown in Figure 3.8 represents the average for the three

experiments completed at different quartz-tube water contents and demonstrates that increasing water content had little effect on TCE recovery.

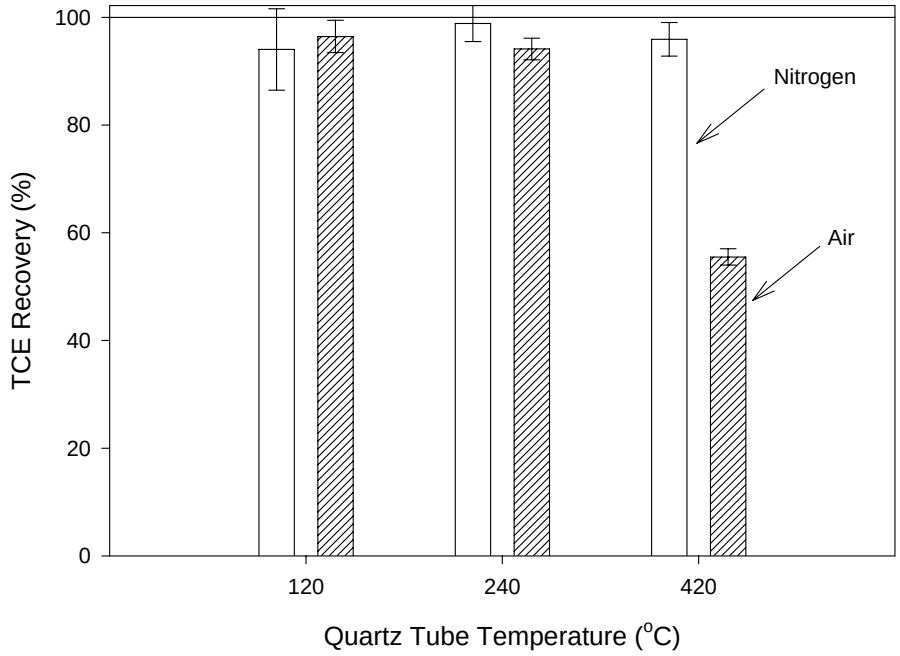

Figure 3.8: Average recovery of TCE as a function of carrier gas oxygen content and quartz tube temperature (fifth flow-through experiment).

Table 3.3 contains the average amount of TCE recovered, along with the standard deviation, as a function of quartz-tube water content with nitrogen as the carrier gas. The low TCE recovery for the 60°C inlet temperature at the 120°C tube temperature was due to a leak in the experimental apparatus and this value was not used to calculate the average recovery at 120°C shown in Figure 3.8. Table 3.4 contains the amount of TCE recovered as a function of quartz-tube water content with air as the carrier gas. The average values found in Tables 3.3 and 3.4 are shown in Figure 3.8.

Table 3.3: TCE Recovery with **Nitrogen** as the Carrier Gas (Recovery = TCE in DCM Trap ÷ TCE injected × 100%)			
Inlet Temperature (°C)	Quartz Tube Temperature (°C)		
	120	240	420
22	91.2±6.0[a]	98.7±1.3	93.1±1.9
60	[b]68.0±4.6	101.7±2.9	95.5±1.5
100	96.9±4.5	96.2±1.0	99.1±1.9
Average ± Standard Deviation	94.0±7.6[c]	98.8±3.3	95.9±3.1

[a]Analytical variability: standard deviation based on three samples.
[b]Leak in experimental system, average based on 22 and 100°C inlet temperatures.
[c]Experimental variability: standard deviation of TCE recovery for differing water contents.

Table 3.4: TCE Recovery with **Air** as the Carrier Gas (Recovery = TCE in DCM Trap ÷ TCE injected × 100%)			
Inlet Temperature (°C)	Quartz Tube Temperature (°C)		
	120	240	420
22	95.3±1.2[a]	96.2±1.2	52.4±1.2
60	97.7±2.1	94.1±0.6	54.6±0.2
100	96.3±1.7	92.0±1.5	51.7±0.9
Average ± Standard Deviation	96.4±3.0[b]	94.1±2.0	52.9±1.5

[a]Analytical variability: standard deviation based on three samples.
[b]Experimental variability: standard deviation of TCE recovery for differing water contents.

TCE recovery of less than 100% is one indication that TCE degradation had occurred within the experimental apparatus. However, accounting for the amount of missing TCE with the amount of degradation products detected (i.e., mass balance) provides a greater level of confidence to conclude that TCE had been degraded as opposed to lost from the experimental apparatus via a gas leak or condensed in fittings and not recovered. The amount of each TCE degradation product detected is presented in Sections 3.6.2.2 through 3.6.2.5 and the balance between the missing amount of TCE

from each experimental temperature and the amount of degradation products detected is provided in Section 3.6.2.6.

3.6.2.2 Compounds in the DCM Trap

The carrier gas leaving the quartz tube apparatus (i.e., the effluent) passed through an ice cooled, 40 mL vial filled with dichloromethane (DCM) to trap condensable TCE degradation products that were soluble in DCM. These products were expected to include PCE, CCl_4, hexachlorobutadiene, and hexachlorobenzene based on the results of the first four preliminary flow-through experiments and work by Yasuhara and Morita (1990) presented in Section 2.4.5. Samples from the DCM trap for each experimental temperature were initially analyzed by GC/FID and TCE was the only compound detected in the DCM trap for the 120 and 240^{o}C experiments regardless of carrier gas or quartz tube water content. Thus no degradation products were detected in the DCM trap for quartz tube temperatures below 240^{o}C in the fifth flow-through experiment.

The chromatograms from the analysis of DCM trap samples from each 420^{o}C experiment with nitrogen as the carrier gas contained up to four unidentified peaks in addition to the peak for TCE. The GC/MS analysis of samples from each DCM trap showed that in addition to TCE, up to four other compounds were present in the DCM trap liquid including titanium tetrachloride ($TiCl_4$), pentachlorobutadiene (C_4HCl_5), hexachlorobutadiene (C_4Cl_6), and pentachlorobenzene (C_6HCl_5). These compounds are thought to represent TCE degradation products since no other organic compounds were detected in the DCM rinse of the quartz tube apparatus prior to introducing TCE.

Table 3.5: Concentration (ppmv) of Compounds Detected in the DCM Trap for the 420°C Experiments with **Nitrogen** as the Carrier Gas			
Inlet Temperature (°C)	22	60	100
TCE[a]	24,010±491[b]	24,517±397	25,992±501
titanium tetrachloride ($TiCl_4$)	864±37	524±30	186±26
pentachlorobutadiene (C_4HCl_5)	395±7.0	305±5.0	175±3.0
hexachlorobutadiene (C_4Cl_6) *	14±0.0	5±0.3	1<
pentachlorobenzene (C_6HCl_5)	22±0.4	1<	1<
Total	24,571	24,905	26,192

Values reported as **ppmv** in the quartz tube (mL gas phase compound÷30 min×4.3 min÷500 mL).
[a]Amount determined using calibration solutions. Amount of other compounds was estimated.
[b]Analytical variability: standard deviation based on three samples.

The gas phase concentration (ppmv or uL/L gas) for each compound detected in the DCM trap is reported in Table 3.5 and was calculated using the ideal gas law to convert the amount of each compound detected [i.e., the number of moles (n)] into a gas phase volume at 25°C and 1 atm (V = n×82.06×298.15÷1). The calculated volume of gas for each compound was normalized to the duration of TCE injection (30 minutes) and the gas residence time (4.3 minutes) in the quartz tube (500 mL). The value is intended to represent the concentration of each compound that would be measured in a gas sample collected from the quartz tube during TCE injection. The purpose of reporting the results as gas phase concentrations is to gain insight into conditions during thermal remediation where these compounds are anticipated to be present in the gas phase. Thus TCE would be the dominant compound present (>97% by volume) with relatively minor amounts (<1% by volume) of penta- and hexachlorobutadiene, and pentachlorobenzene in a subsurface volume contaminated with TCE that was heated to 420°C and was devoid of oxygen.

The amount of pentachlorobutadiene and pentachlorobenzene shown in Table 3.5 were estimated using a GC/FID response factor of 3.0 (concentration of compound/chromatogram area). This response factor was justified by the observation that the average response factor determined using calibration solutions for TCE, PCE, hexachloroethane, and hexachlorobutadiene was 3.01±0.41.

Water was introduced into the apparatus in effort to decrease the Cl/H ratio which was anticipated to result in the formation of less chlorinated TCE degradation products. Increasing the quartz tube water content led to a decrease in the number and amount of degradation products detected (Table 3.5) that was also matched with an increase in TCE recovery (Table 3.3, r^2=0.994 and P-Value=0.05). Thus increasing the amount of water in the apparatus at 420^{o}C with nitrogen as the carrier gas did not shift the TCE degradation products toward less chlorinated compounds, but had the effect of decreasing the amount of TCE degraded based on the DCM trap results.

Titanium tetrachloride was detected in all three experiments performed at 420^{o}C without oxygen present and the amount of titanium tetrachloride was estimated using the response factor that was determined for CCl_4. Titanium tetrachloride was thought to form due to a reaction between the gas phase chlorine from the degradation of TCE and titanium in the 316-SS Cajon connectors. Since the Cajon connectors are located outside of the tube oven (Figure 3.1), the detection of $TiCl_4$ potentially means that TCE, or reactive intermediates formed during the degradation of TCE, was able to travel outside the heated zone (420^{o}C) and react with the steel connectors.

Table 3.6: Concentration (ppmv) of Compounds Detected in the DCM Trap for the 420°C Experiments with **Air** as the Carrier Gas				
Inlet Temperature (°C)	22 I	22 II	60	100
*TCE	15,339±1,395[a]	13,709±1,722	14,474±1,450	13,568±1,442
Unknown (reported as $C_2H_4Cl_2$)	675±128	854±54	683±45	95±25
*chloroform ($CHCl_3$)	276±12	257±3	209±9	205±5
*carbon tetrachloride (CCl_4)	1,639±52	1,145±54	984±41	281±34
*tetrachloroethylene (C_2Cl_4)	822±26	829±35	863±17	365±18
trichloroacetic acid methyl ester ($Cl_3C_2O_2CH_3$)	34±2	37±1	1<	1<
tetrachloropropene ($C_3H_2Cl_4$)	19±1	18±1	19±0	21±1
pentachlorocyclopropane (C_3HCl_5)	93±5	109±3	110±0	27±1
perchlorocyclobutenone (C_4Cl_4O)	30±2	39±5	52±2	24±1
*hexachloroethane (C_2Cl_6)	226±8	288±5	261±1	81±1
tetrachlorobutadiene ($C_4H_2Cl_4$)	92±5	97±3	102±1	44±1
titanium tetrachloride ($TiCl_4$)	1<	1<	1<	1<
pentachlorobutadiene (C_4HCl_5)	38±2	33±1	35±0	42±2
hexachloropropene (C_3Cl_6)	30±0	28±1	24±1	6±0
*hexachlorobutadiene (C_4Cl_6)	65±4	69±3	57±0	18±1
hexachlorobutene (C_4Cl_6)	7±0	11±0	12±0	1<
pentachlorobenzene (C_6HCl_5)	1<	1<	1<	1<
Total	19,386	17,523	17,883	14,777

Values reported as **ppmv** in the quartz tube (mL gas phase compound÷30 min×4.3 min÷500 mL)
*Amount determined using calibration solutions. Amount of other compounds was estimated.
[a]Analytical variability: standard deviation based on three samples.

With air as the carrier gas, there were up to 14 peaks in the GC/FID chromatograms, in addition to the peak for TCE, from the analysis of DCM trap samples after the 420°C experiments. The identity of the compounds associated with the unknown GC/FID peaks were determined by GC/MS analysis (Table 3.6) with the exception of the peak with retention time of 2.05 minutes which could not be identified due to interference from DCM co-elution. The compound with retention time of 2.05 minutes may have been dichloroethane ($C_2H_4Cl_2$) based on the elution order for a test mix of chlorinated solvents

available in the chromatogram library from Supleco. The concentration of chloroform, CCl_4, PCE, hexachloroethane, hexachlorobutadiene, and hexachlorobenzene were determined using calibration solutions prepared from A.C.S. grade, high purity reagents (Sigma-Aldrich, Inc., Milwaukee, WI). The concentrations of other compounds were estimated using a response factor of 3 as with the results shown in Table 3.5.

Two experiments were completed with the inlet at 22^{o}C (22 I and 22 II) with air as the carrier gas and the quartz tube operated at 420^{o}C. The 22 II experiment was completed with the addition of an aniline trap located in-line after the effluent DCM trap to determine the amount of phosgene leaving the quartz tube. Although the two experiments (22 I and 22 II) could be considered replicates, the addition of the aniline trap resulted in a pressure increase within the quartz tube from 1.058±0.001 to 1.072±0.013 bar. Based on the results shown in Table 3.6, a gas sample collected from the quartz tube at 420^{o}C with air as the carrier gas would primarily contain TCE (>80% by volume). The gas sample would also contain significant amounts of CCl_4 (2 to 8% by volume), PCE (2.5 to 5% by volume), hexachloroethane (0.5 to 2% by volume), and chloroform (~1.5% by volume).

Increasing the water content in the quartz tube apparatus operated at 420^{o}C with air as the carrier gas did not affect the amount of TCE degraded (r^2<0.5 and P-Value>0.5) in contrast to the result with nitrogen as the carrier gas. There was a decrease in some of the chlorinated TCE degradation products with increasing water content: most notably CCl_4 and hexachloroethane. However, non-chlorinated TCE degradation products such as ethane (C_2H_6) were not detected in the DCM trap, which were expected due to the decrease in Cl/H ratio with the addition of water. Thus increasing the water content of the

apparatus did not result in a shift from chlorinated to non-chlorinated TCE degradation products based on the DCM trap analysis. Water did, however, have an effect on the amounts of other TCE degradation products as detailed in the following sections.

3.6.2.3 Compounds in the Tedlar Bag

The entire volume of carrier gas that passed through the experimental apparatus during each trial was collected in Tedlar bags. The gas was collected after passing through the ice-cooled DCM trap and aniline trap, when used. The purpose of collecting the gas phase leaving the quartz tube was to determine TCE degradation products that were not retained within the DCM trap. The degradation products were expected to include CO, CO_2, and phosgene ($COCl_2$) based on past experimental results as described in Section 2.4.7.

Table 3.7: Concentration of Compounds Detected in the Tedlar Bag and Phosgene Trap for the 420°C Experiments with **Air** as the Carrier Gas

Inlet Temperature (°C)	CO (uL/L)	CO_2 (uL/L)	Phosgene (uL/L)	
			gravimetrically	UV 254
22 I	8640	2120	NA	NA
22 II	8712	1755	7964	1067
60	9410	2285	929	836
100	8846	4395	15	345

The amount of CO and CO_2 formed was determined by GC/TCD analysis of a 60 mL gas sample from each 1.6 L Tedlar bag. Carbon monoxide (CO) and CO_2 were detected only after passing TCE through the quartz tube heated to 420°C with air as the carrier gas (Table 3.7).

A 250 uL gas sample from the Teldar bag was collected during the 420°C experiment with inlet temperature of 22°C (i.e., 22 I) and was analyzed by GC/MS. The presence of phosgene ($COCl_2$) was identified by mass spectrum match with the NIST98 library. An aniline trap was added to determine the amount of phosgene formed as per EPA method TO-6 (U.S. EPA, 1999) and the experiment was repeated (i.e., 22 II). The amount of phosgene formed was determined gravimetrically and by determining the concentration of carbanilide formed (see Section 3.6.1.3). The volume of phosgene was calculated at 25°C and 1 atm using the ideal gas law ($V = n \times 82.06 \times 298.15 \div 1$) based on the moles (n) of phosgene detected and the gas phase phosgene concentration is reported in Table 3.7 for a 1.6 L volume.

The aniline trap was used for experiments completed at 420°C with air as the carrier gas to evaluate the effect of increasing water content on the amount of phosgene detected. Phosgene concentrations were found to decrease with increasing quartz-tube water content (Table 3.7). However, the compound formed after passing the quartz tube effluent through the aniline trap may not have been due to phosgene alone. For example, O'Mara et al. (1971) found that gas phase HCl formed during the combustion of vinyl chloride caused aniline to polymerize in a liquid trap and form a compound that had a UV absorbance of 254 nm which interfered with the detection of phosgene. While the concentration of HCl in the quartz tube effluent was not determined, the amount of chloride found in the water rinse (Section 3.6.2.4, Figure 3.9) suggests that gas phase HCl was present in the quartz tube effluent. Thus the decrease in phosgene concentration with increase in quartz tube water content shown in Table 3.7 may have been due to phosgene

hydrolysis alone, or may represent a reduction in effluent HCl concentration along with phosgene hydrolysis.

Table 3.8: Change in the Amount of CO_2 and Phosgene Detected with Increase in Water Content for the 420°C Experiments with **Air** as the Carrier Gas

Inlet Temperature (°C)	CO_2 (mmol)	CO_2 Gain $CO_2 - CO_2$ (22II)	Phosgene (mmol)	
			gravimetrically	UV 254
22 I	0.28	-0.05	NA	NA
22 II	0.23	0.00	0.52	0.07
60	0.30	0.07	0.06	0.05
100	0.58	0.35	0.00	0.02

NA – not analyzed.

Phosgene is reported to react with water to yield CO_2 according to (Ryan et al., 1996):

$$COCl_2 + H_2O \rightarrow CO_2 + 2HCl \quad (3.2)$$

There was an increase in the amount of CO_2 with increase in quartz tube water content while the concentration of CO in the effluent (8,902±349 ppmv) and TCE recovery remained consistent implying a shift in degradation product distribution with phosgene being converted to CO_2 as expected according to Equation 3.2. Table 3.8 contains the moles of CO_2 and phosgene formed along with the difference between the amount of CO_2 found with the inlet at 22°C (22 II), at 60°C, and at 100°C. The amount of CO_2 gained with increase in quartz tube water content (CO_2 Gain, Table 3.8) was approximately 33% of the amount of phosgene lost between the inlet temperatures of 22°C and 100°C based on the phosgene gravimetric analysis, but was 6 times greater than the amount of phosgene lost based on the UV 254 analysis. The gravimetric analysis results suggesting

that the increase in CO_2 was primarily due to phosgene hydrolysis. However, the UV 254 analysis results suggest that not all the solids formed in the aniline trap represented carbanilide or phosgene.

3.6.2.4 Compounds in the Water Rinse

Approximately 30 mL of freshly dispensed DI water was used to rinse the quartz tube apparatus after cooling to room temperature (22°C). The water rinse was performed to determine the water-soluble TCE degradation products formed after passing TCE through the heated quartz tube. The expected degradation products included chloride due to the loss of chlorine atoms from TCE (i.e., dechlorination) and haloacetic acids such as dichlororacetate based on the past experimental work described in Section 2.4.2.

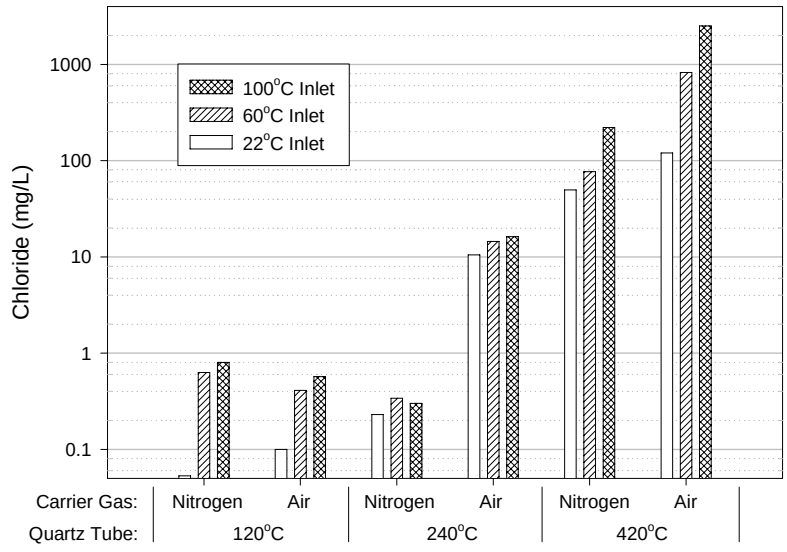

Figure 3.9: Concentration of chloride in the water rinse completed after each temperature trial for the fifth flow-through experiment.

The concentration of chloride in the water rinse as a function of quartz tube temperature, carrier gas, and inlet temperature (water content) is shown in Figure 3.9. Chloride was detected in the water rinse from each isothermal experiment regardless of carrier gas used. This result potentially indicates that TCE was degraded, to some degree, in all the quartz tube experiments performed in the fifth flow-through experiment. The concentration of chloride in the 120^{o}C experiment with the inlet temperature at 22^{o}C and nitrogen as the carrier gas was 0.05 mg/L which was below the method detection limit (MDL) of 0.06 mg/L and the concentration of chloride with air as the carrier gas was 0.10 mg/L with a MDL of 0.05 mg/L; all other chloride concentrations were at least an order-of-magnitude above their MDL. The concentration of chloride increased with increasing quartz tube water content (i.e., inlet temperature), even for experiments completed at the lowest quartz tube temperature of 120^{o}C where TCE recovery was greater than 94% (Figure 3.8) and no TCE degradation products were detected in the DCM trap. The amount of chloride measured in the 240 and 420^{o}C experiments with air as the carrier gas was greater than the amount of chloride detected in experiments with nitrogen as the carrier gas which was consistent with the lower TCE recovery noted in Figure 3.6 with air as the carrier gas. The concentration of chloride was greatest in the water rinse after the 420^{o}C experiments which also had the lowest TCE recovery and greatest number of TCE degradation products detected in the DCM trap.

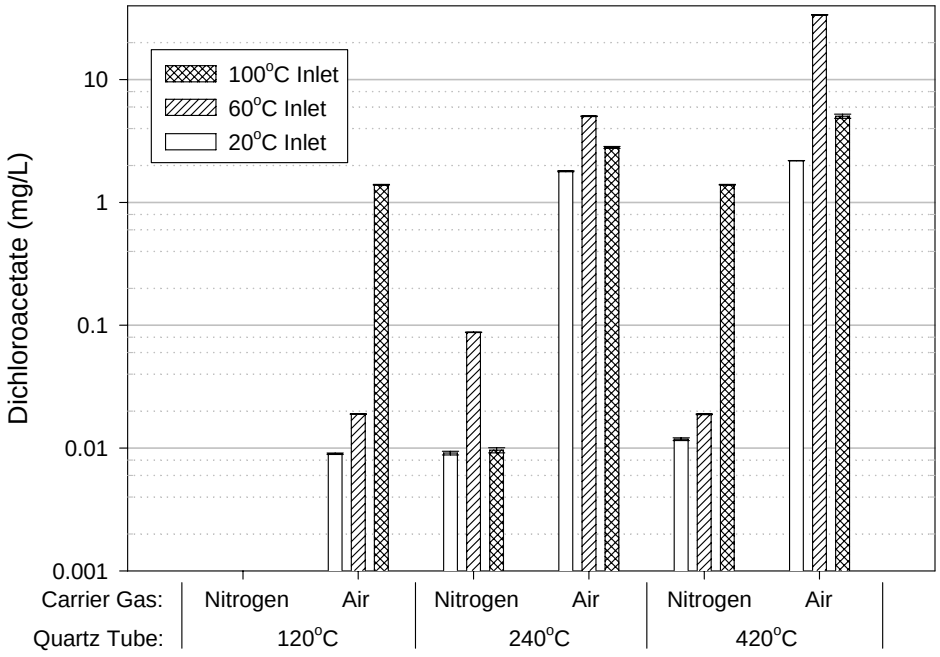

Figure 3.10: Concentration of dichloroacetate in the water rinse completed after each temperature trial for the fifth flow-through experiment.

The dichloroacetate ($Cl_2HC_2OO^-$) concentration as a function of quartz tube temperature, carrier gas, and inlet temperature (water content) is shown in Figure 3.10. As mentioned in Section 2.4.2, DCAA has been classified as a probable human carcinogen with a practical drinking water treatment level of 0.06 mg/L. No haloacetic acids (e.g., dichloroacetate) were detected in the water used to rinse the quartz tube operated at 120°C with nitrogen as the carrier gas and the minimum concentration of DCAA detected with air as the carrier gas was 0.009 mg/L which was near the MDL of 0.005 mg/L. The concentration of dichloroacetate (DCAA) measured with air as the carrier gas was greater than the concentration of DCAA detected in experiments completed with nitrogen as the carrier gas.

Table 3.9: Concentration of Haloacetic Acids in the Water Rinse from the 240°C and 420°C Experiments with **Air** as the Carrier Gas				
Inlet Temperature (°C)	Quartz Tube Temperature (°C) – Air as Carrier Gas			
	240		420	
	DCAA (mg/L)	TCAA (mg/L)[a]	DCAA (mg/L)	TCAA (mg/L)
20	1.79±0.01[b]	1.29	2.20±0.003	10.16
60	5.04±0.03	2.85	33.67±0.06	31.61
100	2.80±0.05	1.52	5.04±0.2	20.33
[a]TCAA concentration estimated based on ratio of TCAA to DCAA chromatogram peak area. [b]Analytical variability: standard deviation based on three samples.				

Trichloroacetate ($Cl_3C_2COO^-$) was also detected in the water rinse from the quartz tube operated at 240 and 420°C with air as the carrier gas (Table 3.9) whereas no trichloroacetate (TCAA) was detected in experiments with nitrogen as the carrier gas. TCAA was identified by mass spectrum match with the NIST02 library after GC/MSD analysis and the concentration of TCAA was estimated based on the ratio of chromatogram peak areas between DCAA and TCAA along with the concentration of DCAA that was determined using calibration solutions. The concentration of TCAA was similar to DCAA for the 240°C experiments and the concentration of TCAA exceeded the DCAA concentration for the 420°C experiments with inlet temperature of 22 and 100°C. The water rinse from each 420°C experiment with air as the carrier gas had a pale yellow color and a strong solvent odor while the water rinse with nitrogen as the carrier gas was clear.

After processing the water rinses for haloacetic acid analysis, the MTBE extract was analyzed by GC/MSD which revealed the presence of additional chlorinated compounds (Table 3.10). Each compound was identified by mass spectrum match with the NIST02 library and the concentration of each compound was estimated based on the

ratio of chromatogram peak area to the peak area for DCAA. The estimated concentration of hexachlorobenzene in the water rinse was at least an order-of-magnitude greater than the reported aqueous solubility limit of 0.008 mg/L (Schwarzenbach et al., 2003) while the estimated pentachlorobenzene concentration was close to the reported aqueous solubility limit of 0.66 mg/L (Schwarzenbach et al., 2003). The estimated hexachlorobenzene concentration may have been in excess since it was greater than its reported aqueous solubility limit while the estimated pentachlorobenzene concentration appears reasonable since it is within an order-of-magnitude of its reported aqueous solubility limit.

Table 3.10: Estimated Concentration (mg/L) of Compounds in Water Rinse from 420°C Experiment with **Air** as the Carrier Gas

Compound	Water Solubility (mg/L) at 20°C	Inlet Temperature (°C)			
		22 I	22 II	60	100
tetachloroethylene (C_2Cl_4)	141.1	nd	nd	1.34	2.94
1,1,2,2-tetrachloroethane ($C_2Cl_4H_2$)	3274	nd	nd	nd	0.52
hexachloroethane (C_2Cl_6)	49.5	nd	nd	0.57	nd
3,4-dichloro-3-butene-2-one ($C_4Cl_2OH_4$)	unknown	1.44	0.51	6.25	58.77
pentachlorobutadiene (C_4Cl_5H)	unknown	0.58	0.84	0.57	0.63
hexachlorobutadiene (C_4Cl_6)	2	nd	nd	0.27	nd
pentachloro-1-propene (C_3Cl_5)	unknown	2.81	nd	0.98	nd
hexachlorobutene ($C_4Cl_6H_2$)	unknown	nd	4.56	6.40	1.00
pentachlorobenzene (C_6Cl_5H)	0.66	0.58	0.92	1.85	1.30
hexachlorobenzene (C_6Cl_6)	0.008	nd	0.21	0.72	0.14
tetrachloro-1,3-cyclopentadiene-5-dichloromethylene (C_6Cl_6)	unknown	nd	1.49	0.37	nd

Water solubility from Schwarzenbach et al., 2003 except for hexachlorobutadiene (Booker and Pavlostathis, 2000).
nd – not detected in the chromatogram.

Based on the results shown in Figures 3.9 and 3.10, a water sample collected from the quartz tube at 240^{o}C and 420^{o}C with nitrogen as the carrier gas would contain chloride and dichloroacetric acid (DCAA). With air as the carrier gas, a water sample collected from the quartz tube operated at 240^{o}C would contain DCAA and TCAA (Table 3.9) and a water sample from the quartz tube at 420^{o}C would contain the chlorinated hydrocarbons pentachlorobutadiene, hexachlorobutene, and pentachlorobenzene (Table 3.10) in addition to DCAA and TCAA.

3.6.2.5 Compounds in the Iso-Octane Rinse

The DI water rinse was immediately followed by rinsing the sealed apparatus with approximately 30 mL of iso-octane for period of 5 minutes. The iso-octance rinse was performed to determine the organic TCE degradation products that had condensed within the experimental apparatus while passing TCE through the heated quartz tube. The expected degradation products included hexachlorobutadiene and hexachlorobenzene based on the past experimental work described in Section 2.4.5.

The iso-octane rinse samples were initially analyzed by GC/MS to identify the TCE degradation products present whereas the concentration of each product in each iso-octane rinse was determined by GC/FID analysis. No TCE degradation products were detected in the iso-octane rinse for the 120 and 240^{o}C experiments regardless of carrier gas or water content.

There were up to three products detected in the 420^{o}C experiment with nitrogen as the carrier gas with the mass (mg) of each compound detected reported per mass (kg) of dry soil in Table 3.11. The concentration of each degradation product was calculated assuming that the quartz tube was filled with 500 mL of dry soil with bulk density of 1.6

g/mL. Note: no solids were present in these experiments. Reporting this theoretical value is intended to represent the maximum concentration of each compound that would be measured if soil were present in the quartz tube during the experiment. The purpose of reporting the results as soil phase concentrations is to gain insight into post thermal remediation conditions where these compounds are anticipated to condense onto soils.

Table 3.11: Concentration (mg/kg) of Compounds in the Iso-Octane Rinse from the 420°C Experiments with **Nitrogen** as the Carrier Gas

Inlet Temperature (°C)	22	60	100
hexachlorobutadiene (C_4Cl_6)	0.04<	0.04<	0.04<
hexachlorobutene (C_4Cl_6)	0.04<	0.04<	0.04<
pentachlorobenzene (C_6Cl_5H)	0.23±0.00[a]	0.04<	0.04<
heptachlorocyclohexane ($C_6H_5Cl_7$)	0.22±0.00	0.04<	0.04<
hexachlorobenzene (C_6Cl_6)	1.77±0.01	0.56±0.01	0.04<

Values reported as **mg/kg** assuming the quartz tube was full of soil with dry bulk density of 1.6 g/mL.
[a]Analytical variability: standard deviation based on analysis of three samples.

For example, hexachlorobenzene would be the dominant compound present in a TCE contaminated subsurface volume with low moisture and oxygen content after heating to 420°C based on the results in Table 3.11. Increasing the quartz tube water content (i.e., inlet temperature) led to a decrease in the number and amount of degradation products detected with nitrogen as the carrier gas which was matched by an increase in TCE recovery (r^2=0.994, Table 3.3). There were no degradation products detected by GC/FID analysis in the iso-octane rinse of the 420°C experiment with the inlet temperature at 100°C which represented the maximum water content for the fifth flow-through experiment.

There were up to five compounds detected in the 420°C experiments with air as the carrier gas (Table 3.12). Hexachlorobutadiene and hexachlorobutene were detected in addition to penta- and hexachlorobenzene in the iso-octane rinse for the inlet temperature of 22°C. An iso-octane rinse of the experiment with the inlet at 60°C was collected in a 40 mL glass vial and placed in a 4°C chamber for storage. The vial was found to have been broken during storage and the iso-octane rinse was lost and thus no analysis result is reported for this inlet temperature. Although increasing the water content of the quartz tube at 420°C with air as the carrier gas did reduce the concentration of compounds detected in the iso-octane rinse, penta- and hexachlorobenzene were detected in the iso-octane rinse with the inlet at 100°C. These compounds were also detected in the MTBE extract of the water rinse (Table 3.10) that was completed prior to the iso-octane rinse for the 420°C experiment with air as the carrier gas.

Table 3.12: Concentration (mg/kg) of Compounds in the Iso-Octane Rinse from the 420°C Experiments with **Air** as the Carrier Gas

Inlet Temperature (°C)	22 I	22 II	60	100
hexachlorobutadiene (C_4Cl_6)	0.22	0.15±0.00[a]	NA	0.04<
hexachlorobutene (C_4Cl_6)	0.51±0.01	0.41±0.00	NA	0.04<
pentachlorobenzene (C_6Cl_5H)	0.29±0.01	0.23±0.00	NA	0.20±0.01
heptachlorocyclohexane ($C_6H_5Cl_7$)	0.04<	0.04<	NA	0.04<
hexachlorobenzene (C_6Cl_6)	1.51±0.03	1.49±0.01	NA	0.55±0.01

Values reported as **mg/kg** assuming the quartz tube was full of soil with dry bulk density of 1.6 g/mL.
NA – not analyzed, sample broken during storage.
[a]Analytical variability: standard deviation based on analysis of three samples.

Based on the results in Table 3.11 and 3.12, hexachlorobenzene is expected to be the dominant compound present in a TCE contaminated subsurface volume heated to

420°C and increasing the amount of water vapor entering the heated soil would decrease the amount of TCE degradation products formed.

3.6.2.6 Mass Balance

The amount of TCE as moles of carbon (moles carbon = 2 × moles TCE) detected in the DCM trap with respect to the moles of TCE as carbon that were introduced into the experimental apparatus operated at 420°C with nitrogen as the carrier gas is provided in Table 3.13 as "%Carbon in Feed." Similarly, the amount of TCE recovered as moles of chlorine (moles chlorine = 3 × moles TCE) with respect to the moles of TCE as chlorine introduced into the apparatus is also provided in Table 3.13 as "%Chlorine in Feed."

Table 3.13: Distribution of Carbon and Chlorine for the 420°C Experiments with **Nitrogen** as the Carrier Gas

Inlet Temperature (°C) or Water Content		22	60	100	22	60	100
Phase	Compound	%**Carbon** in Feed			%**Chlorine** in Feed		
Compounds in DCM Trap	TCE	93.1±1.9[a]	95.5±1.5	99.1±1.9	93.1±1.9	95.5±1.5	99.1±1.9
	All Other	3.4±0.1	2.4±0.0	1.3±0.0	7.3±0.2	4.7±0.2	1.1±0.0
Compounds in Gas Phase	CO/CO_2	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4
Condensed in Quartz Tube	Water + Iso-Octane Rinses	0.5±0.0	0.1±0.0	0.0±0.0	0.8±0.1	0.9±0.1	2.2±0.3
Net Recovery		97.1±1.9	98.1±1.5	100.4±1.9	101.2±1.9	101.1±1.6	102.4±1.9

[a]Propagated analytical variability: propagated as the square root of the sum of squared standard deviations.

The amount of TCE degradation products detected in the DCM trap and quartz tube rinses are also reported in Table 3.13 as moles of carbon and chlorine with respect to the amount of carbon and chlorine delivered to the quartz tube apparatus as TCE. The purpose of reporting the amount of carbon or chlorine detected is to show the distribution of each TCE degradation product in the apparatus and to determine if all the carbon and

chlorine atoms were accounted for (i.e., mass balance). For example, while 93.1% of the carbon delivered during the experiment with the inlet at 22°C was detected in the DCM trap as TCE (Table 3.13), 3.4% of the carbon delivered was detected in the DCM trap as TCE degradation products that were presented in Table 3.5, and 0.5% of the carbon delivered was detected in the quartz tube rinses as TCE degradation products as listed in Table 3.11. Thus, the net recovery of TCE introduced with the inlet at 22°C increased from 93.1% when TCE recovery alone was considered to 97.1% on a carbon basis and 101.2% on a chlorine basis when the TCE degradation products were included.

TCE was the predominant (>93%) compound detected in the DCM trap and there were more chlorinated TCE degradation products condensed within the DCM trap than found in the water or iso-octane rinses of the 420°C experiments with nitrogen as the carrier gas. Increasing the quartz-tube water content resulted in a decrease in the amount of TCE degradation products in the DCM trap while the amount of chloride found in the water rinse increased. Overall, there was good recovery of TCE on a carbon (>97%) and chlorine (>100%) basis in the 420°C experiments with nitrogen as the carrier gas.

The distribution of carbon and chlorine in the experimental apparatus operated at 420°C with air as the carrier gas is provided in Table 3.14. For the experiment with inlet temperature of 22°C, 18.4% of the carbon introduced as TCE was converted to CO and CO_2 while 20.2% consisted of chlorinated hydrocarbons detected in the DCM trap and as phosgene. Increasing the quartz tube water content resulted in a decrease in the amount of chlorinated carbon compounds in the DCM trap from 13.2 to 3.2% as carbon and from 20.3 to 4.9% on a chlorine basis. The decrease in chlorinated compounds was matched with an increase in the amount of CO and CO_2 from 18.4 to 23.2% on a carbon basis. The

increase in chlorine content of the water and iso-octane rinses from 2.0 to 17.8% on a chlorine basis was primarily due to the increase in chloride found in the water rinse.

Table 3.14: Distribution of Carbon and Chlorine for the 420°C Experiments with **Air** as the Carrier Gas

Inlet Temperature (°C) or Water Content		22 II	60	100	22 II	60	100
Phase	Compound	%**Carbon** in Feed			%**Chlorine** in Feed		
Compounds in DCM Trap	TCE	52.4±1.2[a]	54.6±0.2	51.7±0.9	52.4±1.2	54.6±0.2	51.7±0.9
	All Other	13.2±0.3	11.9±0.2	3.2±0.1	20.3±0.4	18.0±0.3	4.9±0.1
Compounds in Gas Phase	CO/CO_2	18.4	20.3	23.2	0.0	0.0	0.0
	Phosgene	7.0	0.8	0.0	14.0	1.1	0.0
Condensed in Quartz Tube	Water + Iso-Octane Rinses	0.6±0.0	0.6±0.0	1.0±0.0	2.0±0.0	6.7±0.4	17.8±1.8
Net Recovery		91.5±1.2	88.1±0.3	79.1±0.9	88.8±1.3	80.5±0.5	74.6±2.0

[a]Propagated analytical variability: propagated as the square root of the sum of squared standard deviations.

The net recovery of carbon and chlorine decreased from 91.5 to 79.1% on a carbon basis and from 88.8 to 74.6% on a chlorine basis with increasing quartz tube water content for the 420°C experiments with air as the carrier gas (Table 3.14). The amount of missing carbon and chlorine were nearly equal, therefore, the missing compounds could have consisted of chlorinated hydrocarbons. It is suspected that the missing chlorinated hydrocarbons were present in the Tedlar bag and went undetected during the GC/TCD analysis for CO/CO_2 content due adsorption on the Carboxen 1010 capillary column. The lack of 100% mass balance and uncertainty in the phosgene analysis led to completion of the sixth flow-through experiment described in the following sections.

3.7 TCE Degradation in a Quartz Tube Heated to 120, 240, 380, 420, and 800°C with Increasing Water Vapor Content (Sixth Flow-Through Experiment)

The sixth flow-through experiment was designed based on the results of the fifth flow-through experiment with the goal of closing the mass balance for experiments with air as the carrier gas. Experiments were completed at temperatures of 120, 240, 380, and 420°C as a function of quartz tube water vapor content. Two additional experiments were completed at 800°C, without water, to determine the products formed at the maximum temperature reportedly used during in situ thermal conductive heating.

3.7.1 Sixth Flow-Through Experiment Methods

As with the fifth flow-through experiment, the residence time through the quartz tube was fixed at approximately 4.3 minutes for all experimental temperatures used during the sixth flow-through experiment. This represented a gas flow rate of approximately 85 mL/min (at 22°C) with the empty quartz tube at 120°C, 65 mL/min (at 22°C) for the empty quartz tube at 240°C, 51 mL/min (at 22°C) with the quartz tube at 380°C, 48 mL/min (at 22°C) with the quartz tube at 420°C, and 31 mL/min for the quartz tube at 800°C.

The analysis of CO and CO_2 was completed using a GC with equipped with a custom made methanizer that converted CO and CO_2 into methane for analysis using a flame ionization detector (FID). The methanizer was built by loading a 1/16 OD 316-SS tube with 100 mesh nickel powder (Sigma-Aldrich, Milwaukee, WI) and installing the tube into a housing that contained a cartridge heater (McMaster-Carr, Atlanta, GA). The methanizer was heated to 420°C and hydrogen was used as the capillary column carrier gas for the catalytic reduction of CO and CO_2 to methane (CH_4) by the nickel within the

methanizer. This technique achieved a detection limit of 16 uL/L (ppmv) for CO and 37 uL/L for CO_2, which decreased the detection limit by an order-of-magnitude as compared the GC/TCD method employed in the fifth flow-through experiment described in Section 3.6.1.3.

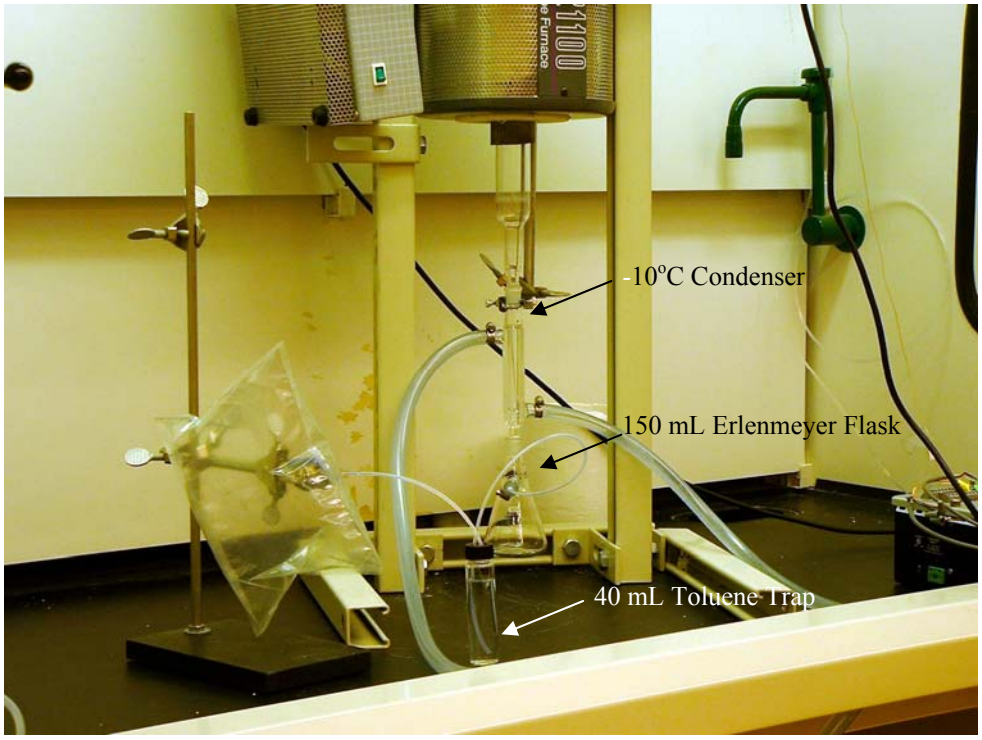

Figure 3.11: Picture of the two stage cold trap used during the sixth flow-through experiment.

The most significant change in the methods used for the sixth flow-through experiment involved replacing the DCM trap with a two stage cold-trap that was connected to a 40 mL vial filled with toluene in effort to trap phosgene for direct GC/ECD analysis (Figure 3.11). The cold trap was used to eliminate DCM which co-elutes with some of the TCE degradation products during GC analysis thereby limiting quantification of all degradation products and potentially impacting the mass balance.

The cold trap also facilitated using toluene as a trap fluid by isolating the potentially explosive toluene vapors from the heated quartz tube.

The cold-trap consisted of two stages: the first stage was maintained at -10°C and the second stage at -78°C. The first stage of the cold trap consisted of a 10 cm long by 1 cm ID jacketed short-path condenser that was cooled to -10°C by pumping a 1:1 (by volume) mixture of water and ethylene glycol through the jacket using a recirculation bath. The second stage of the cold trap was a 150 mL Erlenmeyer vacuum flask with aspirator that was place in an insulated container filled with crushed dry ice. The temperature within the Erlenmeyer flask was -78°C, measured by a K-type thermocouple placed into the flask after 15 minutes of cooling. This two stage cold-trap was expected to

Table 3.15: Melting and Boiling Point Temperatures for Select TCE Degradation Products
(data from Linstrom and Mallard, 2005)

Compound	Melting Temperature (°C)	Boiling Temperature (°C)
Phosgene	-128	8
Dichloroacetylene	-126	NA
toluene	-95	111
TCE	-85	87
Chloroform	-63	61
CCl_4	-23	77
PCE	-23	121
Hexachlorobutene	11	NA
Hexachloroethane	185	185 (sublimes)
Dichloroacetic acid	11	194
Hexachlorobutadiene	NA	215
hexachlorobenzene	227	325

NA – not available

retain compounds with a melting temperature of greater than -78°C such as chloroform, carbon tetrachloride (CCl_4), and PCE (Table 3.15). Phosgene was expected to pass through the cold trap necessitating additional collection measures. A 40 mL vial was filled with approximately 30 mL of toluene (Optima grade, Fisher Scientific, Fair Lawn, NJ) and was connected to the aspirator nipple on the Erlenmeyer flask via 1/8-inch OD Teflon tubing so that gas leaving the cold trap bubbled through the toluene before being captured in a 1.6L Tedlar bag. Toluene was chosen since phosgene is known to be soluble in toluene (Ryan et al., 1996) and because a phosgene calibration standard prepared in toluene was obtained from Sigma-Aldrich, Inc. (Milwaukee, WI).

The compounds condensed within the two-stage cold trap were collected by repeatedly rinsing the condenser and Erlenmeyer flask with fresh aliquots of toluene. The process began by disconnecting the cold trap from the quartz tube and pouring approximately 30 mL of toluene through the condenser while connected to the Erlenmeyer flask. The condenser opening was then sealed with a glass ground-joint stopper and allowed to reach room temperature (25°C). The external 40 mL toluene trap remained attached to the cold-trap to collect any compounds that were volatilized during the warming process. After reaching room temperature the toluene in the cold-trap was collected in a 100 mL volumetric flask and the cold-trap was rinsed 3 additional times with fresh toluene, which was also collected in the 100 mL flask. Samples were then collected from the 100 mL flask after filling to the volumetric mark and placed in 2 mL autosampler vials for analysis by GC methods. Separate samples were collected from the 40 mL toluene trap.

The toluene samples from the cold-trap were analyzed for TCE content using the GC/FID method described in Section 3.1.5. However, TCE calibration standards were prepared in the 3,000 to 6,000 mg/L range using toluene as the solvent and 1,2,3-trichloropropane was used as the internal standard. The samples from the cold-trap and 40 mL toluene trap were also analyzed using a GC equipped with an ECD to achieve more sensitive analysis of TCE degradation products such as phosgene. Certified calibration stock solutions were obtained from Supelco (Bellefonte, PA) for chloroform, hexachloroethane, hexachlorobutadiene, hexachlorobenzene, chloroacetate, and trichloroacetate. These stock solutions were used to prepare calibration standards in the 10 to 500 mg/L range.

3.7.2 Sixth Flow-Through Experiment Results

The amount of TCE recovered after each experimental temperature trail is provided in Table 3.16 and shown in Figure 3.12. The average recovery of TCE for the experiments completed at 120^{o}C using the cold-trap was identical (96.4±3.0) to the recovery obtained when the DCM trap was used (Table 3.4). Thus the cold trap proved to be as good at collecting TCE after it passed through the heated quartz tube as the DCM trap. The one exception was the relatively low (93.1%) TCE recovery when the inlet temperature was at 100^{o}C or the maximum water vapor content. In this case, the toluene in the 40 mL trap was pulled into the cold-trap during a carrier gas flow interruption caused by water droplets falling into the heated quartz tube. Since no toluene was in the 40 mL trap for a period of time, some TCE passed through the trap and was not collected, this is reflected in the low TCE recovery for the experiment with inlet temperature of 100^{o}C.

Table 3.16: TCE Recovery with **Air** as the Carrier Gas (Recovery = TCE in Cold-Trap ÷ TCE injected × 100%)				
Inlet Temperature (°C)	Quartz Tube Temperature (°C)			
	120	240	380	420
dry	nd	98.3±1.8	nd	nd
22	98.7±2.2[a]	97.9±0.6	81.7±2.3	61.1±1.0
60	97.5±2.2	99.7±2.2	82.6±1.1	58.7±0.3
100	93.1±1.8	102.2±1.9	91.1±1.6	84.0±1.1
Average ± Standard Deviation	96.4±3.0[b]	99.5±1.9	84.8±4.6	67.9±13.9

nd – not determined
[a]Analytical variability: standard deviation based on analysis of three samples.
[b]Experimental variability: standard deviation of TCE recovery for differing water contents.

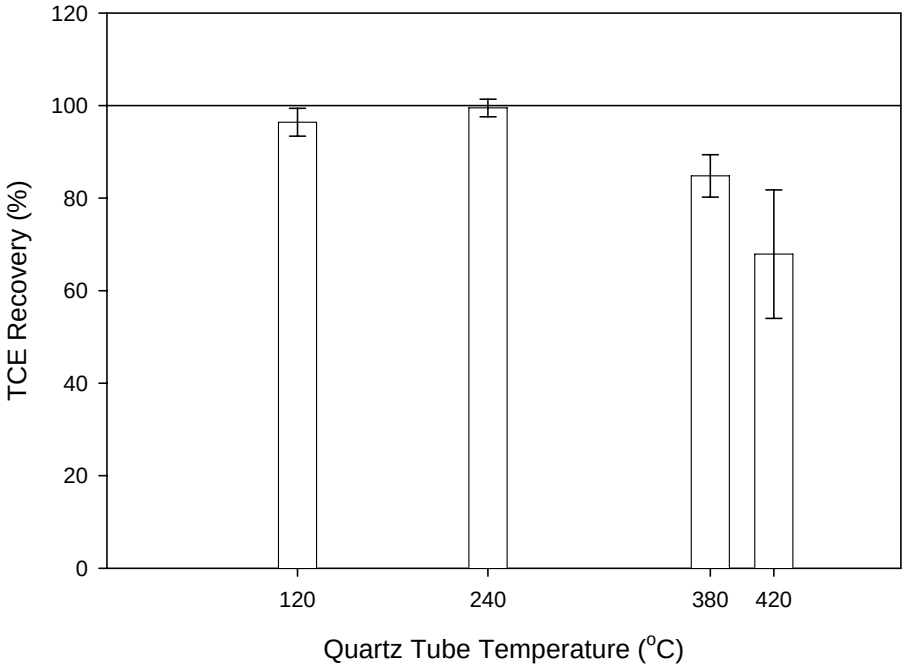

Figure 3.12: Recovery of TCE as a function of quartz tube temperature for the sixth flow-through experiment.

The average recovery of TCE in the 240°C experiments with the cold-trap improved to 99.5% which was better than the 94.1% recovery with the DCM trap (Table

3.4). The recovery of TCE also improved in the 420°C experiments with an average of 67.9% with the cold-trap as compared to the 52.9% with the DCM trap.

Table 3.17: Carbon Balance for the **380°C** Experiments with **Air** as the Carrier Gas			
Compound	Inlet Temperature (°C) or Water Content		
	22	60	100
TCE	81.7±2.3[a]	82.6±1.1	90.1±1.6
CO	6.1	5.7	2.7
Phosgene	4.0±0.1	0.6±0.0	0.2±0.0
CO_2	1.2	1.4	1.6
Hexachloroethane	0.8±0.2	1.0±0.0	0.3±0.0
PCE	0.6±0.1	0.7±0.0	0.1±0.0
Hexachlorocyclopropane	0.4±0.1	0.5±0.1	0.2±0.0
Chloroform	0.1±0.0	0.1±0.0	0.1±0.0
CCl_4	0.1±0.0	0.1±0.0	0.0±0.0
Dichloroacetate	0.02	*Lost*	0.00
Trichloroacetate	0.07	*Lost*	0.00
Net Recovery (%)	95.1±2.6	92.8±1.2	95.2±1.7
Lost – Sample lost during dervatization process due to vial failure. [a]Analytical variability: standard deviation based on analysis of three samples.			

Table 3.17 contains the compounds detected in experiments completed at 380°C with air as the carrier gas. The predominant TCE degradation products included CO, phosgene, CO_2, and hexachloroethane, on a carbon basis. The overall carbon balance was greater than 90% for each experiment completed at 380°C. The amount of TCE recovered increased from 81.7 to 90.1% with an increase in quartz tube water content from inlet temperature of 22 to 100°C. The increase in TCE recovery was matched by a decrease in the amount of TCE degradation products formed: CO decreased from 6.1 to 2.7%, phosgene from 4.0 to 0.2%, and hexachloroethane from 0.8 to 0.3%, while CO_2 levels increased from 1.2 to 1.6%.

Table 3.18: Carbon Balance for the **420°C** Experiments with **Air** as the Carrier Gas			
Compound	Inlet Temperature (°C) or Water Content		
	22	60	100
TCE	61.1±1.0[a]	58.7±0.3	84.0±1.1
CO	14.3	15.7	7.7
Phosgene	8.7±0.4	1.9±0.0	0.5±0.1
CO_2	2.6	6.0	4.0
Hexachloroethane	4.2±0.1	3.8±0.1	0.5±0.0
PCE	2.8±0.1	2.8±0.1	0.5±0.0
CCl_4	1.0±0.1	0.7±0.0	0.1±0.0
Hexachlorocyclopropane	0.6±0.0	0.5±0.1	0.2±0.0
Pentachlorobutadiene	0.4±0.0	0.4±0.0	0.1±0.0
Hexachlorobutadiene	0.4±0.0	0.4±0.0	0.1±0.0
Hexachlorobutane	0.4±0.0	0.3±0.0	0.1±0.0
Hexachlorobenzene	0.3±0.0	0.2±0.0	0.1±0.0
Chloroform	0.1±0.0	0.1±0.0	0.2±0.0
Dichloroacetate	0.02	0.04	0.00
Trichloroacetate	0.22	0.02	0.00
Net Recovery (%)	97.1±1.9	91.7±0.6	98.1±1.2
[a]Analytical variability: standard deviation based on analysis of three samples.			

Along with an increase in the recovery of TCE in the 420°C experiment, there was also better accounting of the TCE degradation products which resulted in an improvement in the mass balance (Table 3.18). The greatest net recovery of carbon reported for the 420°C experiments completed with the DCM trap was 91.5% (Table 3.14) whereas the lowest net carbon recovery in experiments completed with the cold trap was 91.7%. The improvement in carbon balance was in part due to use of the more sensitive GC/ECD for the analysis of TCE degradation products; the less sensitive GC/FID was used for the DCM trap experiments. However, the greatest change was in the increased TCE recovery in the experiment with greatest water content: the 100°C inlet

experiment. TCE recovery was 51.7% with the DCM trap and increased to 84.0% when the cold-trap was used.

The effect of increasing the water content of the quartz tube heated to 420^{o}C with air as the carrier gas resulted in an increase in TCE recovery and a decrease in the amount of phosgene, hexachloroethane, and other chlorinated compounds. These trends are similar to those found for experiments completed at 420^{o}C that used the DCM trap as reported in Table 3.14. The one difference was the decrease in CO and CO_2 levels in the experiment with inlet temperature of 100^{o}C. The combined CO/CO_2 levels decreased from 21.7% (60^{o}C inlet) to 11.7% (100^{o}C inlet) when the cold trap was used, while they increased from 20.3 to 23.2% with the DCM/Aniline trap. The cause of this difference between experimental results is unknown. The one difference between experimental systems was that with the DCM trap, most of the water introduced into the quartz tube as vapor remained in the system while with the cold trap, the vapor could exit the quartz tube and condense within the cold-trap.

Two additional experiments were completed with the quartz tube heated to 800^{o}C using air as the carrier gas. The carrier gas was not humidified as the stability of the quartz tube heated to this temperature was a concern. The initial experiment used a toluene trap in series after the cold trap; the same configuration used for the previous experiments described in this section. The only compounds detected after passing TCE through the quartz tube heated to 800^{o}C were CO_2, CO, and phosgene. No other compounds were found in the cold-trap, the toluene trap, or in the toluene rinse of the quartz tube. Unfortunately, these compounds only accounted for 77.3% of the carbon introduced as TCE (Table 3.19).

Table 3.19: Carbon Balance for the 800°C Experiments with **Air** as the Carrier Gas		
Compound	Toluene Trap	Water Trap
TCE	Not detected	Not detected
CO_2	42.0	49.8
CO	34.6	33.7
Phosgene	0.6	0.1
Net Recovery (%)	77.3	83.6

A second 800°C experiment was completed using a 40 mL vial filled with DI water in place of the toluene trap. The water trap was added in attempt to account for the chlorine liberated during TCE degradation. While the amount of CO_2 increased from 42.0 to 49.8% and the amount of phosgene decreased from 0.6 to 0.1% when the toluene trap was replaced by a water trap, the carbon balance was still not complete with 16.4% of the carbon unaccounted for. The pH of the water in the trap decreased from 7.0 to 1.20, which was expected to indicate that HCl had formed as a product of TCE degradation. However, chloride (Cl^-) was not detected in the water trap or the quartz tube rinse above the colorimetric analysis method detection limit of 0.1 mg/L (Section 3.6.1.4). The water in the trap had a characteristic order that was similar to that described for Cl_2 gas. A 1 mL gas sample collected from the Tedlar bag was injected into a GC/MS and in addition to a chromatogram peak identified as phosgene; there was another elution peak that had a mass spectrum base peak with m/z of 70, which is characteristic for the Cl_2 molecule. The location of the missing carbon is unknown at this time.

3.8 Discussion

The goal of the quartz tube experiments was to determine the identity and amount of TCE degradation products formed after exposing gas phase TCE to temperatures from 60 to 800°C. The purpose of performing these experiments was to anticipate the

compounds that may form during in situ thermal treatment of subsurface environments contaminated with TCE. These experiments were designed to simulate conditions that occur as the TCE enriched vapor (Figure 2.2) travels through the heated subsurface toward extraction wells. This vapor phase recovery is common to the three thermal treatment technologies: steam flushing, electrical conductive heating, and thermal conductive heated as described in Sections 2.3.1 through 2.3.4. The following sections contain a discussion of how the results of the experiments described in the previous sections apply to each of the three thermal remediation technologies.

3.8.1 Implications for Steam Flushing

The maximum in-situ temperatures achieved during steam flushing are not expected to exceed 140^{o}C based on the description of past technology applications provided in Section 2.3.1. At 120^{o}C, greater than 94% of the TCE introduced into the quartz tube was recovered in each of the 9 experimental trails (3 with nitrogen as carrier gas and 6 with air as carrier gas). Compounds other than TCE were not detected in the DCM trap or cold trap, and CO and CO_2 were not detected in the Tedlar bag for the 120^{o}C experiments. The only indication that TCE was being degraded while passing through the quartz tube heated to 120^{o}C was the presence of chloride and chloroacetic acids in the DI water used to rinse the quartz tube; no compounds were detected in the solvent (iso-octane or toluene) rinses of the quartz tube.

Table 3.20 contains the amount of chloride (umol) and DCAA detected (umol) in the water rinses from the 120^{o}C experiments. The detection limit for chloride was 0.07 umol and was determined using the standard deviation of 12 measurements of a 2 uM calibration standard collected over a one month period and the student's t value of 2.718

(n=11, alpha=0.01). The detection limit for the DCAA was determined using the standard deviation of 12 measurements of a 12 ug/L calibration standard analyzed over a 15 day period.

Table 3.20: Amount of Chloride and DCAA in the Water Rinse from the 120°C Experiments (Fifth Flow-Through Experiment)

Inlet Temperature (°C)	Nitrogen as Carrier Gas (DCM trap)		Air as Carrier Gas (DCM and cold trap)	
	*Cl^- (umol)	DCAA (umol)	Cl^- (umol)	DCAA (umol)
22	<0.07	<0.005	0.15±0.06[a]	0.003±0.000
60	0.74	<0.005	0.28±0.24	0.006±0.000
100	0.94	0.008	0.34±0.20	0.32±0.00

*No estimate of uncertainty, only one Cl^- measurement performed.
[a]Analytical variability: standard deviation based on two samples.

The amount of chloride and DCAA detected in the DI rinse after each experiment represents less than 0.01% of the TCE introduced into each experiment on a carbon basis. These minor amounts of chloride and DCAA may, or may not, indicate that TCE degradation occurred within the quartz tube system, but do point out the potential for DCAA to form after heating TCE to 120°C. The concentration of DCAA detected in the DI rinse of the 120°C experiment with air as the carrier gas and equipped with the DCM trap was 1.4±0.01 mg/L, which is 20 times greater than the current drinking water standard of 0.06 mg/L for DCAA. Thus there is a potential to form this unwanted compound at the temperatures used for steam flushing.

3.8.2 Implications for Electrical Resistive Heating

The maximum in situ temperatures achieved during electrical resistive heating can theoretically approach 200°C (Section 2.3.2). The results for the 120°C experiments

described above suggest that TCE would not be expected to degrade with the exception of forming minor amounts of chloride and DCAA. Experiments completed at 240°C, above the maximum temperature expected for electrical resistive heating, demonstrate that greater than 94.1% of the TCE introduced into the quartz tube operated at 240°C was recovered over 9 experimental trails (3 with nitrogen as carrier gas and 6 with air as carrier gas). As with the experiments completed at 120°C, no compounds were detected in the DCM or cold trap, no CO or CO_2 was detected in the Tedlar bag, and no compounds were found in the solvent rinse of the quartz tube for the experiments completed at 240°C with nitrogen or air as the carrier gas. The only indication that TCE was degraded in the 240°C experiments was the detection of chloride, DCAA, and trichloroacetic acid (TCAA) (Table 3.21).

Table 3.21: Amount of Chloride, DCAA, and TCAA in the Water Rinse from the 240°C Experiments (Fifth Flow-Through Experiment)

Inlet Temperature (°C)	Nitrogen as Carrier Gas		Air as Carrier Gas		
	Cl^- (umol)	DCAA (umol)	Cl^- (umol)	DCAA (umol)	TCAA (umol)
22	0.27	0.03±0.001[a]	11.2±0.9	0.53±0.004	0.3
60	0.36	0.02±0.001	15.5±2.2	1.48±0.008	0.7
100	0.34	0.03±0.001	14.9±0.2	0.71±0.01	0.3

[a]Analytical variability: standard deviation based on two samples.

Increasing the tube temperature to 240°C did not substantially increase the amount of chloride detected with nitrogen as the carrier gas as compared to the amount detected in the 120°C experiments (Table 3.20). The presence of oxygen in the 240°C experiments resulted in an increase in the amount of DCAA, TCAA, and chloride detected relative to the experiments completed with nitrogen as the carrier gas (Figures

3.9 and 3.10). These results demonstrate that TCE was not appreciably degraded at 240°C, the amount of chloride and chloroacetic acids formed represented less than 0.2% of the TCE introduced into the quartz tube on a carbon basis. However, these results also point to the potential to form chloroacetic acids during in-situ thermal treatment of TCE contaminated subsurface environments.

3.8.3 Implications for Thermal Conductive Heating

There are three broad temperature regions that develop during thermal conductive heating (Section 2.3.3) including a 100 to 250°C region located between heater wells, a 500 to 700°C region for soil within a one-foot radius of heater wells, and the 745 to 900°C region located within heater wells. The experiments performed at 120 and 240°C suggest that TCE would not be expected to degrade at these temperatures; however, the formation of unwanted chloroacetic acids may occur. As gas phase TCE flowed through soil heated to greater than 380°C, the potential to degrade TCE would be anticipated based on the results obtained from experiments completed at 380, 420, and 480°C.

In environments heated to 420°C where oxygen is absent, TCE degradation is not expected to be appreciable as greater than 93% of the TCE was recovered after passing through the quartz tube heated to 420°C with nitrogen as the carrier gas (Table 3.3). The primary TCE degradation products formed at this temperature included pentachlorobutadiene (Table 3.5) at up to 3.1% of the amount of TCE introduced into the quartz tube and hexachlorobenzene (Table 3.11) at up to 0.4% on a carbon basis.

Increasing the water content of the quartz tube at 420°C with nitrogen as the carrier gas resulted in an increase in TCE recovery, an increase in the amount of chloride detected in the water rinse, and a decrease in the amount of degradation products detected

in the DCM trap and in the iso-octane rinse (Table 3.22). These results indicated that increasing the amount of water in the quartz tube at 420°C resulted in a decrease in the amount of TCE degraded. The increase in quartz tube water content also caused an increase in the concentration of chloroacetic acids in the water rinse (Figure 3.10), with the maximum concentration of DCAA at 1.4 mg/L in the 420°C experiment completed with inlet temperature of 100°C with nitrogen as the carrier gas.

Table 3.22: Distribution of Carbon in the DCM Trap and Iso-Octane Rinse, and Chloride in the Water Rinse for the 420°C Experiments with **Nitrogen** as the Carrier Gas (Fifth Flow-Through Experiment)

Inlet Temperature (°C) or Water Content	22	60	100
TCE Recovery (%)	93.1±1.9[a]	95.5±1.5	99.1±1.9
Carbon in DCM trap other than TCE (umol)	251.6	176.7	99.7
Carbon in iso-octane rinse (umol)	38.0	9.4	0.0
Carbon in water rinse (umol)	0.01	0.01	0.84
Chloride in water rinse (umol)	52.0	83.9	242.7

Note: No CO or CO_2 was detected in the experiments with nitrogen as the carrier gas.
[a]Analytical variability: standard deviation based on analysis of three samples.

In subsurface environments where oxygen is present, TCE is anticipated to readily degrade at temperatures in excess of 380°C based on results from the sixth flow-through experiment where the quartz tube was heated to 380 and 420°C with air as the carrier gas. The average amount of TCE recovered after passing through the quartz tube heated to 380°C was 84.8% and decreased to 67.9% with the quartz tube heated to 420°C. The primary TCE degradation products at 380°C and 420°C with oxygen present included CO, phosgene, and CO_2 (Table 3.17 and 3.18). These compounds would be expected to remain in the gas phase once formed and travel to subsurface volumes that were at lower

pressure. A properly designed and operated vapor extraction system would be expected to recover these compounds.

At 420°C, chlorinated compounds in addition to phosgene were found after passing TCE through the quartz tube with air as the carrier gas. Hexachloroethane, PCE, and CCl_4 were present at greater than 1% of the amount of TCE introduced into the quartz tube (Table 3.18). A general guide for removing a compound from soil via ex situ thermal treatment is that the soil must be heated to at least the boiling point temperature of the compound (Mechati et al., 2004). The boiling point temperature for hexachloroethane, PCE, and CCl_4 are all less than 420°C (Table 3.15), therefore, these compounds would be expected to remain in the gas phase once formed. Assuming that the vapor recovery systems used during thermal remediation was capable of capturing these TCE degradation products, then they would be anticipated to travel toward the in situ well heated to 800°C.

The experiments completed by heating the quartz tube to 800°C with air as the carrier gas represented an ideal system where the compounds formed during TCE degradation were expected to be recovered based on the net carbon recovery of greater than 91.7% for experiments completed at 380 and 420°C. In the 800°C experiment, TCE passed from room temperature (25°C) through an approximate 10 inch long region of increasing temperatures before entering the 800°C zone within the quartz tube, then through a decreasing temperature region, and ending up in the cold trap at -78°C. TCE was degraded to CO, CO_2, and a small amount (<1% carbon basis) of phosgene (Table 3.19) while no hexachloroethane, PCE, or CCl_4 was detected in the experiments completed at 800°C with air as the carrier gas. Despite the fact that the compounds found

in the lower temperature experiments (e.g., hexachloroethane) probably formed during the 800^{o}C experiment, they were not found in the cold trap employed to capture TCE degradation products or in the toluene rinse of the quartz tube. Thus, these compounds were degraded in the quartz tube heated to 800^{o}C. However, the amount of missing carbon in the well controlled 800^{o}C experiments (~17%) makes the prospect of recovering all the TCE degradation products doubtful.

CHAPTER 4

AMPULE EXPERIMENTS

The flow-through experiments described in Chapter 3 focused on the degradation of TCE after residing in a heated quartz tube for approximately 4.3 minutes. However, subsurface environments can remain at elevated temperatures for extended periods of time, reported to be up to one year in duration (Section 2.3). The experiments described in this chapter involved heating TCE and PCE contaminated water within sealed glass-ampules in the temperature range from 22 to 120^{o}C for periods of up to 75 days. The ampules were prepared with deionized water under either anoxic or oxic conditions and were amended with TCE or PCE at concentrations below their solubility limits. Ampules with TCE dissolved in anoxic deionized water were also amended with Ottawa sand or Ottawa sand with 1% (wt) goethite (FeOOH) to measure the effect of solids on the rate of TCE degradation. Goethite was selected as a solid-phase additive because it is known to react with halogenated hydrocarbons (Elsner et al., 2004) and is a common mineral in natural soils (Sposito, 1989; Cornell and Schwertmann, 2003). Ampules were also prepared with soil and groundwater samples collected from the Camelot Cleaners Superfund Site located in West Fargo, ND that were contaminated with PCE. The ampules were destructively sampled over time to obtain aqueous and gas-phase constituent data, which were used to assess the rate of TCE and PCE disappearance and the degradation products formed.

In all, six ampule experiments were performed with five involving dissolved phase TCE and one with dissolved phase PCE (Table 4.1). The experiments were

completed using glass ampules filled with TCE or PCE contaminated water and sealed by melting the ampule neck with a propane-oxygen torch (flame sealed). Approximately three-quarters of the ampule volume was filled with contaminated water while the remaining one-quarter volume contained gas, thus TCE or PCE was present in both the dissolved and gas phase during the experiments.

Table 4.1: Completed Ampule Experiments

Experimental Series		Variables	Purpose
Preliminary	1	Dissolved Oxygen, Hydroxide Ions	Demonstrate that ampules can retain oxygen and identify TCE reaction products.
	2	Dissolved Oxygen	Develop sample analysis techniques.
	3	Dissolved Oxygen Solids	Room temperature controls, solids, evaluation of TCE introduction method.
4		Dissolved Oxygen, Hydroxide Ions Solids	Determine rate of TCE disappearance and degradation products as function of oxygen, hydroxide ion, and solids content.
5		Dissolved Oxygen Solids Temperature	Determine rate of PCE disappearance and degradation products as a function of oxygen and solids content at four different temperatures.
6		Solids	Determine rate of TCE disappearance and degradation products with sand and goethite.

The initial three experiments were performed to develop methods and procedures to produce repeatable experimental results and are termed preliminary experiments. The first preliminary ampule experiment was performed to demonstrate that dissolved oxygen levels could be maintained in flame-sealed ampules by measuring the dissolved oxygen concentration before and after heating water-filled ampules to 120^{o}C over a period of 6 days. The second preliminary ampule experiment involved developing analytical methods to determine the aqueous phase concentrations of TCE and dichloroacetic acid (DCAA), one of the anticipated TCE degradation products. The third preliminary ampule

experiment introduced solids into the ampules along with room temperature control ampules and involved an evaluation of the method used to introduce TCE into the ampules. The fourth ampule experimental was designed to determine the rate of TCE disappearance along with the identity and amount of each TCE degradation product as a function of 1) dissolved oxygen concentration, 2) hydroxide ion concentration, and 3) ampule solids content. The fifth experiment used TCE contaminated deionized water amended with sand and goethite in an effort to verify the findings from the fourth ampule experiment. The sixth ampule experiment involved measuring PCE degradation in deionized water and in contaminated soil and ground samples from the Camelot Cleaners site. This was in effort to evaluate the rate of PCE degradation and products that might form during the application of electrical resistive heating at that site.

The following section (Section 4.1) describes the ampule experimental system along with the methods used to prepare the ampules. Experimental methods and results specific to each of the initial three preliminary experimental series are given in Sections 4.2 through 4.4. The methods and results for the fourth (Section 4.5), fifth (Section 4.6), and sixth (Section 4.7) ampule experiments are presented separately due to the expanded efforts employed to identify degradation products. The final section (Section 4.8) provides a discussion of how the ampule experimental results apply to each of the three thermal remediation technologies.

4.1 Ampule Experimental Methods

The ampule experiments were conducted in clear, 25 mL (Kimble-Kontes, Vineland, NJ) or 50 mL (Wheaton Science Products, Millville, NJ) borosilicate glass ampules (Figure 4.1). The 25 mL ampules were used for the initial three experimental

series and the 50 mL funnel-top ampules were used for the fourth experiment to minimize the amount of carbon monoxide and carbon dioxide (CO/CO_2) introduced during the flame sealing process. The 25 mL ampules were used again for the fifth and sixth experimental series because the 50 mL funnel top ampules were no longer available from Wheaton Science Products.

4.1.1 Ampule Preparation and Sealing

The ampules were autoclaved with 17 psi of steam (121^{o}C) for 25 minutes, then rinsed with deionized (DI) water (>18 MΩ/cm), and dried in an oven at 200^{o}C for 2 hours. The ampules were then removed from the oven and placed in a glass desiccator that contained approximately 100 grams of indicator drierite (97 % $CaSO_4$ and 3% $CoCl_2$) to maintain water free conditions. For the anoxic and oxic experiments, the desiccator was evacuated to 750 mm Hg of vacuum and then backfilled with either argon gas or ultra zero grade air (UZA), respectively. Each ampule was then flushed with argon or UZA just prior to filling with aqueous solution. Each water-filled ampule was temporarily sealed with aluminum foil until a complete batch of ampules was prepared (~10 minutes). Ampules containing solids were prepared in an identical fashion, but filled with either sand, sand+1% goethite, or Camelot soil as they were removed from the desiccator.

The ampules were flame sealed using a propane-oxygen torch (BernzOMatic, Medina, NY) that has a maximum flame temperature of approximately 2,500^{o}C. The flame sealing process consisted of heating the ampule neck using the outer portion of the torch flame to vaporize any water droplets present within the neck followed by melting the glass using the inner portion of the torch flame. The flame seal location was

approximately 3 cm above the gold band (Figure 4.1) in accordance with Wheaton Science instructions. The vaporization of water required approximately 10 seconds, while melting the glass to form the seal required less than 5 seconds. The sealed ampule was then placed in a rack and allowed to cool to room temperature.

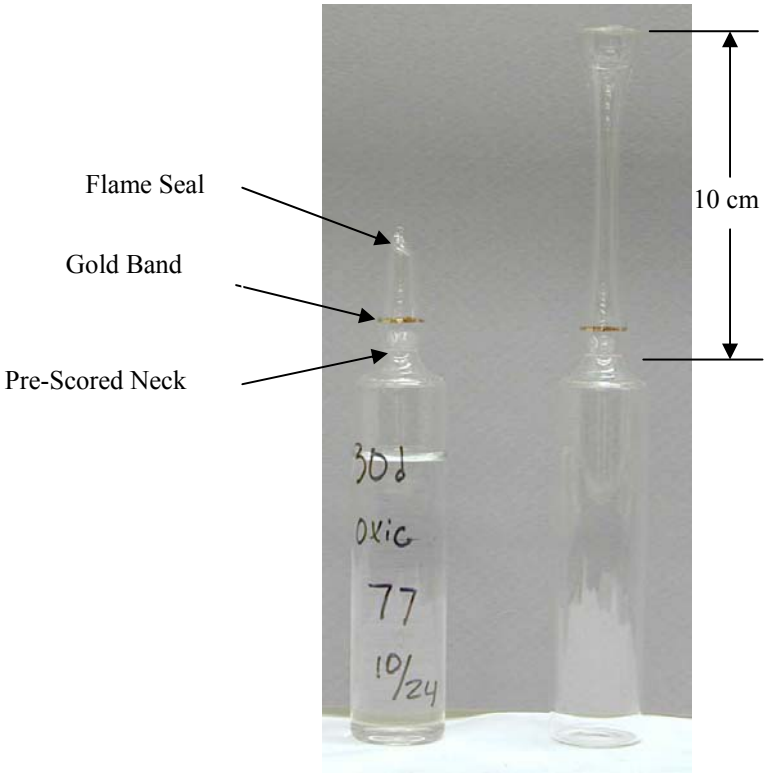

Figure 4.1: Picture of the 50 mL funnel-top ampule before and after sealing.

Each ampule was labeled with a permanent marker to indicate the sequential ampule number, preparation date, and ampule contents. The ampules were then weighed using an analytical balance (Model# AG245, Mettler-Toledo, Columbus, OH) after checking the balance accuracy with an ASTM E617 class 2 certified traceable 20±0.0001 gram weight (Cat. # 820000.2, Denver Instruments, Denver, CO).

4.1.2 Preparation of Aqueous Solutions

All aqueous solutions (except for Camelot ampules) were prepared with deionized (DI) water that was freshly dispensed from a Nanopure® analytical deionization system (model D4741, Barnstead International, Dubuque, IA). The Nanopure® system has four inline purification cartridges that produce organic free, Type I reagent grade water in accordance with the specifications provided in the ASTM D1193-99e1, "Standard Specification for Reagent Water." The DI water was dispensed only after the electrical resistance of the water was greater than 18 MΩ-cm at room temperature (22°C) and through a 0.2 μm pore size filter.

Aqueous solutions with low dissolved oxygen content (<0.3 mg/L), referred to as anoxic water, were prepared prior to each experiment by sparging freshly dispensed DI-Nanopure water with argon gas (Airgas-South, Inc., Marietta, GA) after passing through an oxygen trap (part# 4001, Alltech Associates, Inc., Deerfield, IL). The anoxic water was sparged with argon for at least 1 hour and had a dissolved oxygen concentration between 0.2 and 0.3 mg/L as indicated by the Rhodazine D method (part# K7501, CHEMetrics, Inc., Calverton, VA). Oxygen-saturated water, referred to as oxic water, was prepared by sparging DI-Nanopure water with ultra zero grade air (UZA) (Airgas-South, Inc., Marietta, GA). The oxic water was sparged with UZA for at least 1 hour and had a dissolved oxygen concentration between 8 and 10 mg/L as indicated by the Indigo Carmine method (part# K7512, CHEMetrics, Inc., Calverton, VA). Gas sparging was accomplished by passing the carrier gas through a glass tube fitted with a fritted glass disk that generated small bubbles to enhance gas transfer. Sparging was completed within

a 4 L aspiration carboy that had been autoclaved with 17 psi of steam (121^{o}C) for 25 minutes prior to each use.

4.1.3 Sample Collection Process

The ampule sampling process was initiated by removing the ampules from the oven and placing them in a darkened vent hood to allow the hot ampules to cool to room temperature. The ampules were then weighed using the same analytical balance used to determine the initial ampule weight (Section 4.1.1). The ampule opening method consisted of inverting the ampule and measuring the distance of the gas-filled space to estimate the volume of gas in each ampule (Step 1, Figure 4.2). The ampule neck was then broken by hand along the pre-scored line (Step 2, Figure 4.2), the water within the ampule body did not drain out since gas could not flow past the water that blocked the ampule opening which was smaller in diameter than the ampule body. The opened ampule was then placed into a custom made sampling collection apparatus that was filled with a stream of argon gas flowing at 500 mL/min to minimize the introduction of oxygen and carbon dioxide during sample collection (Step 4, Figure 4.2). The sample collection apparatus consisted of a 60 mL plastic syringe body that was cut in half with an 18-gauge, 30 cm long stainless steel needle affixed to the syringe body. A 10 mL syringe (Becton Dickinson and Co., Franklin Lakes, NJ) was attached to the 30 cm long needle via a luer lock connection in effort to collect a gas sample from the inverted ampule.

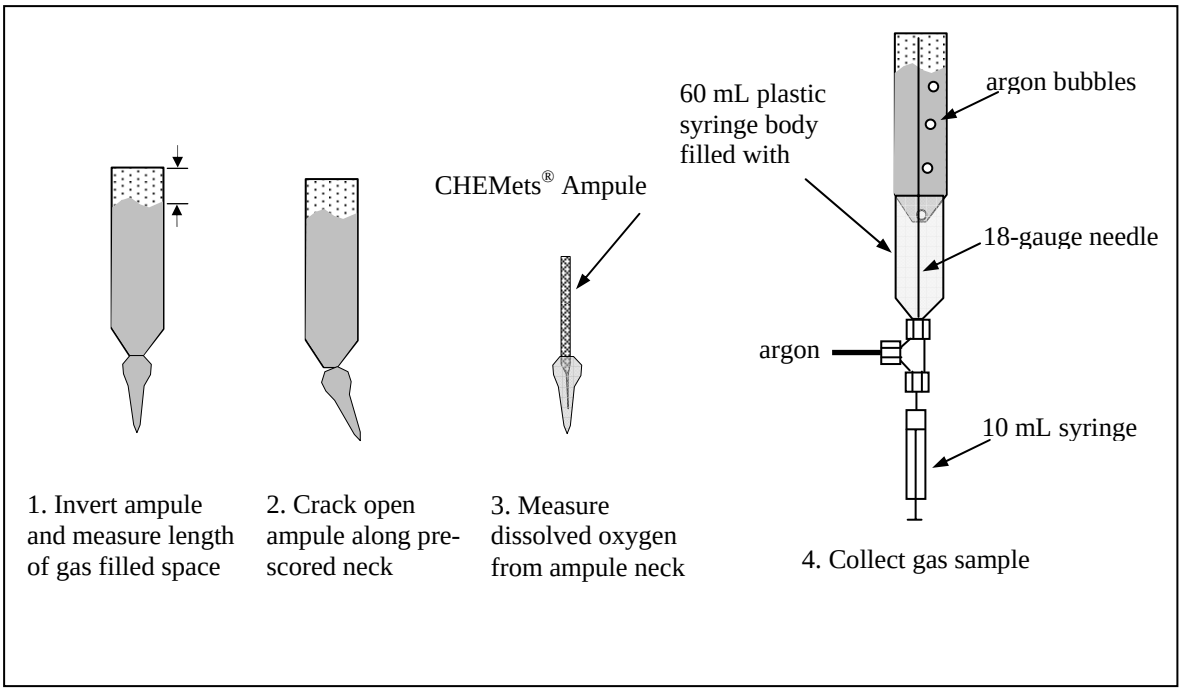

Figure 4.2: Illustration of the ampule gas sample collection method.

The dissolved oxygen (DO) concentration was determined using a membrane-covered voltammetric sensor (YSI 5010 BOD Probe, YSI, Inc. Yellow Springs, OH) during the initial three experiments. This method required transferring the aqueous phase from each ampule into a second vial that could accommodate the YSI probe body.

The dissolved oxygen concentration of ampules in the fourth and subsequent experiments was determined using the Rhodazine D method (part# K7501, CHEMetrics, Inc., Calverton, VA) for DO between 0 and 1 mg/L or the Indigo Carmine method (part# K7512, CHEMetrics, Inc., Calverton, VA) for DO between 1 and 10 mg/L. The CHEMets method was contained within a self-filling ampule that was inserted into the ampule neck (Step 3, Figure 4.3) to determine the DO concentration while waiting for argon to flush ambient air from the 60 mL syringe body. A sample of the gas within the ampule was then collected by slowly retracting the syringe plunger (5 mL in 30 seconds)

and allowing the argon gas to bubble through the liquid-filled portion of the ampule and backfill the gas-filled space as the gas sample was being removed. The gas sample was analyzed within 60 seconds of collection using a gas chromatograph (HP 6890) equipped with a thermal conductivity detector (TCD) as describe in Section 3.6.1.3. The ampule was then removed from the 60 mL syringe body and placed upright to allow for collection of liquid samples. The water within the ampule was then transferred into a pre-washed 50 mL borosilicate glass vial and sealed with a Teflon lined septum affixed with an open-top screw cap. The pH of the ampule water was measured in the 50 mL glass vial by placing a DI water rinsed pH probe (Fisher Scientific, Fair Lawn, NJ) into the vial and waiting approximately 5 minutes before recording the pH value. The vial was then labeled using a permanent marker and stored in a 4^{o}C chamber.

4.2 Degradation of TCE in Ampules Amended with Oxygen and Sodium Hydroxide (First Preliminary Ampule Experiment)

The first preliminary ampule experiment consisted of filling each of 4, 25 mL ampules with 20 mL of DI-Nanopure water (>18 MΩ-cm), leaving approximately 5 mL of gas headspace in each ampule. Two (2) ampules were filled with nitrogen sparged water with initial dissolved oxygen (DO) concentration of less than 0.5 mg/L (anoxic water) and 2 ampules were filled with ultra zero grade air (UZA) sparged water with initial DO concentration of 8.17 mg/L (oxic water). Approximately 1.4 uL of neat TCE was then injected into each of the 4 ampules through a temporary aluminum film seal to create aqueous solutions containing approximately 100 mg/L of TCE. The ampule with anoxic water and TCE represented the control since Knauss et al. (1999) had found that dissolved oxygen affected the rate of TCE disappearance. Two (2) of the 4 ampules were amended with solid sodium hydroxide (NaOH) chips to adjust the solution pH to

approximately 11. No duplicate ampules were prepared in this first preliminary ampule experiment. All 4 ampules were flame-sealed and placed in an oven maintained at 120°C for a period of 6 days.

Table 4.2: Results of the First Preliminary Ampule Experiment After 6 Days at 120°C

Ampule Contents	Initial DO (mg/L)	Final DO (mg/L)	Final pH	CO_2 in Gas Phase (uL/L)
Water and TCE	<0.5	<0.5	6.74	1032
Water and TCE	8.17	7.8	6.60	1000
Water, TCE, and NaOH	<0.5	<0.5	11.24	nd
Water, TCE, and NaOH	8.17	7.9	10.75	nd

nd – below detection limit (~200uL/L).

At the end of 6 days the oven was turned off and allowed to cool for 12 hours to room temperature (22°C). The ampules were destructively sampled using the method described in Section 4.1.3 and the gas-phase CO_2 concentrations was determined using a GC (HP 6890) equipped with a gas sampling valve, a Supel-Q PLOT capillary column (Supelco, Bellefonte, PA), and a thermal conductivity detector (TCD). The Supel-Q PLOT column was only capable of separating CO_2 from the ampule gas and using this column resulted in a detection limit of 200 ppmv for CO_2. The DO concentration of each sample was determined using a membrane-covered voltammetric sensor (YSI 5010 BOD Probe, YSI, Inc. Yellow Springs, OH). Aqueous samples were collected from each ampule and injected into a GC (Varian 3600CX) equipped with a Varian Saturn 2000 mass spectrometer (MS) to analyze for TCE degradation products.

Carbon dioxide (CO_2) was detected in the 2 ampules without NaOH, regardless of the initial dissolved oxygen content (Table 4.2). No TCE was detected in water samples

collected from the NaOH amended ampules while TCE was present in the ampules without NaOH, the concentration of TCE was not determined. The absence of CO_2 and TCE in the NaOH amended ampules indicated that other TCE degradation products had formed, which was suspected to include dichloroacetic acid (DCAA) based on the past experimental work presented in Section 2.4.3. Additional aqueous phase samples were collected from the NaOH amended ampules and the pH of the samples were adjusted to less than 1 by adding concentrated sulfuric acid. The pH adjustment was performed to convert any organic ions that may have been present from the anionic to the acid form because organic acids can be detected using an ultraviolet (UV) light spectrophotometer. After adjusting the pH of each sample to less than 1, the water samples from the NaOH amended ampules absorbed light at 270 nm in a Varian UV-visible spectrophotometer, which, based on the similarity to work by Mertens and von Sonntag (1994), suggested that DCAA was present.

The first preliminary ampule experiment demonstrated that DO levels in the ampules could be maintained with greater than 95% of the initial amount of the DO detected after incubating the sealed ampules for 6 days at 120^{o}C. In addition, the importance of NaOH on the rate of TCE disappearance was demonstrated in that no TCE was detected in NaOH amended ampules after 6 days at 120^{o}C, while TCE was detected in the ampules without NaOH. It was evident that a method to determine the DCAA content of water solutions needed to be developed based on the observation of UV light absorbance in water samples from the NaOH amended ampules. A method to determine the concentration of TCE in water was also found to be necessary in an effort to determine if small changes in TCE content were equal to the amount of CO_2 detected.

4.3 Degradation of TCE as a Function of Ampule Oxygen Content (Second Preliminary Ampule Experiment)

The second preliminary ampule experiment consisted of filling each of 8, 25 mL ampules with 20 mL of DI-Nanopure water, leaving approximately 5 mL of gas headspace in each ampule. Four (4) ampules were filled with nitrogen sparged water with initial DO concentration of 0.68 mg/L (anoxic water) as measured using the YSI voltammetric sensor, and 4 ampules were filled with UZA sparged water with initial DO of 9.8 mg/L (oxic water). Approximately 1.4 uL of neat TCE was added to 7 of the 8 ampules to achieve an initial aqueous phase TCE concentration of approximately 100 mg/L, while one ampule with oxic water was TCE-free to serve as a control. All of the ampules were flamed sealed and placed in an oven at 120^{o}C for a period of 10 days. One ampule with anoxic water and TCE was broken during the flame sealing process, leaving 7 ampules for incubation.

After cooling to room temperature, the ampules were destructively sampled to determine the amount of CO_2 in the gas phase and the concentration of DO, TCE, and DCAA in the aqueous phase. Gas samples from 3 of the 7 ampules were not analyzed (na, Table 4.3) because these ampules were damaged during the opening process which resulted in the ampule contents being exposed to ambient air (~500 uL/L CO_2) and potentially biasing the amount of CO_2 in those samples. The TCE content of the ampule aqueous phase was determined by injecting a 1 uL water sample from each ampule directly into a gas chromatograph (GC) equipped with a flame ionization detector (FID) (See Section 4.5.1.2). The DCAA concentration of the ampule water was determined using the modified EPA method 552.2 (described in Section 3.6.1.4).

Table 4.3: Results of Second Preliminary Ampule Experiment After 10 Days at 120°C						
Ampule Contents	Initial DO (mg/L)	Final DO (mg/L)	Initial pH	Final pH	Weight Change (%)	CO_2 (uL/L)
Water and TCE*	0.68	na	7.34	na	0.0006	1,007
Water and TCE*	0.68	na	7.34	6.1	0.0006	na
Water and TCE	0.68	na	7.34	na	0.0006	na
Water and TCE	9.08	7.5	7.15	6.3	0.0003	na
Water and TCE*	9.08	8.55	7.15	6.47	0.0006	879
Water and TCE	9.08	8.43	7.15	6.16	0.0000	739
Water	9.08	8.52	7.15	8.19	0.0006	nd

DO – dissolved oxygen.
*DCAA detected in water samples near detection limit of 5 ug/L.
na – not analyzed, contents lost after breaking ampule neck.
nd – not detected, below detection limit of ~200 uL/L.

The ampules with oxic water had DO at concentrations ranging from approximately 7.5 to 8.6 mg/L after 10 days at 120°C (Table 4.3) as determined using the YSI voltammetric sensor. The similarity between initial and final DO concentrations of the control ampule (9.08 vs. 8.52 mg/L), and minimal changes in ampule weights (# 0.0006%) were taken to indicate that the flame-sealed ampules provided a gas-tight environment over the 10-day, 120°C incubation period. For ampules that contained TCE, the pH decreased from 7 to approximately 6.2, and CO_2 was detected in the ampules with both anoxic and oxic water. As anticipated, CO_2 was not detected in the gas headspace of the TCE-free control ampule. Dichloroacetic acid (DCAA) was detected at concentrations near the method detection limit (~5 ug/L) in 3 of the 7 ampules.

The pH of the TCE-free control ampule increased from 7.15 to 8.19, which was attributed to the thermal enhanced dissolution of silica (SiO_2) from the borosilicate glass ampule walls. As SiO_2 dissolves into water it forms silicic acid (H_4SiO_4), which is a weak acid with an initial dissociation constant of $pK_a = 9.5$ ($H_4SiO_4 \rightarrow H_3SiO_4^- + H^+$) (Stumm

and Morgan, 1996). Thus the dissociation of silicic acid would cause the pH of the solution to increase as SiO_2 was dissolved from the ampule walls.

Table 4.4: Initial and Final TCE Concentration in Ampules from the Second Preliminary Ampule Experiment

Ampule Contents	Initial TCE (mg/L)[a]	Final TCE (mg/L)[b]	Relative Standard Deviation (%RSD)
Water and TCE*	110.0	57.9	3.4
Water and TCE*	95.0	66.5	0.5
Water and TCE	105.0	42.9	5.2
Water and TCE	100.0	49.5	0.6
Water and TCE*	100.0	60.2	3.2
Water and TCE	115.0	65.3	4.7
Water	*not added*	nd	*not determined*

[a]Calculated based on the mass of TCE added to each ampule and volume of water in each ampule.
[b]Determined using direct GC injection technique.
nd – not detected.

The initial concentration of TCE was not determined using the direct GC injection technique but was in the 95 to 115 mg/L range as estimated based on the mass of TCE added to each ampule and the volume of water in each ampule (Table 4.4). The concentration after incubating the ampules at 120^{o}C for 10 days was determined using the direct GC injection technique and was less than the initial, calculated TCE concentration. The relative standard deviation (%RSD= standard deviation ÷ average × 100) is one measure of the precision associated with an analysis method. A %RSD of less than 15% is considered adequate for determining the concentration of TCE in aqueous samples (U.S. EPA, 1996). The %RSD values shown in Table 4.4 were determined by analyzing three separate water samples collected from each ampule and shows that the direct GC

injection method was capable of determining aqueous phase TCE concentration with adequate precision.

There appeared to be a significant reduction in amount of TCE after 10 days at 120^{o}C based on the results shown in Table 4.4, however, the small amount of CO_2 detected and DCAA indicated that the apparent reduction in TCE was due to an overestimation in the initial concentration of TCE. This led to the conclusion that the initial concentration of TCE should be measured rather than estimated and an additional set of ampules should be maintained at room temperature to help in quantifying any temperature induced changes in TCE content.

4.4 Degradation of TCE as a Function of Ampule Oxygen Content (Third Preliminary Ampule Experiment)

The third preliminary ampule experiment was designed to incorporate a set of room temperature controls, introduce solids (20-30 mesh Ottawa sand) into the ampules, and evaluate the method of introducing TCE into the ampules. The experiment involved 25 mL ampules that contained 20 mL of DI-Nanopure water and approximately 5 mL of gas headspace. Twelve (12) ampules contained anoxic water and nitrogen gas, and a matching set of 12 ampules contained oxic water and UZA gas for a total of 24 ampules. Approximately 10 grams of 20-30 mesh Ottawa sand were added to 8 ampules, 4 with anoxic water and 4 with oxic water. Approximately 1.4 uL of neat TCE was introduced into 10 of the 12 ampules with anoxic water, while the remaining 2 ampules were TCE free. TCE was introduced into 10 of the 12 oxic ampules as a 100 mg/L aqueous solution that was prepared by adding neat TCE to a 250 mL volumetric flask filled with UZA-sparged DI-Nanopure water and a Teflon-coated stir bar. The 250 mL flask was sealed,

placed on a magnetic stir plate, and the contents mixed for 12 hours at room temperature (22^oC) before filling each ampule with 20 mL of the solution via glass pipette.

After filling the ampules with aqueous solution, a 100 uL aqueous sample was collected from each ampule in effort to determine the initial concentration of TCE. The samples were analyzed using a mass spectrometer (ITS40, Thermo-Finnegan, Waltham, MA) equipped with a vial sparge module that allowed TCE to be purged from water in a 40 mL vial directly into the mass spectrometer (MS) per EPA method 8265 (U.S. EPA, 2002). The vial sparge method was being evaluated as an alternative to the direct GC injection method for determining aqueous-phase TCE concentration. After collecting a sample to determine the initial TCE concentration, each ampule was flame sealed using a propane torch and 19 of the ampules were placed in an oven maintained at 120^oC. The remaining 5 ampules were wrapped with aluminum foil and stored in a vented hood at room temperature (22^oC). The 19 ampules were removed from the oven after 10 days and allowed to cool to room temperature and then all 24 ampules were destructively sampled on the same day in numerical order. The gas phase from each ampule was initially analyzed for CO_2 content followed by the analysis of aqueous phase samples to determine the concentration of TCE, DO, DCAA, and chloride ions. The concentration of TCE in each ampule after the 10 day period was determined using the vial sparge method and a headspace method that involved collecting a 1 mL aqueous sample from each ampule and injecting the sample into a previously sealed headspace vial for analysis by a GC equipped with a headspace autosampler (See Section 4.5.1.2).

Table 4.5: Initial and Final TCE Concentration in Anoxic Ampules from the Third Preliminary Ampule Experiment 1.4 uL of TCE added to each ampule, Initial DO = 0.79 mg/L					
Contents	Temperature (^{o}C)	Initial TCE (mg/L)		Final TCE (mg/L)	
		Estimated	Vial Sparge	Vial Sparge	Headspace
TCE, water	120	110±7.1[a]	58.2±15.9	62.4±6.2	61.5±3.7
	22	110	77.8	80.6	69.9
TCE, water, sand	120	107±7.6	87.9±12.2	62.5±5.1	63.2±5.7
	22	110	84.8	80.6	81.2
[a]Experimental variability: standard deviation based on duplicate ampule results.					

The initial concentration estimated by the mass of TCE added was greater than the concentration determined by the vial sparge method (Table 4.5). The difference between the estimated and measured TCE concentration was thought to be due to non-equilibrium between the neat TCE droplet that was added to each ampule and the ampule water because the sample used to determine the initial TCE concentration was collected within 30 minutes of injecting the neat TCE. The non-equilibrium condition between the neat TCE droplet and ampule water was indicated by the significant difference (P-value=0.01) between the initial TCE concentration determined for Ampule 1 (46.9±1.0 mg/L) and for the other identically prepared ampules (69.4±3.8 mg/L for Ampule 2 and 69.4±3.8 mg/L for Ampule 3) even thought a similar amount of neat TCE was added to each ampule (2.1, 2.3, and 2.2 mg TCE, respectively). The difference in the initial concentration between ampules indicated that the neat TCE in Ampule 1 was not completely dissolved into the ampule water at the time when the water sample was collected in effort to estimate the initial TCE concentration. The concentration of TCE in Ampule 1 measured after 10 days at 120^{o}C increased from 46.9 mg/L to 66.7 mg/L which

supports the conclusion that a portion of the neat TCE was not dissolved when the sample used to establish the initial TCE concentration was collected. In addition to the non-equilibrium condition, there must have been a loss of TCE mass after injecting the neat TCE droplet into each ampule since the concentration, as determined by the vial sparge method, was less than the concentration estimated from the mass of TCE added to each ampule. Thus it was concluded that injecting neat TCE to establish an initial mass of TCE was not desirable since estimating the initial concentration of TCE was complicated by the non-equilibrium condition and loss of TCE mass during the loading process.

Table 4.6 contains the initial and final concentration of TCE in the ampules filled with oxic water. Here, instead of amending each ampule with 1.4 uL of neat TCE, as done with the ampules filled with anoxic water (Table 4.5), the ampules with oxic water were filled with an aqueous mixture that had been prepared by mixing neat TCE with water at room temperature for a period of 12 hours. The average concentration of TCE in the mixture was 71.7±4.1 with a %RSD of 5.7. This average was calculated based on the analysis of a 100 uL sample collected from each of the 10 ampules after filling with the aqueous TCE mixture, which shows the adequate precision of the vial sparge analysis method and degree of TCE homogeneity in the mixture. The vial sparge method was not used in subsequent experiments since there was no substantial improvement in analysis precision over the direct GC injection or headspace methods and because the vial sparge method was time consuming due to the manual sample-injection step. TCE and PCE were introduced into each ampule in the subsequent experiments as an aqueous solution that was prepared by mixing neat TCE or PCE with a 2 L volume of water for at least 24 hours at room temperature.

Table 4.6: Initial and Final TCE Concentration in Oxic Ampules from the Third Preliminary Ampule Experiment TCE mixed into 250 mL of water prior to addition to each ampule, Initial DO = 8.22 mg/L				
Contents	Temperature (^{o}C)	Initial TCE (mg/L)	Final TCE (mg/L)	
		Vial Sparge	Vial Sparge	Headspace
TCE, water	120	72.5±6.0[a]	57.2±3.6	59.9±1.2
	22	73.3	69.1	65.7
TCE, water, sand	120	69.9±3.5	58.3±3.2	64.7±1.3
	22	71.4	58.0	66.8
[a]Experimental variability: standard deviation based on duplicate ampule results.				

The concentration of TCE increased in the ampules with anoxic water from 58.2 to 62.4 mg/L after 10 days at 120^{o}C while it decreased from 87.9 to 62.5 mg/L in ampules that contained Ottawa sand and anoxic water (Table 4.5), however, these changes are in comparison to the initial TCE concentration which, as described above, did not represent the true initial condition due to non-equilibrium between neat TCE and water. In ampules with oxic water (Table 4.6), there was a significant decrease in TCE concentration (P-value= 0.01) from 72.5 to 57.2 mg/L after 10 days at 120^{o}C and from 69.9 to 58.3 mg/L in ampules with sand and oxic water, which may have indicated that TCE was being degraded. However, there was also a decrease in TCE concentration in the matching ampules stored at 22^{o}C where TCE was not expected to degrade over 10 days. No statistical comparison between the 22^{o}C and 120^{o}C results was possible as only one ampule was stored at 22^{o}C for each experimental variable thus the variability (the basis for statistical tests) of the TCE concentration in the ampules stored at 22^{o}C was unknown. A matching number of 22^{o}C control ampules were prepared in the subsequent experiment to allow for statistical comparisons between 22^{o}C and 120^{o}C results. If TCE was being degraded in the ampules incubated at 120^{o}C, the rate of disappearance, based

on the results shown in Table 4.6, was approximately 1.5 mg/L·day, which meant that 24 days would have been required to degrade 50% of the initial amount of TCE, assuming a zero-order reaction model. The subsequent experiment was extended up to 40 days in effort to observe a greater change in TCE concentration potentially caused by the degradation of TCE.

Table 4.7: Third Preliminary Ampule Experiment Results for Anoxic Ampules
1.4 uL of TCE added to each ampule
Initial DO = 0.79 mg/L

Contents	Temperature (^oC)	Final pH (Initial pH=7.73)	Final DO (mg/L)	CO_2 (uL/L)	DCAA (ug/L)
water	120	7.46	4.5	na	nd
TCE, water	120	6.46±0.18[a]	6.7±0.5	838±104	0.7±0.6
TCE, water	22	4.85	na	2,320	5.4
sand, water	120	3.17	na	2,783	nd
TCE, water, sand	120	3.86	3 (n=1)	3,493±144	6.0±1.6
TCE, water, sand	22	3.14±0.06	na	646	10.3

na – not analyzed.
nd – below detection limit (~0.2 ug/L).
[a]Experimental variability: standard deviation based on duplicate ampule results.

The final CO_2 content of the gas phase, and the aqueous phase concentration of DO and DCAA along with the final pH for the ampules with anoxic water are shown in Table 4.7 and in Table 4.8 for the ampules with oxic water. The pH of the aqueous solution decreased from 7.73 to 6.46 in ampules with anoxic water that contained TCE and were incubated at 120^{o}C, while the pH decrease was less than 0.3 pH units in the TCE-free ampule with anoxic water (Table 4.7). A similar decrease in the pH of ampules with oxic water was observed with the pH decreasing from 7.80 to 6.55 for ampules incubated at 120^{o}C (Table 4.8). The pH also decreased in ampules that contained both

anoxic and oxic water along with TCE and were stored at 22°C, the pH decreased to values lower than expected based on the results from ampules incubated at 120°C.

Table 4.8: Third Preliminary Ampule Experiment Results for Oxic Ampules
TCE mixed into 250 mL of water prior to addition to each ampule
Initial DO = 8.22 mg/L

Contents	Temperature (°C)	Final pH (Initial pH=7.80)	Final DO (mg/L)	CO_2 (uL/L)	DCAA (ug/L)
water	120	7.63	7.7	nd	nd
TCE, water	120	6.55±0.07[a]	6.7±0.6	847±369	nd
TCE, water	22	6.45	6.9	1,103	nd
water, sand	120	3.09	na	2,845	nd
TCE, water, sand	120	3.25±0.03	2.8±0.2	2,187±392	nd
TCE, water, sand	22	3.94	6.0	1,733	nd

na – not analyzed.
nd – below detection limit (~0.2 ug/L).
[a]Experimental variability: standard deviation based on duplicate ampule results.

The decrease in pH was matched with the detection of CO_2 in the gas phase. This could either indicate that TCE was being degraded or that CO_2 was introduced during the flame sealing process from the torch combustion products; CO_2 can dissolve in water to form carbonic acid and thus decrease the pH. Since TCE was not expected to degrade in the ampules stored at 22°C where the pH decreased and CO_2 was detected, it was suspected that the ampule contents were being exposed to the torch flame combustion-products during the flame sealing process. To test this hypothesis, several empty 25 mL ampules were flame sealed and CO_2 was subsequently detected in the ampules after destructive sampling. Thus the CO_2 detected in the ampules may have been introduced during the flame sealing process and not from the degradation of TCE. This finding

prompted the use of "funnel top" ampules in the subsequent experiment, which can be flame sealed without exposing the ampule contents directly to the torch flame.

The pH of the water in the ampules that contained sand decreased from approximately 7.7 to less than 4.0 regardless of TCE content, initial DO concentration, or incubation temperature. It was suspected that the 20-30 mesh Ottawa sand, which had been treated by soaking in a 0.5 N nitric acid solution and then rinsed with DI water, contained residual nitric acid due to an inadequate DI rinse. A separate test was performed by placing 100 grams of the acid treated Ottawa sand in a beaker and adding enough freshly dispensed DI-Nanopure water to cover the sand. The pH of the DI water decreased from 7.7 to 4.2 indicating that the DI rinse after the 0.5 N nitric acid treatment was not sufficient to remove the residual nitric acid. This result prompted additional rinsing procedures in subsequent experiments that included rinsing the sand until the rinse water was at pH 7.

The chloride content of the water samples was determined using an ion selective electrode (ISE). However, the ISE failed to yield consistent values for the 1 mM chloride solution used to check probe response during measurements. As a result, chloride data are not reported here, and alternative analytical methods that included a colorimetric technique by Bergmann and Sanik (1957) and use of Ion Chromatography as described in Section 3.6.1.4 were employed in the subsequent experiments.

The DO concentration in ampules filled with anoxic water increased from 0.79 to greater than 4.5 (Table 4.7). The DO concentration was determined using the YSI voltammetric sensor that was used in the first and second ampule experiments, which required exposing the sample to air followed by vigorous stirring thus potentially

introducing oxygen into the samples. To minimize exposure to oxygen during the measurement process, a colorimetric titration method, described in Section 4.1.2, for measuring dissolved oxygen was adopted for the subsequent ampule experiments.

The results of the first, second, and third preliminary ampule experiments were used to design the fourth ampule experiment described in the follow section.

4.5 Degradation of TCE as a Function of Ampule Oxygen, Solids, and Sodium Hydroxide Content (Fourth Ampule Experiment)

The fourth ampule experiment was undertaken to determine the rate of TCE degradation and the degradation products formed after incubating dissolved-phase TCE at 120^{o}C for up to 40 days. The experimental matrix was expanded compared to the initial three experiments and included the following experimental variables: 1) dissolved oxygen concentration, 2) hydroxide ion concentration, and 3) solids content (Table 4.9).

Table 4.9: Experimental Matrix Used for the Fourth Ampule Experiment

Liquid Content (~50 mL)	Solids Content (20g total solids)	Headspace Gas (~20 mL)	Experimental Variable
Anoxic water, pH 7	None	Argon	Control
Oxic water, pH 7	None	Air	Oxygen
Anoxic water pH 10	None	Argon	Hydroxide Ion
Anoxic water, pH 7	ASTM 20-30 Sand	Argon	Solids
Anoxic water, pH 7	20-30 Sand + 1% Goethite	Argon	Goethite

Of particular note, the solids were expanded to include goethite, a common Fe-containing soil mineral which is known to be chemically reactive. The experimental methods were refined or modified based on the results of the initial three ampule

experiments. Hence, the following sections describe preparation of solids and solutions, analytical methods, and the experimental variables considered for each batch of ampules.

4.5.1 Fourth Ampule Experimental Methods

Several batches of ampules were prepared over a period of two weeks to evaluate the experimental variables listed in Table 4.9. The ampules prepared with TCE were designed to evaluate the rate of TCE degradation and the degradation products formed. Ampules prepared without TCE or solids were intended to determine if CO and CO_2 were being introduced during the flame sealing process. Ampules without TCE but with solids were intended to determine the amount of CO_2 that could be attributed to the presence of solids. The number of ampules prepared and the date of preparation for each experimental batch are listed in Table 4.10.

Table 4.10: Summary of Ampules Prepared for the Fourth Ampule Experiment

Date Prepared (Batch No.)	Number of Ampules Prepared		Nominal Initial TCE Concentration (mg/L)	Oxygen Content	Solids Content	Ampule Number
	with TCE	without TCE				
10/21/03 (1)	21	18	1,000	Anoxic	None	1 – 36
10/23/03 (2)	18	6	1,000	Oxic	None	37 – 61
10/24/03 (3)	18	18	100	Oxic	None	62 – 97
10/25/03 (4)	18	18	100	Anoxic	None	98 – 133
11/05/03 (5)	18	18	100	Anoxic	None (pH 10)	134 – 170
11/13/03 (6)	18	17	100	Anoxic	Sand+ 1% Goethite	171 – 188 209 – 225
11/13/03 (7)	18	18	100	Anoxic	Sand	189 – 207 226 – 243

An initial TCE concentration of 100 mg/L was intended for all experiments, however, a miscalculation led to the preparation of a 1,000 mg/L TCE solution used for

the initial 2 batches of ampules (Ampules 1-61), which were added to the experimental matrix. Three (3) additional ampules (Nos. 3a, 6a, and 10a) were prepared in the first batch (10/21/03) to replace ampules that had to be re-sealed. These 3 re-sealed ampules were retained to evaluate the effect of exposing the ampule contents the propane-oxygen flame. Only 6 TCE-free ampules were prepared in the second batch (10/23/03) instead of the 18 that were planned since the 1,000 mg/L TCE concentration was in addition to the planned 100 mg/L concentration. In Batch 6 and 7, prepared on 11/13/03, one of the TCE-free sand and one of goethite-containing ampules cracked open during preparation and were not replaced. In all, 242 ampules were prepared for the fourth ampule experiment.

4.5.1.1 Preparation of Ampule Solids and Solutions

Two solids compositions were used in the fourth ampule experiment including 20-30 mesh Ottawa sand and a mixture of 20-30 mesh Ottawa sand and 1% goethite. The solids were prepared by soaking approximately 2,000 g of sand from Ottawa, IL (ASTM 20-30 Sand, U.S. Silica Co., Berkeley Springs, WV) in 1 N nitric acid solution as described in Section 3.1.3. However, the DI rinse method employed was improved to remove residual nitric acid from the sand. The DI rinse consisted of placing small volumes of sand into the top of a 20-30-100 mesh ASTM sieve stack and running DI water over the sand. The sand was then placed back into a drying tray and DI water was added to cover the sand. The pH of the DI water covering the sand was measured with a pH probe (Accumet Model 50, Fisher Scientific, Fair Lawn, NJ) and the water rinse was repeated until the pH of the standing DI water was 7. The sand was then placed into a drying oven and heated to 130^{o}C for 3 hours to remove excess moisture and then baked at

200°C for 2 hours. The oven temperature was lowered to 100°C and the sand was allowed to cool for 3 hours.

Approximately 1,000 g of the acid-washed sand was placed into a second glass drying tray to which 10 grams of goethite powder was added to create a uniform 1% (wt) mixture. Research grade goethite chips, approximately 1 gram each, were obtained from Ward's Natural Science (Rochester, NY), and were reported to have been collected from Grants County, New Mexico. The goethite chips were ground into a fine power (silt to clay size particles) using a mortar and pestle prior to mixing with the sand. The drying trays were then autoclaved with steam at 17 psi (121°C) for 25 minutes and the water from the autoclave process was allowed to vent from the trays for a period of approximately 30 minutes. Ampules that had been autoclaved and cooled in a desiccator according to procedures outlines in Section 4.1.1 where loaded with approximately 20 grams of either Ottawa sand or Ottawa sand+1% goethite and the sealed with aluminum foil.

Stock solutions of TCE were prepared by transferring either argon- or air-sparged DI-Nanopure water from a 4 L carboy (Section 4.1.2) via gravity drainage into 2 L volumetric flasks. The 2 L flasks were prepared prior to use by autoclaving with steam at 17 psi (121°C) for 25 minutes, rinsing with DI-Nanopure water (>18 MΩ/cm), and drying at 200°C for 2 hours. The flasks were allowed to cool to room temperature within the drying oven and were then flushed with argon gas prior to filling with sparged DI-Nanopure water. Argon was used instead of nitrogen due to the greater density of argon, 0.98 g/mL for argon vs. 0.68 g/mL for nitrogen at 25°C (calculated using the ideal gas law), which was thought to minimize the introduction of atmospheric oxygen during

anoxic ampule preparation. A Teflon-coated stir bar was placed into each water-filled flask, to which neat TCE was added using a gas-tight syringe. Approximately 1.37 mL of TCE was added to create 1,000 mg/L solutions (1.37 mL×1.46 g/mL÷2 L = 1000 mg/L), and 0.14 mL of TCE was added to create 100 mg/L solutions (0.14 ml×1.46 g/mL÷2 L = 102 mg/L). The 2 L flasks were then sealed with glass stoppers and then the stoppers were wrapped with parafilm. The 2 L flasks were wrapped in aluminum foil to minimize exposure to light, and placed on a magnetic stir plate where the contents of each flask were mixed at room temperature for at least 24 hours.

The pH 10 stock solution was prepared by adding 10 mL of a NaOH solution (901.4 mg/L) to the 2 L flask containing 100 mg/L of TCE just prior to ampule loading. The resulting NaOH concentration was 0.26 mM in the 2 L volume with 100 mg/L of TCE. American Chemical Society (A.C.S.) certified NaOH obtained from Fisher Scientific (Fair Lawn, NJ) was used to prepare the stock solution.

4.5.1.2 Analytical Methods

Aqueous phase concentrations of TCE were determined by gas chromatography (GC) using a headspace method and a direct GC injection method. The headspace method consisted of transferring a 1 mL aqueous sample into a 20 mL vial that was sealed with a Teflon-lined, butyl rubber stopper (West Pharmaceutical Services, Inc., Lionville, PA) affixed with an aluminum crimp cap. The headspace vials were placed in an autosampler (HP 7694) that was programmed to heat each sample to 70^{o}C for a period of 15 minutes prior to transferring the headspace gas into an HP 6890 GC for analysis. The GC was equipped with a 30 m long by 0.32 mm OD DB-624 column (Agilent Technologies, Palo Alto, CA) connected to a flame ionization detector (FID). Calibration standards

containing 60, 80, and 100 mg/L TCE were analyzed with each experimental sample batch. The calibration standards were prepared by injecting small volumes of 10,000 mg/L TCE methanol stock solution into 100 mL flasks that contained DI-Nanopure water cooled to 4^{o}C. The direct GC injection method involved introducing 1 uL of aqueous solution into a HP 6890 GC equipped with a 990 uL inlet liner, a 30 m long by 0.32 mm OD DB-5 column (Agilent Technologies, Palo Alto, CA), and a FID. The inlet was operated at 200^{o}C with a constant helium pressure of 20 psi and a 2:1 split ratio: these inlet parameters served to minimized water vapor back-flash after injecting the 1 uL aqueous sample.

The concentration of formate ($CHOO^-$), glycolate ($HOH_2C_2OO^-$), sulfate (SO_4^{2-}), and chloride (Cl^-) in aqueous phase samples from the ampules were determined using a Dionex DX-100 Ion Chromotograph (IC) equipped with an AS14A IonPac column with 8 mM Na_2CO_3/1 mM $NaHCO_3$ eluent concentrate flowing at 1 mL/min. Organic acid calibration standards were prepared from 1 M stock solutions in the concentration range from 0.02 to 0.50 mM. Formate and glycolate solutions were prepared from 99% grade solids (glycolic acid and sodium formate, ACROS Organics, Morris Plains, NJ). One limitation of IC analysis is the relatively high detection limit: the average method detection limits for glycolate and formate were 0.86 mg/L and 0.31 mg/L, respectively. The chloride ion content of aqueous samples was determined by IC analysis to allow for comparisons with chloride concentrations measured using the titration method of Bergmann and Sanik (1957) (Section 3.6.1.4).

The dissolved oxygen (DO) concentration of water held within the ampule neck was measured immediately after opening using the CHEMets ampules (Step 3, Figure

4.2, Section 4.1.3). The aqueous phase concentration of DCAA was determined using the modified EPA method 552.2 as described in Section 3.6.1.4.

4.5.1.3 Initial TCE Concentration

The initial concentration of TCE in the ampules was determined by analyzing 1 mL aqueous samples collected from each of three randomly-selected ampules in each experimental batch of 18 ampules just prior to flame sealing. The average TCE concentration measured immediately prior to sealing the ampules was considered to be representative of the initial aqueous phase TCE concentration. The average initial TCE concentration for Batch 1 was 893±21 mg/L, 878±44 for Batch 2, 95.2±3.5 mg/L for Batch 3, 85.3±2.5 mg/L for Batch 5, and 77.0±6.4 mg/L for Batch 4 based on the direct GC analysis method as the headspace GC equipment was unavailable. The solids-containing ampules had an average initial TCE concentration of 87.5±3.6 mg/L, as both the Ottawa sand and Ottawa sand+1%goethite ampules (Batches 6 and 7) were prepared using the same anoxic TCE solution.

Table 4.11: Initial Ampule TCE Concentration

Date Prepared (Batch No.)	Initial TCE Concentration (mg/L)	Oxygen Content
10/21/03 (1)	893±21	Anoxic
10/23/03 (2)	878±44	Oxic
10/24/03 (3)	95.2±3.5	Oxic
10/25/03 (4)	77.0±6.4*	Anoxic
11/05/03 (5)	85.3±2.5	Anoxic
11/13/03 (6)	87.5±3.6	Anoxic
11/13/03 (7)	87.5±3.6	Anoxic

(#) – Batch number corresponds to Table 4.10.
*Analyzed using the direct GC injection method, all other ampules by headspace analysis.

The average initial TCE concentration for the 1,000 mg/L solutions prepared for Batch 1 and 2 was less than 1,000 mg/L as was the TCE concentration in the 100 mg/L solutions prepared for Batches 3 through 7 (Table 4.11). Thus the 1,000 mg/L and 100 mg/L ampules are in name only (i.e., nominal), with the actual initial concentrations provided in Table 4.11.

4.5.1.4 Ampule Incubation Schedule

After flame-sealing the ampules in each batch, the ampules were divided in half so that 18 ampules (9 with TCE and 9 without TCE) were incubated at 120^{o}C in a convection oven (VWR Model 1320, VWR International, West Chester, PA), while the remaining 18 ampules (9 with TCE and 9 without TCE) were stored at room temperature (22^{o}C) in the dark. The ampules for oven incubation were contained in a 3 L Pyrex glass drying tray that was placed in the convection at 120^{o}C where the oven temperature was measured using a certified traceable thermometer (Fisher Scientific, Fair Lawn, NJ) located within the oven enclosure. The ampules stored at room temperature were placed in a storage rack located inside an insulated container (ice chest) to minimize exposure to light.

Ampules with TCE and without TCE were removed from the oven and room temperature storage at 10 and 20 day intervals for destructive sampling according to the schedule listed in Table 4.12 and 4.13. On 17 November 2003, 4 days after placing the solids filled ampules in the convection oven, an explosion occurred that destroyed the 82 ampules being incubated within the oven. On 18 November 2003, the 82 ampules that were stored at room temperature (Table 4.13) were moved to a 4^{o}C chamber to minimize the formation of potentially explosive TCE degradation products.

Table 4.12: Schedule for Convection Oven Ampule Incubation				
Oxygen Content	Start Date No. of Ampules	10 day Date Removed No. of Ampules	20 day Date Removed No. of Ampules	30 day Date Removed No. of Ampules
Anoxic	10/21/03 (1) 18 [9]	10/31/03 6 [3]	11/11/03 6 [3]	*oven exploded* 6 [3] *Lost*
Oxic	10/23/03 (2) 12 [9]	11/03/03 4 [3]	11/13/03 4 [3]	*oven exploded* 4 [3] *Lost*
Oxic	10/24/03 (3) 18 [9]	11/04/03 6 [3]	11/15/03 6 [3]	*oven exploded* 6 [3] *Lost*
Anoxic	10/25/03 (4) 18 [9]	11/06/03 6 [3]	*oven exploded* 6 [3] *Lost*	*oven exploded* 6 [3] *Lost*
Anoxic	11/05/03 (5) 18 [9]	*oven exploded* 6 [3] *Lost*	*oven exploded* 6 [3] *Lost*	*oven exploded* 6 [3] *Lost*
Anoxic	11/13/03 (6) 18 [9]	*oven exploded* 6 [3] *Lost*	*oven exploded* 6 [3] *Lost*	*oven exploded* 6 [3] *Lost*
Anoxic	11/13/03 (7) 18 [9]	*oven exploded* 6 [3] *Lost*	*oven exploded* 6 [3] *Lost*	*oven exploded* 6 [3] *Lost*
(#) – Batch number corresponds to Table 4.10. [#] – Number of ampules that contained TCE.				

Following the explosion, the remaining 1,000 mg/L ampules that had been stored at room temperature (on 12/06/06, Table 4.13) along with the 20-day, 100 mg/L oxic ampules that had been removed from the oven just prior to the explosion were destructively sampled to determine if dichloroacetylene (C_2Cl_2) had formed. Dichloroacetylene (DCA) is reportedly a spontaneously explosive compound (Urben et al., 1999) and was suspected to have caused the oven explosion. DCA was one of the TCE degradation products detected during the high temperature degradation of TCE in quartz tubes (Wu and Lin, 2004; Kim and Choo, 1983) but was not anticipated to form in the ampules at 120^{o}C with water present. DCA was detected in the gas phase from the

100 mg/L oxic ampules that had been incubated at 120°C in the convection oven and thus the ampule experiment was considered to be an explosion hazard. As a consequence, an explosion-resistant incubation apparatus was constructed to incubate the 72, 100 mg/L ampules that were being stored in the 4°C chamber.

Table 4.13: Schedule for Room Temperature Ampule Storage

Oxygen Content	Start Date No. of Ampules	10 day Date Removed No. of Ampules	20 day Date Removed No. of Ampules	30 day Date Removed No. of Ampules
Anoxic	10/21/03 (1) 21 [12]	10/31/03 8 [5]	11/11/03 7 [4]	12/06/03 6 [3]
Oxic	10/23/03 (2) 12 [9]	11/03/03 4 [3]	11/13/03 4 [3]	12/06/03 4 [3]
Oxic	10/24/03 (3) 18 [9]	11/04/03 6 [3]	11/15/03 6 [3]	*11/18/04* 6 [3]
Anoxic	10/25/03 (4) 18 [9]	11/06/03 6 [3]	*11/18/04* 6 [3]	*11/18/04* 6 [3]
Anoxic	11/05/03 (5) 18 [9]	*11/18/04* 6 [3]	*11/18/04* 6 [3]	*11/18/04* 6 [3]
Anoxic	11/13/03 (6) 17 [9]	*11/18/04* 6 [3]	*11/18/04* 6 [3]	*11/18/04* 5 [3]
Anoxic	11/13/03 (7) 18 [9]	*11/18/04* 6 [3]	*11/18/04* 6 [3]	*11/18/04* 6 [3]

(#) – Batch number corresponds to Table 4.10.
[#] – Number of ampules that contained TCE.
11/18/04 – Date that ampules stored at 22°C were moved to 4°C chamber.

The explosion-resistant apparatus consisted of a block of aluminum into which 2 inch diameter holes were drilled to accommodate the ampules. The aluminum block was heated using a standard bench top hot plate (Fisher Scientific, Fair Lawn, NJ) and the

temperature of the block was determined using a K-type thermocouple connected to a data logger (Model# CR23X, Campbell Scientific, Inc., Logan, UT), which automatically recorded the temperature at 15-minute intervals. As shown in Figure 4.3, the hot plate and aluminum block were located behind a 2 by 2 foot, by 1/2 inch thick sheet of polycarbonate (McMaster-Carr, Atlanta, GA) that served to shield laboratory personnel from exploding ampules. The ampules were manipulated behind the polycarbonate sheet using an 18-inch long pair of metal tongs. In addition, laboratory personnel wore a polycarbonate face shield (Fisher Scientific, Fair Lawn, NJ) when manipulating ampules.

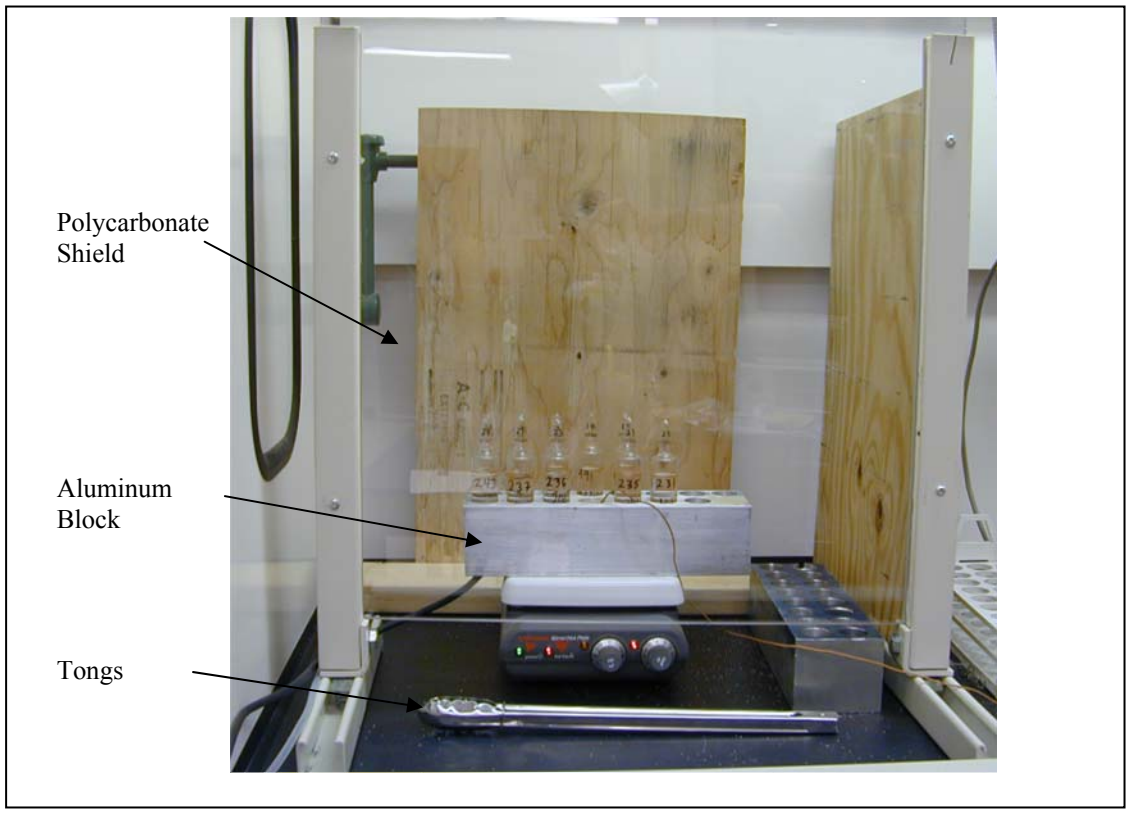

Figure 4.3: Photograph of the explosion-resistant ampule incubation apparatus.

Incubation of the ampules that were stored in the 4^{o}C chamber began on 26 April 2004 according to the schedule given in Table 4.14. The ampules had been stored in the

4°C chamber for approximately 5 months prior to incubating in the explosion-resistant apparatus. The ampules that contained Ottawa sand+1% goethite (Batch 6) were incubated first with the duration of incubation at 120°C limited to 4 days since the oven explosion occurred 4 days after placing the solids-filled ampules in the oven. The ampules containing pH 10 water (Batch 5) were then incubated over a 4-day period beginning on 30 April 2004. The ampules with sand (Batch 7) were incubated for 40 days at 120°C after significant levels of DCA had been detected in the pH 10 ampules. The remaining oxic ampules (Batch 3) were then incubated at 120°C for 30 days and the anoxic ampules (Batch 4) for 30 and 41 days. A limited number of ampules from each batch were stored at room temperature including: 4 of the sand+goethite, 4 of the pH 10, 4 of the sand, 2 of the oxic, and 4 of the anoxic ampules.

Table 4.14: Schedule for Explosion-Resistant Apparatus Ampule Incubation

Ampule Content	Start Date No. of Ampules	1 Date Removed No. Ampules	2 Date Removed No. Ampules	3 Date Removed No. Ampules	4 Date Removed No. Ampules
Sand+ Goethite (6)	4/26/04 12 [6]	4/27/04 {1} 4 [2]	4/28/04 {2} 4 [2]	4/30/04 {3} 4 [2]	--
pH 10 (5)	4/30/04 14 [7]	5/01/04 {1} 4 [2]	5/02/04 {2} 4 [2]	5/03/04 {3} 4 [2]	5/04/04 {4} 2 [1]
Sand (7)	5/04/04 14 [7]	5/15/04 {10} 4 [2]	6/02/04 {30} 4 [2]	6/13/04 {40} 6 [3]	--
Oxic (3)	6/13/04 3 [2]	7/14/04 {30} 3 [2]	--	--	--
Anoxic (4)	6/13/04 8 [4]	7/14/04 {30} 4 [2]	7/25/04 {41} 4 [2]	--	--

(#) – Batch number corresponds to Table 4.10.
[#] – Number of ampules that contained TCE.
{#} – Number of incubation days.

4.5.2 Fourth Ampule Experimental Results

The following sections describe results obtained from 38 ampules that were incubated at 120°C in the convection oven prior to the oven explosion (Table 4.12), 51 ampules incubated at 120°C in the explosion resistant apparatus (Table 4.14), and 67 ampules that were stored at 22°C (Table 4.13). No results were obtained from the convection oven incubation of the pH 10 or the solids-filled ampules (Batch 5, 6 and 7) because these ampules were destroyed in the oven explosion.

4.5.2.1 Change in TCE Content

The average amounts of TCE in the 1,000 mg/L (nominal) ampules with time are provided in Table 4.14. The amount of TCE in each ampule was calculated based on the aqueous phase TCE concentration and the estimated gas phase TCE concentration. The gas phase TCE concentration was estimated using Henry's law ($C_g = HC_w$), assuming equilibrium conditions, with C_w equal to the TCE aqueous phase concentration as determined by GC analysis, and the dimensionless Henry's Law constant (H) equal to 0.318 at 22°C (Staudinger and Roberts, 2001). These estimates were performed to correct for the differences in the volume of gas (headspace) between ampules that was due to slight differences in the volume of water initially added to each ampule. The amount of TCE (i.e., micro moles or umol) in each ampule was then calculated based on the concentration of TCE and the volume of water and volume of gas in each ampule. The volume of water in each ampule was determined by the difference between the weight of the sealed ampule and the weight of the empty ampule and neck after destructive sampling along with a density of water equal to 0.997 g/mL. The volume of gas in each ampule was estimated based on the length of gas filled space and the ampule diameter

that was equal to 3 cm. The amount of TCE in the ampules shown in Table 4.15 is the average along with the standard deviation (i.e., average±S.D.) calculated from the number (n) ampules at each time period.

Table 4.15: Amounts (Aqueous and Gas Phases) of TCE in 1,000 mg/L (nominal) Anoxic (Batch 1) and Oxic (Batch 2) Ampules

Content	Day	Total TCE (umol)				P-Value (120 vs. 22°C)
		120°C	n	22°C	n	
Anoxic Initial TCE (umol) = 368±8	10	202±49*	3	175±49*	3	0.22
	20	337±22	2†	276±55	3	0.09
	30	*Lost*		317±12	3	--
Oxic Initial TCE (umol) = 350±17	10	355±14	3	338±2	3	0.09
	20	337±26	2‡	343±22	3	0.40
	30	*Lost*		342±11	3	--

n – Number of ampules used to calculate average and standard deviation.
*TCE by direct GC injection.
Lost – Ampules destroyed in oven explosion.
†Ampule 7 contents lost during opening.
‡Ampule 58 results excluded due to significant difference in TCE content.

There was more TCE in the 1,000 mg/L ampules incubated at 120°C than stored at 22°C (Table 4.15), with the exception of the oxic 20-day ampules. However, a paired t-test performed on these data suggest that the difference between the average amount of TCE in the 1,000 mg/L ampules incubated at 120°C and stored at 22°C was not significant (P-Values>0.22). Thus there was no apparent change in the TCE content for the 1,000mg/L ampules. The one exception was Ampule 58 from Batch 2, which had a 50.9% reduction in the amount of TCE after 20 days at 120°C. The result from Ampule 58 was not used in calculating the 20 day average shown in Table 4.15.

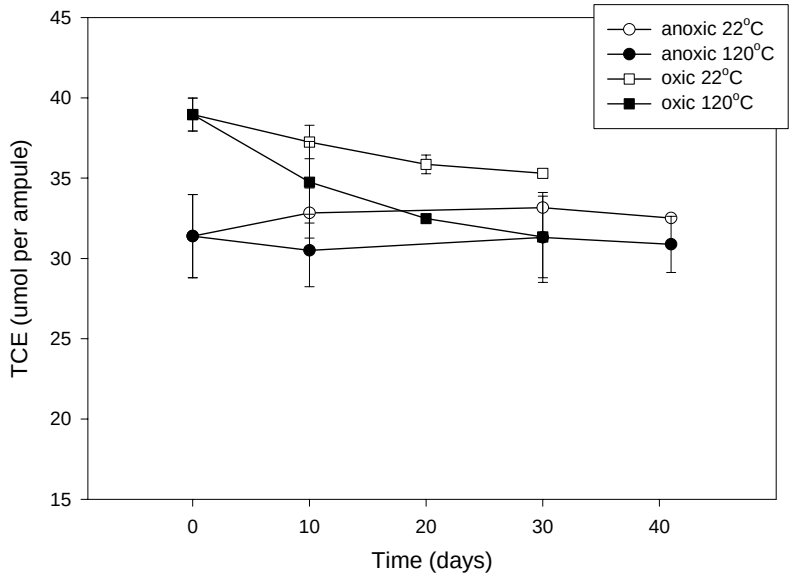

Figure 4.4: Amounts of TCE in the 100 mg/L anoxic (Batch 4) and oxic (Batch 3) ampules stored at 22°C and incubated at 120°C.

The average amounts of TCE in the 100 mg/L (nominal) anoxic (Batch 4) and oxic (Batch 3) ampules, based on the amount detected in the aqueous phase and that estimated in the gas phase, are shown in Figure 4.4 as a function of incubation time. There was little change in the amount of TCE in the anoxic ampules (Batch 4) incubated at 120°C or stored at 22°C over the 41 day period. However, no statistical significance could be assigned to this claim as the P-Values were greater than 0.05 (data not shown) from the comparison between the initial amount of TCE in Batch 4 vs. the amount of TCE in ampules at 22°C and 120°C for each time period. There was no statistical difference (P-Values>0.05, Table 4.16) between the amount of TCE in the anoxic

ampules incubated at 120°C and stored at 22°C over 41 days, which supports the claim that there was little change in the amount of TCE in the anoxic ampules.

In contrast, there was a decrease in the amount of TCE in the oxic ampules that contained 100 mg/L of TCE after 10, 20, and 30 days at 22°C and 120°C (P-Value<0.05) as compared to the initial amount of TCE in Batch 3. There was less TCE in the oxic ampules incubated at 120°C than was present in the ampules stored at room temperature after 10 and 20 days (P-Values<0.05, Table 4.16). These results suggest that the presence of oxygen affected the amount of TCE found in the ampules incubated at 120°C and stored at 22°C.

Table 4.16: Amounts (Aqueous and Gas Phases) of TCE in 100 mg/L (nominal) Anoxic (Batch 4) and Oxic (Batch 3) Ampules

Content	Day	Total TCE (umol)				P-Value (120 vs. 22°C)
		120°C	n	22°C	n	
Anoxic Initial TCE (umol) = 31.4±2.6*	10	30.5±2.3	3	32.8±1.6	3	0.12
	30†	31.3±2.8	2	33.2	1	0.34
	41†	30.9±1.7	2	32.5	1	0.29
Oxic Initial TCE (umol) = 39.0±1.0	10	34.8±2.5	3	37.3±1.0	3	0.06
	20	32.5±0.3	3	35.9±0.6	3	0.01
	30†	31.3±2.5	2	35.3	1	0.21

n – Number of ampules used to calculate average and standard deviation.
*TCE by direct GC injection.
†Incubated using the explosion resistant apparatus, all other ampules incubated in convection oven.

The average amounts of TCE decreased in the anoxic ampules that contained solids (Batches 6 and 7) as a function of time as shown in Figure 4.5. The amount of TCE detected in the ampules that contained either Ottawa sand alone or Ottawa sand+1% goethite and were incubated at 120°C was significantly less (P-Value>0.05) than the

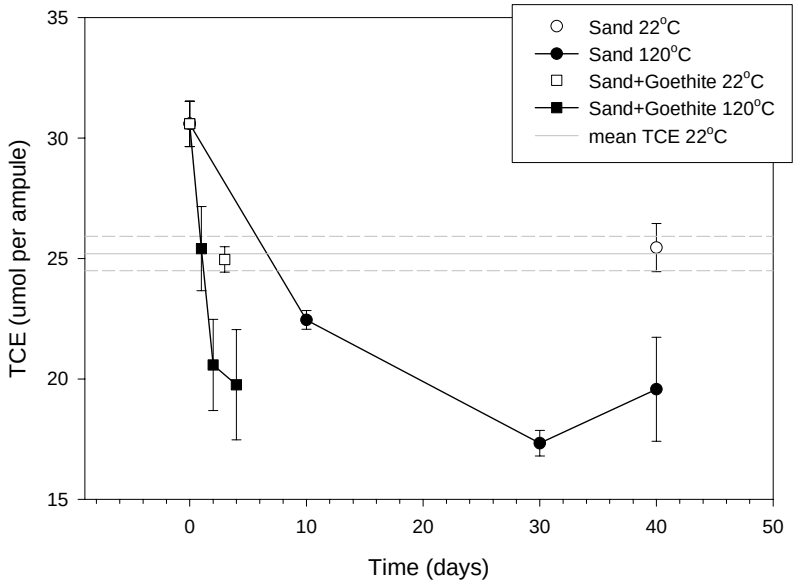

Figure 4.5: Amounts of TCE in anoxic 100 mg/L ampules with Ottawa sand (Batch 6) and Ottawa sand+1% goethite (Batch 7) stored at 22°C and incubated at 120°C.

Table 4.17: Amounts (Aqueous and Gas Phases) of TCE in 100 mg/L (nominal) Anoxic Ampules with Sand (Batch 6) and Sand+1% Goethite (Batch 7)

Content	Day	Total TCE (umol)				P-Value (120 vs. 22°C)
		120°C	n	22°C	n	
Sand Initial TCE (umol) = 30.6±0.9	10	22.5±0.4	2			0.04
	20	17.3±0.5	2			0.04
	30	19.6±2.2	3	25.4±1.0	2	0.01
Sand + 1% Goethite Initial TCE (umol) = 30.6±0.9	1	25.4±1.7	2			0.35
	2	20.6±1.9	2			0.07
	3			25.0±0.5	2	--
	4	19.8±2.3	2			0.07

n – Number of ampules used to calculate average and standard deviation.

amount in the corresponding ampules stored at 22°C (Table 4.17). There was 22.8% less TCE in the ampules with sand after 30 days at 120°C with 20.8% less TCE in the ampules with sand+1%goethite after 4 days at 120°C as compared to the amount in the ampules stored at 22°C. This result indicated that the rate of TCE disappearance was greater in the ampules that contained Ottawa sand+1% goethite as compared to ampules with Ottawa sand alone.

The average amounts of TCE in the anoxic ampules that contained water amended with NaOH to achieve a pH of 10 (Batch 5) decreased as a function of time as shown in Figure 4.6. There was 10.8% less TCE in the pH 10 ampules after 4 days at 120°C compared to the amount of TCE in the 22°C ampules. (Table 4.18)

Table 4.18: Amounts (Aqueous and Gas Phases) of TCE in 100 mg/L (nominal) Anoxic Ampules Amended with NaOH (0.26 mM) to pH 10 (Batch 5)

Content	Day	Total TCE (umol)				P-Value (120 vs. 22°C)
		120°C	n	22°C	n	
NaOH Initial TCE (umol) = 35.3±1.0	1	28.5±0.7	2			0.09
	2	26.8±1.7	2			0.01
	3	24.4±4.1	2			0.07
	4	28.0	1	31.4±1.9	2	--

n – Number of ampules used to calculate average and standard deviation.

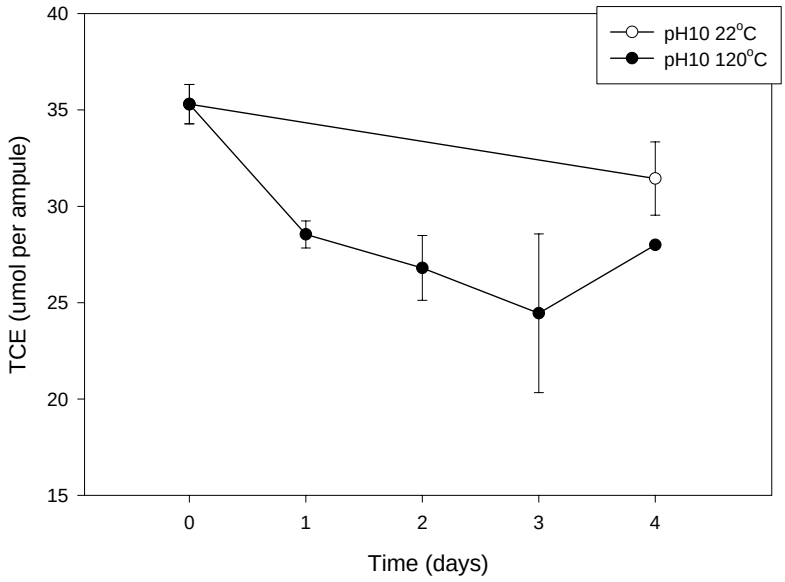

Figure 4.6: Amounts of TCE in 100 mg/L anoxic ampules amended with NaOH (0.26 mM) to pH 10 (Batch 5) stored at 22°C and incubated at 120°C.

4.5.2.2 Change in pH

The pH of ampules was expected to decrease with the degradation of TCE. Assuming that all the TCE initially present was transformed into CO_2 and chloride, then the pH in ampules would have decreased from 7 to approximately 2 based on the initial amount of TCE present in the 1,000 mg/L ampules and from 7 to 3 in ampules with 100 mg/L. The aqueous phase pH of anoxic (Batch 1) and oxic (Batch 2) ampules with 1,000 mg/L (nominal) of TCE are shown in Figure 4.7. The pH decreased in both the anoxic and oxic ampules from 7.0 to 4.34±0.08 (n=2) and 3.65±0.19 (n=2), respectively, after 20 days at 120°C. The pH of the oxic 1,000 mg/L ampules stored at 22°C also decreased,

from 7.0 to 4.74±0.35 (n=3) after 20 days but did not substantially decrease after an additional 10 day period. In contrast, the pH of the anoxic 1,000 mg/L ampules stored at 22°C increased from 7.0 to 7.43±0.82 (n=3) after 20 days (Figure 4.7). The pH of the TCE-free anoxic and oxic ampules (controls) increased from 7.0 to 8.45±0.16 (n=12), this average was calculated from the pH of TCE-free ampules after 10, 20, and 30 days at 22°C and 120°C. The pH measurements for the TCE-free controls were from 12 of the 24 ampules that were initially prepared in Batch 1 and 2 (Table 4.12). The pH increase in TCE-free ampules was thought to represent the dissolution of SiO_2 from the ampule glass walls as discussed in Section 4.3, whereas the pH decrease in TCE containing ampules was thought to represent the release of hydrogen atoms from TCE molecules due to the degradation of TCE.

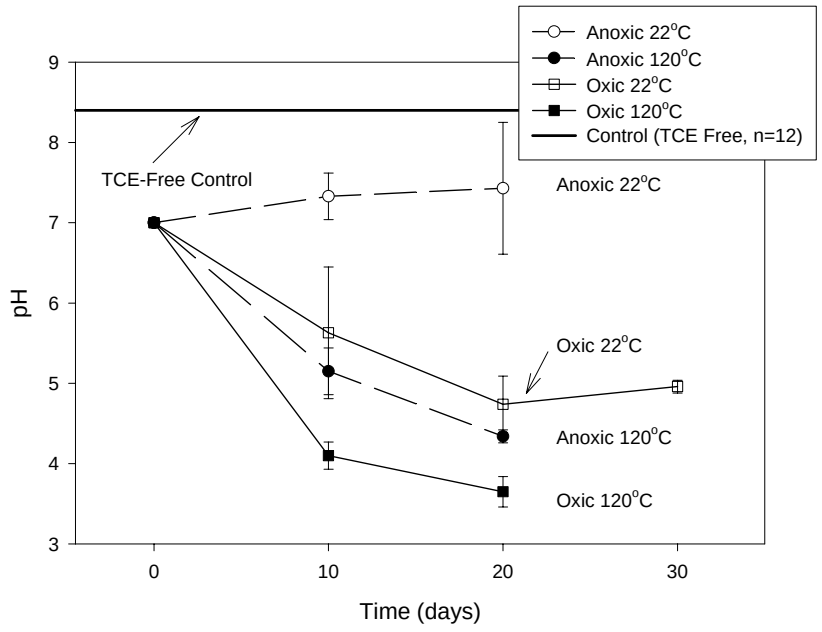

Figure 4.7: The pH of anoxic (Batch 1) and oxic (Batch 2) ampules with 1,000 mg/L of TCE and TCE-free controls stored at 22°C and incubated at 120°C.

The aqueous phase pH of anoxic (Batch 4) and oxic (Batch 3) ampules with 100 mg/L (nominal) of TCE are shown in Figure 4.8. The pH of the anoxic (Batch 4) ampules incubated at 120°C decreased from 7.0 to 4.69±0.04 (n=3) after 10 days, to 6.60±0.04 (n=2) after 30 days, and to 6.36±0.08 (n=2) after 40 days. It should be noted that the 30 and 41 day results for the anoxic 100 mg/L ampules were obtained using the explosion resistant incubation apparatus, while the 10 day results were obtained from the convection oven prior to the explosion. There was a difference in the ampule temperature profile between heating methods with the ampule necks at an average temperature of 100°C while the ampule body was at 120°C (see Figure 4.3) whereas the entire ampule was exposed to 120°C in the convection oven.

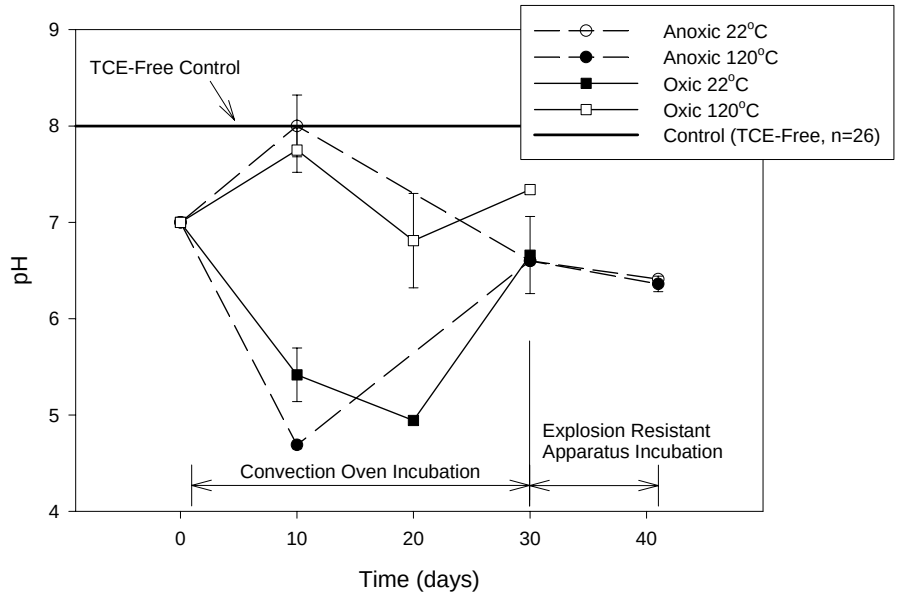

Figure 4.8: The pH of anoxic (Batch 4) and oxic (Batch 3) ampules with 100 mg/L of TCE and TCE-free controls stored at 22°C and incubated at 120°C.

In the oxic 100 mg/L ampules (Batch 3), the pH decreased from 7.0 to 5.42±0.28 (n=3) after 10 days, to 4.95±0.04 (n=3) after 20 days, and to 6.66±0.40 (n=2) after 30 days, with the 10 and 20 day results obtained from the convection oven and the 30 day results obtained from the explosion resistant apparatus. The pH of the 100 mg/L anoxic and oxic ampules stored at room temperature (22°C) increased to 8.0±0.32 (n=3) and 7.75±0.23 (n=3), respectively, after 10 days but then decreased to 6.36 (n=1) and 7.34 (n=1), respectively, after 30 days at 22°C. The average pH of the anoxic and oxic TCE-free control ampules that were stored at 22°C and incubated at 120°C was 8.00±0.70 (n=26) over 41 days which shows that the pH did not substantially change in ampules

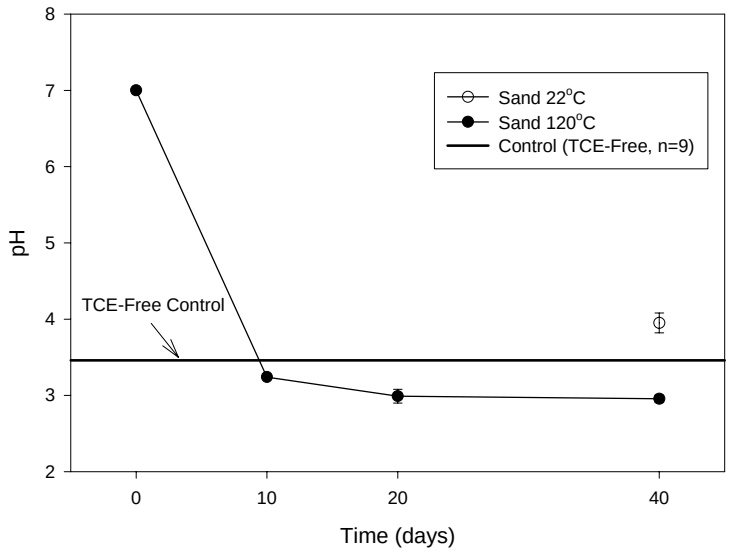

Figure 4.9: The pH of anoxic ampules that contained acid-washed Ottawa sand with 100 mg/L of TCE (Batch 6) and TCE-free controls stored at 22°C and incubated at 120°C.

without TCE. The pH measurements for the TCE-free controls were from 26 of the 36 ampules that were initially prepared in Batches 3 and 4 (Table 4.12).

The pH of anoxic ampules that contained acid washed, 20-30 mesh Ottawa sand (Batch 6) are shown in Figure 4.9. After 40 days at 120^{o}C, the pH decreased in ampules with TCE and TCE-free ampules, from an initial value of 7.00 down to 2.96±0.05 (n=3) and 3.21±0.13 (n=3), respectively. The lower pH in the ampules with TCE was significantly different (P-Value=0.01) than the pH in the TCE-free ampules indicating that TCE was being degraded. However, the Ottawa sand also served as a source of hydrogen atoms since the pH of the TCE-free control ampules was less than 4 after 10, 20, and 40 days. The pH decrease was not believed to be from the nitric acid used during sand pre-treatment since the sand was rinsed with DI water after the acid wash until the rinse water in contact with sand yielded a pH of 7.

One explanation for the pH decrease in the ampules with sand is related to the detection of sulfate ions (SO_4^{2-}) in the ampule aqueous phase (presented in Section 4.5.2.6), which led to the hypothesis that the Ottawa sand contained pyrite (FeS_2). Pyrite is known to dissolve in water and form sulfuric acid (H_2SO_4), a strong acid with a pK_a of approximately -3 (Stumm and Morgan, 1996), which could have caused the observed decrease in pH. A sample of the acid treated Ottawa sand was sent to the U.S. Silica Co. Corporate Laboratory in Berkeley Springs, WV where the sand was analyzed by X-ray diffraction analysis (Dr. Matt Paige, facsimile communication, 30 August 2004). The mineral phases identified in the sand included pyrite, marcasite (FeS_2 - polymorph of pyrite), and hematite (Fe_2O_3), however, no estimate of the relative amount of the minerals (i.e., mg/kg) was provided. Transformation of the sulfur in pyrite and marcasite into

sulfate requires a source of dissolved oxygen or ferric iron (Fe^{3+}) (Stumm and Morgan, 1996). While no measurement for ferric iron was performed, the hematite identified in the Ottawa sand may have served as a source of ferric iron and thus accounts for the detection of sulfate in the anoxic ampules.

Another source of acidity was the CO_2 found after incubating ampules amended with Ottawa sand (Section 4.5.2.4). Assuming that gas phase CO_2 was in equilibrium with the ampule water at 22°C and using a value of 0.0339 M/atm for the Henry's coefficient (Stumm and Morgan, 1996) between CO_2(g) and dissolved phase CO_2(aq), which is assumed to transform into carbonic acid (H_2CO_3), results in a decrease from pH 7 to approximately 4 in the ampules with Ottawa sand. Thus there are at least two potential sources of acidity in the Ottawa sand that could account for the observed decrease in ampule pH.

The pH of anoxic ampules that contained acid-washed Ottawa sand+1% goethite (Batch 7) is shown in Figure 4.10. The pH decreased from 7.00 to 3.64±0.05 (n=2) in ampules with 100 mg/L of TCE after 4 days at 120°C and to 4.44±0.18 after 3 days at 22°C. The pH in TCE-free ampules stored at 22°C and incubated at 120°C decreased to 4.79±0.35 (n=8). The pH of the anoxic ampules that contained water amended with NaOH to achieve an initial pH of 10 (Batch 5) is shown in Figure 4.11. At 120°C, the pH of NaOH-amended ampules that contained 100 mg/L of TCE decreased from 10.0 to 7.06 (n=1) after 4 days. In contrast, the pH of the TCE-free control ampules remained at 9.03±0.11 (n=9) and the ampules with 100 mg/L TCE were at pH of 9.37±0.04 (n=2) after 4 days at 22°C (Figure 4.11).

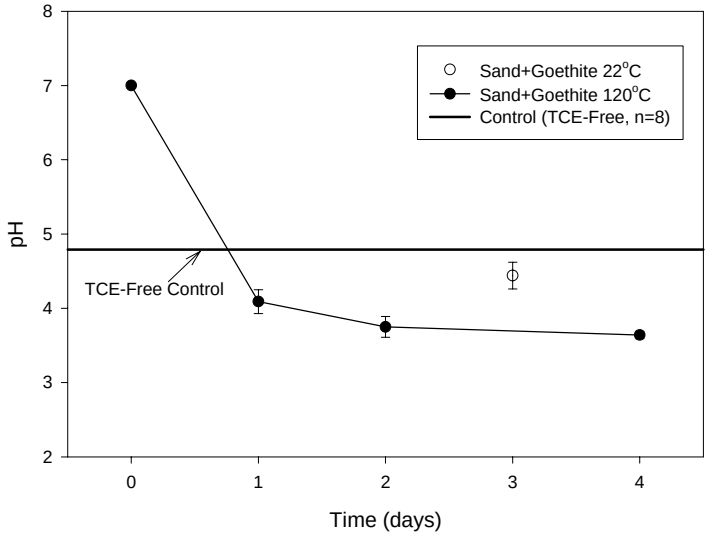

Figure 4.10: The pH of anoxic ampules that contained acid-washed Ottawa sand+1%goethite with 100 mg/L of TCE (Batch 7) and TCE-free controls stored at 22°C and incubated at 120°C.

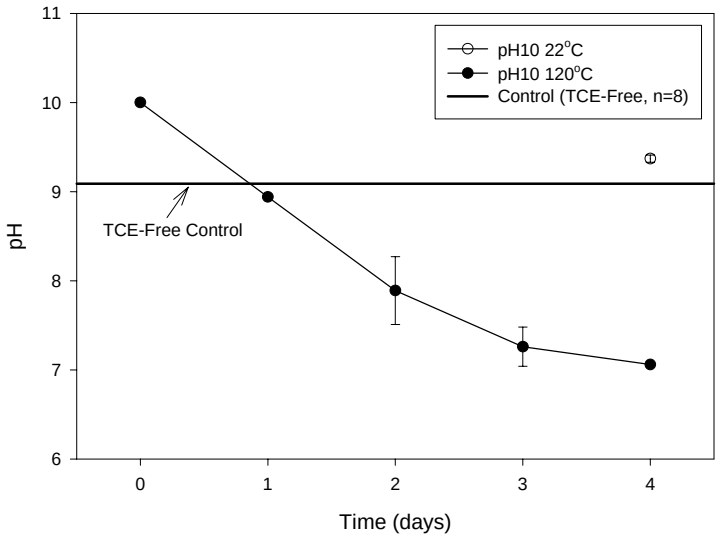

Figure 4.11: The pH of anoxic ampules amended with NaOH (0.26 mM) to pH 10 and 100 mg/L of TCE (Batch 5) along with TCE-free controls stored at 22°C and incubated at 120°C.

4.5.2.3 Change in Dissolved Oxygen

Dissolved oxygen (DO) was determined using a colorimetric method that reports DO concentration (mg/L) in a range between two values (e.g., 6 to 8 mg/L). An estimate of the average DO concentration range for each set of ampules, as a function of time, was made based on the colorimetric analysis result for each vial (Table 4.19). The DO concentration in the oxic ampules (Batches 2 and 3) remained constant (6-8 mg/L) or

Table 4.19: Dissolved Oxygen (DO) Concentration Range for Anoxic and Oxic Ampules with 1,000 and 100 mg/L of TCE (Batches 1-4)

Ampule Temperature (^{o}C)	Time (days)	1,000 mg/L anoxic (1)	1,000 mg/L oxic (2)	100 mg/L anoxic (4)	100 mg/L oxic (3)
Initial	0	0.2 to 0.3	6 to 8	0.2 to 0.3	6 to 8
120	10	4 to 5	6 to 8	2 to 3	6 to 8
22		3 to 5	6 to 8	2 to 3	6 to 8
120 and 22 (Controls)		1 to 3	6 to 8	2 to 3	6 to 8
120	20	1 to 3	8 to 10*	NA	8 to 10
22		2 to 3	8 to 10		8 to 10
120 and 22 (Controls)		3 to 4	8 to 10		8 to 10
120	30	*Lost*	*Lost*	0.8 to 1.0	6 to 8
22		4 to 5	8 to 10	0.8 to 1.0	6 to 8
120 and 22 (Controls)		5 to 6	8 to 10	0.8 to 1.0	6 to 8
120	41	NA	NA	0.8 to 1.0	NA
22				0.8 to 1.0	
120 and 22 (Controls)				0.8 to 1.0	

(#) – Batch number.
Controls – TCE-free ampules.
*Excludes Ampule 58 results, DO between 0.6 and 0.8 mg/L after 20 days at 120^{o}C.
Lost – Ampules destroyed in oven explosion.
NA – No ampules analyzed for DO at time interval.

increased by one increment (8-10 mg/L) over the 30-day incubation period, with the exception of Ampule 58 (1,000 mg/L TCE). The DO concentration in Ampule 58 decreased from 6-8 mg/L to 0.6-0.8 mg/L after incubation at 120°C for 20 days. This result suggests that oxygen was not consumed during ampule incubation at 120°C, with the exception of Ampule 58 where oxygen was consumed in conjunction with a greater than 50% decrease in TCE content after 20 days at 120°C.

Table 4.20: Dissolved Oxygen (DO) Concentration Range for Anoxic Ampules that Contained Solids (Ottawa sand and Ottawa Sand+1% Goethite) or NaOH (pH 10) (Batches 5-7)

Ampule Temperature (°C)	Time (days)	Sand (6)	Time (days)	Sand+1%Goethite (7)	pH 10 (5)
Initial	0	0.2 to 0.3	0	0.2 to 0.3	0.2 to 0.3
120	10	NA	1	NA	0.8 to 1.0
120 (Controls)		0.8 to 1.0		1 to 2	0.4 to 0.6
120	30	NA	2	NA	0.8 to 1.0
120 (Controls)		0.6 to 0.8		1 to 2	0.4 to 0.5
22	40	NA	3	NA	0.8 to 1.0
120 (Controls)		0.3 to 0.4		1 to 2	0.4 to 0.6
22 (Controls)		0.8 to 1.0		1 to 2	0.8 to 1.0

(#) – Batch number.
Controls – TCE-free ampules.
NA – Did not measure DO in solids filled ampules that contained TCE.

The DO concentration tended to increase in anoxic ampules with TCE and without TCE (TCE-free). The DO concentration increased in anoxic ampules that contained 1,000 mg/L of TCE (Batch 1) from an initial value of 0.2-0.3 mg/L to final values up to 4-5 mg/L after 30 days at 22°C and 120°C. The DO concentration also increased in TCE-free controls for the Batch 1 ampules from 0.2-0.3 mg/L to 5-6 mg/L over the course of the incubation period. Anoxic ampules with 100 mg/L of TCE and

without TCE (Batch 4) exhibited slight increases in oxygen content on day 10 (2-3 mg/L), followed by declines on day 30 (0.8-1.0 mg/L).

The DO concentrations of ampules that contained Ottawa sand (Batch 6), Ottawa sand+1% goethite (Batch 7), and amended with NaOH (Batch 5) are provided in Table 4.20. All of the sampled ampules exhibited a slight increase in dissolved oxygen concentration, ranging from the initial anoxic condition (0.2-0.3 mg/L) up to 1-2 mg/L for the TCE-free control ampules containing Ottawa sand+1% goethite (Batch 6). However, the observed increases in dissolved oxygen concentration in ampules containing solids and NaOH (Batches 5-7) were less than in the anoxic ampules containing 1,000 mg/L TCE (Batch 1, Table 4.18). For Batch 6 and 7 ampules, solids filled the ampule neck thus preventing the measurement of dissolved oxygen using the procedures illustrated in Figure 4.2. Hence, the DO concentration for these ampules had to be made within the main ampule body to gain access to sand-free water, and for this reason, DO was measured in ampules that contained solids but not TCE where the CHEMets reagents may have led to interferences during subsequent analyses for TCE degradation products.

4.5.2.4 CO and CO_2 in the Gas Phase

A 10 mL gas sample was collected from each ampule using a gas-tight syringe and approximately 6 mL of the gas sample was analyzed by a GC/TCD equipped with a Carboxen 1010 capillary column capable of separating CO and CO_2 from the ampule gas samples. Carbon monoxide (CO) and CO_2 were anticipated TCE degradation products based on the past experimental work presented in Section 2.4.3. The amount (umol) of CO and CO_2 in each ampule was calculated based on the gas-phase concentration

determined for CO and CO_2, and the estimated volume of headspace gas in each flame-sealed ampule. The amount of CO_2 reported does not include the amount of CO_2 dissolved in the aqueous phase, which was expected to be substantial given the Henry's law coefficient of 0.83 M(aq)/M(g) for 25°C (Stumm and Morgan, 1996, p. 214). Using the average gas volume of 20 mL and liquid volume of 45 mL for the ampules shows that the amount of dissolved CO_2 is expected to be 1.7 times greater than the amount in the gas phase. The additional amount of dissolved CO_2 was incorporated in calculating the rate of TCE degradation based on the rate of carbon products formed (Table 4.23).

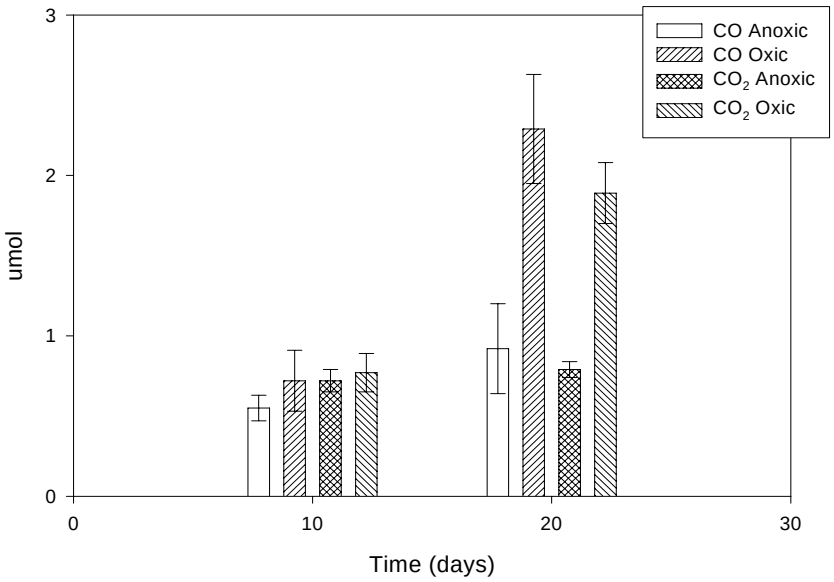

Figure 4.12: Amounts of CO and CO_2 in anoxic (Batch 1) and oxic (Batch 2) ampules with 1,000 mg/L of TCE and incubated at 120°C.

The amounts of CO and CO_2 in ampules that initially contained 1,000 mg/L of TCE (Batch 1 and 2) and were incubated at 120°C are shown in Figure 4.12. The CO and

CO_2 content of the ampules increased during the 120°C incubation period, with nearly identical amounts of CO and CO_2 detected in all of the ampules after 10 days regardless of the initial oxygen content (anoxic or oxic). After 20 days of incubation at 120°C, the amounts of CO and CO_2 detected in the oxic ampules nearly doubled, while the amounts detected in the anoxic ampules remained similar to the 10-day incubation values. The average amounts of CO and CO_2 shown in Figure 4.12 excludes the amounts detected in Ampules 9, 55, and 58, which were incubated at 120°C. In the case of Ampule 9, an anoxic ampule with 1,000 mg/L of TCE from Batch 1, there was a significant difference (P-Value=0.02) between the amount of CO and CO_2 detected after 20 days ($CO+CO_2$ = 12,386 ppmv) compared to the amounts detected in the companion replicate

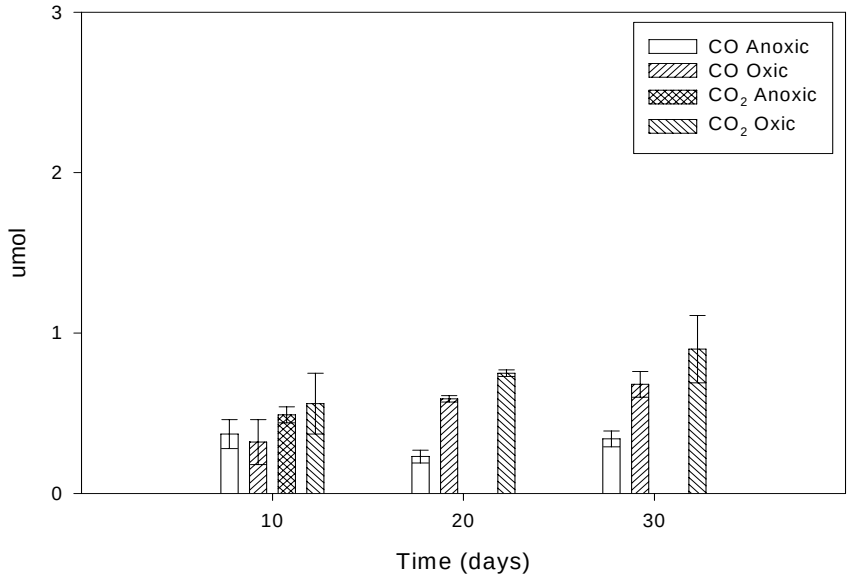

Figure 4.13: Amounts of CO and CO_2 in anoxic (Batch 1) and oxic (Batch 2) with 1,000 mg/L of TCE and stored at 22°C.

ampules, Ampules 7 and 8 (2,057±387 ppmv). There was a significant difference (P-Value=0.06) between the amount of CO and CO_2 detected after 10 days in Ampule 55 (4,250 ppmv) and in replicate Ampules 53 and 54 (1,983±419 ppmv), oxic ampules with 1,000 mg/L of TCE from Batch 2. In this case, Ampule 55 had to be flame sealed a second time during preparation thus the ampule contents may have been exposed to the propane-oxygen flame. The greatest difference for the amount of CO and CO_2 between replicate Batch 2 ampules was obtained after 20 days for Ampule 58 (123,143 ppmv) and Ampules 56 and 57 (4,515±304 ppmv).

The amounts of CO and CO_2 detected in anoxic (Batch 4) and oxic (Batch 3) ampules that initially contained 100 mg/L of TCE and were incubated at 120°C for up to

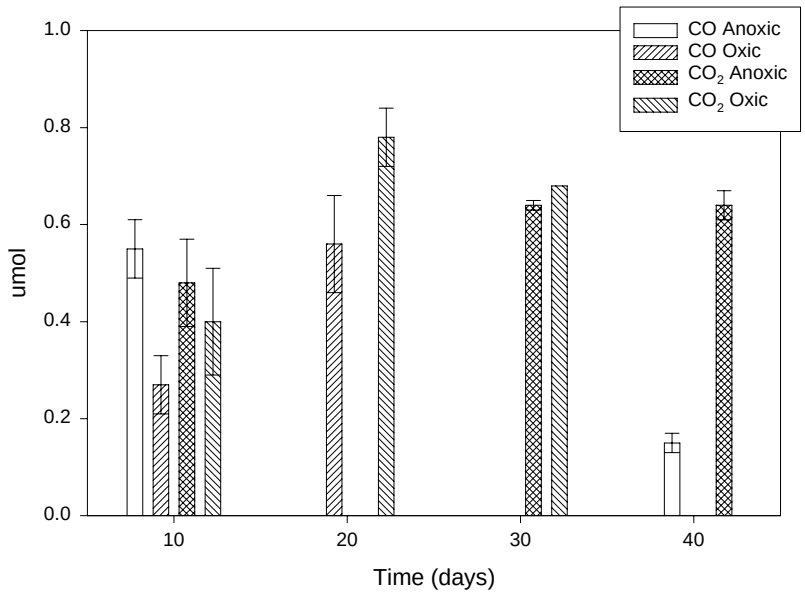

Figure 4.14: Amounts of CO and CO_2 in anoxic (Batch 4) and oxic (Batch 3) ampules with 100 mg/L of TCE and incubated at 120°C. No CO or CO_2 was detected in ampules stored at 22°C.

41 days are shown in Figure 4.14. Carbon monoxide (CO) and CO_2 were not detected in ampules stored at 22°C that contained 100 mg/L of TCE and were without TCE (TCE-free). Carbon monoxide (CO) was detected in ampules that contained TCE and were incubated at 120°C using the convection oven, whereas CO wasn't detected in ampules using the explosion resistant apparatus until 41 days at 120°C. This result may indicate that the difference in temperature profile between the two incubation systems led to differences in the rate of TCE degradation.

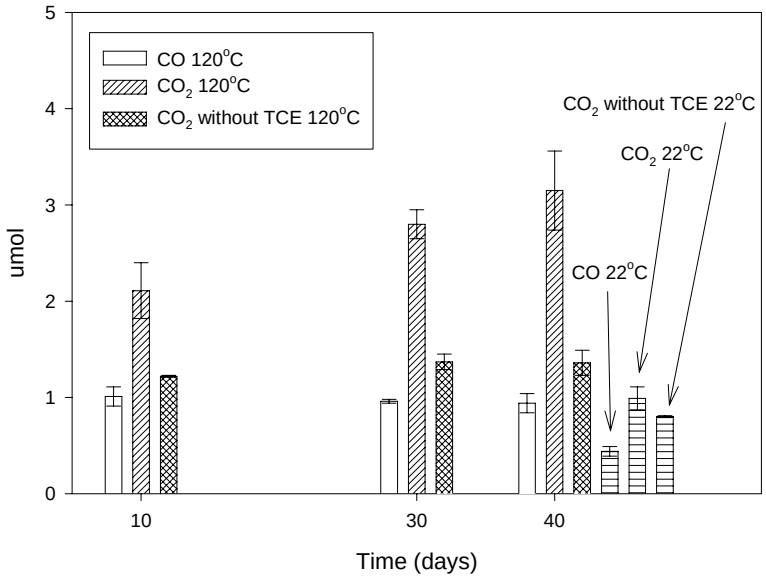

Figure 4.15: Amounts of CO and CO_2 in anoxic ampules with Ottawa sand and 100 mg/L of TCE (Batch 6) stored at 22°C and incubated at 120°C.

The amounts of CO and CO_2 detected in anoxic ampules that contained 20-30 mesh Ottawa sand (Batch 6) are shown in Figure 4.15. The average amount of CO detected (0.97±0.08 umol) in ampules that contained TCE and were incubated at 120°C

over a 40-day period was approximately twice the amount detected in the ampules stored at 22°C for 40 days. Carbon monoxide (CO) was not detected in ampules without TCE that were stored at 22°C and incubated at 120°C. For the ampules incubated at 120°C, the amount of CO_2 increased with incubation time, with amount of CO_2 detected in ampules with TCE in excess of the amount of CO_2 detected in ampules without TCE.

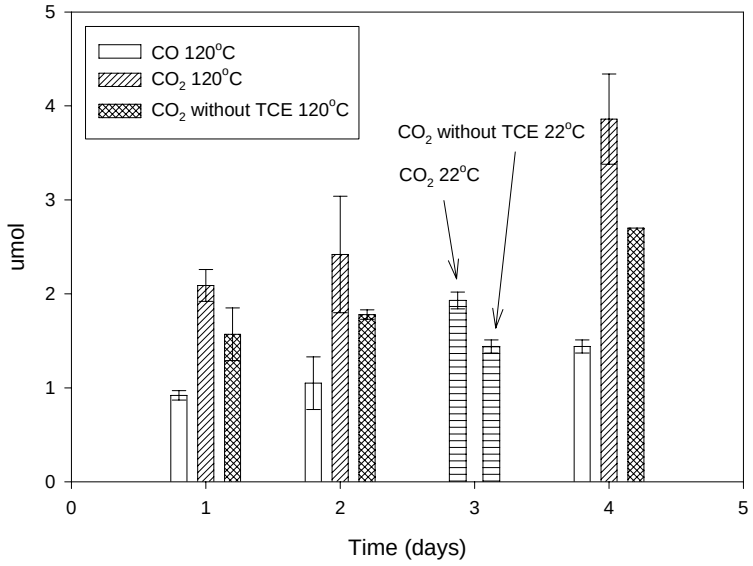

Figure 4.16: Amounts of CO and CO_2 in anoxic ampules with Ottawa sand+1%goethite and 100 mg/L of TCE (Batch 7) stored at 22°C and incubated at 120°C.

The amounts of CO and CO_2 detected in anoxic ampules that contained 20-30 mesh Ottawa sand + 1% goethite (Batch 7) are shown in Figure 4.16. The amount of CO increased during incubation over 4 days at 120°C. In contrast, no CO was detected in TCE-free ampules that were stored at 22°C. At 120°C, the amount of CO_2 increased with incubation time in excess of the amount of CO_2 detected in the TCE-free ampules.

Relative the data shown in Figure 4.15, the amount of CO_2 generated in the presence of 1% goethite was greater than detected in ampules that contained Ottawa sand alone. Figure 4.17 shows the amounts of CO and CO_2 detected in the ampules that contained 0.26 mM of NaOH. The amount of CO increased over the initial 2 days of the incubation period at 120^{o}C and then decreased over the last 2 days. No CO was detected in the ampules without TCE at 120^{o}C and with TCE that were stored at 22^{o}C. The amount of CO_2 increased with incubation time until reaching a plateau of approximately 0.8 umol on day 3 and 4.

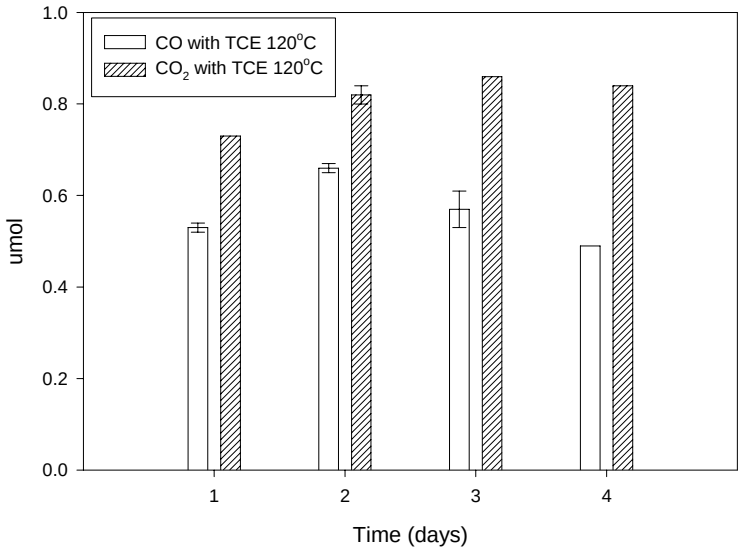

Figure 4.17: Amounts of CO and CO_2 in anoxic ampules amended with NaOH (0.26mM) to pH 10 (Batch 5) and 100 mg/L of TCE incubated at 120^{o}C.

4.5.2.5 Other Gas Phase Compounds

After analyzing 6 mL of the 10 mL gas sample for CO/CO_2 content, the 10 mL syringe with 4 mL of gas sample was removed from the GC/TCD injection loop and the syringe needle tip was sealed with a rubber septum. Approximately 1 mL of the gas sample was then injected directly into the inlet of a Varian 3600CX GC equipped with a 30 m long by 0.32 mm OD Varian CP-Sil 8MS column connected to a Varian Saturn 2000 mass spectrometer (MS). The purpose of injecting the gas sample directly into the GC/MS was to screen for the presence of compounds other than CO, CO_2, and TCE. This analysis step was added after the oven explosion had occurred to determine if potentially explosive TCE degradation products were present in the ampule gas phase. The first gas

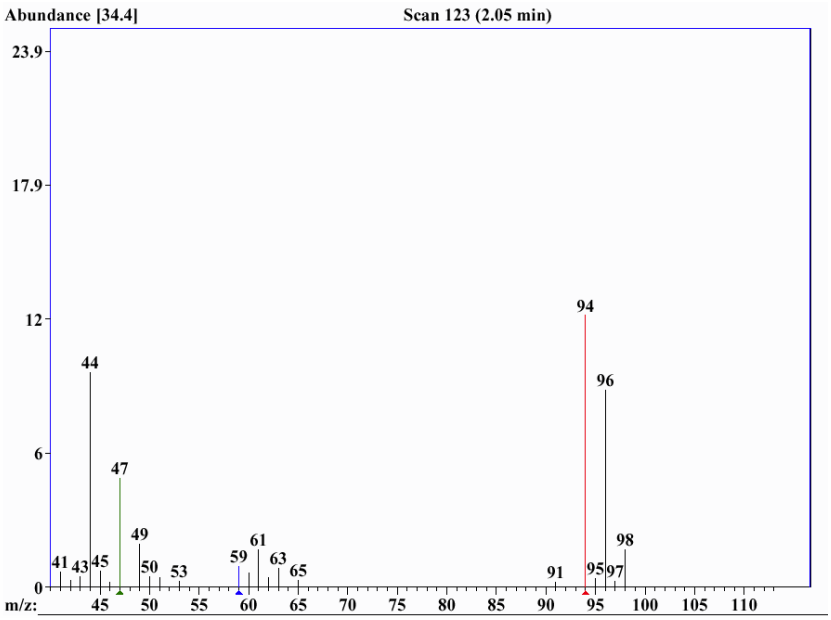

Figure 4.18: Mass spectrum of the 2.05 min chromatogram peak from the analysis of 1 mL of gas from Ampule 83.

samples analyzed by GC/MS were from Ampules 83, 84, and 85 (Batch 3), oxic ampules that contained 100 mg/L of TCE and had been incubated at 120°C for 20 days in the convection oven. The gas samples were found to contain dichloroacetylene (DCA), CO_2, and TCE. Dichloroacetylene was identified by mass spectrum match with the NIST98 library (Figure 4.18).

The concentration of DCA was not determined, as this compound is unstable and difficult to prepare for calibration purposes. The abundance of dichloroacetylene was less than 1% of the TCE present (base peak). Dichloroacetylene (DCA) was not present in the gas samples from Ampules 95, 96, and 97, the matching 100 mg/L oxic ampules that were stored at 22°C. Dichloroacetylene (DCA) was consistently identified in gas samples from ampules that were incubated at 120°C for Batch 3 through 7, no gas samples from Batch 1 or 2 ampules were analyzed by GC/MS. The greatest amount of DCA was detected in the gas phase of the pH 10 ampules (Batch 5) by GC/MS analysis. An unidentified peak was present in the headspace GC/FID chromatogram from the analysis of 1 mL water samples collected from the pH 10 ampules. The identity of the GC/FID peak was assigned to DCA based on the GC/MS results and the dissolved phase DCA concentration was 1.8±0.5 mg/L for the pH 10 ampules incubated at 120°C, estimated using the headspace response factor for TCE.

4.5.2.6 Aqueous Phase Compounds

The amount of chloride detected in both anoxic and oxic ampules incubated at 120°C increased for all experimental conditions considered and in excess of the amount measured in paired ampules stored at 22°C (Figures 4.19 through 4.23). Thus increasing the temperature of ampules resulted in an increase in the rate of TCE degradation since

TCE was the only source of chloride within the ampules. The presence of oxygen appeared to affect the amount of TCE degraded in the 1,000 mg/L ampules (Batches 1 and 2) as there was a greater amount of chloride (P-Value=0.001) in the 1,000 mg/L ampules with oxygen after 10 and 20 days at 120°C (Figure 4.19). However, there was no discernable difference (P-Value=0.66) between the amount of chloride in the anoxic (Batch 4) and oxic (Batch 3) ampules with 100 mg/L of TCE after 10 and 30 days at 120°C (Figure 4.20). The amount of chloride detected in the 100 mg/L oxic (Batch 3) ampules increased from 7.6±1.3 umol after 10 days to 9.9±0.6 umol after 20 days at 120°C using the convection oven incubation but was 6.0±0.1 umol after 30 days using the explosion resistant apparatus. There was a similar trend for chloride in the anoxic 100 mg/L ampules with more chloride detected after 10 days in the convection oven that after 30 and 41 days in the explosion resistant apparatus.

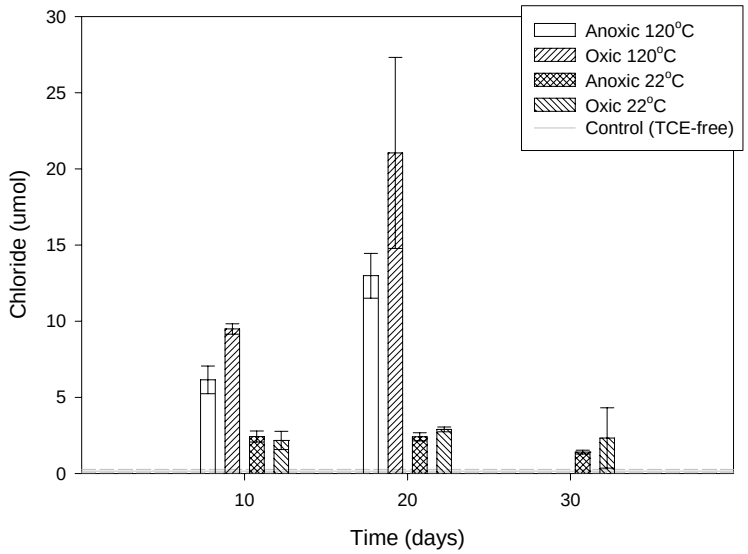

Figure 4.19: Amounts of chloride in anoxic (Batch 1) and oxic (Batch 2) ampules with 1,000 mg/L of TCE stored at 22°C and incubated at 120°C.

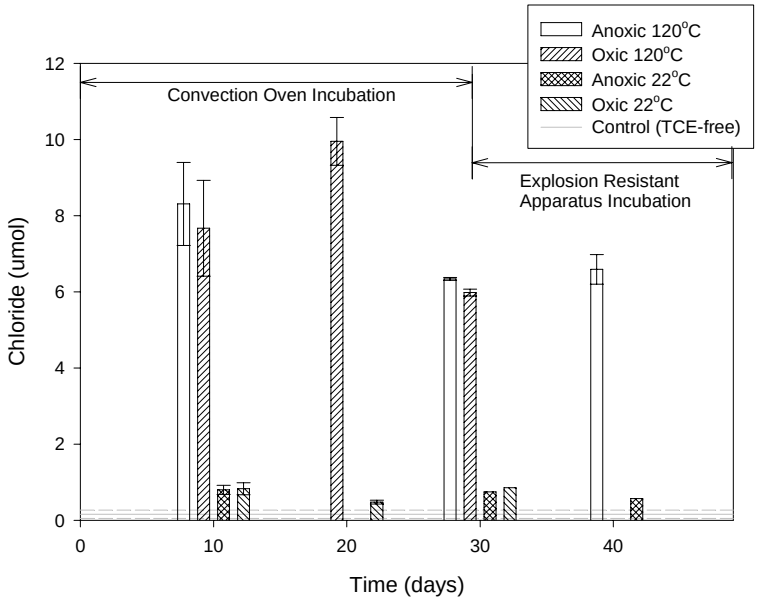

Figure 4.20: Amounts of chloride in anoxic (Batch 4) and oxic (Batch 3) ampules with 100 mg/L of TCE stored at 22°C and incubated at 120°C.

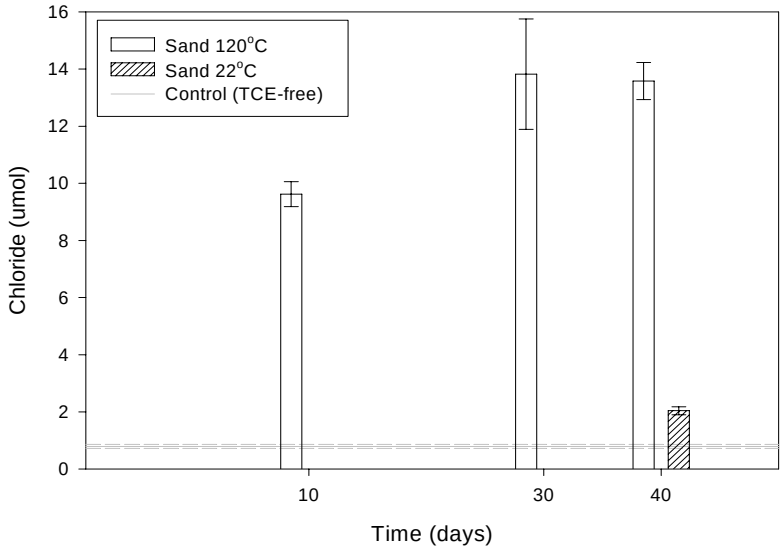

Figure 4.21: Amounts of chloride in anoxic ampules with Ottawa sand and 100 mg/L of TCE (Batch 6) stored at 22°C and incubated at 120°C.

The presence of 20-30 mesh Ottawa sand (Batch 6) caused an increase in the amount of chloride (Figure 4.21) in ampules incubated at 120°C compared to the amount of chloride in the anoxic (Batch 4) ampules that were without sand (Figure 4.20); both batches were incubated in the explosion resistant apparatus. There was 13.8±1.9 umol of chloride detected in the anoxic ampules that contained 20-30 mesh Ottawa sand after 30 days at 120°C as compared to 6.3±0.0 umol of chloride in the ampules with anoxic water alone. The addition of goethite to the Ottawa sand resulted in 6.8±1.7 umol of chloride (Figure 4.22) after 4 days at 120°C while the amount of chloride in the pH 10 ampules was 13.8 umol (n=1) after 4 days at 120°C (Figure 4.23).

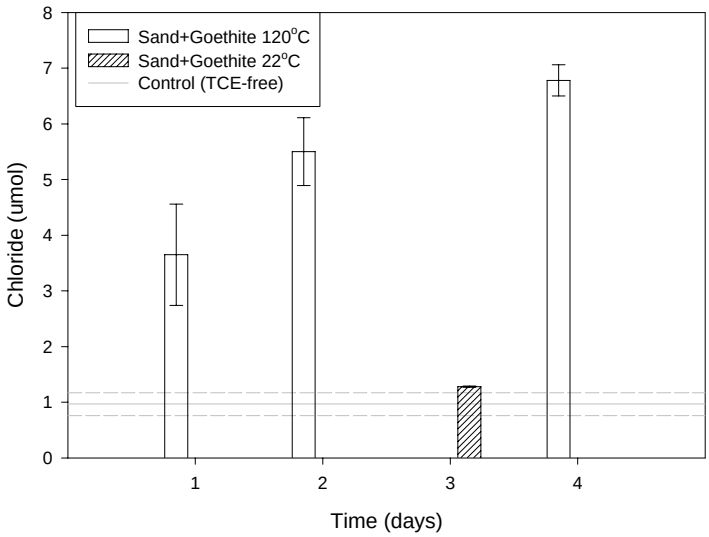

Figure 4.22: Amounts of chloride in anoxic ampules with Ottawa sand+1%goethite and 100 mg/L TCE (Batch 7) stored at 22°C and incubated at 120°C.

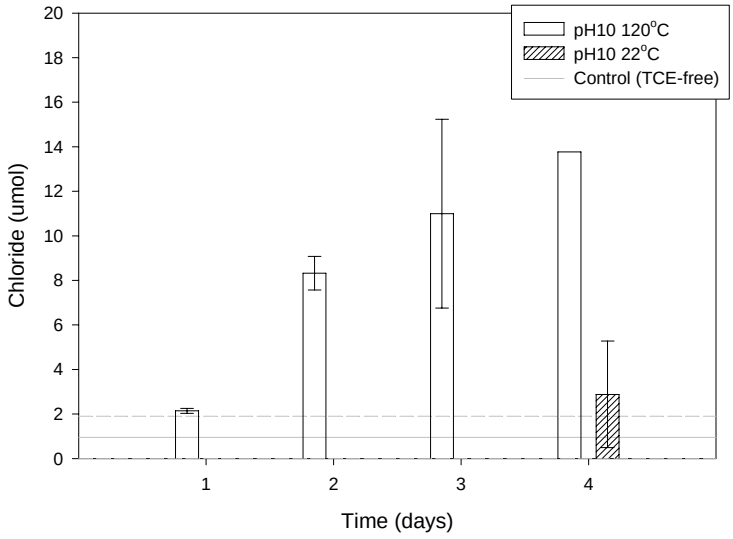

Figure 4.23: Amounts of chloride in anoxic ampules amended with NaOH (0.26 mM) to pH 10 with 100 mg/L of TCE (Batch 5) stored at 22°C and incubated at 120°C.

Aqueous samples collected from the ampules were analyzed for haloacetic acid content, including chloroacetate ($ClH_2C_2OO^-$), dichloroacetate ($Cl_2HC_2OO^-$), and trichloroacetate ($Cl_3C_2OO^-$). While dichloroacetate (DCAA) was not detected (>2 ug/L) in any of the ampules containing 100 mg/L of TCE (Batches 3-7), DCAA was detected in several of the ampules containing 1,000 mg/L of TCE (Batch 1 and 2). In 3 of the anoxic ampules, DCAA was detected at the following concentrations: 16 ug/L after 10 days at 22°C, 7 ug/L after 20 days at 120°C, and 6.1 ug/L after 30 days at 22°C. The one exception was the 125 ug/L of DCAA detected in Ampule 9, the 1,000 mg/L anoxic ampule that also had more CO and CO_2 than in its companion replicate ampules. DCAA was detected in all of the oxic ampules with 1,000 mg/L of TCE (Batch 2), with the

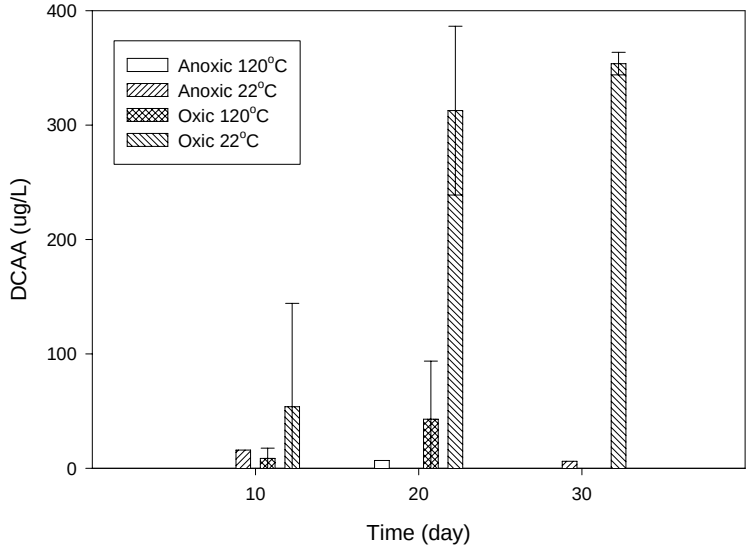

Figure 4.24: Concentration of dichloroacetate (DCAA) in the anoxic (Batch 1) and oxic (Batch 2) ampules with 1,000 mg/L of TCE stored at 22°C and incubated at 120°C.

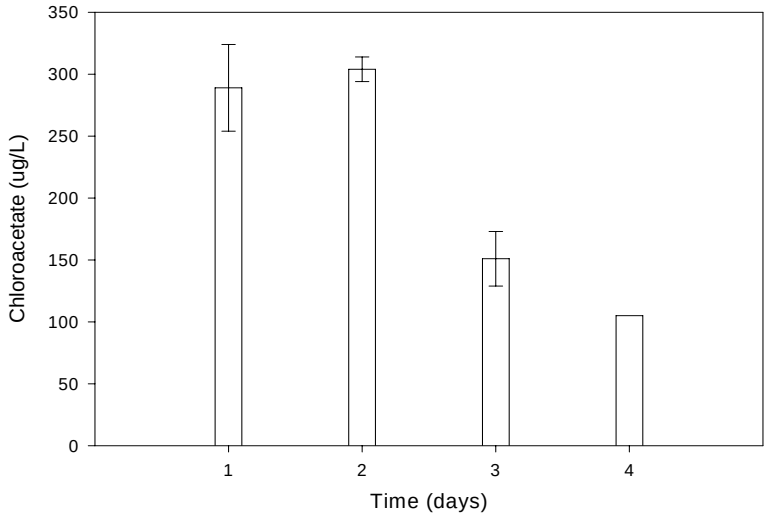

Figure 4.25: Concentration of chloroacetate in ampules amended with NaOH (0.26 mM) to pH 10 and 100 mg/L TCE (Batch 5) incubated at 120°C.

largest DCAA concentration detected in ampules that were stored at 22°C (Figure 4.24). DCAA was detected in the ampules that contained solids (Batch 6 and 7), but at relatively low concentrations (i.e., <5 ug/L). Chloroacetate was detected in pH 10 ampules that were incubated at 120°C (Figure 4.25), whereas the chloroacetate concentration in the pH 10 ampules stored at 22°C were less that 5 ug/L.

The aqueous solution that remained after the haloacetic acid and chloride analysis (~5 mL) was analyzed by Ion Chromatography (IC) to determine if other anionic species were present. The IC chromatogram contained three elution peaks with retention times of 3.35, 3.73, and 4.75 minutes. The 4.75 minute peak was attributed to chloride based on comparison with the elution time for a 1 mM chloride standard solution. The 3.35 and 3.73 minute peaks were attributed to formate ($HCOO^-$) and to glycolate ($HOH_2C_2OO^-$),

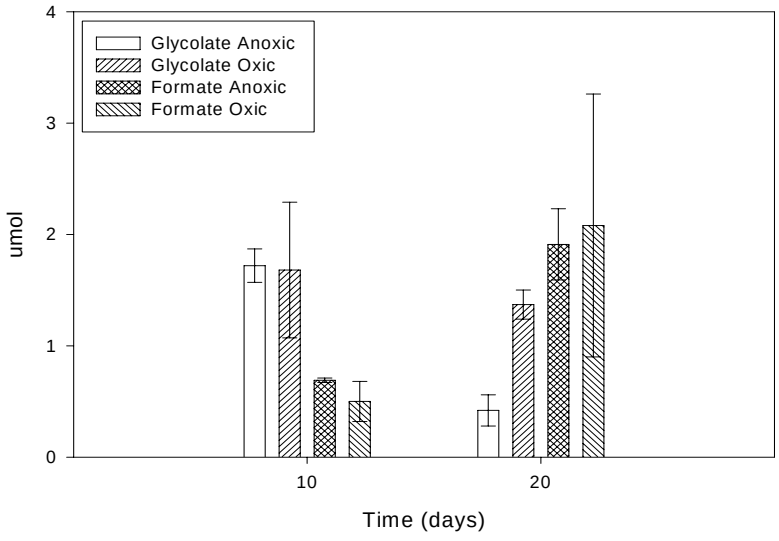

Figure 4.26: Amounts of glycolate and formate in anoxic (Batch 1) and oxic (Batch 2) ampules with 1,000 mg/L of TCE incubated at 120°C.

respectively, based on comparison with elution times for a solution containing 1 mM of glycolate, acetate, and formate. Glycolate and formate were detected in all ampules that contained 1,000 mg/L of TCE (Batch 1 and 2) and were incubated at 120°C (Figure 4.26).

The average values shown in Figure 4.26 do not include the results from Ampules 9, 55, and 58 as the results from these ampules were significantly different from the other ampules as discussed in Section 4.5.2.4. The amount of formate increased with time at 120°C in the oxic and anoxic ampules that contained 1,000 mg/L of TCE while the amount of glycolate decreased with incubation time. There was more glycolate than formate after 10 days in all the 1,000 mg/L ampules, while there was more formate than glycolate after 20 days. Glycolate and formate were not detected in ampules stored at 22°C that contained 1,000 mg/L of TCE or in the TCE-free control ampules.

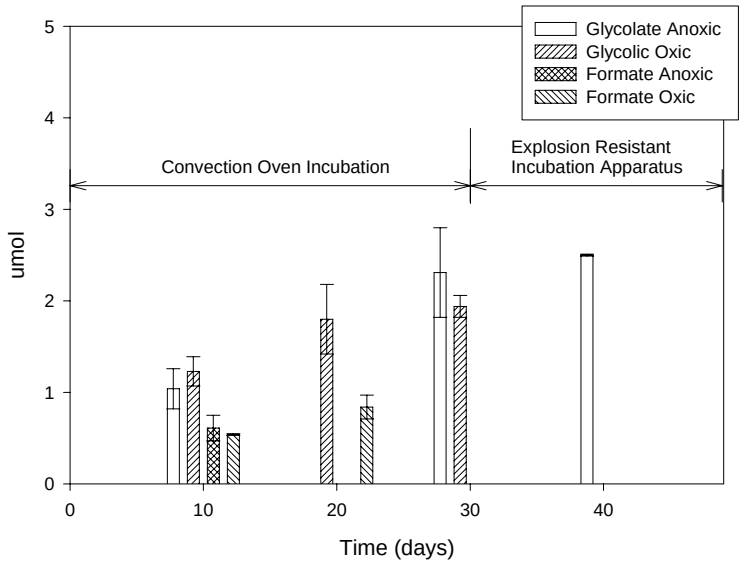

Figure 4.27: Amounts of glycolate and formate in anoxic (Batch 4) and oxic (Batch 3) ampules with 100 mg/L of TCE incubated at 120°C.

Glycolate and formate were detected in both the anoxic (Batch 4) and oxic (Batch 3) ampules that contained 100 mg/L of TCE and were incubated at 120°C (Figure 4.27). Formate was not detected in either the anoxic or oxic ampules with 100 mg/L of TCE after 30 days at 120°C. Another indication that there was a difference in the rate of TCE degradation between ampules incubated in the explosion resistant incubation apparatus and the convection oven. Glycolate and formate were not detected in the anoxic and oxic ampules that contained 100 mg/L of TCE and were stored at 22°C or in the TCE-free control ampules.

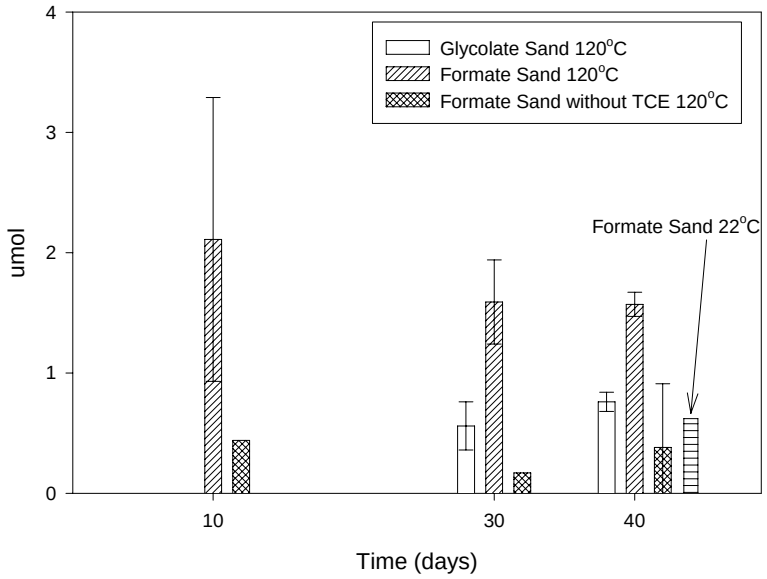

Figure 4.28: Amounts of glycolate and formate in anoxic ampules with Ottawa sand and 100 mg/L of TCE (Batch 6) stored at 22°C and incubated at 120°C.

The amount of formate detected in the anoxic ampules that contained 20-30 mesh Ottawa sand and 100 mg/L of TCE (Batch 6) decreased with time at 120°C, while the

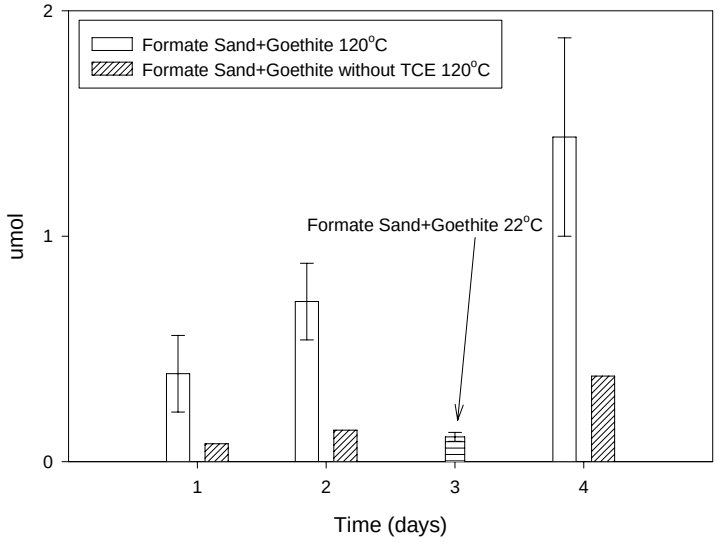

Figure 4.29: Amounts of formate in anoxic ampules with Ottawa sand+1%goethite and 100 mg/L of TCE (Batch 7) stored at 22°C and incubated at 120°C.

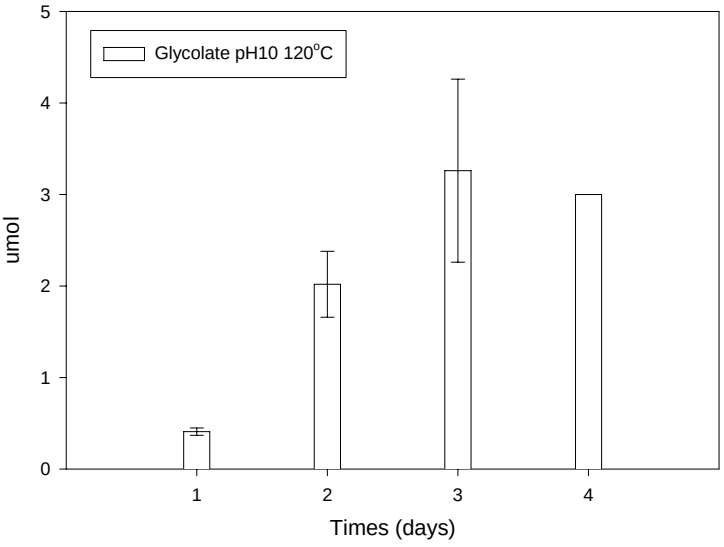

Figure 4.30: Amounts of glycolate in anoxic ampules amended with NaOH (0.26 mM) to pH 10 and with 100 mg/L of TCE (Batch 5) incubated at 120°C.

amount of glycolate increased over the 40-day incubation period (Figure 4.28). Formate was the only organic acid detected in the ampules that contained Ottawa sand+1% goethite (Batch 7) and the amount of formate increased over the 4-day incubation period at 120°C (Figure 4.29). Glycolate was the only organic acid detected in the 100 mg/L ampules with NaOH (Batch 5) that were incubated at 120°C as shown in Figure 4.30.

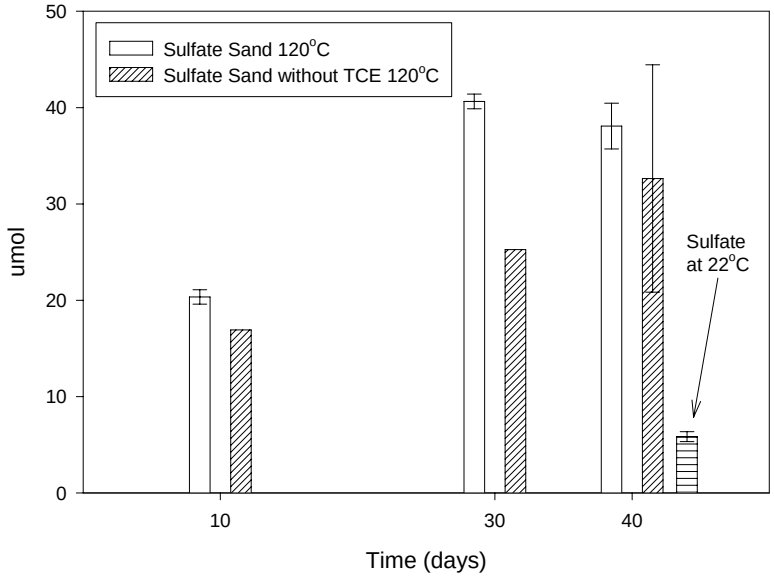

Figure 4.31: Amounts of sulfate in anoxic ampules with Ottawa sand and 100 mg/L of TCE (Batch 6) stored at 22°C and incubated at 120°C.

Sulfate (SO_4^{2-}) was an additional anion detected in ampules that contained solids. The amounts of sulfate detected in anoxic ampules with 20-30 mesh Ottawa sand that were stored at 22°C and incubated at 120°C are shown in Figure 4.31. Sulfate was present at aqueous phase concentrations of greater than 1 mM and is hypothesized to have been

formed from the thermal decomposition of pyrite and marcasite (FeS_2), which were found to be present in the 20-30 mesh Ottawa sand (Dr. Matt Paige, facsimile communication, 30 August 2004) as discussed in Section 4.5.2.2. Similar amounts of sulfate were detected in ampules that contained goethite in addition to 20-30 mesh Ottawa sand (data not shown).

4.5.2.7 Mass Balance

A balance between the loss of TCE and the moles of carbon and chloride detected in ampules incubated at 120°C is provided in Table 4.21. The moles of TCE lost was determined by subtracting the moles of TCE detected after each 120°C incubation period from the initial moles of TCE as determined immediately prior to flame sealing the ampules. The moles of carbon lost was calculated as twice the moles of TCE lost (2×TCE lost) and the moles of chlorine lost as three times the moles of TCE lost (3×TCE lost). The mass balance is a unitless ratio of the moles of TCE lost divided by the moles of degradation products detected with a value of 1 indicating an ideal balance between what was lost and what was found. A value of less than zero corresponds to a gain in the moles of TCE present in the ampule.

The results shown in Table 4.21 indicate that more TCE was lost than could be accounted for by the moles of carbon detected in the gas phase as CO and CO_2, and in the aqueous phase as formate, glycolate, and haloacetic acids (i.e., mass balance > 1). There was also more TCE lost that could be accounted for by the moles of chlorine detected in the aqueous phase as chloride. The failure to achieve mass balance could be attributed to the following explanations: 1) more organic compounds were present than were detected, 2) experimental error occurred during the analysis of TCE, and/or degradation products,

or 3) losses occurred during the sample collection process, in particular volatile degradation products.

Table 4.21: Mass Balance Between Carbon and Chloride Lost as TCE and Detected as Degradation Products in Ampules Incubated at 120°C

Ampule Content (Batch No.)	Incubation Time (days)	C lost/C detected	Cl lost/Cl detected
Anoxic 1000 mg/L TCE (1)	10	6.4±13.0	6.9±14.4
	20	3.7±2.7	2.9±0.6
Oxic 1000 mg/L TCE (2)	10	-2.5±5.2	-1.0±4.1
	20	2.7±4.4	2.4±3.1
Oxic 100 mg/L TCE (3)	10	1.9±1.1	1.8±1.2
	20	1.8±0.0	2.0±0.2
	30	2.5±0.7	3.9±1.2
Anoxic 100 mg/L TCE (4)	10	0.4±1.0	0.3±0.8
	30	0.1±0.9	0.1±1.3
	41	0.2±0.5	0.2±0.8
Ottawa Sand 100 mg/L TCE (6)	10	1.2±1.6	1.0±1.2
	30	2.3±1.4	1.9±2.2
	40	1.6±2.5	1.4±2.4
Ottawa Sand + 1% Goethite 100 mg/L TCE (7)	1	-0.2±1.8	-0.4±2.0
	2	2.0±2.2	3.2±2.0
	4	1.8±2.5	2.7±2.4
pH 10 100 mg/L TCE (5)	1	2.5±0.2	3.5±0.3
	2	1.7±0.2	1.9±0.3
	3	2.1±1.2	2.6±1.8
	4	1.4 (n=1)	1.4 (n=1)

The ratio of the TCE degradation products—moles of chloride divided by the moles of carbon as CO, CO_2, formate and glycolate—provides another measure to determine if all degradation products were detected and has the advantage of being independent of the TCE analysis. The ideal ratio of chlorine to carbon (Cl/C), assuming TCE is the only parent compound, is 1.5 (3Cl/2C). The values for Cl/C shown in Table

4.22 are all close to 1.5, suggesting that the compounds detected represent the majority of the TCE degradation products. Therefore, the poor overall mass balance results shown in Table 4.21 most likely reflect losses in TCE during sample collection and analysis.

Table 4.22: Amount of Carbon and Chloride Detected as Degradation Products and the Cl/C Ratio for Ampules Incubated at 120°C.

Ampule Content (Batch No.)	Incubation Time (days)	C detected (umol)	Cl detected (umol)	Cl/C
Anoxic 1000 mg/L TCE (1)	10	6.5±0.3	5.6±0.3	0.9±0.1
	20	6.0±0.7	13.0±1.5	2.2±0.3
Oxic 1000 mg/L TCE (2)	10	5.3±1.7	9.5±0.3	1.8±0.6
	20	9.0±2.0	21.1±6.3	2.3±0.9
Oxic 100 mg/L TCE (3)	10	4.5±0.5	7.7±1.3	1.7±0.2
	20	7.3±1.0	9.9±0.6	1.4±0.1
	30	6.1±0.2	6.0±0.1	1.0±0.0
Anoxic 100 mg/L TCE (4)	10	4.7±0.6	8.3±1.1	1.8±0.2
	30	6.6±1.0	6.3±0.0	1.0±0.1
	41	7.1±0.1	6.6±0.4	0.9±0.1
Ottawa Sand 100 mg/L TCE (6)	10	5.2±1.2	8.8±0.4	1.7±0.4
	30	7.1±0.8	13.1±1.9	1.8±0.3
	40	7.3±0.8	12.7±0.6	1.7±0.2
Ottawa Sand + 1% Goethite 100 mg/L TCE (7)	1	3.3±0.5	2.7±0.9	0.8±0.3
	2	4.5±1.1	4.3±0.6	1.0±0.3
	4	5.9±0.8	6.0±0.3	1.0±0.1
pH 10 100 mg/L TCE (5)	1	5.5±0.1	5.8±0.1	1.1±0.0
	2	9.8±0.7	13.6±0.7	1.4±0.1
	3	11.1±2.0	14.2±4.8	1.3±0.5
	4	10.1 (n=1)	16.2 (n=1)	1.6

*Corrected for the moles of carbon found in paired ampules without TCE

4.5.2.8 Rate of TCE Degradation

Previous studies performed by Knauss et al. (1999) and Jeffers and Wolfe (1996) reported the rate of TCE disappearance based on the first-order reaction rate model. Thus the rate of TCE disappearance is reported in Table 4.23 based on a fit of the natural log of TCE concentration vs. incubation time, and a fit of the natural log of total carbon and chlorine degradation products vs. incubation time. The rate for ampules with 1,000 mg/L of TCE (Batches 1 and 2) are not presented as these results were from only 2 time periods. The first-order rate coefficients for the loss of TCE was determined after correcting for the non-degradative loss of TCE that occurred after cooling the 120°C ampules to room temperature (22°C), which was potentially due to sorption to ampule walls or solids, when present. The correction involved subtracting the amount of TCE detected in the ampules at 120°C from the amount measured in ampules stored at 22°C to yield the effective amount of TCE lost due to degradation alone at each incubation time. The rate coefficient (k) for the disappearance of TCE was determined by fitting the measured amount of TCE at each incubation time (t) using Equation 4.1:

$$\ln\left(\frac{\mathrm{TCE}_0 - \left[\mathrm{TCE}\ 22^{\circ}\mathrm{C} - \mathrm{TCE}\ 120^{\circ}\mathrm{C}\right]}{\mathrm{TCE}_0}\right) = kt \qquad (4.1)$$

The rate of TCE degradation was also determined based on the amount of reaction products detected. The rate of TCE degradation based on the carbon products, represented by the sum of CO, CO_2, H_2CO_3, formate, and glycolate, was determined by fitting the calculated amount of TCE at each incubation time using Equation 4.2:

$$\ln\left(\frac{TCE_0 - \frac{\Sigma[Carbon]}{2}}{TCE_0}\right) = kt \qquad (4.2)$$

The rate of TCE degradation based on the amount of chloride detected was determined by fitting the calculated amount of TCE at each incubation time using Equation 4.3:

$$\ln\left(\frac{TCE_0 - \frac{\Sigma[Chloride]}{3}}{TCE_0}\right) = kt \qquad (4.3)$$

Table 4.23: Rate of TCE Disappearance from the 100 mg/L Ampules at 120°C

Basis	Decrease in TCE		Increase in Carbon		Increase in Chloride	
Rate	Rate (1/day) $k \times 1000$	Half-Life (days)	Rate (1/day) $k \times 1000$	Half-Life (days)	Rate (1/day) $k \times 1000$	Half-Life (days)
Anoxic (4)	No Change	--	2.6±0.8[a] $r^2 = 0.83$	262	1.2±1.3 $r^2 = 0.30$	591
Oxic (3)	3.4±0.8 $r^2 = 0.89$	201	2.8±1.2 $r^2 = 0.72$	248	1.8±1.6 $r^2 = 0.37$	393
Sand (6)	6.2±2.6 $r^2 = 0.74$	111	2.8±1.0 $r^2 = 0.80$	244	3.5±1.2 $r^2 = 0.81$	200
Sand+ 1%Goethite (7)	53.4±20.1 $r^2 = 0.78$	13	23.3±6.3 $r^2 = 0.87$	30	15.8±3.2 $r^2 = 0.92$	44
NaOH (5)	34.0±21.9 $r^2 = 0.45$	20	39.9±11.9 $r^2 = 0.79$	17	42.0±8.1 $r^2 = 0.90$	17
Knauss et al. (1999)	606	1.1	*Not Reported*	--	*Not Reported*	--
Jeffers and Wolfe (1996)	0.8	858	*Not Reported*	--	*Not Reported*	--

[a] Standard Error

There was no statistically significant change in TCE mass observed in the anoxic ampules that were incubated at 120°C or stored at 22°C. The first-order TCE degradation rate coefficients based on the rate of carbon degradation product appearance in anoxic, oxic, and anoxic ampules containing Ottawa sand were similar at 2.6 to 2.8×10^{-3} day^{-1} corresponding to a half-life of about 250 days. The TCE degradation rate coefficient based on the rate of chloride formation was also similar for the anoxic, oxic, and anoxic ampules containing Ottawa sand ranging from 1.2 to 3.5×10^{-3} day^{-1}, with corresponding half-lives ranging from 591 to 200 days. These findings suggest that the presence of either oxygen or quartz sand had little influence on TCE degradation for the experimental system evaluated herein. In contrast, TCE disappearance and product formation in ampules containing 1% goethite occurred rapidly, yielding first-order rate coefficients ranging from 23.3×10^{-3} day^{-1} (half-life = 30 days) based on the rate of carbon formation to 53.4×10^{-3} day^{-1} (half-life = 13 days) based on the rate of TCE disappearance. Therefore, the addition of goethite resulted in more than a one order-of-magnitude increase in the rate of TCE degradation compared to the other systems investigated, and suggests that iron bearing soil minerals have the potential to substantially increase rates of TCE degradation during thermal treatment.

The first-order rate coefficient for TCE disappearance reported by Jeffers et al. (1989 and 1996), for experiments conducted at 120 °C in Pyrex tubes containing water and headspace was 0.8×10^{-3} day^{-1} (half-life = 858 days). The coefficient is approximately 4 to 8 times less than the values obtained for the anoxic and oxic ampules absent of solids reported Table 4.23. In contrast, the coefficient for the rate for TCE disappearance interpolated from data reported by Knauss et al. (1999) was 0.61 day^{-1} (half-life = 1.1

days), which is approximately 11 times greater than the average value obtained for the ampules containing 1% geothite.

The first-order rate coefficients determined for the ampule experiments reported herein represent the rate of thermally induced TCE degradation for a three-phase system containing gas, aqueous, and solid phases. These conditions are expected during treatment of unconfined aquifers or where steam is used and a gas phase is expected to form during thermal treatment. The rate determined by Knauss et al. (1999) represents a system with only aqueous phase present at elevated pressure, which may be applicable to confined aquifers where a gas phase is not expected to form at elevated temperatures.

4.6 Degradation of TCE in Ampules with Ottawa Sand and Goethite (Fifth Ampule Experiment)

The fifth ampule experiment was completed to verify the rate of TCE degradation and products formed in ampules amended with Ottawa sand and goethite. This work was a partial repeat of the fourth ampule experiment where the results for the sand+1% goethite were based on just 8 ampules: 6 incubated at 120^{o}C in the explosion resistant apparatus and 2 stored at room temperature (22^{o}C). The number of ampules was limited because 8 from the original batch of 16 ampules were destroyed in the oven explosion that occurred during the fourth experimental series. However, the limited results showed that the addition of goethite to the Ottawa sand increased the rate of TCE degradation by greater than one order-of-magnitude. Thus repeating the sand with goethite experiment was justified due to the importance of this finding.

4.6.1 Fifth Ampule Experimental Methods

This experiment utilized the same methods along with the same batch of Ottawa sand and goethite as described for the fourth ampule experiment with the following modifications. The 50 mL Wheaton funnel top ampules, which are no longer manufactured or available, were replaced with 25 mL Kontes ampules. This change resulted in a decrease in the amount of sand and water loaded into each. The average amount of sand was 5.6±1.0 grams with 13.6±1.3 mL of water as compared to the 20 grams of sand and 40 mL of water used during the fourth ampule experiment. The initial TCE concentration was 83.5±5.1 mg/L based on the analysis of 1 mL aqueous samples using the headspace GC method that were collected from 12 randomly chosen ampules just prior to flame sealing. A total of 55 ampules were prepared, 40 with TCE and 15 without TCE so that 5 ampules with TCE and 3 TCE-free controls could be destructively sampled at each incubation interval along with 3 TCE-containing ampules maintained at 25^{o}C.

The ampules were incubated at 120^{o}C within a custom made enclosure consisting of a steel box lined with 2 inch thick mineral wool insulation, fitted with 1/4 inch OD stainless steel tubing all obtained from McMaster-Carr (Atlanta, GA). The tubing was connected to a recirculation bath heater (Barnstead International, Dubuque, IA) filled with silicon oil. The temperature within the heated enclosure was recorded at 2 hour intervals using a K-type thermocouple connected to a datalogger.

The incubation schedule was designed around the rate of TCE degradation determined from the fourth ampule experiment (Table 4.23) where 50% of the TCE should have been degraded after 13 days based on the rate of TCE disappearance vs. 30

days based on the rate of carbon appearance. Ampules were collected after incubating for 2.2, 5.8, 9.8, 21.8, and 46.8 days.

Concentrations of carbon monoxide (CO) and carbon dioxide (CO_2) in gas phase samples were determined using a HP6890 GC equipped with a heated gas sampling valve with a 250 uL sample loop and Carboxen-1010 column (Supleco, Bellefonte, PA) connected to custom made methanizer and FID as described in Section 3.7.1. This technique achieved a detection limit of ca. 16 uL/L (ppmv) for CO and 37 uL/L for CO_2. The GC/methanizer/FID was calibrated using a serial dilution of certified gas mixture (Scotty Specialty Gases, Plumsteadville, PA) that contained carbon dioxide (15%), carbon monoxide (7%), oxygen (5%), and nitrogen (73%). Calibration standards were prepared using a 500 mL syringe (Hamilton Company, Reno, NV) with nitrogen as the dilution gas.

The concentration of ferrous iron [iron(II)] and total iron was determined using the ferrozine method (Stookey, 1970; Violler et al., 2000) where a 100 uL aqueous phase sample from the ampules filled with Camelot soil (Batch 3) was transferred into a 2 mL vial that contained 900 uL of nitrogen sparged DI water with 0.5 M of HCl. After 10 minutes, 300 uL of the aqueous phase extract was added to 2.7 mL buffer solution of 0.4 mM ferrozine [97%, 3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p'-disulfonic acid monosodium salt hydrate, Sigma-Alrich, Milwaukee, WI] with 50 mM HEPES [99.5%, N-(2-Hydroxyethyl)piperazine-N'-(2-ethanesulfonic acid), Sigma-Aldrich, Milwaukee, WI] in a quartz cuvette. The absorbance at 562 nm was measured using a Cary 3E Spectrophotometer (Varian, Palo Alto, CA). The concentration of total iron was determined by adding 300 uL of extract to 2.7 mL of buffer solutions with 64 mM

hydroxylamine sulfate (99.98%, Fisher Scientific, Fair Lawn, NJ), 0.4 mM ferrozine, and 50 mM HEPES in a quartz cuvette followed by measuring the light absorption at 562 nm. The ferrozine method was calibrated using freshly prepared aqueous solutions of ferrous ammonium sulfate (Certified ACS, Fisher Scientific, Fair Lawn, NJ) at the concentrations of 4, 12, 28, and 40 mg/L.

The concentration of sulfide (S^{-2}) was determined using the methylene blue method (Haddad and Heckenberg, 1988) which involved adding 1 mL of Batch 3 ampule water to a 2 mL autosampler vial followed by 50 uL of a methylene blue/sulfuric acid solution and then 1 drop of ferric chloride solution. The vial was capped with a Teflon lined crimp and inverted once. After allowing the sulfide to react with methylene blue (98%, N,N-Dimethyl-p-phenylenediamine Hemioxalate salt, Fisher Scientific, Fair Lawn, NJ), 0.5 ml of the solution from the 2 mL autosampler vial was added to 2.5 mL of DI water in a quartz cuvette and the light adsorption at 664 nm was measured. The methylene blue method was calibrated using a solution of sodium sulfide (ACS reagent, Fisher Scientific, Fair Lawn, NJ) in nitrogen sparged DI water at concentrations of 1, 10, and 100 mg/L.

After determining the pH of the aqueous phase for each ampule, the water was decanted to a sterile container. A 10 mL volume of 50 mM potassium diphosphate (A.C.S. grade, Fisher Scientific) solution was then transferred to the ampule in effort to recover chloride and organic acids adsorbed to the Ottawa sand. Concentrations of formate ($CHOO^-$), glycolate (COH_3COO^-), acetate (CH_3COO^-), oxalate ($COOHCOO^-$), sulfate (SO_4^{2-}) and chloride (Cl^-) in the ampule aqueous phase and in the phosphate

extracts were determined using a Dionex DX-100 ion chromatograph (IC) equipped with an AS14A IonPac column (Section 4.5.1.2).

4.6.2 Fifth Ampule Experiment Results

The amounts of TCE in ampules (aqueous and gas phases) after 2.2 and 5.8 days of incubation at 25 and 120°C (Table 4.24) were not significantly different from the initial amount of TCE (P-Values>0.05). Although there was a significant decrease in the amounts of TCE in ampules after 9.8, 21.8, and 46.8 days of incubation (P-Values<0.05) with respect to the initial amount present, there was no difference between the amounts of TCE found in ampules incubated at 120°C and stored at 25°C (P-Values>0.05) at these intervals. These results show that TCE was disappearing from the ampules at 120°C and 25°C, and are inconclusive regarding an increase in the rate of TCE degradation at 120°C.

Table 4.24: Amounts (Aqueous and Gas Phases) of TCE in 100 mg/L (nominal) Anoxic Ampules with Sand+1% Goethite (Fifth Ampule Experiment)

Content	Day	Total TCE (umol)				P-Value (120 vs. 25°C)
		120°C	n	25°C	n	
Sand + 1% Goethite Initial TCE (umol) = 8.3±0.5	2.2	8.1±0.3	5	8.0±0.7	3	0.42
	5.8	8.7±0.7	5	8.8±0.2	3	0.48
	9.8	7.7±0.8	5	7.1±0.9	3	0.17
	21.8	7.2±0.9	5	7.6±0.5	3	0.29
	46.8	7.1±0.9	5	7.5±0.7	3	0.30

n – Number of ampules used to calculate average and standard deviation.

While TCE levels did not provide an indication that TCE was being degraded, the amount of chloride steadily increased with incubation time in TCE containing ampules incubated at 120°C (Figure 4.32). The amounts of chloride in ampules with 100 mg/L

TCE were in excess of that in the TCE containing ampules stored at 25°C and the TCE-free ampules incubated at 120°C. The chloride levels reported in Figure 4.32 are the sum of the chloride found in the ampule aqueous phase and in the 50 mM phosphate solution used to extract the chloride adsorbed to the Ottawa sand.

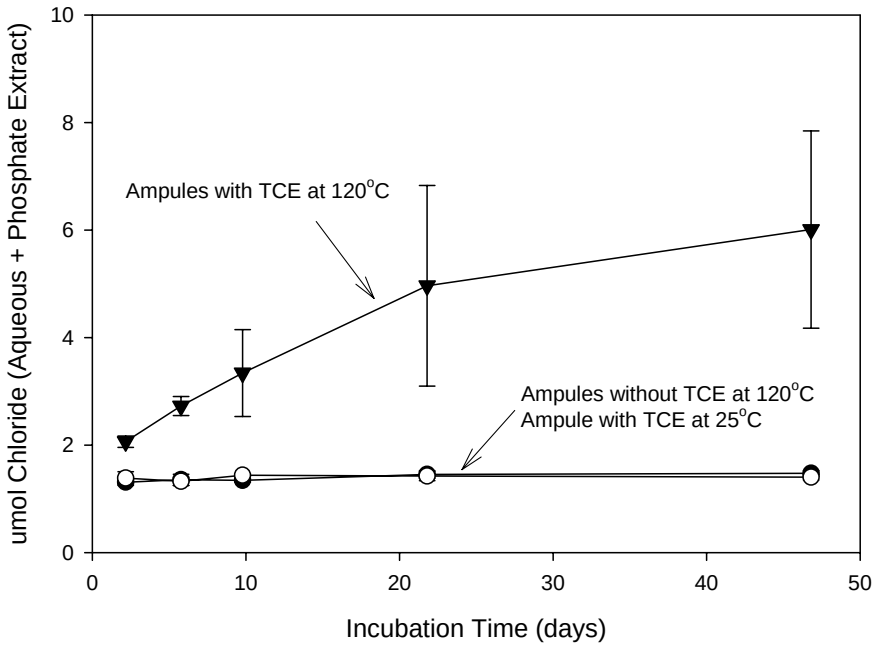

Figure 4.32: Amounts of chloride in anoxic ampules with Ottawa sand+1%goethite and 100 mg/L TCE stored at 25°C and incubated at 120°C along with ampules that were TCE-free and incubated at 120°C.

Another indication that TCE was being degraded in the anoxic ampules with Ottawa sand+1%goethite that were incubated at 120°C was the increase in the amounts of CO and CO_2 with incubation time (Figure 4.33). Here, the total amount of CO_2 is reported as Ct which accounts for the amount of carbonic acid (H_2CO_3) in equilibrium with the ampule aqueous phase as estimated using a Henry's coefficient of 0.0339 M/atm (Stumm and Morgan, 1996). The total amounts of CO_2 were greater in ampules that

contained 100 mg/L of TCE and were incubated at 120°C than in TCE-free ampules or in ampules with 100 mg/L TCE that were stored at 25°C. Carbon monoxide (CO) was only detected in ampules incubated at 120°C with 100 mg/L of TCE.

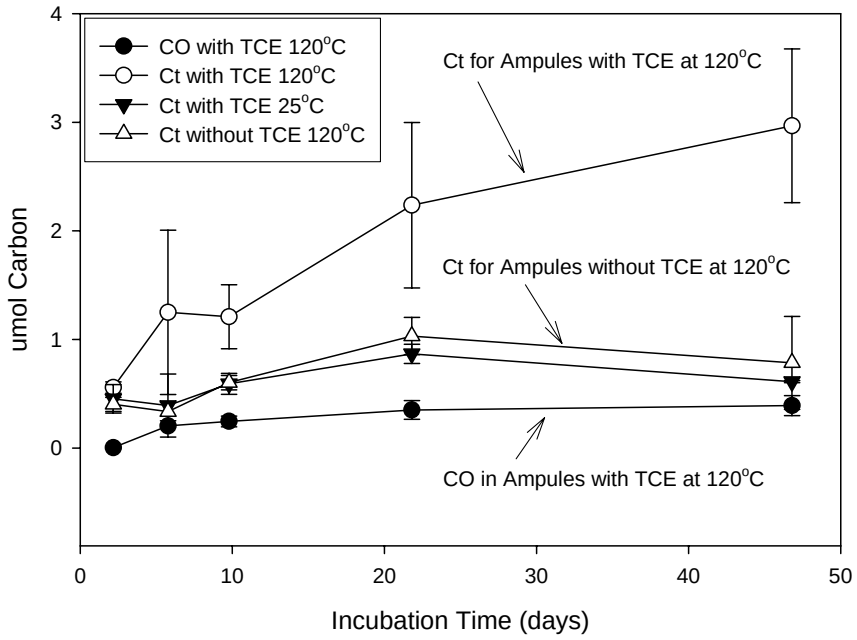

Figure 4.33: Amounts of CO in anoxic ampules with Ottawa sand+1%goethite and 100 mg/L TCE incubated at 120°C along with amounts of total CO_2 (Ct) in ampules with TCE stored at 25°C and incubated at 120°C, and in ampules that were TCE-free and incubated at 120°C.

In addition to CO and CO_2, formate was found in the aqueous phase of ampules incubated at 120°C (Figure 4.34) and was not detected in ampules stored at 25°C. The amounts of formate in the ampules with 100 mg/L TCE that were incubated at 120°C represent the sum of aqueous phase formate and formate detected in the 50 mM phosphate extract solution. Although formate was detected in the aqueous phase of the TCE-free ampules incubated at 120°C, none was detected in the phosphate extract for these ampules.

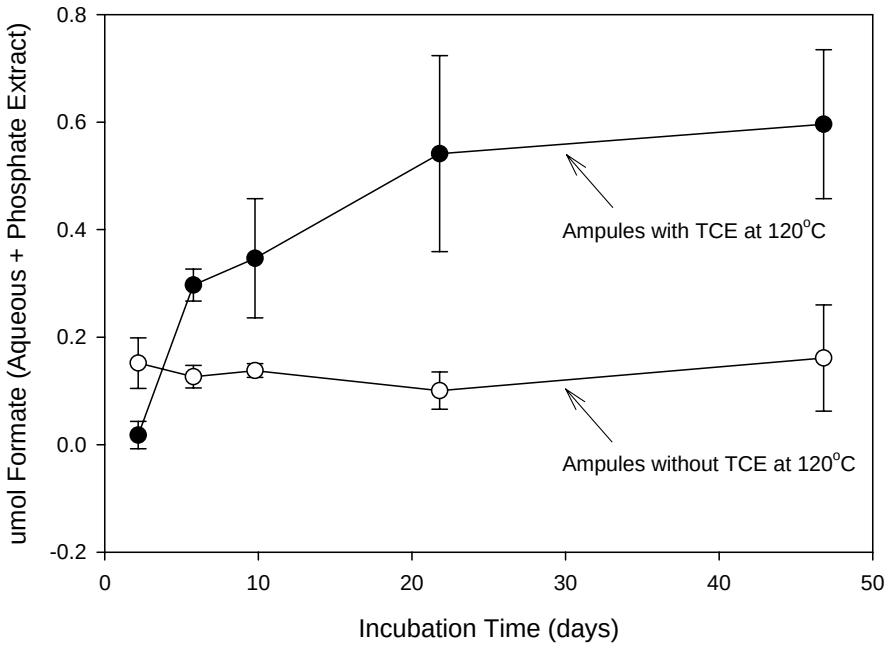

Figure 4.34: Amounts of formate in anoxic ampules with Ottawa sand+1%goethite incubated at 120°C with 100 mg/L TCE and were TCE-free.

The rate of TCE degradation in ampules incubated at 120°C was calculated after correcting for ambient levels of carbon compounds and chloride found in TCE-free ampules incubated at 120°C. Table 4.25 provides the amount of chloride and carbon at each incubation interval for the ampules that contained TCE and were TCE-free, the same values shown in Figures 4.32, 4.33, and 4.34. Also shown in Table 4.25 is the difference between the amount of chloride and carbon for the ampules incubated at 120°C where the standard deviation represents one standard deviation (SD) of the root mean squared (rms) propagated error according to:

$$SD = avg\sqrt{\sum\left(\frac{SD_i}{avg_i}\right)^2} \tag{4.4}$$

Table 4.25: Total Amounts of Chloride and Carbon in Anoxic Ampules with Sand+1% Goethite (Fifth Ampule Experiment)						
day	Chloride (umol) at 120°C			Total Carbon (umol) at 120°C		
	With TCE	TCE-free	Difference (With TCE – TCE-free)	With TCE	TCE-free	Difference (With TCE – TCE-free)
2.2	2.1±0.1[a]	1.4±0.1[a]	0.7±0.1[b]	0.6±0.8[a]	0.6±0.2[a]	0.0±0.0[b]
5.8	2.7±0.2	1.3±0.1	1.4±0.1	1.7±1.1	0.5±0.1	1.3±0.9
9.8	3.3±0.8	1.4±0.0	1.9±0.5	1.8±0.8	0.7±0.1	1.1±0.5
21.8	5.0±1.9	1.4±0.1	3.5±1.3	3.1±1.7	1.1±0.4	2.0±1.3
46.8	6.0±1.8	1.4±0.1	4.6±1.4	3.9±1.6	0.9±0.8	3.0±2.7
[a]Experimental variability [b]Propagated error						

The rate of TCE degradation was then calculated by subtracting the amount of chloride or carbon formed (difference column in Table 4.25) from the initial amount of TCE present according to Equations 4.2 and 4.3. The disappearance of TCE was then fit using a first-order decay model.

Table 4.26: Rate of TCE Disappearance from Anoxic Ampules with Sand+1% Goethite (Fifth Ampule Experiment)				
Day	TCE at 25°C	TCE at 120°C	TCE Based on Chloride	TCE Based on Carbon Products
0	8.3±0.5	8.3±0.5	8.3±0.5	8.3±0.5
2.2	8.0±0.7	8.1±0.3	8.0±0.5	8.2±0.5
5.8	8.8±0.2	8.7±0.7	7.8±0.5	7.6±1.0
9.8	7.1±0.9	7.7±0.8	7.6±0.7	7.7±0.7
21.8	7.6±0.5	7.2±0.9	7.1±1.4	7.3±1.4
46.8	7.5±0.7	7.1±0.9	6.7±1.5	6.8±2.8
Rate (1/day) $k \times 1000$	2.1±1.9	3.6±1.3	4.2±0.6	4.1±0.7
r^2	0.22	0.64	0.91	0.90
Half-Life (days)	335	194	164	168

The first-order rate coefficient (k) for the degradation of TCE within initial concentration of 83 mg/L in ampules with Ottawa sand and 1% goethite was 4.2×10^{-3} day^{-1} based on the amount of chloride detected and 4.1×10^{-3} day^{-1} based on the amount of carbon degradation products formed. These rate coefficients are approximately 6 and 4 times slower, respectively than the coefficients determined during the fourth ampule experiment (Table 4.23).

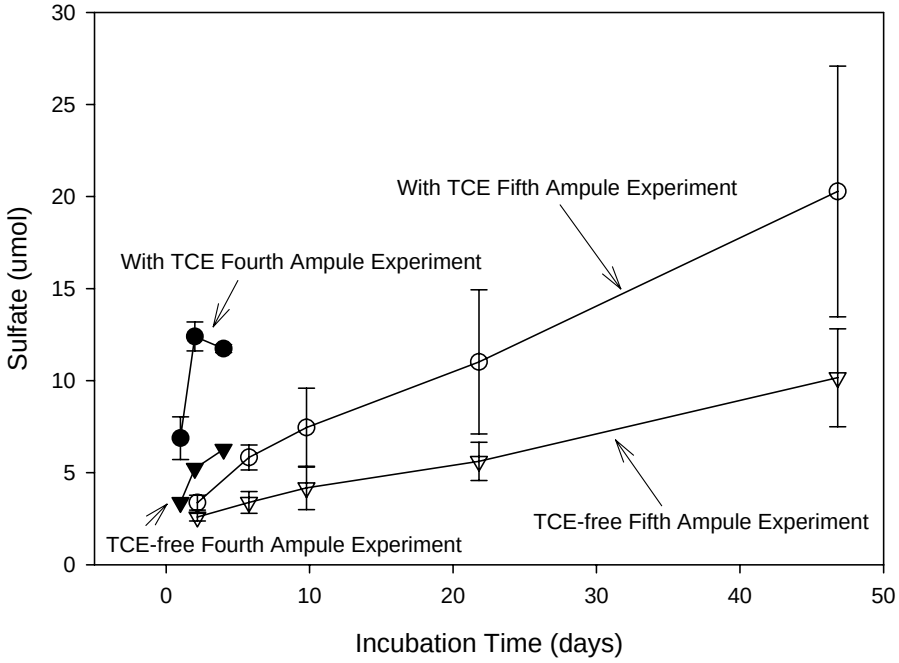

Figure 4.35: Amounts of sulfate in anoxic ampules with Ottawa sand+1%goethite incubated at 120°C with 100 mg/L TCE and were TCE-free.

The decrease in TCE degradation rate between the fourth and fifth ampule experiments may have been due to the decrease in surface area of Ottawa sand due to the difference in ampule volume between experiments (50 mL in the fourth vs 25 mL in the fifth). Another explanation for the difference in TCE degradation rates could be related to

the observation that the amount of sulfate in ampules with TCE was greater than (P-Values<0.05) the amount of sulfate in ampules that were TCE-free (Figure 4.35).

The sulfate observed during the fourth ampule experiment was thought to be caused by the dissolution of pyrite (FeS_2) that was present in the Ottawa sand. If pyrite was undergoing dissolution, then Fe(II) or Fe(III) would have been expected to form, however, none was detected using the Ferrozine analysis method. The observation that sulfate levels were greater when TCE was present and that TCE was being oxidized suggests that a sulfur based oxidant was present in the Ottawa sand. Persulfate ($S_2O_8^{2-}$) and peroxymonosulfate (HSO_5^{1-}) are compounds that are activated by heat (Fossey et al., 1995) to form sulfate radicals which are capable of oxidizing dissolved-phase TCE (Liang et al., 2004). Persulfate is also activated when transition metals (e.g., Fe[II], Ag[I]) are present to serve as electron donors or reductants (Fossey et al., 1995). Since TCE is being oxidized (loss of electrons) in the ampules, TCE may serve as the electron donor resulting in sulfate production.

4.7 Degradation of PCE as a Function of Ampule Oxygen and Solids Content (Sixth Ampule Experiment)

This experiment was initiated at the request of William Health, Chief Technical Officer, Current Environmental Solutions (CES) who wanted an evaluation of the rate of PCE degradation and products that could be expected to form while using electrical resistive heating to remediate PCE contamination at the Camelot Cleaners Superfund site located in West Fargo, ND. The sixth ampule experiment involved incubating dissolved-phase PCE at 25, 55, 75, and 95^{o}C for up to 75 days. The experiment was completed using three batches of 25 mL Kontes ampules (Table 4.27). One batch of ampules contained PCE contaminated DI water with low oxygen content (anoxic) and a second

batch was amended with oxygen at ambient levels (oxic). A third batch of ampules was prepared with soil and groundwater samples that were collected from the Camelot Cleaners site by CES personnel.

The ampules were destructively sampled at four incubation intervals and the chemical constituents in each ampule phase were determined using the methods described in the previous sections with modifications as described in the following sections.

Table 4.27: Experimental Matrix for the Sixth Ampule Experiment

Batch No.	Aqueous Phase	Headspace Gas	Solids	No. of Ampules
1	Dionized water DO = 0.2-0.3 mg/L	Argon	none	80
2	Dionized water DO = 8-10 mg/L	Air (21% O_2)	none	80
3	Camelot Groundwater	Nitrogen	Camelot Soil (homogenized)	90 (10 with $HgCl_2$)

DO = dissolved oxygen

4.7.1 Sixth Ampule Experimental Methods

The total number of ampules per batch was increased from the 36 used in the fourth ampule experiment to 80 so that there would be 5 ampules collected at each of the four incubation time intervals (5 amps×4 times×4 temperatures = 80). The number of replicate ampules was increased was due to the inherent variability associated with field samples and therefore, additional samples were required to characterize the range of PCE and degradation product concentrations.

4.7.1.1 Preparation of DI Water Solutions and Ampules

Stock solutions of PCE were prepared by transferring either argon- or UZA-sparged DI-Nanopure water from a 4 L carboy (Section 4.1.2) via gravity drainage into 2 L volumetric flasks. The 2 L flasks were prepared prior to use by autoclaving with steam at 17 psi (121^{o}C) for 25 minutes, rinsing with DI-Nanopure water (>18 MΩ/cm), and drying at 200^{o}C for 2 hours. The flasks were allowed to cool to room temperature within the drying oven and were then flushed with argon gas prior to filling with sparged DI-Nanopure water. A Teflon-coated stir bar was placed into each water-filled flask, to which neat PCE (99.5% unstabilized ACS grade, Sigma-Aldrich, Milwaukee, WI) was added using a gas-tight syringe. Approximately 0.013 mL of PCE was added to create 10 mg/L solutions (0.013 mL×1.62 g/mL÷2 L = 10 mg/L). The 2 L flasks were then sealed with glass stoppers and the stoppers were wrapped with parafilm. The 2 L flasks were covered with a dark plastic bag to minimize light exposure. The contents of the flasks were mixed for a period of at least 36 hours at room temperature (25^{o}C).

Batch experiments were conducted in clear, 25 mL borosilicate glass ampules (Kimble-Kontes, Vineland, NJ). Prior to use, the ampules were autoclaved for 25 min at 121^{o}C and then rinsed with DI water. The ampules were placed in a glass desiccator that was then evacuated under a vacuum of 750 mm Hg for a period of 1 h and flushed with either argon gas or ultra zero grade air (UZA) to achieve anoxic or oxic conditions, respectively. The ampules were filled with approximately 20 mL of the 10 mg/L PCE stock solution, which was dispensed under positive pressure through a 1/8 inch OD section of Teflon tubing from the appropriate (i.e., anoxic or oxic) 2 L flask. The ampules

were flame sealed using a propane-oxygen torch (BernzOMatic, Medina, NY) that had a maximum flame temperature of ca. 2,500^{o}C.

4.7.1.2 Preparation of Camelot Ampules

Soil and groundwater samples were collected from the Camelot Cleaners site by personnel working for Current Environmental Solutions (CES). CES is firm that specializes in electrical resistance heating remediation and these soil and water samples were collected during the installation of a thermal treatment system. The soil samples were collected from a single location designated as E17 and consisted of 2 soil cores (about 1 kg each) that were contained in acetate liners (18 in long by 2 in dia.); one core was collected from 45 feet below ground surface (bgs) and the other from 56 feet bgs. The cores where shipped to Georgia Tech (Atlanta, GA) where the ampule experiments were completed. At Georgia Tech, the cores were transferred into autoclaved mason jars under anoxic conditions within an argon filled glove bag and 4 soil subsamples were collected from each core to determine the initial PCE content. Each soil subsample has a mass of approximately 15 grams and was placed in a 40 mL vial that contained 10 mL of methanol.

Two methods were evaluated for preparing the soil samples prior to loading into ampules: Method 1 involved loading the ampules with undisturbed Camelot soil and in Method 2, with soil that had been homogenized. Although Method 1 was more physically realistic as PCE was not uniformly distributed in the soil, the initial amount of PCE in each ampule would have been unknown. The sticky nature of the wet soil also complicated the ampule loading and sealing process in that the thin layer of soil which coated the ampule neck interior led to inconsistent flame seal integrity and the potential

to generate radical initiator compounds. Method 1 was abandoned due to uncertainty in the initial PCE content and the poor seal caused by loading the wet soil into each ampule. Instead, the soil was dried and homogenized (Method 2) in preparation for loading into the Batch 3 ampules to minimize interference with the ampule walls and create a more uniform initial PCE content. To dry the soil, the cores were placed in a sterilized glass tray and left in a laminar flow hood for 12 hours at room temperature (25^{o}C). The soil was then homogenized using a mortar and pestle to break up clumps and then thorough mixed in the sterilized glass tray. The average concentration of PCE in the soil after being homogenized was 14.7±7.0 mg/kg based on the analysis of methanol extracts of 12 randomly collected soil samples. The mass of homogenized soil loaded into each ampule (which were prepared as described in the previous section) was determined using an analytical balance (PG503-S, Mettler-Toledo, Inc., Columbus, OH) resulting in an average of 8.7±1.4 g of soil per ampule.

The groundwater was collected from a monitoring well located at the Camelot site; however, no groundwater was present at location E17 where the soil samples were collected. At Georgia Tech, the groundwater was transferred to a 2 L glass flask that had been autoclaved and then rinsed with DI water. Approximately 600 mL of DI water was added to the groundwater to bring the total volume to 1.6 L, enough so that each ampule would receive 15 mL of aqueous solution. A Teflon coated stir bar that had been rinsed with methanol was added to the flask and the flask was placed on a magnetic stir plate to mix the groundwater solution while transferring 15 mL aliquots of water into each soil filled ampule using a volumetric pipette.

After filling 80 of the Batch 3 ampules with approximately 1,200 mL of water, the 400 mL of groundwater remaining in the 2 L flask was amended with 988 mg of mercuric chloride ($HgCl_2$, Fisher Scientific, Fair Lawn, NJ) to create a solution with 2,470 mg $HgCl_2$/L. Trevors (1996) recommended 500 mg of $HgCl_2$ per kg soil if effort to sterilized soil. Using the 2,470 $HgCl_2$/L solution prepared for this experiment resulted in a soil loading of 3,700 mg $HgCl_2$/kg soil based on the 15 mL of water and 10 mg of soil in each ampule. The $HgCl_2$ amended groundwater was added to 10 of the Batch 3 ampules of which 5 were stored at room temperature (25^{o}C) for 75 days and the remaining 5 were incubated at 95^{o}C for 75 days.

4.7.1.3 Analytical Methods

The amount of PCE in the Camelot soil was determined by collecting 5 to 15 gram soil samples and placing them in pre-weighed vials that contained 10 mL of methanol (Optima grade, Fisher Scientific, Fair Lawn, NJ). Each vial was sealed with a screw top lid after wiping the vial lip to remove soil grains, the vial was shaken to mix the soil and methanol, and then the mass of the vial with soil was recorded. These methanol extracts were allowed to sit overnight in a 4^{o}C chamber and then 3, 2 mL samples were collected from each vial for analysis using a Hewlett-Packard (HP) Model 6890 gas chromatograph (GC) equipped with a 30 m by 0.32 mm DB-5 column (Agilent Technologies, Palo Alto, CA) connected to a electron capture detector (ECD). The PCE content of soil at each incubation period was determined using a similar method: 10 mL of methanol was added to each ampule, the methanol and soil were mixed with a metal spatula, and then transferred to a 40 mL vial that was sealed with screw top lid.

The remaining 1 mL of gas from each ampule filled with Camelot soil and groundwater after 75 days of incubation was analyzed for H_2 content instead of the GC/MS analysis. The H_2 content of gas samples was determined using a reduction gas analyzer (RGA3, Trace Analytical, Menlo Park, CA). The analyzer was calibrated using H_2 gas in the 0.1 to 50 uL/L range and was periodically checked using the H_2 present in ambient air.

4.7.1.4 Initial PCE Content

Immediately prior to flame sealing, 1 mL water samples were collected from 4 randomly selected DI water filled ampules to determine the initial aqueous phase PCE concentration for Batch 1 and 2 ampules. The samples were analyzed using the headspace GC method described in Section 4.5.1.2. PCE calibration standards containing 0.5, 1, 5, and 10 mg/L of PCE were analyzed with each sample batch. The calibration standards were prepared by injecting small volumes of 10,000 mg/L PCE methanol stock solution into 100 mL flasks that contained DI-Nanopure water cooled to 4^{o}C. The initial concentration of PCE in the anoxic ampules (Batch 1) was 7.0±0.9 mg/L while the concentration in oxic ampules (Batch 2) was 6.8±0.6 mg/L.

The initial PCE content of soil cores was determined by the analyzing methanol extracts from 4 sub-samples collected from each core (E17-45 and E17-56). The compounds present in the methanol extract from each soil sample were initially determined by injecting 1 uL of the methanol into a GC/MS (Varian). There was PCE in addition to toluene and xylene present in the methanol extracts from soils samples collected from E17-45, however, no contaminants were present in the methanol extracts

from E17-56. The concentration of PCE in the E17-45 soil core was 1,082±924 mg/kg based on the analysis of 4, 15 g soil samples collected from the 1 kg core.

The initial concentration of PCE in the ampules filled with Camelot soil (Batch 3) was determined by measuring the PCE content in methanol extracts from 12 samples collected after homogenizing the soil (Section 4.7.1.2). The average initial PCE content of the soil in the Batch 3 ampules was 14.7±7.0 mg/kg.

4.7.1.5 Ampule Incubation Schedule

Ampules were incubated at 55, 75, and 95 ^{o}C within custom made enclosures that consisted of ice chests fitted with 1/4 inch OD copper tubing. The copper tubing was connected to constant temperature recirculation bath heaters (Barnstead International, Dubuque, IA) filled with food grade mineral oil (STE Oil Co., San Marcos, TX). Enclosure temperatures were recorded every hour using K type thermocouples connected to a data logger (Campbell Scientific, Inc., Logan, UT) where the average enclosure temperatures were 53.7±0.6, 77.1±0.5, and 96.7±0.6 ^{o}C. Ampules were also stored in an ice chest at room temperature (25±1 ^{o}C).

Ampules with anoxic and oxic DI water were prepared on 2 November 2004 while the ampules with Camelot soil and water were prepared on 22 November 2004. Twenty ampules were to be collected from each batch at each of four incubation intervals: 5, 10, 20, and 40 days after placing ampules in the incubation enclosures. However, the incubation durations were extended as reported in the following results section due to the lack of PCE degradation.

4.7.2 Sixth Experimental Series Results

The following sections describe the results for experiments completed to determine the thermal induced degradation of PCE dissolved in deionized water (DI) and in field samples collected from the Camelot Cleaners Superfund site.

4.7.2.1 PCE Degradation in DI Water

The amount of PCE in each ampule was calculated based on the aqueous phase PCE concentration and the estimated gas phase PCE concentration. The gas phase PCE concentration was estimated using Henry's law ($C_g = HC_w$), assuming equilibrium conditions, with C_w equal to the PCE aqueous phase concentration as determined by GC analysis, and the dimensionless Henry's Law constant (H) equal to 0.699 at 25°C (Staudinger and Roberts, 2001). These estimates were performed to correct for the

Table 4.28: Amount of PCE in Anoxic (Batch 1) Ampules

Incubation Time (days)	Incubation Temperature (°C)			
	25	55	75	95
0	1.10±0.16[a] (IV)[b]	1.10±0.16 (IV)	1.10±0.16 (IV)	1.10±0.16 (IV)
6	1.04±0.03 (V)	1.19±0.13 (III) 0.02[c]	1.08±0.07 (V) 0.15	1.03±0.04 (V) 0.19
14	1.02±0.05 (V)	1.06±0.11 (IV) 0.22	1.10±0.01 (IV) 0.01	1.08±0.03 (V) 0.07
37	0.97±0.03 (IV)	1.06±0.08 (V) 0.02	1.01±0.07 (V) 0.27	1.04±0.03 (V) 0.03
70	0.78±0.02 (V)	0.93±0.11 (V) 0.02	0.77±0.05 (V) 0.38	0.79±0.01 (IV) 0.17

[a]average amount of PCE (umol) ±standard deviation.
[b]number of ampules provide in roman numerals.
[c]P-Value for one-sided t-test between amount of PCE in 25°C ampules and amount in ampules at other incubation temperatures.

differences in the volume of gas (headspace) between ampules that was due to slight differences in the volume of water initially added to each ampule. The amount of PCE (i.e., umol) in each ampule was then calculated based on the concentration of PCE and the volume of water and volume of gas in each ampule. The volume of water in each ampule was determined by the difference between the weight of the sealed ampule and the weight of the empty ampule after destructive sampling along with a density of water equal to 0.997 g/mL. The volume of gas in each ampule was determined based on the mass of water required to fill the ampule minus the amount of water in the ampule during incubation. The amount of PCE in the ampules shown in Table 4.28 is the average along with the standard deviation (i.e., average±S.D.) calculated from the number (n) of ampules at each time period.

The initial amount of PCE in the Batch 1 ampules was 1.10±0.16 umol based on the analysis of aqueous samples collected from 4 randomly selected ampules just prior to flame sealing. There was a decrease in the amount of PCE in ampules after 6 days at all incubation temperatures with the exception of the ampules at 55^{o}C where the amount of PCE increased to 1.19 umol. The amount of PCE decreased steadily in the ampules stored at 25^{o}C with a first-order rate of $4.7\pm0.8\times10^{-3}$ 1/day ($r^2 = 0.92$) for an apparent half-life of 148 days. The amount of PCE also decreased with incubation time in ampules maintained at 55, 75, and 95^{o}C, however, the rate of decrease was less than that for PCE in ampules maintained at 25^{o}C.

The average recovery of PCE from the Batch 1 ampules is shown in Figures 4.36, and represents the average amount of PCE at each incubation time with respect to the initial average amount of PCE. The error bars shown in Figure 4.36 represent one

standard deviation (SD) of the root mean squared (rms) propagated error according to Equation 4.1. There was little change in the average amount of PCE in ampules with anoxic DI water as indicated by PCE recoveries near 100% over incubation times up to 37 days. There was a substantial decrease (~30%) in the amount of PCE after 70 days for all incubation temperatures. However, the average amount of PCE in ampules at 75 and 95°C was not significantly different (P-Value>0.05, Table 4.28) from that found in ampules stored at 25°C. Thus there was no difference between the loss of PCE from ampules stored at room temperature (25°C), where PCE degradation was not expected, and ampules incubated at 75 and 95°C.

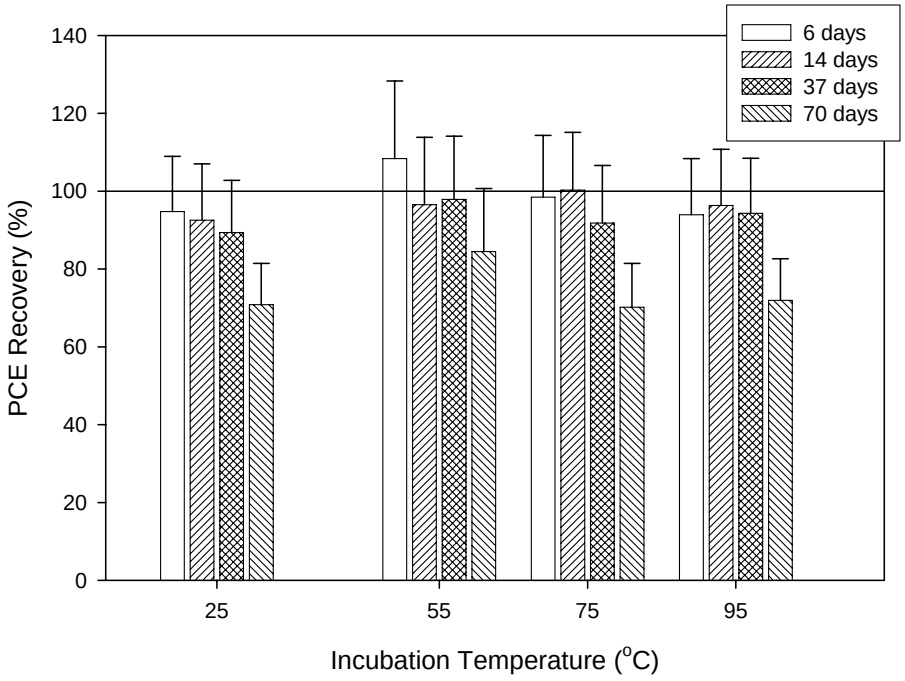

Figure 4.36: PCE recovery from ampules filled with anoxic DI water (Batch 1).

The initial amount of PCE in the Batch 2 ampules was 1.06±0.09 umol based on aqueous samples collected just prior to flame sealing from 3 randomly selected ampules.

The amount of PCE decreased after 6 days in ampules maintained at 25 and 95°C, was unchanged in the 55°C ampules, and increased in the 75°C ampules. After 14 days, the amount of PCE increased relative to the amount detected after 6 days in ampules maintained at 25, 55, and 95°C where the amount of PCE in ampules at 75°C was greater than found when the ampules were initially prepared. The amount of PCE in ampules after incubating for 41 days was similar to that found after 14 days with the exception of a slight increase in the amount of PCE in the 75°C ampules. The only appreciable decrease in the amount of PCE was detected after incubating the ampules at 55, 75, and 95°C for 75 days where there was an 18% decrease in PCE content relative to the initial amount. This results was similar to that found for the anoxic (Batch 1) ampules; however,

Table 4.29: Amount of PCE in Oxic (Batch 2) Ampules

Incubation Time (days)	Incubation Temperature (°C)			
	25	55	75	95
0	1.06±0.09[a] (III)[b]	1.06±0.09 (III)	1.06±0.09 (III)	1.06±0.09 (III)
6	1.01±0.05 (V)[b]	1.06±0.06 (III) 0.12[c]	1.16±0.07 (V) 0.02	1.02±0.04 (V) 0.29
14	1.05±0.04 (V)	1.19±0.08 (V) 0.03	1.07±0.06 (III) 0.34	1.04±0.04 (V) 0.28
41	1.06±0.04 (V)	1.11±0.10 (V) 0.21	1.14±0.03 (V) 0.00	1.04±0.08 (V) 0.00
75	1.00±0.03 (V)	0.87±0.08 (V) 0.02	0.87±0.05 (V) 0.00	0.87±0.04 (IV) 0.00

[a]average amount of PCE (umol) ±standard deviation.
[b]number of ampules provide in roman numerals.
[c]P-Value for one-sided t-test between amount of PCE in 25°C ampules and amount in ampules at other incubation temperatures.

in this case, there was a significant difference between the amount of PCE in oxic ampules incubated at 55°C and above and the amount in the ampules maintained at 25°C (P-Values<0.05, Table 4.29). This decrease in PCE content of ampules incubated at greater than 25°C may be due to thermal induced PCE degradation.

The average recovery for the Batch 2 ampules is shown in Figure 4.37 which demonstrates that there was little change in the PCE content of oxic ampules over a 41 day period with a significant decrease in PCE levels after 75 days of incubation at temperatures greater than 25°C.

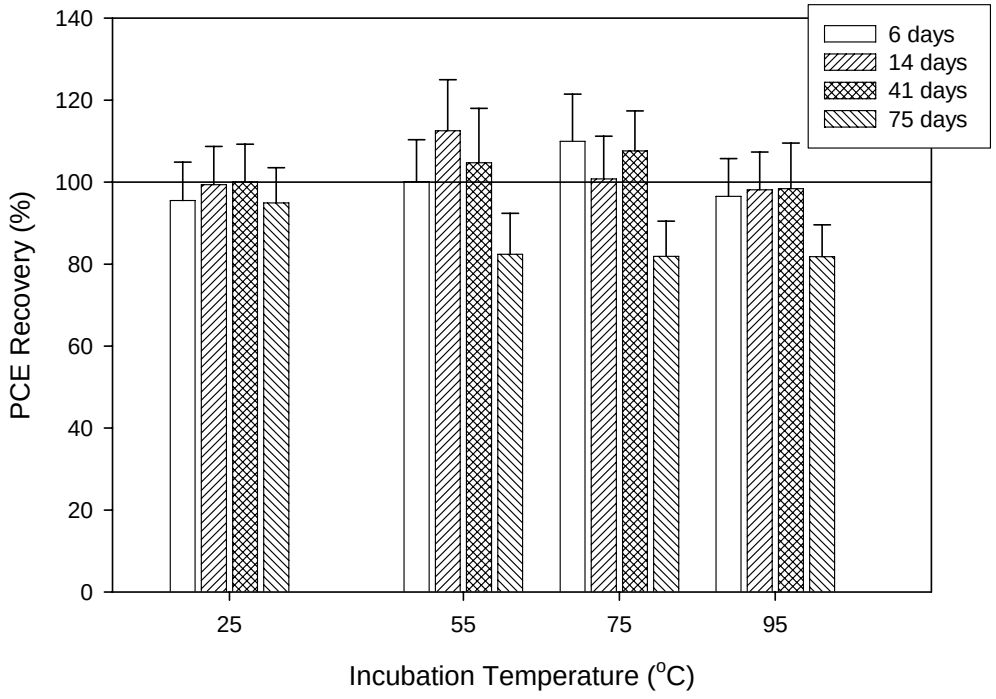

Figure 4.37: PCE recovery from ampules filled with oxic DI water (Batch 2).

If PCE were being degraded via a dechlorination reaction, then the amount of chloride in the ampules was expected to increase with incubation time. The average amounts of chloride in the Batch 1 ampules are shown in Figure 4.38 with the chloride in

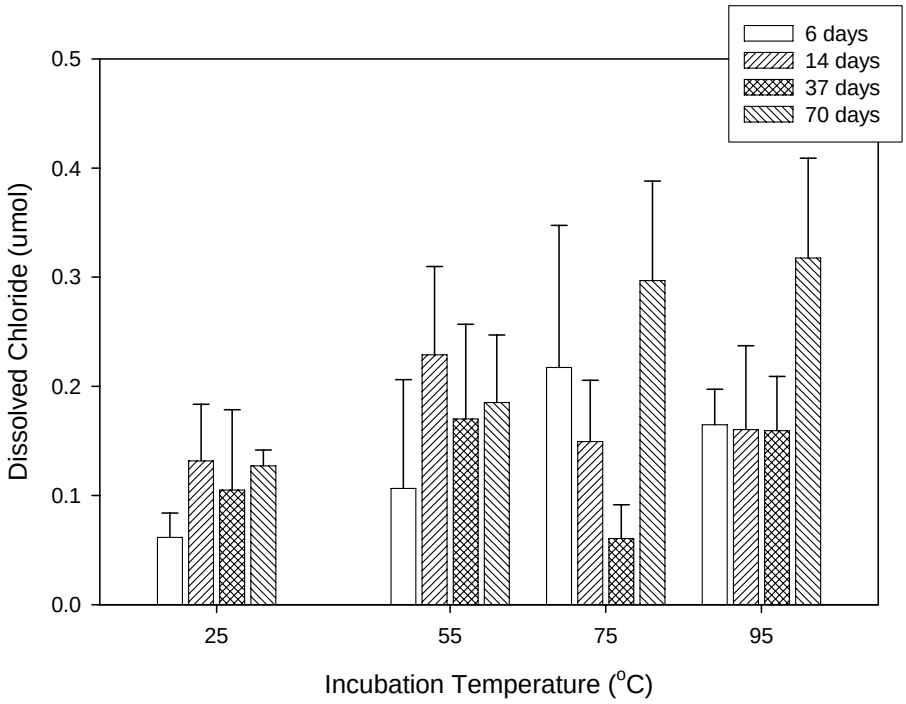

Figure 4.38: Amounts of aqueous phase chloride in Batch 1 ampules (anoxic).

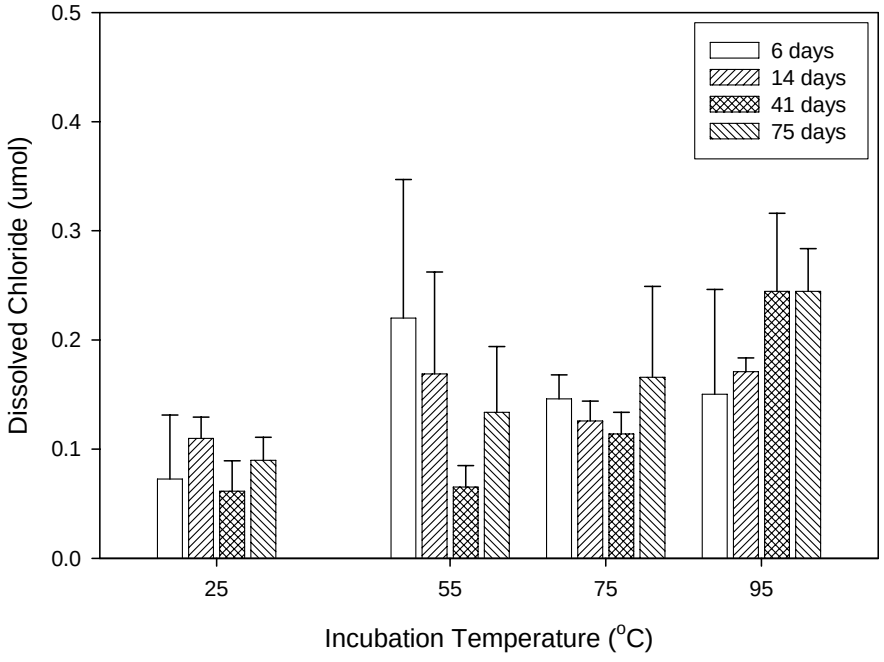

Figure 4.39: Amounts of aqueous phase chloride in Batch 2 ampules (oxic).

Batch 2 ampules shown in Figure 4.39. The least amount of chloride was found in the ampules maintained at 25°C with more found in the ampules incubated at 55, 75, and 95°C in both the anoxic and oxic ampules. The amount of chloride increased with incubation time in the anoxic ampules maintained at 25°C, which when combined with the observation that the amount of PCE decreased in these ampules with incubation time (Table 4.25) might lead to the conclusion that PCE was being degraded in the 25°C anoxic ampules. The same argument regarding the degradation of PCE in the oxic ampules incubated at 95°C could be made based on the increase in chloride with incubation time at 95°C (Figure 4.39) along with the significant decrease in PCE content after 75 days at 95°C (Figure 4.37).

If the chloride detected in ampules during incubation represented PCE degradation then carbon degradation products would be expected to form. The gas phase from the ampules was analyzed for CO and CO_2 content and injected into a GC/MS to determine the presence and identify of other gas phase compounds. The amounts of CO_2 detected in the anoxic (Batch 1) ampules are shown in Figure 4.40 with the amounts of CO_2 found in the oxic (Batch 2) ampules shown in Figure 4.41. Instead of increasing with incubation time, the amount of CO_2 was remarkably consistent over all temperatures with the average concentration of 84±16 uL/L (ppmv) determined from the analysis of 69 of the 80 anoxic ampules. The 11 ampules that were excluded from this analysis had CO_2 levels that were significantly different (P-Values<0.05) than their companion ampules, which combined with the fact that CO was also present in these 11 ampules, led to the conclusion that the interior of these ampules was inadvertently exposed to the propane-oxygen flame during the sealing process. The average concentration of CO_2 over all

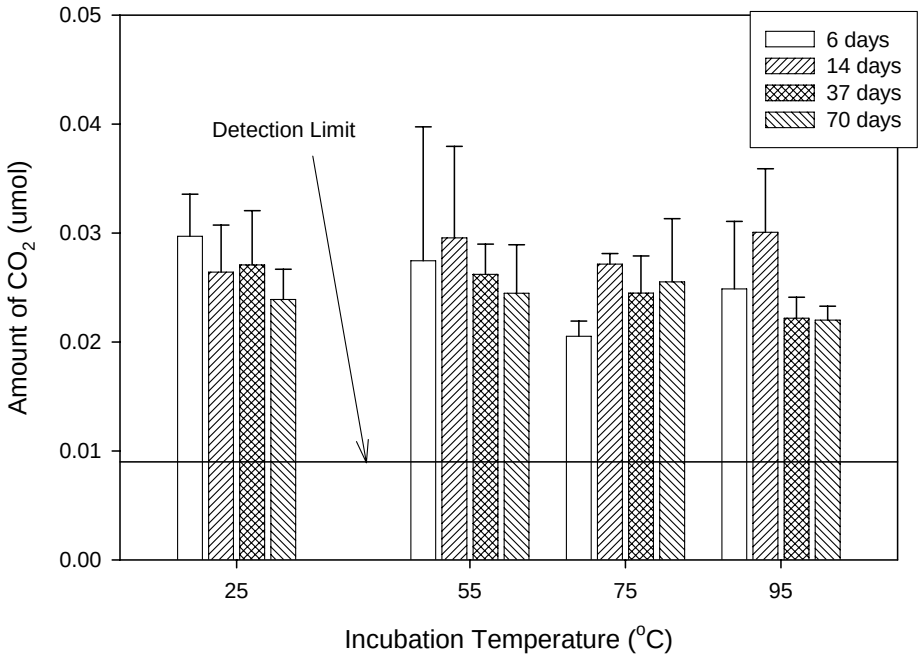

Figure 4.40: Amounts of CO_2 in gas phase of Batch 1 ampules (anoxic).

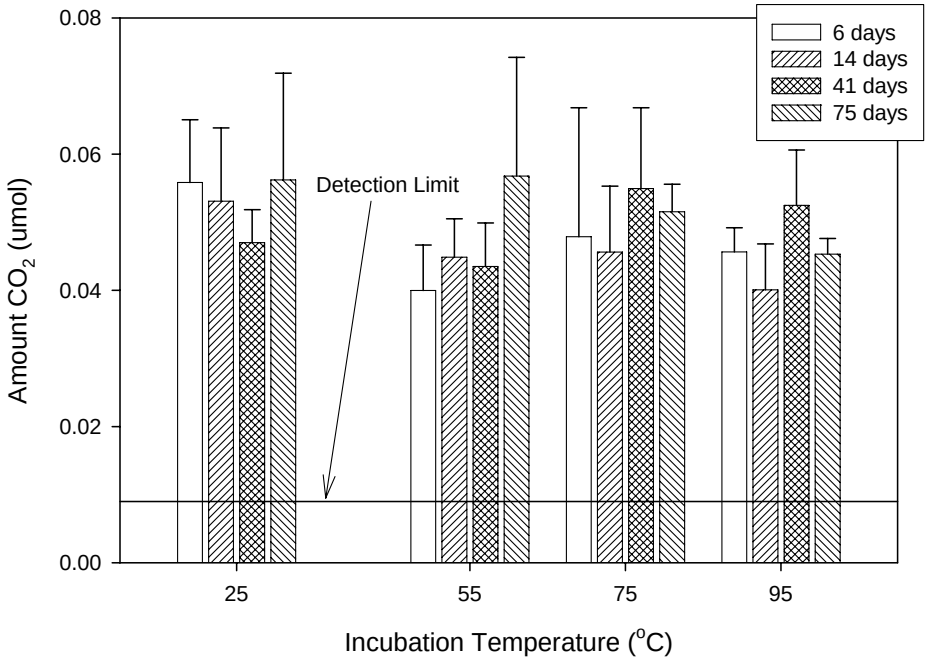

Figure 4.41: Amounts of CO_2 in gas phase of Batch 2 ampules (oxic).

incubation times and temperatures for the oxic ampules was slightly greater at 152±29 uL/L (ppmv) determined from 76 of the 80 ampules, but was also consistent.

Carbon monoxide (CO), another potential PCE degradation product, was not detected above its 16 uL/L detection limit, except in ampules suspected of being exposed to the propane-oxygen torch. Tetrachloroethylene (PCE) was the only compound detected in the GC/MS analysis of ampule gas samples. In addition to the gas phase samples, select aqueous samples were analyzed using ion chromatography and were processed to determine the chloroacetic acid content. The aqueous phase samples were found to be free of organic acids such as formate, acetate, and glycolate as well as chloroacetic acids including chloroacetate, dichlororacetate, and trichloroacetate (Table 4.30).

Table 4.30: Average Concentrations for Expected PCE Degradation Products

Ampules	CO (uL/L)	CO_2 (uL/L)	Organic Acids (mg/L)	Chloroacetic Acids (ug/L)
Anoxic (Batch 1)	< 16 (n = 68)	84±16 (n = 69)	< 1	< 10
Oxic (Batch 2)	< 16 (n = 76)	152±29 (n = 76)	< 1	< 10

While an argument could be made that PCE was degraded based on the change in PCE content combined with slight increases in chloride levels, the lack of change in CO_2 levels combined with the absence of CO, organic acids, and chloroacetic acids—compounds found during TCE degradation experiments—weakens the argument for PCE degradation. Thus it was concluded that PCE was not degraded in the DI water filled ampules over a period of 75 days and at incubation temperatures of up to 95^{o}C. This conclusion is more consistent with the results of Jeffers et al. (1989) who reported a first-order half-life of 75,200 years for PCE degradation at 95^{o}C and stated that "PCE is

essentially inert" (Jeffers et al., 1994, p. 829). The lack of PCE degradation in these experiments is contrasted by the findings of Knauss et al. (2000b) who stated that PCE was readily degraded in their experiments.

4.7.2.2 PCE Degradation in Contaminated Soil and Groundwater

The Camelot ampules (Batch 3) contained groundwater and soil collected from the Camelot Cleaners Superfund site located in West Fargo, ND. The ampules were filled with approximately 8.7±1.4 g of Camelot soil that had an average PCE concentration of 14.7±7.0 mg/kg which resulted in an average initial PCE loading of 0.78±0.39 umol per ampule. PCE was not detected in the groundwater used to fill the ampules. The average aqueous phase PCE concentration in the Camelot ampules, as determined by headspace/GC analysis of a 1 mL aqueous sample collected from each ampule, increased with incubation temperature (Figure 4.42). However, comparing the aqueous-phase PCE concentrations between ampules at the same incubation temperature shows that there was no change in PCE concentration with incubation time (P-Values>0.05) with the exception of the 95^{o}C ampules. These results suggest that increasing ampule temperature resulted in an increase in the amount of PCE that partitioned to the aqueous phase from the solid phase (i.e., desorption of PCE).

After draining the water from each ampule, 10 mL of methanol was added and the solids and methanol were mixed for about 30 seconds. The methanol-soil slurry was then transferred to a 40 mL vial that was sealed with a Teflon lined septum and stored for 24 hours at 4^{o}C; similar to the method used to estimate the initial soil PCE content. PCE was the only compound detected in the methanol extracts and the average solid phase PCE concentrations are shown in Figure 4.43.

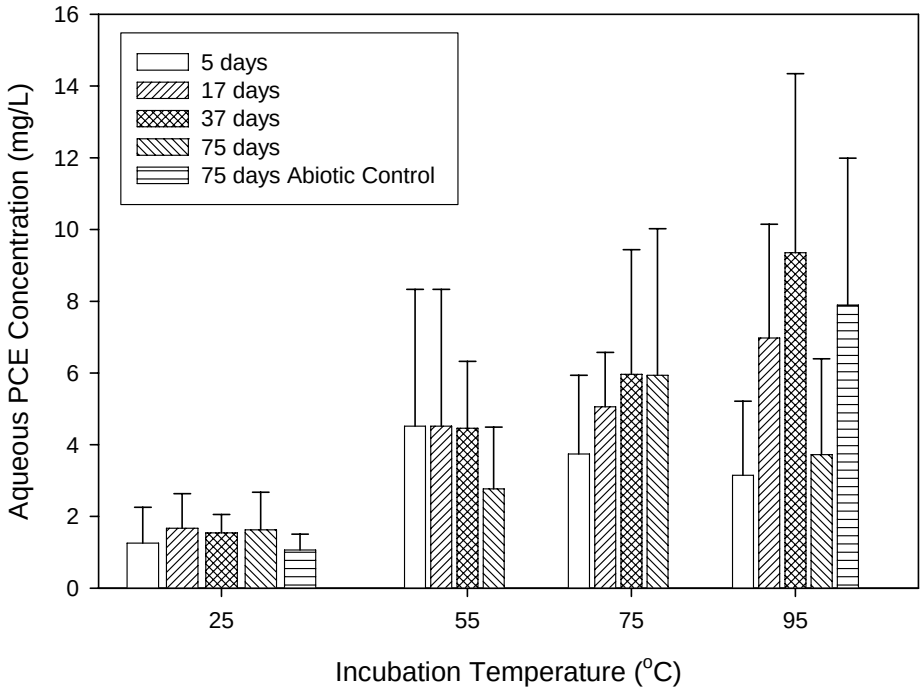

Figure 4.42: Concentrations of PCE in the aqueous phase of Camelot ampules (Batch 3).

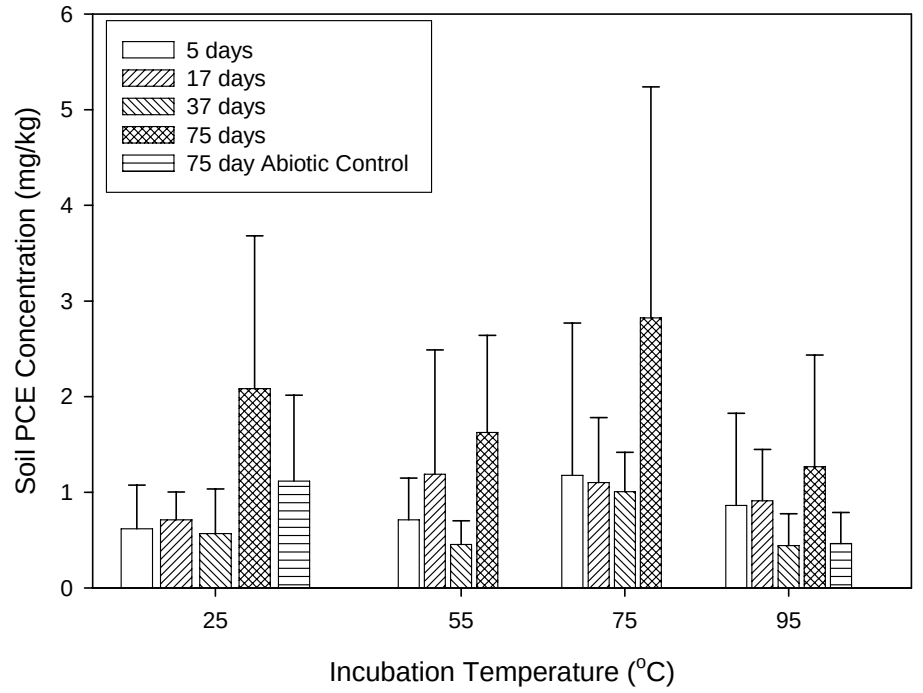

Figure 4.43: Concentrations of PCE in soil from Camelot ampules (Batch 3).

While the concentrations of PCE increased in the ampule aqueous phase with increasing incubation temperature, there was no apparent change in soil-phase PCE concentrations with temperature (P-Values>0.05). These two observations are not compatible within a closed system where the total amount of PCE should remain constant: the concentration of PCE in the soil should have decreased to compensate for the increase in aqueous phase PCE. This assumes the initial amount of PCE in the soil as estimated using methanol extracts was accurate or that the methanol extracts were capable of recovering all the PCE present in the Camelot soil.

Table 4.31: Amount of PCE in Camelot (Batch 3) Ampules

Incubation Time (days)	Incubation Temperature (^{o}C)			
	25	55	75	95
0	0.78±0.39[a] (XII)[b]	0.78±0.39 (XII)	0.78±0.39 (XII)	0.78±0.39 (XII)
5	0.20±0.15 (V) -- 0.05[d]	0.30±0.10 (III) 0.15[c] 0.30	0.55±0.37 (V) 0.08 0.10	0.47±0.32 (IV) 0.07 0.23
17	0.26±0.14 (V) -- 0.13	0.65±0.57 (IV) 0.09 0.07	0.72±0.21 (V) 0.00 0.00	0.96±0.44 (IV) 0.01 0.00
37	0.23±0.08 (V) -- 0.07	0.60±0.26 (V) 0.01 0.03	0.83±0.46 (V) 0.03 0.01	1.24±0.65 (V) 0.02 0.00
75	0.31±0.21 (V) -- 0.30	0.45±0.28 (V) 0.22 0.26	0.93±0.66 (V) 0.06 0.01	0.55±0.41 (V) 0.18 0.11
75 ($HgCl_2$)	0.20±0.11 (V) -- 0.07	*No Ampules Prepared*	*No Ampules Prepared*	1.05±0.51 (III) 0.00 0.02

[a]average amount of PCE (umol) ±standard deviation.
[b]number of ampules provide in roman numerals.
[c]P-Value for one-sided t-test between amount PCE in 25^{o}C ampules and amount in ampules at other incubation temperatures.
[d]P-Value for one-sided t-test between initial amount of PCE and amount in ampules at other incubation times.

Table 4.31 provides the average total amount of the amount of PCE at each incubation temperature and interval in effort to evaluate if more PCE was initially present than was recovered by methanol extracts. The amount of PCE shown in Table 4.31 is the sum of that found in the aqueous and gas phases along with the amount detected in methanol extracts, which represents the total amount of PCE in each ampule. Increasing the ampule temperature caused an increase in the total amount of PCE within ampules and was due to the greater amounts found in the aqueous phase (Figure 4.42). There was more PCE in the ampules after 37 and 75 days of incubation at 75^{o}C and after 17 and 37 days at 95^{o}C than was initially estimated to be present. These results suggest that heating the ampules to at least 75^{o}C caused PCE, which was not extractable by methanol at 4^{o}C, to partition into the ampule aqueous phase. This is an important observation because one of the advantages touted for thermal remediation is that applying heat to the subsurface can increase the rate of contaminant desorption from soil (Davis, 1997).

In terms of PCE degradation, the only indication that PCE was degraded came from the decrease in PCE level after 75 days at 95^{o}C relative the amount found at 37 days and in ampules amended with $HgCl_2$ which were incubated for 75 days at 95^{o}C. This decrease in total PCE content may have represented PCE degradation at 95^{o}C or it may have been that these five ampules were prepared with soil that had lower initial PCE content than the soil used for the 37 day ampules incubated at 95^{o}C. However, there was no significant difference between the mean amount of PCE at each destructive sampling interval for the 25 ampules maintained at 25^{o}C (P-Values>0.05), which were prepared sequentially after the ampules incubated at 95^{o}C. The similarity in the amount of PCE in these 25 room temperature ampules suggests that the decrease in PCE content between 37

and 75 days at 95°C may have been caused by something other than differences between initial PCE contents.

Chloride levels could be tracked to account for the degradation of TCE in ampule experiments completed with low-chloride DI water. The chloride levels in the Camelot ampules were on the order of 300 mg/L, approximately 50 times greater than the amount of PCE (as chloride) introduced into the ampules. The elevated chloride levels in the Camelot ampules obscured the relatively small increases in chloride content that might be attributed to PCE degradation. For example, the amount of chloride in ampules after 37 days at 95°C was 158±22 umol and decreased to 146±25 umol after 75 days at 95°C. Thus changes in chloride levels in the Camelot ampules could not be used to infer PCE degradation.

Carbon monoxide (CO), a degradation product found during the thermal degradation of TCE, might prove useful for tracking PCE degradation in field samples. In fact, CO levels steadily increased, but only in Camelot ampules incubated at 95°C (Figure 4.44). A separate experiment to evaluate the source of CO was performed using the soil collected from 56 feet below ground surface at the Camelot site which was found to be PCE free (Section 4.7.1.4). Twenty-four ampules were prepared with PCE-free Camelot soil and DI-Nanopure water and then incubated at 95°C over a 75 day period. The amount of CO formed in these PCE-free ampules was similar (P-Values>0.05) to that found in the ampules that contained PCE (Figure 4.44). Thus, CO was a likely a product of soil degradation and not necessarily due to PCE degradation in ampules at 95°C.

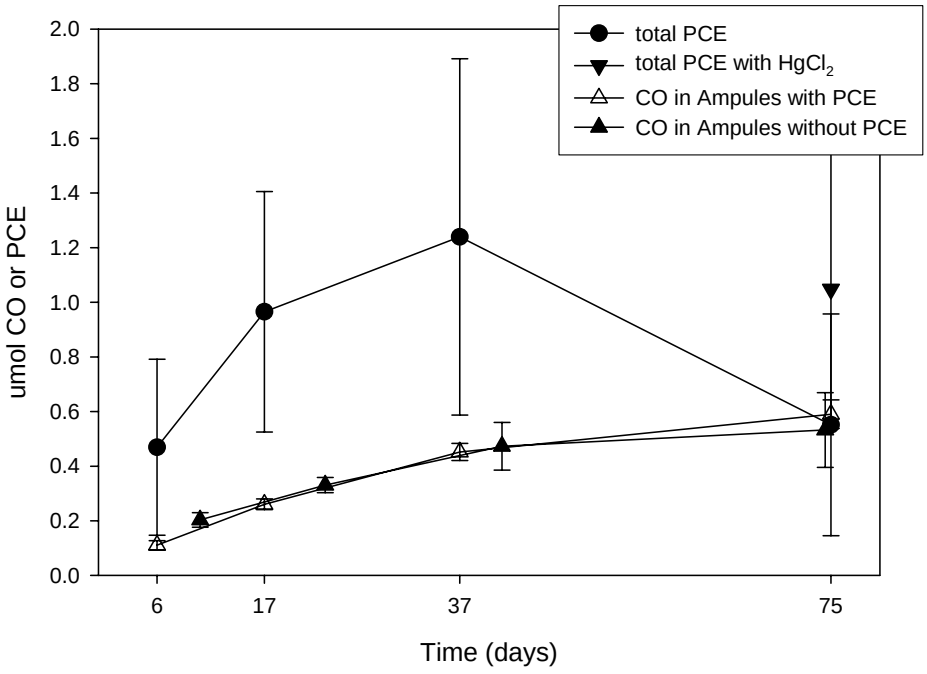

Figure 4.44: Amounts of CO and PCE measured in Camelot ampules incubated at 95°C.

Other potential PCE degradation products were detected in aqueous samples from ampules incubated at 95°C and included TCE, cis-1,2-dichloroethylene (cis-DCE), and 1-butene. These compounds were not found in soil methanol extracts before or during incubation. Trichloroethylene (TCE), cis-DCE, and 1-butene have been detected as products from the reductive dechlorination of PCE in experiments with zero valent iron (Arnold and Roberts, 1998 and 2000). However, 1-butene, like CO, may represent thermal degradation of the organic carbon present in Camelot soil.

While the amounts of CO detected in ampules at 95°C were similar (Figure 4.44), there was more 1-butene detected in ampules with PCE and less in the PCE-free ampules (Figure 4.45). The concentration of 1-butene was determined using the headspace-GC which was calibrated using standards prepared in a 500 mL gas-tight syringe from 1-

butene gas (99.8%. Sigma-Aldrich, Milwaukee, WI). The difference in the amounts of 1-butene, shown in Figure 4.45, may have been due to PCE degradation or to differences in the aqueous phase composition of ampules since the PCE-free ampules were filled with DI water while the ampules with PCE contained groundwater from the Camelot site. The groundwater may have contained additional sources of 1-butene. The fact that 1-butene was detected in ampules with Camelot soil and were PCE-free makes this compound a poor candidate for indicating PCE degradation.

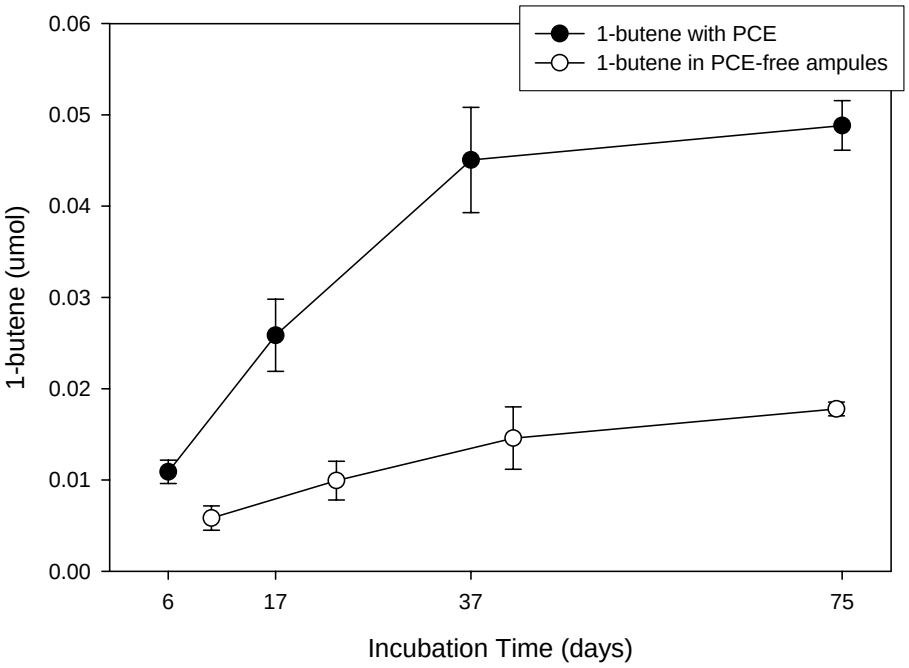

Figure 4.45: Amounts of 1-butene in ampules with Camelot soil that contained PCE and were PCE-free.

Trichloroethylene (TCE) may represent a PCE degradation product or may have been present in the Camelot soil but was not recovered during methanol extraction. TCE was only detected in aqueous samples from ampules incubated at 55, 75, and 95^{o}C and its concentration decreased with incubation temperature and time (Figure 4.46). Although

the source of TCE is unknown, it's suspected to have been initially present in the soil and was not recovered in the methanol extracts. Thus, TCE was not thought to represent PCE degradation. The working hypothesis is that heating the ampules caused TCE to partition into the aqueous phase and resulted in its detection during ampule incubation. If true, this observation supports the idea that heat aids in desorbing contaminants from soil.

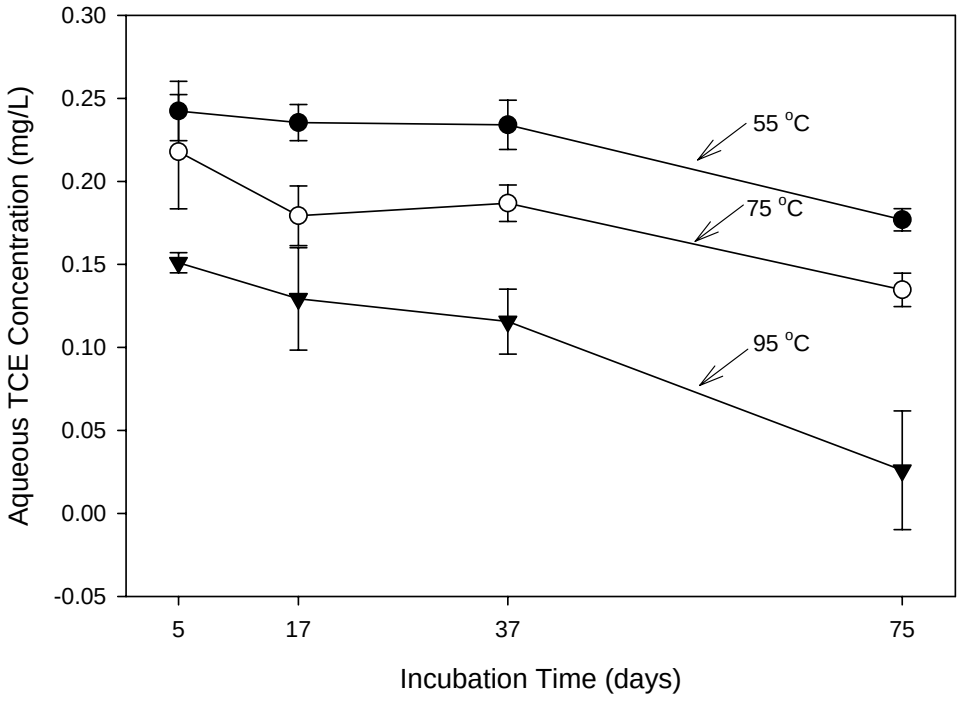

Figure 4.46: Concentration of TCE in aqueous phase of Camelot ampules (Batch 3).

While TCE was not thought to indicate PCE degradation, the amount of TCE decreased with increasing incubation temperature and time (Table 4.32), which suggests that TCE was being degraded, with the greatest degradation rate in the ampules at 95°C.

Table 4.32: Amount of TCE in Camelot (Batch 3) Ampules				
Incubation Time (days)	Incubation Temperature (^{o}C)			
	25	55	75	95
0	<0.001 (XII)[a]	<0.001 (XII)	<0.001 (XII)	<0.001 (XII)
5	<0.001 (V)	0.035[b]±0.003 (III)	0.031±0.005 (V) 0.16[c]	0.022±0.001 (IV) 0.00
17	<0.001 (V)	0.034±0.002 (IV)	0.026±0.003 (V) 0.00	0.019±0.005 (IV) 0.01
37	<0.001 (V)	0.033±0.002 (V)	0.027±0.001 (V) 0.00	0.017±0.003 (V) 0.00
75	<0.001 (V)	0.026±0.001 (V)	0.020±0.001 (V) 0.00	0.003±0.005 (V) 0.00
75 ($HgCl_2$)	<0.001 (V)	*No Ampules Prepared*	*No Ampules Prepared*	<0.001 (III) 0.00

[a]number of ampules provide in roman numerals.
[b]average amount of TCE (umol) ±standard deviation.
[c]P-Value for one-sided t-test between amount TCE in 55^{o}C ampules and amount in ampules at other incubation temperatures.

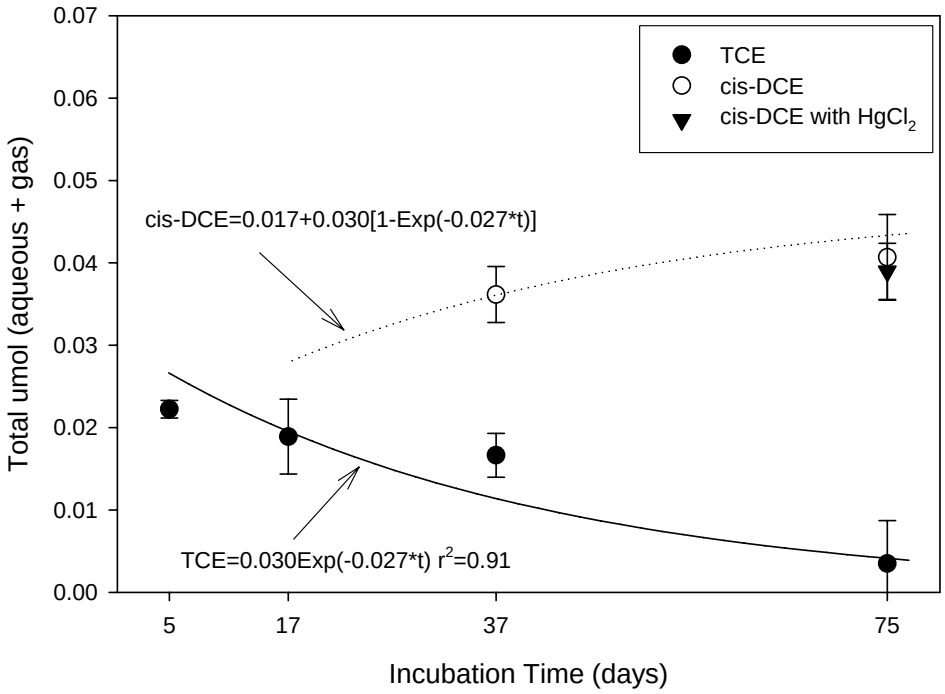

Figure 4.47: Amounts of TCE and cis-DCE in aqueous phase of Camelot ampules (Batch 3).

In the ampules incubated at 95°C, the amount of cis-DCE increased with incubation time and coincided with the decrease in the amount of TCE (Figure 4.47). There are several plausible explanations for the observed decrease in TCE and concurrent increase in cis-DCE. The first hypothesis involves the sequential degradation of PCE (C_2Cl_4) to TCE (C_2HCl_3) and then TCE degrading to form cis-DCE ($C_2H_2Cl_2$):

$$(+IV)C_2Cl_4 \xrightarrow[k_1]{H_2} (+II)C_2HCl_3 + HCl \xrightarrow[k_2]{H_2} (0)C_2H_2Cl_2 + HC \qquad (4.5)$$

where the carbon oxidation number is shown in the parenthesis preceding each carbon containing molecule. Equation 4.5 illustrates that in addition to the formation of hydrogen chloride (HCl), this reaction requires a source of hydrogen (H_2) to complete the reductive dechlorination of PCE to TCE and TCE to cis-DCE.

For the reaction in Equation 4.5 to describe the data shown in Figure 4.47 would require that k_2, the first order rate constant for TCE to cis-DCE, be greater than k_1 so that the amount of TCE continuously decreases and the amount of the degradation product, cis-DCE, continuously increases. However, the approach described in Equation 4.5 results in an over prediction of the amount of cis-DCE with incubation time. The second hypothesis used to explain the decrease in TCE and increase in cis-DCE with incubation time extends the first hypothesis by introducing the degradation of cis-DCE with the formation of 1-butene (C_4H_6):

$$C_2Cl_4 \xrightarrow[k_1]{H_2} C_2HCl_3 + HCl \xrightarrow[k_2]{H_2} C_2H_2Cl_2 + HCl \xrightarrow[k_3]{H_2} 0.5C_4H_6 + 2HCl \qquad (4.6)$$

The degradation of cis-DCE with formation of 1-butene would bring the predicted amount of cis-DCE more in line with the measured amounts. However, 1-butene was found in ampules with and without PCE. The third potential hypthesis for the observed TCE and cis-DCE behavior requires that no PCE degradation occurred; the only degradation reaction is that of TCE degrading to cis-DCE:

$$\text{TCE} + H_2 \xrightarrow{k_1} \text{cis-DCE} + \text{HCl} \qquad (4.7)$$

This third hypothesis requires that TCE was initially present in the Camelot soil samples and not a product of PCE degradation. This reaction (Eq. 4.7) was best described by a first-order model that also included an initial amount of cis-DCE based on the fit of data shown in Figure 4.47. A similar amount of cis-DCE was also noted in the ampules amended with mercuric chloride indicating that this is a thermally induced abiotic reaction.

The degradation of TCE to cis-DCE was evident only in the 95^{o}C ampules as no cis-DCE was detected in the ampules incubated at 55 or 75^{o}C. This indicates the reaction did not follow the expected Arrehnius behavior where the reaction rate was expected to increase with temperature and implies that a reactive species may have formed at 95^{o}C and cause the reaction to proceed. One finding was that the level of hydrogen (H_2) in gas samples from the Camelot ampules incubated at 95^{o}C was significantly greater than for ampules incubated at lower temperatures (Table 4.33). The presence of the additional amount of hydrogen in the 95^{o}C ampules along with the added thermal energy may have led to the addition of hydrogen to TCE along with elimination of Cl to form cis-DCE.

The concentration of other potential reductants including ferrous iron (Fe[II]) and sulfide were below the method detection limit (Table 4.33).

Table 4.33: Summary of Reductant and Oxidant Levels in the 75 day Camelot Ampules

Incubation Temperature (^{o}C)	Hydrogen (ppmv)	Ferrous Iron Fe(II) (mg/L)	Total Iron (mg/L)	Sulfide (mg/L)	Dissolved Oxygen (mg/L)
25	1.2±0.3	<1	6.0±9.6	<1	2 to 3
25 with $HgCl_2$	6.8±6.0	<1	4.9±8.3	<1	4 to 5
55	1.2±0.3	<1	0.6±0.3	<1	1 to 2
75	1.9±1.1	<1	2.0±2.9	<1	0.5 to 1
95	37.1±12.6	<1	3.3±5.4	<1	1 to 2
95 with $HgCl_2$	25.5±2.7	<1	3.5±4.9	<1	0.5 to 1

In summary, there was no clear evidence to suggest that PCE was being degraded in the ampules that contained Camelot soil and groundwater. However, there was evidence to suggest that TCE was being degraded to cis-DCE via a hydrogenolysis reaction to form cis-DCE.

4.8 Discussion

The primary objectives of the ampule experiments were to determine the rate of dissolved-phase PCE and TCE degradation and the identity of the degradation products formed at temperatures of up to 120^{o}C for periods of up to 75 days. The following sections provide a discussion of possible cause of the oven explosion, comparisons between the ampule experimental results obtained herein and those of Knauss et al. (1999), and implications for thermal remediation.

4.8.1 Oven Explosion

The oven explosion is hypothesized to have been caused by the detonation of dichloroacetylene (DCA) which was detected in the gas phase of ampules after the oven explosion. Reichert et al. (1975) showed that DCA is stable in the presence of excess TCE, however, once the ratio of DCA to TCE exceeds 1:2, a spontaneous reaction occurs with oxygen. The explosion occurred 4 days after introducing the sand, sand+1% goethite, and pH 10 ampules into the oven, and 20 days after incubation of the 1,000 and 100 mg/L ampules began. The explosion scenario involves the formation of DCA in many ampules and in excess of TCE in at least one ampule. Some event then occurred to initiate the rapid DCA decomposition resulting in the detonation of at least one ampule and the force from that one ampule exploding is thought to have caused the other ampules to break open and release additional DCA into the air resulting in an explosion that destroyed the oven.

Goethite was initially suspected of having caused the formation of DCA in an amount in excess of TCE. However, the goethite ampules contained argon sparged water and argon gas, meaning that the oxygen content was limited to approximately 3 umol. The reaction of 3 umol of DCA with oxygen to yield CO, CO_2, and phosgene would have released approximately 1.4 J of energy based on the heats of reaction (Zhu and Bozzelli, 2002) which is estimated to result in a 1 bar pressure increase within an ampule. The ampules have a rated pressure capacity of approximately 14 bar, thus the estimated 1 bar pressure increase in the ampules with goethite would be insufficient to cause an ampule to break open. In addition to the goethite ampules, there were ampules with 1,000 mg/L of TCE that contained air sparged water with air in the headspace and had been in the

oven for 24 days. There was approximately 100 umol of oxygen in these oxic ampules and a reaction with DCA would have released approximately 48 J of energy or an estimated pressure increase of 47 bar, about three times greater than the rated pressure capacity of the ampules.

A significant amount of DCA could have been generated in the sand+1% goethite or pH 10 ampules, rendering these ampules potentially explosive. However, the amount of oxygen present in these ampules was limited to less than 3 umol making it unlikely that they initiated the oven explosion. The 1,000 mg/L oxic ampules that had been incubating for a period of 24 days at 120^{o}C are more likely to have initiated the explosion due to the presence of approximately 100 umol of oxygen.

4.8.2 Comparison to Knauss et al. (1999) Results

The in-situ transformation of TCE to CO_2 and chloride ions has been claimed to occur during the thermal treatment of subsurface environments contaminated with TCE according to researchers working in the Applied Geology and Geophysics Group at the U.S. Department of Energy, Lawrence Livermore National Laboratory (LLNL). The LLNL group based their claim on experimental results obtained by measuring the disappearance of dissolved-phase TCE along with the appearance of dissolved phase CO_2 and chloride ions. The experiments were completed over a period of up to 43 days within a heated, constant pressure, gold-walled reactor that was completely water filled (Knauss et al., 1999). The ampule experiment reported herein was conducted, in part, to independently evaluate the conclusions reached by the LLNL group.

The results of the gold-walled experiments conducted by Knauss et al. (1999) were significantly different than those reported herein. TCE concentrations decreased to

50% of the initial concentration within 2 days in the gold-walled reactor operated at 90°C. In contrast, approximately 80.2% of the initial amount of TCE (Table 4.16) remained after 30 days of incubation at 120°C in the oxic ampules. Knauss et al. (1999) stated that chloride and carbonate were the only TCE degradation products detected in the gold-walled experiment. The primary compounds detected in the ampule experiments included CO and CO_2 in the gas phase, chloride, hydronium, glycolate, and formate in the aqueous phase. Knauss et al. (1999) analyzed the aqueous phase from their gold-walled reactors using a direct infrared spectroscopic method and a high pressure liquid chromatograph (HP 1090) connected to a conductivity detector. Details regarding operation conditions for these methods were not provided, but if chloride were detected then organic acids, such as glycolate and formate, should have been detected if present. However, Gu and Siegrist (1997) reported that the liquid chromatography method had a detection limit of 50 mg/L for glycolate, which is at least twice the initial concentration of TCE used by Knauss et al. (1999). Therefore, organic acids may have formed in the Knauss et al., (1999) experiments, but may have been well below detection limit of the analytical method.

The difference in experimental results between these two studies may also be associated with the differences in reactor wall materials. While the gold-walled reactor is supposedly chemically "inert" (Seyfried et al., 1979), gold power has also been used as a catalyst to increase the rate of reactions. The glass ampules used herein may not be entirely chemically "inert" either. The use of the 2,500°C flame to seal the ampule may have generated radical species that caused an increase in the rate of TCE degradation. For example, there was a 50.9% reduction in the amount of TCE in Ampule 58 along with a

consumption of dissolved oxygen and a reduction in the amount of gas phase oxygen by an estimated 50%. The half-life for TCE degradation in Ampule 58 was approximately 20 days, similar to the disappearance rate reported by Knauss et al. (1999) for an initial TCE concentration of 1,000 mg/L.

There were other significant differences between the Knauss et al. (1999) gold-walled experiment and the ampule experiment reported herein. The gold-walled experiment used a completely water-filled reactor under a pressure of 10 bar. The ampule experiments were completed in glass ampules that were partially filled with water at a pressure of approximately 1.4 bar at 120^{o}C. The gold-walled experiment involved measuring the concentration of TCE in a single gold-walled vessel every day over a period of days. The ampule experiment used destructive sampling of individually prepared ampules after incubation periods to determine the TCE degradation products.

Due to these differences, a direct comparison regarding the rate of TCE degradation determined by Knauss et al. (1999) and the results reported herein is not possible. However, the results of both studies can be used to conclude that TCE can be degraded in sealed containers incubated at elevated temperatures for up to 40 days.

4.8.3 Implications for Thermal Remediation

TCE was found to degrade in ampules incubated at 120^{o}C, therefore, TCE is expected to degrade during thermal treatment. For all treatments, no more than 15% of the initial amount of TCE was degraded, resulting in the formation of several non-chlorinated products including chloride, CO, CO_2, glycolate, and formate. First-order rate coefficients for TCE disappearance based on the rate of carbon and chloride formation were between 1.1 and 3.5×10^{-3} day^{-1} at 120^{o}C, and were not dependent upon oxygen

content or the presence of Ottawa sand. However, the rate of TCE disappearance at 120^{o}C increased to 4.2 and 5.7×10^{-3} day^{-1} based on the rate of carbon and chloride formed in ampules containing 1% (wt.) goethite and Ottawa sand. These results indicate that the rate of TCE degradation in heated, three-phase systems is relatively insensitive to oxygen content, but may increase substantially in the presence of iron bearing minerals. Given that the rate of TCE degradation in these experiments was not rapid, with first order half-lives between 123 and 591 days, and that none of these experiments demonstrated the complete degradation of TCE, it would be prudent to recommend the use of optimization techniques to recover dissolved phase TCE instead of relying on thermal induced degradation to achieve cleanup goals.

While dissolved-phase TCE is expected to degrade during in situ thermal treatment, dissolved-phase PCE was not found to undergo thermal degradation based results from experiments performed with deionized water and field samples contaminated with PCE. Therefore, PCE is not expected to degrade during in situ thermal treatment at temperatures below 95^{o}C and additional optimization measures would need to be employed to recover dissolved phase PCE.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Thermal remediation involves heating subsurface environments and collecting fluids in order to recover contaminants such as tetrachloroethylene (PCE) and trichloroethylene (TCE). While increasing subsurface temperature can lead to changes in the distribution of contaminants between the solid, liquid, and gas phases, there is also an increased potential for PCE and TCE to degrade. This work was performed to determine the rate of PCE and TCE degradation and products formed in laboratory-scale experiments designed to simulate thermal remediation conditions. Experiments were completed using two laboratory-scale experimental systems where the flow-through experiments simulated the conditions that occur during recovery of gas phase contaminants and the ampule experiments simulated heating dissolved phase contaminants for extended periods of time. The following sections provide conclusions specific to each experimental system followed by recommendations for future work.

5.1 Flow-Through Experiments

A series of six flow-through experiments were completed to determine the TCE degradation products formed after passing through a quartz tube operated at set temperatures between 60 and 800^{o}C. The purpose of these experiments was to evaluate the claim that TCE is completely oxidized to non-toxic CO_2 and chloride during in situ thermal remediation. Specific experiments were conducted to investigate the effects of temperature, water vapor content, solids (Ottawa sand), and oxygen content on TCE degradation and product formation. Degradation of TCE was not evident at temperatures

of less than 240°C based on TCE recoveries of greater than 94% regardless of quartz tube oxygen or water content. The only indication that TCE was being degraded while passing through the quartz tube heated to temperatures below 240°C was the small amount (<0.2% of TCE) of chloride and chloroacetic acids detected in the deionized water used to rinse the quartz tube after cooling to room temperature. Thus, gas phase TCE is not anticipated to degrade during steam flushing or electrical resistive heating where in situ temperatures are less than 200°C during field applications. These results demonstrate the potential for chloroacetic acids to form during the thermal remediation of sites contaminated with TCE.

Trichloroethylene (TCE) readily degraded while passing through the quartz tube heated to greater than 300°C where the yields and composition of degradation products were dependent on the oxygen, water, and solids content of the quartz tube. With nitrogen as the carrier gas, up to four TCE degradation products were identified in the liquid-trap fluids and quartz tube rinses, with no CO or CO_2 was detected for experiments completed at 420°C with water present. The amount of carbon recovered for the 420°C experiments with nitrogen as the carrier gas was greater than 97%, with up to 3.4% detected as chlorinated hydrocarbon degradation products. The amount of chlorine recovered was greater than 100%, with up to 7% as chlorinated degradation products. The degradation products detected contained 4 and 6 carbon atoms with greater than 5 chlorine atoms per molecule. Although increasing the quartz tube water content resulted in an increase in TCE recovery concurrent with a decrease in TCE degradation products, 1.3% of the TCE introduced was transformed into unwanted chlorinated carbon degradation products in an atmosphere of nitrogen saturated with boiling water, the

maximum water content expected during thermal remediation. These results demonstrate that water was not an effective source of hydrogen at 420^{o}C since chlorinated carbons were found instead hydrogenated carbon compounds (e.g., C_2H_4).

With air as the carrier gas, there was an increase in the amount of TCE degraded and the number of degradation products detected as compared with experiments completed with nitrogen as the carrier gas. The average recovery of TCE decreased to approximately 68% in the 420^{o}C experiments with air (i.e., 21% O_2) as the carrier gas and CO, CO_2, and phosgene were detected with the addition of oxygen. The presence of CO and CO_2 with oxygen present demonstrated that water was not an effective source of oxygen at 420^{o}C since CO and CO_2 were not detected in experiments with humid nitrogen as the carrier gas. With air as the carrier gas at 420^{o}C, TCE degradation products were not limited to CO_2 and chloride but ranged from single carbon compounds with 3 chlorine atoms (i.e., chloroform) to compounds with up to 6 carbons and 6 chlorine atoms (i.e., hexachlorobenzene). The average amount of carbon recovered for the 420^{o}C experiments with air as the carrier gas was 95.6% which indicated that nearly all the TCE degradation products had been accounted for. Increasing the quartz tube water content improved TCE recovery in the 420^{o}C experiments with air as the carrier gas concurrent with a decrease in the amount of degradation products formed. However, even at the maximum water content anticipated during in site thermal remediation (i.e., boiling water), 2.4% of the TCE introduced into the quartz tube at 420^{o}C was transformed into unwanted chlorinated hydrocarbons.

Increasing the amount of Ottawa sand within the quartz tube at 420^{o}C was found to decrease TCE recovery and increase the amount of chlorinated carbon degradation

products formed. Unfortunately, these results are based on a limited number of experiments due to quartz tube failures caused by the presence of calcium in the Ottawa sand.

The experiments completed at 420^{o}C demonstrated that unwanted chlorinated degradation products were formed from TCE regardless of quartz tube oxygen, water, or solids content. However, temperatures of up to 800^{o}C are achieved during thermal conductive heating and the chlorinated degradation products observed at 420^{o}C may not form at higher temperatures. Experiments completed with the quartz tube operated at 800^{o}C demonstrated that CO and CO_2 were the primary TCE degradation products and only a small amount of the unwanted phosgene (>0.1% on carbon basis) was detected. However, up to 22.7% of the carbon introduced as TCE was not recovered and chloride was not detected in experiments completed at 800^{o}C suggesting that recalcitrant high molecular weight chlorinate carbon compounds (i.e., tar and soot) had formed. Therefore, TCE was not completely transformed to CO_2 and chloride after passing through the quartz tube heated to 800^{o}C. Although the composition of the missing carbon is unknown, the fact that greater than 17% of the carbon was not recovered from this controlled laboratory system makes the prospect of recovering all the TCE degradation products from field soils heated to 800^{o}C doubtful.

5.2. Ampule Experiments

Five series of ampule experiments were completed to investigate the effects of oxygen and solids (Ottawa sand and goethite) content on the degradation of dissolved phase TCE at temperatures of 22 and 120^{o}C for periods of up to 47 days. These experiments were performed to evaluate the claim that dissolved phase TCE was rapidly

degraded to CO_2 and chloride during thermal remediation. The results of the ampule experiments demonstrate that TCE was degraded within sealed glass ampules which contained gas, water, and solids. The rates of TCE degradation in ampules with anoxic water, both with and without sand, and in oxic water were similar, with a first order half-life on the order of 200 days at 120^{o}C. The degradation rate in ampules with anoxic water and sand was increased by adding 1 % (wt.) goethite, with a first order half-life on the order of 20 days at 120^{o}C. However, the rate determined in a follow on experiment using the same batch of Ottawa sand and 1 % (wt.) goethite was slower with a first order half-life of 164 days at 120^{o}C. The decrease in degradation rate between experiments may have been due to the difference in the amount of sand used between experiments. The rates of thermal induced TCE degradation determined in these ampule experiments were slow, thus an appreciable decrease in dissolved phase TCE mass would only be expected during thermal remediation applications where elevated temperatures are maintained for extended periods of time.

The primary TCE degradation products in all experiments included CO and CO_2 in the gas phase and chloride, hydronium ions, formate, glycolate in the aqueous phase. Minor amounts (<1 mg/L) of dichloroacetic acid (DCAA) were detected in select ampules, most consistently in ampules that that were stored at 22^{o}C and initially contained 1,000 mg/L TCE along with oxygen. Dichloroacetylene (DCA) was detected in minor amounts (i.e., DCA < 1% of TCE) in ampules that contained TCE and were incubated at 120^{o}C.

One experiment was performed to determine the rate of PCE degradation at 25, 55, 75, and 95^{o}C in deionized water and in field samples from the Camelot Cleaners

Superfund site, West Fargo, ND that were contaminated with PCE. These experiments were performed to evaluate the rate of PCE degradation and products that could be expected to form during application of electrical resistive heating at the Camelot Cleaners site. While PCE was found to partition into the ampule aqueous phase at 55^{o}C and above, no evidence was found to conclude that PCE was degraded over 75 days at temperatures up to 95^{o}C. Thus, the concentration of PCE in groundwater is expected to increase during electrical resistive heating of the Camelot Cleaners site but PCE is not expected to degrade based on the ampule experiment results.

5.3 Recommendations for Future Work

The results of the flow-through experiments demonstrate that degrading TCE at temperatures greater than 300^{o}C results in the formation of unwanted chlorinated hydrocarbons. However, these results are primarily based on experiments completed without field soils which may substantially alter the degree of chlorinated degradation products formed. The work should be extended by completing experiments with field soils. This is not an easy task and would require finding a tube material that can withstand the thermal stress and variety of chemicals formed while heating soil to temperatures of up to 800^{o}C. The purity of the quartz tube made it susceptible to common soil ions (e.g., Ca^{2+}) and the known reactivity of steel makes it a poor choice. Soils are primary composed of SiO_2 (quartz) but there can also be significant amounts of aluminum oxide (Al_2O_3), thus a tube made from aluminum oxide may be suitable for simulating subsurface conditions.

The ampule experiments demonstrated that TCE was degraded at 120^{o}C and resulted in the formation of non-chlorinated degradation products. However, the rate of

degradation was slow and is not expected to result in appreciable decreases of TCE mass during thermal remediation. The experiment completed with sodium hydroxide demonstrated that the rate of TCE degradation could be increased. While sodium hydroxide is not expected to be present in subsurface environments, other common groundwater anions (e.g., nitrate) may increase the rate of TCE degradation. Additional ampule experiments should be performed using field soils and groundwater samples that may contain chemicals which may increase the rate of TCE degradation at elevated temperatures.

The source of sulfate found in the fifth ampule experiment with Ottawa sand and 1 % (wt.) goethite was suggested to be persulfate or peroxymonosulfate. The rate of sulfate production from these compounds can be induced at room temperature in solutions that contain transition metals where the rate of sulfate production from persulfate is greatest with Ag(I) and greatest from peroxymonosulfate with Co(II) (Anipsitakis and Dionyiou, 2004). Experiments should be performed with Ottawa sand in solution with Ag(I) and CO(II) along with deionized water to determine the rate of sulfate produced from Ottawa sand and to determine if there is a difference in the rate of production between the different metals. If the transition metals increase the rate of sulfate production from Ottawa sand with respect to Ottawa sand in deionized water, then this may direct further research on naturally occurring oxidants that can be activated by elevated temperatures to degrade contaminants.

Tetrachloroethylene (PCE) was not found to degrade during ampule experiments, however, PCE degradation may be induced under acidic conditions. Ampule experiments using sulfuric acid combined with a chloride counter ion (e.g., Ag[I], Fe[III]) would be a

reasonable starting point to determine if dissolved phase PCE degradation could be initiated and what degradation products could be expected.

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