

LABORATORY STUDY ON THE TRANSFORMATION OF TRICHLOROETHYLENE UNDER THERMAL SOURCE ZONE REMOVAL CONDITIONS

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Abstract. Removal of separate-phase organic liquids from the subsurface has been hypothesized to reduce the long-term contamination of ground-water resources. Thermal source zone treatment is one remedial method being used to recover organic liquids from the subsurface. *In-situ* oxidation of organic contaminants is thought to occur during thermal treatment, resulting in the formation of benign reaction byproducts including carbon dioxide and water. This work presents the results from an ongoing laboratory investigation of the chemical transformation of trichloroethylene (TCE), a common source zone contaminant, as a function of temperature. The objective of this study is to quantify the TCE degradation products formed in a laboratory-scale reactor containing three phases (air, water, and solids) heated over a temperature range from 22 to 480°C to simulate subsurface conditions under thermal source zone treatment. Preliminary experimental results show that TCE reacts to form tetrachloroethylene (PCE), an unwanted byproduct, at temperatures greater than 300°C. Future experimental efforts will focus on the effect of granular medium and moisture content on chemical transformations.

INTRODUCTION

Trichloroethylene (TCE) is a solvent used primarily for degreasing of metal parts, but is also used for paint stripping and chemical manufacturing (Watts, 1998). TCE is one of three volatile organic compounds included in the National Exposure Registry due to its presence at 25.5% of the National Priorities List sites, toxicity, and potential for human exposure (ATSDR, 1994). TCE was often released into the environment where it migrated into the subsurface and contaminated ground-water resources. If TCE was released at a rate that exceeded the rate of sorption to soil, vaporization to soil gas, and dissolution into ground water, a separate

non-aqueous phase liquid (NAPL) will form in the subsurface. The presence of separate-phase TCE represents a long-term source of subsurface contamination due to the slow rate of mass transfer from the NAPL to soil, soil gas, and ground water. Removal of the NAPL source zone is intended to result in a decrease in the long-term contamination of subsurface environments.

Thermal source zone treatment involves the addition of heat to the NAPL-contaminated subsurface by the injection of steam, heating of buried steel rods (thermal conductive heating), or passing of electrical current through the subsurface (electrical resistive heating). The addition of heat results in an increase in TCE vapor pressure and aqueous solubility. These physical effects lead to enhancements in the rate of TCE mass transfer and rate of recovery from the subsurface. The addition of heat into the subsurface also increases the potential for chemical reactions to occur. The Department of Energy developed and patented (United States Patent No. 6,127,592) a process known as Hydrous Pyrolysis/Oxidation (HPO), which involves the injection of air along with steam to promote the *in-situ* oxidation of organic contaminants at subsurface temperatures between 70 and 120°C. A full-scale demonstration of the HPO process was performed during the summer of 1997 at the Visalia Pole Yard Superfund Site located in Visalia, CA. It was estimated that 7,300 kg of NAPL mass was converted to carbon dioxide *in-situ* based on isotopic analysis of carbon dioxide in vapor recovered from the subsurface (Newmark et al., 1998). The HPO process was applied at the Savannah River Site in Aiken, SC yielding a significant amount of carbon dioxide (e.g., 6 mL/L) in the vapor extracted from the heated, PCE- and TCE-contaminated subsurface. The presence of carbon dioxide along with a decrease in groundwater dissolved oxygen content, an increase in groundwater pH, and chloride ion concentration, was interpreted as an

indication of the *in-situ* degradation of PCE and TCE (Brown et al., 2002). In-Situ Thermal Desorption (ISTD) is a conductive heating technology that has been shown to remove and destroy semi-volatile organic contaminants including polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) (Bierschenk et al., 2001). Vinegar et al. (1999) reported maintaining conductive heater rod temperatures between 745 and 900°C, with corresponding subsurface temperatures ranging from 100 to 250°C. *In-situ* organic contaminant oxidation is thought to occur during ISTD when subsurface vapor passes through a reactive zone consisting of soil heated to greater than 500°C directly adjacent to vapor recovery wells (TerraTherm, 2001).

Knauss et al. (1999) demonstrated the HPO transformation process in a single phase, water-filled reactor, operated in the temperature range between 70 and 100°C, under a constant pressure of 1 MPa, and saturated with dissolved oxygen (8 mg/L). The concentration of TCE in the water-filled reactor decreased with time while the concentration of chloride ions and carbon dioxide increased with time. The rate of disappearance of the dissolved phase TCE was pseudo first-order with a half-life of approximately 13.2 days. Gas phase laboratory studies have been used to simulate combustion conditions within incinerators and have identified the formation of products of incomplete combustion (PICs) (Wark et al., 1998). For example, Yasuhara and Morita (1990) found that passing dry air containing 21% oxygen and saturated with TCE through an empty quartz tube reactor operated from 300 to 800°C yielded PCE as the main thermal reaction product, as well as carbon tetrachloride and hexachlorobenzene as minor products. The combustion of TCE must proceed through reactive intermediates that can potentially combine to form stable compounds (i.e., PCE) in combustion exhaust (Bose and Senkan, 1983). Combustion temperatures of greater than 1200°C are required before the desirable end products of carbon dioxide and chloride ions can be obtained (Thomson et al., 1994). Other combustion experiments have used reactors containing two phases (air and solids) to demonstrate the formation of dibenzofurans and polychlorinated dibenzo-*p*-dioxins from chlorophenol precursors in the temperature range between 500 and 700°C (Mulholland et al., 2000).

Laboratory investigations of thermal source zone treatment traditionally focused on understanding and controlling the physical processes involved in thermally induced fluid-movement. Comparatively fewer studies have been performed to assess potential chemical

reactions that can occur at elevated subsurface temperatures. This work presents the results from an ongoing systematic laboratory study of the chemical transformation of TCE as a function of temperature, granular medium, and moisture content.

EXPERIMENTAL METHODS

Experiments were conducted in a sand-filled and empty quartz tube reactor system (Figure 1) that consisted of a 34 mm diameter by 50 cm long fused quartz tube (General Electric Type 124, Technical Glass Products, Mentor, OH). The quartz tube reactor was placed within a tube oven (Thermolyne Model 21100, Fisher Scientific) that was used to control the system temperature. Laboratory grade TCE (HPLC grade, Sigma-Aldrich, Milwaukee, WI) was mixed with air (21% oxygen) and passed through the heated quartz tube reactor at a rate of 60 mL/min for a period of 16 minutes. The reactor effluent passed through two 40 mL vials arranged in series and filled with methylene chloride (Optima grade, Fisher Scientific) to trap all



Figure 1. Tube oven and sand-filled quartz tube reactor.

reaction products with greater than two carbons (i.e. PCE). Experiments were also completed with 20-30 mesh Ottawa sand positioned within the quartz tube reactor. The 20-30 mesh Ottawa sand was washed in 0.5 N nitric acid, rinsed with deionized water, and baked at 200°C for a period of 2 hours before use. A heated solvent extraction of sand samples and a solvent rinse of the reactor walls were performed to determine the residual organic chemicals present after the reactor cooled to room temperature. The mass of organic chemicals in the reactor effluent and in sand extracts was determined by gas chromatography (GC), using a Hewlett-Packard (HP) Model 6890 GC equipped with an autosampler, a 15-m DB-5 column (J&W Scientific), and a flame ionization detector. The identity of unknown chemicals was determined using a GC (HP 6890 with a 30-m DB-5 column) coupled to a HP 5973 mass selective detector (MS).

EXPERIMENTAL RESULTS

The amount of TCE recovered from the sand-filled and empty reactor operated between 22 and 180°C was less than 100% of the amount introduced (Figure 2). The loss of TCE was believed to be due to adsorption within the quartz glass reactor rather than degradation of TCE since these experiments were completed in a short period of time (16 minutes). The potential for

adsorption losses within the quartz tube reactor was assessed by passing additional volumes of clean air through the empty quartz tube reactor operated at 240°C after the addition of TCE. Approximately 98% of the TCE introduced into the empty reactor operated at 240°C was recovered indicating that the potential for adsorption losses within the reactor was significant. The amount of TCE found in the reactor effluent declined with reactor temperature greater than 300°C and the complete disappearance of TCE occurred at 480°C in agreement with the results of Yasuhara and Morita (1990) that are shown in Figure 2 for comparison. PCE and other byproducts were found in the reactor effluent for the sand-filled and empty quartz-tube reactor operated at temperatures greater than 300°C. The other reaction byproducts (not shown) included, carbon tetrachloride, hexachloroethane, hexachlorobutadiene, and hexachlorobenzene. The presence of the sand in the reactor reduced the number of the other reaction byproducts, but did not alter the amount of PCE formed. Minor amounts of PCE and hexachlorobenzene were found in the sand sample extracts and the reactor rinse solvent.

These preliminary results demonstrate that the complete oxidation of TCE to carbon dioxide and water may not occur in an anhydrous environment with 20-30 mesh Ottawa sand present. This does not necessarily contradict the findings of Knauss et al. (1999) since

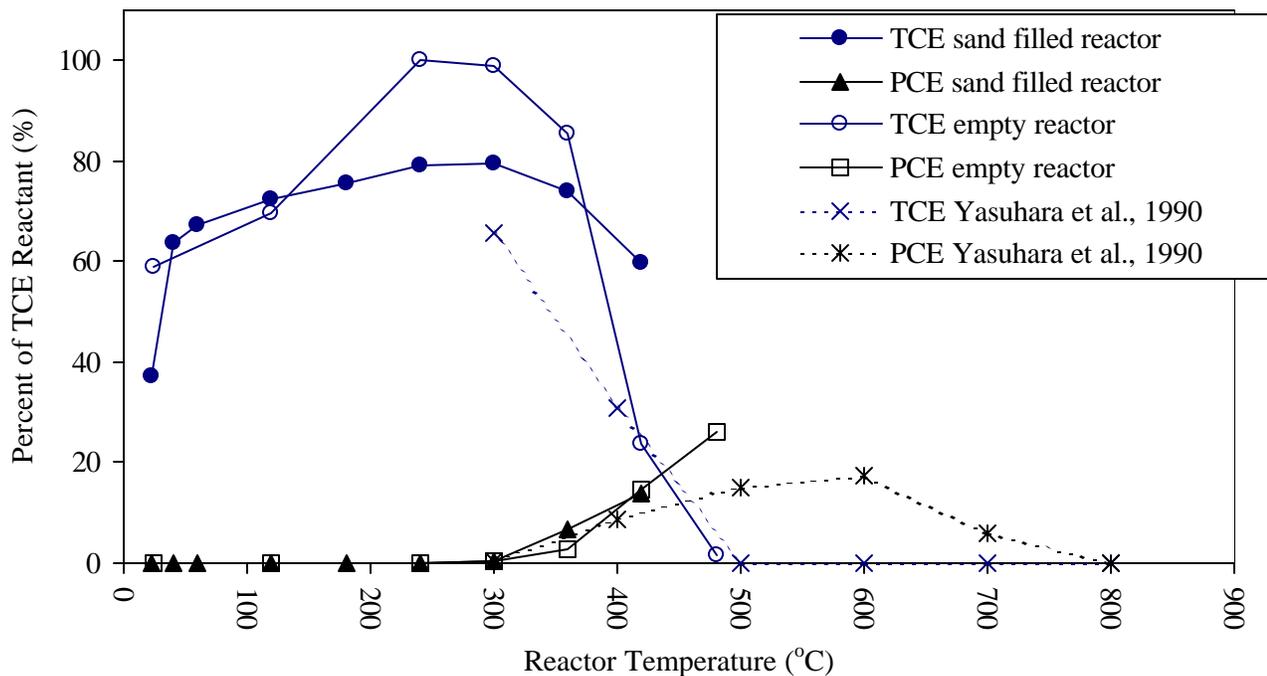


Figure 2. Amount of reaction products after passing air saturated with TCE through the heated quartz tube reactor.

their HPO experiments were performed within a single phase, water-filled reactor operated at temperatures near 100°C. The results suggest that passing TCE vapor through soil or recovery wells heated to between 300 and 500°C may result in the formation of unwanted reaction byproducts along with the disappearance of TCE. The addition of water to the reactor may reduce the amount of unwanted byproducts by providing a hydrogen source leading to the formation of hydrochloric acid, a thermodynamically favored product. The three phase experimental conditions used in this work are suggested to be more representative of thermal source zone treatment conditions where water vapor containing volatile organic compounds will pass through heated, unsaturated soil before being recovered for disposal. Future experiments will involve analyzing for carbon dioxide and hydrochloric acid in the reactor effluent, and introducing water into the reactor influent at relative humidities of 25 and 100% in the temperature range from 22 to 420°C.

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