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Mixed Redox Catalytic Destruction of Chlorinated Solvents in Soils and Groundwater: From the Laboratory to the Field

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Abstract

A new thermocatalytic method to destroy chlorinated solvents has been developed in the laboratory and tested in a pilot field study. The method employs a conventional Pt/Rh catalyst on a ceramic honeycomb. Reactions proceed at moderate temperatures in the simultaneous presence of oxygen and a reductant (mixed redox conditions) to minimize catalyst deactivation. In the laboratory, stable operation with high conversions (above 90% at residence times shorter than 1 s) for perchloroethylene (PCE) is achieved using hydrogen as the reductant. A molar ratio of $H_2/O_2 = 2$ yields maximum conversions; the temperature required to produce maximum conversions is sensitive to influent PCE concentration. When a homologous series of aliphatic alkanes is used to replace hydrogen as the reductant, the resultant mixed redox conditions also produce high PCE conversions. It appears that the dissociation energy of the C–H bond in the respective alkane molecule is a strong determinant of the activation energy, and therefore the reaction rate, for PCE conversion. This new method was employed in a pilot field study in Tucson, Arizona. The mixed redox system was operated semicontinuously for 240 days with no degradation of catalyst performance and complete destruction of PCE and trichloroethylene in a soil vapor extraction gas stream. Use of propane as the reductant significantly reduced operating costs. Mixed redox destruction of chlorinated solvents provides a potentially viable alternative to current soil and groundwater remediation technologies.

Keywords

mixed redox conditions; mixed redox catalysis; catalytic destruction; chlorinated solvents; PCE conversion; reduction; oxidation

Introduction

There is substantial incentive to develop efficient, economic remediation methods for the destruction of halogenated organic compounds, including a variety of chlorinated solvents. This arises from (1) the widespread contamination of soils and groundwater due to historical use and improper disposal of such solvents, and (2) their potentially hazardous effects on human health.

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Conflicts of Interest The authors declare no conflicts of interest.

Acyclic, short-chain halogenated organic compounds are useful solvents in numerous industrial processes and products, such as dry cleaning, metal degreasing, pharmaceuticals, adhesives, and refrigerants. Due to widespread use and improper disposal, such compounds are primary pollutants at thousands of contaminated sites throughout the United States. Of particular prominence are chlorinated solvents, including perchloroethylene (PCE), trichloroethylene (TCE), 1,1,1-trichloroethane, and methylene chloride. These four solvents, according to a survey of water-quality conditions across the conterminous United States,¹ are among the most frequently detected volatile organic compounds (VOCs) in groundwater (sampling carried out between 1985 and 2002). In particular, PCE and TCE are the first and third most frequently detected VOCs in groundwater, with concentrations at or above their maximum contaminant levels (MCLs = 5 ppb).² Not surprisingly, PCE and TCE are the most frequently co-occurring contaminants in groundwater. At U.S. Superfund sites, PCE and TCE are among the top 31 Priority Hazardous Substances that pose significant threats to human health, according to the Department of Health and Human Services.³ In Arizona, chlorinated solvents are the primary contaminants at 90% of the state's Water Quality Assurance Revolving Fund (WQARF) sites.

High doses of PCE or TCE and/or their breakdown products (e.g., vinyl chloride) cause cancer in laboratory animals, and the International Agency for Research on Cancer has determined that both are probable human carcinogens.^{1,3} Many types of cancers (breast, cervix, kidney, liver, lymphomas, prostate, and leukemia) have been associated with exposure to TCE and other chlorinated solvents. Other adverse effects of exposure include disorders of the human central nervous system, immune system, and reproductive system, as well as heart defects in newborns.

In general, chlorinated compounds are difficult to remediate due to their unique physicochemical properties. Chemically, they are relatively stable, and are therefore slow to decompose naturally or biodegrade. They are also semivolatile, sparingly soluble in water, and about 1.5 times denser than water. Taken together, these properties make them mobile, as liquids or gases, in aquifers and vadose zones.

In groundwater, undissolved portions of these solvents can form dense, nonaqueous-phase liquids that tend to sink to the base of aquifers or remain trapped in soil pores, rendering them difficult to access. Biodegradation, for example, can be slow due to limited bioavailability of these compounds to responsible bacteria. In Arizona, slow remediation is exacerbated by the low quantities of dissolved oxygen and dissolved organic carbon in most aquifers.

At about half of U.S. Superfund sites, where soils are contaminated with chlorinated solvents, incineration, or solidification has been the remediation technology of choice.⁴ However, the former can lead to air pollution, while the latter merely separates the contaminants into a different phase. Soil vapor extraction (SVE) has proven useful for recovering semivolatile, immiscible contaminants (including chlorinated solvents) from the vadose zone. However, SVE gases must be treated with activated carbon before their release to the atmosphere, which can significantly increase the overall costs. For groundwater remediation, pump-and-treat is used at more than 90% of contaminated Superfund sites.⁴ Solvents are stripped from recovered groundwater and then trapped on activated carbon, again increasing the overall costs.

New remediation methods are continually being devised, such as using surfactants and alcohols to increase the solubility of target chemicals, using thermal methods to enhance contaminant movement, and injecting reagents to promote chemical and biological transformation of contaminants. By comparison, SVE has been used effectively at many Superfund sites, especially in contaminant source zones, where chlorinated solvents are present as nonaqueous liquids. A key remaining task is to treat SVE gases inexpensively with few or no byproducts.

and minimal contamination to the environment. Nonthermal methods for carbon regeneration have been proposed but are not yet in widespread use.⁵ In this work, a commercial automobile catalyst is used to destroy chlorinated solvents in SVE gases. High removal efficiency, low costs, and environmentally benign end products make this method potentially useful for large-scale field operations. The novelty of this method is the simultaneous presence of oxidizing and reducing conditions; past studies focused on either reduction or oxidation as the dominant mechanism. This was discussed in some detail elsewhere and will be covered here only briefly.⁶

An extensive body of research on catalytic destruction of halogenated compounds has originated from the elegant work of Bond *et al.* in the 1950s.⁷ Catalytic oxidative dehalogenation occurs when an organochlorine compound is oxidized to CO₂ in the presence of an oxidant, such as O₂; primary products are CO₂, H₂O, and Cl₂. Reductive dehalogenation occurs in the presence of a reductant, such as H₂; products include partially or fully dechlorinated hydrocarbons and HCl. Depending on the target compounds to be treated, various catalysts have been used, including supported and unsupported noble metals, metal oxides, and various combinations of these materials. Target contaminants include chlorofluorocarbons, chlorinated aromatics, and chlorinated aliphatics in organic matrices, aqueous, and gas phases. Reductive dehalogenation has the following advantages over oxidation and incineration (in essence, a form of oxidation): (1) reaction products include primarily HCl and hydrocarbons, with minimal environmental impacts—incineration, on the other hand, can produce toxic compounds, such as chlorine, phosgene, dioxins, and furans⁸—(2) reaction rates are typically fast; (3) reaction conditions (temperature and pressure) are typically mild; and (4) there is no NO_x formation due to relatively low temperatures. A summary of previous studies on reductive dehalogenation was provided in Örbay *et al.*⁶

Catalyst poisoning hinders the ability of both reductive and oxidative dehalogenation. This phenomenon is pronounced in the reductive method, mainly due to coking.^{9,10} Since the most effective catalysts so far are supported precious metals, such as Pt and Pd, catalyst lifetime has a substantial effect on process economics and feasibility. In principle, poisonous intermediates from reduction alone can be removed via oxidation to CO₂. Those from oxidation (e.g., Cl₂) can be converted, via reduction, to compounds (e.g., HCl) that are easily removed from the system. This is apparent from previous studies in which hydrogen donors, such as hexane, water, toluene, methane, and propane^{11–15} selectively increase conversion rate and/or efficiency under predominantly oxidative conditions. A primary hypothesis thus arises that is the basis of this work—optimally proportioned mixtures of a reductant and oxidant can prevent catalyst poisoning, increase remediation efficiency and improve process economics.

This chapter describes a laboratory investigation of PCE destruction under simultaneous reducing and oxidizing (hereafter referred to as “mixed redox”) conditions using a commercially available Pt/Rh catalyst. The same thermocatalytic method was applied in a pilot field study for treatment of SVE gases. Operating conditions, destruction efficiencies, catalyst stability and treatment costs are also discussed.

Experimental

Catalyst

The catalyst used in the laboratory was identical to those used in automobile catalytic converters. Pt and Rh are supported, in a 3:1 w/w ratio, on a monolithic honeycomb that is composed of cordierite (90%) and a wash-coat (10%) containing alumina, cerium, zirconium, and other trace constituents. The nominal catalyst loading is 1.85×10^{-4} g total metal/cm³, where volume is based on the total nominal envelope of the catalyst (uncut block was 820 cm³). Cylindrical pieces (2.54 cm diameter $\times$ 2.54 cm long) cut from honeycomb blocks were

used in the reactor described later in the chapter. Control experiments showed that the unamended honeycomb support yields insignificant PCE conversion under typical operating conditions. In the field, the catalyst had the same composition as in the laboratory, although its dimensions were larger. It consisted of two alumina honeycomb blocks of elliptical cross section (11.9 cm in major axis, 8.0 cm in minor axis) measuring 5.1 cm in length.

Laboratory Reactor System

A detailed description and schematics of the laboratory reactor were presented elsewhere.⁶ The reactor was a 50-cm (long) $\times$ 2.54-cm (inner diameter) glass tube, containing a 2.54-cm (long) $\times$ 2.54-cm (outer diameter) honeycomb cylinder. The fixed-bed, tubular reactor was housed in a tube furnace, equipped with automatic temperature control. The length of the furnace was 38 cm. The honeycomb was located inside the reactor at approximately 20 cm from the upstream end of the furnace. The influent gases were heated to the furnace temperature before entering the honeycomb. Temperature was measured using K-type thermocouples at the center of the inlet face of the honeycomb and at the furnace inner wall above the honeycomb (set point for temperature control). An independent measurement verified that the gas temperature at the entrance of the honeycomb block was approximately equal to the furnace temperature at the gas flow rates employed in this work. In the H₂/O₂ redox experiments, a well-mixed gas stream consisting of H₂, O₂, N₂, and PCE was fed to the reactor. Hydrogen (99.95%), oxygen (99.9%), and nitrogen (99.99%) were used as obtained. Flows were regulated by mass flow controllers. Liquid PCE (99.9+%) was placed in a U-tube located in a temperature-regulated water bath (4°C). Nitrogen (20 mL/min) was bubbled through the PCE, resulting in a PCE-loaded N₂ stream, which was then mixed with H₂, O₂, and N₂ at prescribed ratios to obtain the desired flow rates and reactant concentrations. Typical residence times ranged from 1.5 s to 0.2 s, depending on the flow rate and catalyst temperature. Typical concentrations of PCE in the influent were from 200 to 800 ppmv. In the propane/O₂ redox experiments, gas-phase propane (99+%) replaced H₂ in the reactor influent. Effluent gases from the reactor were fed to a scrubber containing alkaline solutions to trap acidic products (mainly HCl).

Analytical

In the laboratory study, an HP 5890 gas chromatograph (Agilent, Santa Clara, CA) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) was used to analyze the influent and effluent streams. Helium was used as the carrier gas. A 0.53- μ m wide-bore capillary column (J&W DB-624, 30 m $\times$ 0.53 mm $\times$ 3.0 μ m; Agilent) with FID was used to measure partially and fully dechlorinated hydrocarbons. A Supelco packed column (60/80 mesh Carboxen-1000, 457 cm $\times$ 0.3175 cm $\times$ 2.1 mm, stainless steel; Sigma Aldrich, St. Louis, MO) with TCD was used to measure CO₂, H₂, and O₂. Injector and detector temperatures were typically 200°C and 250°C.

In the field, influent and effluent gas samples were withdrawn through designated ports using a gas-tight syringe and injected immediately into a HP 5710A gas chromatograph equipped with an FID detector. The gas chromatograph oven temperature was 60°C. The FID inlet and outlet temperatures were 200°C. An isocratic elution program was sufficient to elute TCE at about 2.4 min and PCE at about 4.5 min. In addition, treated soil gas was bubbled into methanol using an impinger tube for 17 h. Within an hour of sampling, the methanol extract was analyzed using an Agilent 6890N gas chromatograph equipped with a 5973 Network mass spectrometer detector. Dioxin, a possible by-product, was not found in the treated soil gas (detection limit at 1 ng/m³).

Laboratory Experiments

In a typical experiment, the initial furnace temperature was 75°C. The influent gas stream was diverted to a bypass line in order to measure the PCE concentration. After stable conditions

were established, flow was directed to the reactor, and the furnace temperature was ramped to the desired final temperature at 2°C/min. Due to the relatively fast reaction characteristic times (of the order of seconds) and the relatively slow rate of temperature change, the reactor was assumed to operate at steady state over the entire temperature range investigated.⁶ The effluent gas stream was periodically sampled and analyzed. At the end of each experiment, all gas streams were turned off except for O₂, and the furnace temperature was held at 450°C for 8 h to clean the catalyst surface. This process successfully maintained catalyst performance characteristics for more than 2 years.

Field Study

The Park-Euclid site, which is located less than one kilometer south of the University of Arizona campus, is one of about 40 Arizona WQARF (State Superfund) sites. Its proximity to the university campus has raised concerns of drinking water quality. Site characterization since the early 1990s has shown that groundwater and vadose zone at the Park-Euclid site are contaminated with a combination of diesel products and VOCs. Detected VOCs include PCE, TCE, and isomeric dichloroethenes (DCEs). Both PCE and TCE are above Aquifer Water Quality Standards (MCLs = 5 ppb). Contaminants are present in the perched aquifer at about 30 m below land surface (BLS), and in the regional aquifer at about 60 m BLS. The source of VOCs is probably previous laundry and dry-cleaning operations. Contamination has prompted the installation of an SVE system to remove contaminated soil gas (500–1000 ppmv), which is treated with granular activated carbon (GAC) and then vented to the atmosphere. The University of Arizona operated a field laboratory adjacent to the SVE system. A side stream of the SVE gas was routed through the thermocatalytic reactor system for treatment and analysis. Two catalytic converters were mounted in parallel. Mixed redox conditions were achieved by combining propane (~ 2%) with the SVE side stream containing 12~18% v/v O₂. The total gas flow rate through a reactor was 100 L/min (under ambient conditions) for a residence time of 0.2 s. Operating temperatures were in the range 450–600°C. Temperature was regulated using mantle heaters that were wrapped around the reactors and attached to a temperature controller. Energy was consumed by the heaters during reactor start-up only. Thereafter, the exothermic nature of the reaction maintained reactor temperature without external energy input.

Results and Discussion

Laboratory Study of the PCE/H₂/O₂ Mixed Redox System

In the mixed redox system where the oxidant is O₂, the reductant is H₂, and PCE is the target VOC, analysis of the reactor effluent suggests that the main end products are a dehalogenated hydrocarbon, CO₂, H₂O, and HCl (and/or Cl₂). Relevant overall reactions, therefore, include:

In addition to ethane (C_2H_6), our analysis indicates that methane and ethylene are produced. Therefore, other reactions also occur and require further investigation. The dominant reaction pathways and exact end products are influenced by, at least, temperature and initial reactant composition. For example, metastable carbonaceous material (coke) may be produced, which, together with other intermediate products, may be further converted, as illustrated below and discussed later:

Reaction (4), among other exothermic reactions, acts as an internal heater to provide the energy needed for this reaction system to be self-sustaining. It was observed that the temperature difference between the catalyst surface and the furnace increased as the H_2/O_2 ratio increased up to a value of 2. This temperature difference reached approximately 100°C when the feed had 800 ppmv PCE, 11% H_2 , and 5% O_2 by volume.⁶ It is expected that internal heating depends on flow rate, initial reactant composition, and degree of reactant conversion, but this was not investigated in detail.

Effects of Temperature and H_2/O_2 Ratio on PCE Conversion—The reaction conversion is defined as $100 \times (1 - C_{\text{out}}/C_{\text{in}})$, where C_{in} and C_{out} are the influent and effluent PCE concentrations measured at room temperature, respectively. Figure 1 shows the PCE percent conversion as a function of two parameters: catalyst surface temperature, and H_2/O_2 ratio. In the range $75\text{--}525^\circ\text{C}$, PCE conversion generally increased with increasing H_2/O_2 ratio and temperature. It should be noted that at $\text{H}_2/\text{O}_2 = 1$, PCE conversion rose rapidly to 93% at around 150°C and then retained this level at higher temperatures. At $\text{H}_2/\text{O}_2 = 2$, PCE conversion rose even more rapidly, reaching near-complete destruction at around 120°C . In comparison, PCE conversions increased more slowly and did not reach maxima until around 320°C in the $\text{H}_2/\text{O}_2 = 0.5$ and 0.25 cases. We believe that the observed substantial drop in PCE conversion with increased oxygen content (Fig. 1) is partly a consequence of competition between PCE and O_2 for active sites on the catalyst surface. A change in mechanism from the more effective reductive dehalogenation to simple oxidation may also play a role in the inhibitive effect of oxygen. In addition, at $\text{H}_2/\text{O}_2 = 2$, the temperature required to reach maximum conversions is highly sensitive to PCE concentration (data not shown; see Örbay *et al.*⁶ for details.)

At this point, it is difficult to provide detailed reaction mechanisms and catalytic processes without further experiments and catalyst surface analysis. However, the trends of PCE conversion with respect to temperature and H_2/O_2 ratio are closely related to catalyst deactivation and regeneration. Earlier experiments show that, in the $180\text{--}450^\circ\text{C}$ range, PCE

conversion was rather low (<30%) under the O₂-only condition, while decreased rapidly to near zero within a few hours under the H₂-only condition.⁶ By comparison, PCE conversion was both high (>67%) and long-lasting (more than a few hours) under the H₂/O₂ mixed redox conditions.

Proposed mechanisms of catalyst deactivation include metal particle sintering,¹⁶ coke deposition, which is particularly pronounced during reduction,^{9,10} and chlorine poisoning, which occurs commonly during oxidation.^{17,18} The latter two mechanisms are the focus of discussions here based on the relevant reactions discussed earlier. In particular, how Cl₂, HCl, and surface chlorides play individual or synergistic roles in poisoning the catalyst is still under investigation. Nevertheless, it is generally believed that either chlorine species or carbonaceous coking materials can adsorb or deposit on the catalyst surface, occupy active sites, and compete with other reactants, leading to catalyst poisoning and eventually lowering conversion. When the catalyst temperature increases, accumulated organic species are volatilized and/or destroyed by O₂, thereby freeing active sites on the catalyst surface. As a result, PCE conversion increases. Furthermore, as the H₂/O₂ ratio increases under mixed redox conditions, heat generated by reaction (4) increases and the catalyst temperature rises more rapidly. In addition, the presence of H₂ prevents accumulation of chlorine on the surface [reaction (5)]. As a result, catalyst poisoning due to coke and chlorine deposition is lessened and PCE conversion increases more rapidly, which is consistent with the trends in Figure 1. Therefore, mixed redox conditions can lower the temperature needed for efficient conversion while preserving catalyst activity for long durations. In our study, the catalyst maintained its activity for over 2 years using only mild regeneration procedures, as described in the Experimental section.

Effect of PCE Concentration on PCE Conversion—The previously noted general trends of PCE conversion with respect to the H₂/O₂ ratio and catalyst temperature have been observed in the same reaction system at different PCE concentrations.⁶ An experiment was carried out to examine the effect of PCE concentration on PCE conversion. Figure 2 clearly shows that PCE conversion decreased as PCE concentration increased, with the temperature held constant at 200°C and H₂/O₂ = 2. The decrease in PCE conversion may be attributed to the existence of a limited number of active sites on the catalyst surface onto which PCE can adsorb and react. The solid line in Figure 2 represents the predictions of a simple model in which PCE in the gas phase is assumed to be at equilibrium with adsorbed PCE through a Langmuir isotherm (which is valid up to saturation of active sites) and the kinetics of the process is simulated by a first-order reaction-rate expression based on adsorbed PCE concentration. As PCE concentration increases, the surface becomes more concentrated in adsorbed PCE, which hinders its ability to further adsorb and react.

Laboratory Study of the PCE/Alkane/O₂ Mixed Redox System

Although the H₂/O₂ redox conditions can give rise to high conversions of PCE on a laboratory scale, the relatively high cost of H₂ and associated handling difficulties hinder its use in field operations. It is necessary to find an alternative reductant to overcome these problems. Our study focuses on testing the homologous series of aliphatic alkanes, some of which were found to improve the conversion of chlorinated solvents by acting as hydrogen donors under the predominantly oxidizing condition.^{11–13, 19} Figure 3 shows the PCE redox conversions, replacing H₂ with methane (CH₄), ethane (C₂H₆), propane (C₃H₈), or *n*-butane (*n*-C₄H₁₀). Clearly, PCE conversion increased with increasing carbon number. Methane did not increase PCE conversion compared with the O₂-only (control) case. The C–H bond dissociation energies (BDE) are 439.3, 420.5, 410.5, and 400.4 kJ/mol for CH₄, C₂H₆, C₃H₈, and *n*-C₄H₁₀, respectively. If the key role of the alkane in a PCE/alkane/O₂ catalytic system is to provide hydrogen to aid dechlorination (detailed mechanism to be investigated), then the ease of the C–H bond dissociation in the alkane should improve PCE conversions. Indeed, the BDE

and the trends shown in Figure 3 support this notion. Prognostic modeling can yield further insight. Two assumptions are made: the reaction rate is first-order with respect to PCE, and the activation energy of the reaction system is a linear function of the corresponding alkane's BDE. Under these assumptions, a simple three-parameter fit can yield optimal activation energy values and the apparent first-order rate constants for PCE conversion (for more details, see Örbay *et al.*⁶) Results of the model calculations are given by the lines in Figure 3. The model reproduces the experimental data reasonably well, suggesting that the assumptions may be valid in these PCE/alkane/O₂ redox systems.

With propane as the reductant, achieving a reasonable PCE conversion (>50%) requires the operating temperature to be at least 400°C. Achieving a high PCE conversion (>90%) requires the operating temperature to be at least 520°C. With *n*-butane as the reductant, the required operating temperatures are lower by about 50°C. Under these temperatures, which are applicable in the field, no harmful byproducts such as furans and dioxins are detected, according to our analytical measurements (data not shown). From the perspective of operating costs, propane becomes the ideal reductant to use in actual field operations. A remaining issue is how much propane should be used to achieve the best operation. In principle, a higher concentration of propane at a given oxygen content increases PCE conversion (a trend similar to that shown in Fig. 1). However, use of excess propane increases costs, and predominantly reducing conditions lead to rapid catalyst deactivation. Systematic tests show that the best volume ratio for propane/O₂ would be 1/5, which is the stoichiometric ratio for the complete oxidation of propane by O₂. For example, for 800 ppmv PCE and at 450°C and a residence time of 0.3 s, PCE conversion dropped from 72% to 36% when the propane/O₂ ratio dropped from 1/5 to 1/10. Similar to Figures 1 and 2, it can be expected that as PCE concentration decreases and temperature increases, PCE conversions will increase.

Field Operation

During the pilot field operation at the Park-Euclid site, our mixed redox catalytic system was used to treat SVE gases from the vadose zone, under semicontinuous (stop–start) conditions, for about 150 days during a period of 240 days in 2006. The main contaminants to be removed from SVE gases included PCE (up to 200 ppmv) and TCE (up to 20 ppmv). Trace levels of other chlorinated solvents, such as isomeric DCEs and diesel fumes, were also present. Since our laboratory study is limited to a single target compound (i.e., PCE), it is difficult to predict whether efficient conversions and catalyst stability can be achieved due to possible matrix effects in the field. For example, other VOCs and/or their reaction products may compete for active sites (thus lowering the conversions) or poison the catalyst surface (thus shortening catalyst lifetime). The actual results are much simpler and quite satisfying. As shown in Figure 4, near-complete conversions of PCE and TCE were achieved during the whole operation. The two catalysts maintained their activities throughout this period with no apparent loss. Even though the amount of propane used (2%) relative to O₂ (12–18%) was less than 1/5, it proved sufficient to produce high conversions, probably due to lower target compound concentrations and higher operating temperatures than in the laboratory. Strikingly, the PCE and TCE concentrations at the inlet increased continuously during the operation. This was likely due to contaminant rebound as the SVE system had been idle for some time prior to this operation.

Because a commercial GAC system was operated side by side with the redox catalytic converter during our pilot study, it is possible to compare treatment costs between the two methods. Neither the soil-vapor pumping costs nor the investment costs for the SVE system are included in this analysis, since they are common to the two treatment methods. The catalyst itself is so inexpensive (<\$50/unit) and it lasts for so long (>2 years) that its acquisition cost is not included either. The concentration of PCE in the soil vapor is taken as 200 ppmv, a typical value from field measurements. In the catalytic method, the most expensive consumable is propane, which

costs about \$0.39/lb (using a 2005 national average price of \$1.674/gal and a propane density of 4.24 lb/gal). This results in a treatment cost of about \$10/lb of PCE destroyed. By comparison, the treatment cost of a typical GAC system is about \$7/lb of PCE adsorbed, according to the recent estimate by Scott Weingarden of U.S. Filter (50 ft³/min flow and an operating temperature of 85°F). At first glance, this is comparable to that of the catalytic system. However, as PCE concentration increases in the SVE gas, the GAC gets saturated faster, leading to proportionately higher unit treatment costs (i.e., costs in treating unit mass of PCE). It is exactly the opposite in the catalytic method, as propane use is independent of the PCE concentration (within the range in the field), which leads to lower unit treatment costs as PCE concentration increases. In addition, the presence of other VOCs (e.g., DCEs) in the soil gas should also increase the overall GAC costs but add no extra costs to the catalytic method. Overall, the redox catalytic method is as cost effective as the GAC method at typical PCE concentrations in the field, but becomes more economical with increasing concentrations of target compounds to be treated.

Conclusions

In the laboratory, the H₂/O₂ mixed redox system yields high conversions of PCE while maintaining catalyst activity using only mild regeneration procedures. A homologous series of aliphatic alkanes are good alternative reductants to replace H₂ (with the exception of CH₄). In a pilot field operation, the propane/O₂ mixed redox system yielded near-complete conversions of PCE and TCE, with no apparent loss of catalyst activity for extended periods (at least 5 months). The presence of other VOCs posed no adverse matrix effects on the conversions of target contaminants. While detailed mechanisms and processes in these redox systems await further study, mixed redox catalysis is a promising new method for highly efficient and economical remediation of soils and groundwater contaminated with chlorinated solvents and other halogenated compounds.

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Figure 1.

PCE conversion as a function of catalyst surface temperature and H₂/O₂ ratio. PCE inlet concentration: 200 ppmv. H₂: 2% by volume. O₂: varies to obtain the respective H₂/O₂ ratios. Flow rate: 2.0 L/min (residence time ~0.2 s). Legend: (▲) 1% O₂. (◇) 2% O₂. (■) 4% O₂. (○) 8% O₂.

Figure 2.

PCE conversion as a function of PCE concentration. The dots are experimental data while the solid line is the model fit. H_2 : 2.7% by volume. O_2 : 1.3% by volume. Flow rate: 1.0 L/min (residence time ~ 0.4 s). Temperature: 200°C.

Figure 3.

PCE conversions in the presence of O₂ (21%) and CH₄ (5%), C₂H₆ (3%), C₃H₈ (2%), and *n*-C₄H₁₀ (1.5%), respectively. PCE in the influent was within the range of 175–200 ppmv. Flow rate: 1.0 L/min (residence time ~0.5 s). Dots are experimental data, while lines are model results. See text for description of the model. Legend: (Δ) O₂-only (control). (●) CH₄. (■) C₂H₆. (◆) C₃H₈. (○) *n*-C₄H₁₀. The solid, dashed, shaded, and dotted lines represent the model fits for CH₄, C₂H₆, C₃H₈, and *n*-C₄H₁₀, respectively.

Figure 4.

PCE and TCE concentrations in the inlet to the catalytic reactor as well as the percent conversions of PCE and TCE during the extended field operation. Operating temperature: $\sim 520^{\circ}\text{C}$. Gas flow rate: 100 L/min. Residence time: ~ 0.2 s. C_3H_8 : $\sim 2\%$ by volume. Legend: (▲) PCE inlet concentration. (■) TCE inlet concentration. (Δ) PCE conversion. (□) TCE conversion.