



ELSEVIER

Journal of Hazardous Materials B87 (2001) 171–186

**Journal of  
Hazardous  
Materials**

www.elsevier.com/locate/jhazmat

## The mechanism and applicability of in situ oxidation of trichloroethylene with Fenton's reagent

Ge Chen<sup>a,1</sup>, George E. Hoag<sup>b</sup>, Pradeep Chedda<sup>b</sup>,  
Farhad Nadim<sup>b,\*</sup>, Bernard A. Woody<sup>c,2</sup>, Gregory M. Dobbs<sup>c</sup>

<sup>a</sup> ELM consulting L.L.C., 304 S Clairborne, Suite 200, Olathe, KS 66062, USA

<sup>b</sup> University of Connecticut, The Environmental Research Institute, Route 44,  
Longley Building 270 Middle Turnpike Unit-5210, Storrs, CT 06269-5210, USA

<sup>c</sup> United Technologies Research Center, 411 Silver Lane, E. Hartford, CT 06108, USA

Received 20 December 2000; received in revised form 1 May 2001; accepted 2 May 2001

### Abstract

Fenton's reagent is the result of reaction between hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ferrous iron ( $\text{Fe}^{2+}$ ), producing the hydroxyl radical ( $\bullet\text{OH}$ ). The hydroxyl radical is a strong oxidant capable of oxidizing various organic compounds. The mechanism of oxidizing trichloroethylene (TCE) in groundwater and soil slurries with Fenton's reagent and the feasibility of injecting Fenton's reagent into a sandy aquifer were examined with bench-scale soil column and batch experiment studies. Under batch experimental conditions and low pH values ( $\sim 3$ ), Fenton's reagent was able to oxidize 93–100% (by weight) of dissolved TCE in groundwater and 98–102% (by weight) of TCE in soil slurries. Hydrogen peroxide decomposed rapidly in the test soil medium in both batch and column experiments. Due to competition between  $\text{H}_2\text{O}_2$  and TCE for hydroxyl radicals in the aqueous solutions and soil slurries, the presence of TCE significantly decreased the degradation rate of  $\text{H}_2\text{O}_2$  and was preferentially degraded by hydroxyl radicals. In the batch experiments, Fenton's reagent was able to completely dechlorinate the aqueous-phase TCE with and without the presence of soil and no VOC intermediates or by-products were found in the oxidation process. In the soil column experiments, it was found that application of high concentrations of  $\text{H}_2\text{O}_2$  with addition of no  $\text{Fe}^{2+}$  generated large quantities of gas in a short period of time, sparging about 70% of the dissolved TCE into the gaseous phase with little or no detectable oxidation taking

\*Corresponding author. Tel.: +1-860-486-4015; fax: +1-860-486-5488.

E-mail addresses: chen.ge@worldnet.att.net (G. Chen), ghoag@aqua.eri.uconn.edu (G.E. Hoag), kousanee@hotmail.com (P. Chedda), fnadim@aqua.eri.uconn.edu (F. Nadim), woodyba@utrc.utrc.com (B.A. Woody), Dobbs@utrc.utrc.com (G.M. Dobbs).

<sup>1</sup>Fax: +1-503-905-9037.

<sup>2</sup>Tel.: +1-860-610-7145; fax: +1-860-610-7911.

place. Fenton's reagent completely oxidized the dissolved phase TCE in the soil column experiment when TCE and Fenton's reagent were simultaneously fed into the column. The results of this study showed that the feasibility of injecting Fenton's reagent or  $\text{H}_2\text{O}_2$  as a Fenton-type oxidant into the subsurface is highly dependent on the soil oxidant demand (SOD), presence of sufficient quantities of ferrous iron in the application area, and the proximity of the injection area to the zone of high aqueous concentration of the target contaminant. Also, it was found that in situ application of  $\text{H}_2\text{O}_2$  could have a gas-sparging effect on the dissolved VOC in groundwater, requiring careful attention to the remedial system design. Published by Elsevier Science B.V.

*Keywords:* Fenton's reagent; In situ chemical oxidation; Groundwater; Soil; Trichloroethylene

---

## 1. Introduction

The in situ chemical oxidation technology uses chemical oxidants that directly destroy dissolved contaminants in a subsurface medium. This results in an increase in the concentration gradient and mass transfer processes between zones of high contaminant concentration and the groundwater containing the oxidant. Because the process is in situ, no surface treatment system for the contaminants is needed and there is no treated groundwater to be discharged. Trichloroethylene (TCE) is a dense non-aqueous phase liquid (DNAPL) with very low water solubility ( $\sim 1100$  mg/l at saturation) [1]. Residual TCE may exist in low permeable zones of the subsurface soil as blobs, globules and lenses. Slow dissolution of residual TCE in groundwater and the slow diffusion of TCE in groundwater trapped in soil micropores may be limiting factors in remediating TCE contaminated sites.

Among various oxidants explored for in situ oxidation of contaminants, Fenton's reagent (a mixture of hydrogen peroxide and ferrous salt) has gained a great amount of attention, due to its strong oxidation capabilities and low environmental impacts [2]. Fenton's oxidation technology has been applied in pilot-scale and full-scale removal of TCE from soil and groundwater at several contaminated sites in the past few years. Some of these studies have claimed to be successful [3,4], some of them found the TCE concentration to rebound a few months after the treatment, and some showed the limitations of this technology caused by subsurface heterogeneity [5]. Weeks et al. studied the use of Fenton's reagent for degradation of TCE in aqueous systems and soil slurries [6]. They used a constant aqueous concentration of 60 mg/l for TCE. However, they did not investigate Fenton's reaction in soil columns and the existing literature does not provide an in-depth understanding of the role of Fenton's reagent in the subsurface oxidation process.

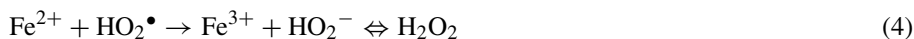
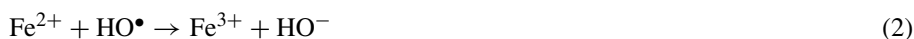
In this study, column experiments were designed to investigate: (1) the decomposition rate of  $\text{H}_2\text{O}_2$  in a heterogeneous sandy soil under continuous flow conditions, (2) the possibility of oxidizing dissolved TCE with soil induced Fenton-type reaction, and (3) the oxidation of aqueous-phase TCE with Fenton's reagent in soil columns packed with undisturbed field samples. The soil induced Fenton-type reaction may be described as the reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  ions naturally present in soil for the generation of hydroxyl radicals. In general, the redox potential (Eh) for deep groundwater is usually sufficiently low that, for a pH of less than about 8, iron is present as the soluble  $\text{Fe}^{2+}$  ion [7]. Therefore, presence of  $\text{H}_2\text{O}_2$  in soils with sufficient iron content may produce a Fenton-type reaction. Batch

experiments were designed to study the competing capabilities of TCE and soil for Fenton's reagent or hydroxyl radicals.

## 2. Chemistry of Fenton's reagent

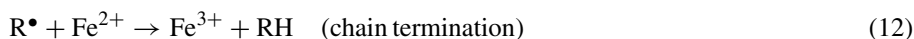
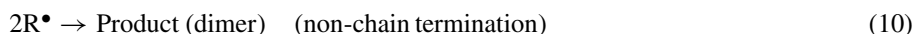
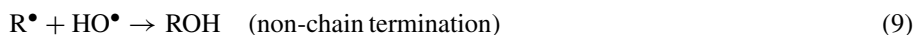
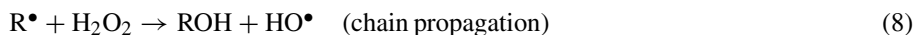
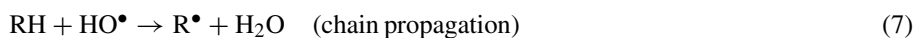
Fenton's reagent is a mixture of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ferrous salt. It produces hydroxyl radicals that are strong oxidizers. Laboratory researchers have shown that Fenton's reagent is capable of oxidizing several chlorinated solvents in aqueous solutions [8,9] including TCE and tetrachloroethylene (PCE) in soil slurries or soil columns [10–12]. It is, therefore, reasonable to presume that Fenton's reagent may have a high potential for in situ applications.

Fenton's reagent is not stable. Once  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  are mixed, several reactions take place simultaneously. These reactions produce hydroxyl radicals ( $\text{HO}^\bullet$ ), hydroperoxyl radicals ( $\text{HO}_2^\bullet$ ),  $\text{Fe}^{3+}$ , and  $\text{O}_2$  (Eqs. (1)–(6)).



Although hydroxyl radicals, hydroperoxyl radicals, hydrogen peroxide, and oxygen are all oxidants, hydroxyl radicals have the strongest oxidation capability, and are considered responsible for oxidizing various organic compounds.

The mixture of organics and Fenton's reagent results in additional reactions, (Eqs. (7)–(12)) [13,14]. Hydroxyl radicals react strongly with the dissolved organic compounds,  $\text{H}_2\text{O}_2$ , and  $\text{Fe}^{2+}$  ions in solution. They also react with other hydroxyl radicals themselves. The reaction rates of hydroxyl radicals are much faster than the generation of these radicals, which gives them a very short life span. Oxidation of the organics initially depends on the selectivity of the hydroxyl radicals for the target organic compounds and then on the selectivity and availability of these radicals to propagate the reaction.



Groundwater constituents and the chemistry of the soil surface may complicate Fenton's chemistry in the oxidation process. This effect was seen in the soil oxidant demand (SOD) when oxidation in DI water, groundwater, soil slurries, and soil columns were compared. During the in situ oxidation process, it is desirable to have little or no SOD, so that oxidants can effectively be distributed throughout the treatment zone. The soil-buffering capacity is an important factor to be considered. This is because where ferrous ions are present the optimal pH for Fenton's reagent for efficient reaction is in the range of 2–4. In order to achieve low pH conditions, soils may need to be acidified. Miller and Valentine conducted a study to investigate the oxidation behavior of quinoline and nitrobenzene in aqueous solutions in the presence of  $\text{H}_2\text{O}_2$  and aquifer material (soil particle sizes of 0.18–0.84 mm) used as a filter media. They observed that reduction of pH in the filter media with acid-hydroxylamine reduced the manganese concentration by 80% and prolonged the lifetime of  $\text{H}_2\text{O}_2$ . Manganese oxides have been shown to be effective catalysts for the decomposition of hydrogen peroxide [15].

### 3. Experimental procedure

Batch experiments were conducted in a zero-headspace reactor (Fig. 1). The reactor was a 100 ml airtight glass syringe (Hamilton part #: 86346) with a Teflon plunger to ensure that reactions were taking place under zero-headspace conditions. A Luer-lock valve (Hamilton part #: 35083) was connected to the syringe with a double-hub needle to facilitate the collection of samples.

Four different experiments in zero-headspace batch reactors were conducted (Table 1). Experiment FTG-B was conducted to study the oxidation of TCE in groundwater. Experiments FTS-B2, and FTS-B3, were conducted to study the impact of soil on the oxidation of TCE. Experiment FTS-B1 was conducted as a control with no addition of TCE. The initial pH levels of all the above experiments were controlled at  $3 \pm 0.05$  with addition of appropriate quantities of 5 M sulfuric acid solution. Groundwater used for the experiments was taken from a site located in North Haven, Connecticut and was tested according to USEPA method-8260B for analysis of volatile organic compounds in soil and water samples, to ensure that it was free of chlorinated solvents or any of the other 60 target VOCs listed in that method [16].

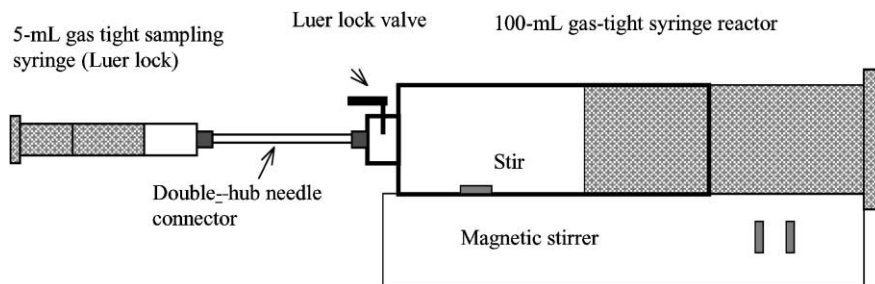


Fig. 1. Schematic of the zero-headspace batch reactor.

Table 1

Experimental conditions for Fenton's reagent oxidizing TCE in groundwater and soil slurries<sup>a</sup>

Experiment (ml)	Groundwater (mg/l)	(H <sub>2</sub> O <sub>2</sub> ) <sub>0</sub> (mg/l)	(Fe <sup>2+</sup> ) <sub>0</sub> (mg/l)	(TCE) <sub>0</sub> (mol:mol)	H <sub>2</sub> O <sub>2</sub> :Fe <sup>2+</sup> (g:g)	Solution:soil
FTG-B	~90	520	15	50	57.1:1	N.A.
FTS-B1 (control)	~90	1000	30	0	54.9:1	10:1
FTS-B2	~80	1000	30	98	54.9:1	10:1
FTS-B3	~45	1000	30	416	54.9:1	10:1

<sup>a</sup> F: Fenton's reagent; T: TCE; G: groundwater; S: soil; N.A.: not applicable.

### 3.1. Column experiments

In order to assess the feasibility of Fenton's reagent application as an in situ oxidant for subsurface remediation, experiments were conducted in stainless steel columns with the dimensions of 76 mm (3 in.) long and an internal diameter of 43 mm (1.7 in.) (Fig. 2). Due to the short life span of H<sub>2</sub>O<sub>2</sub>, the column dimensions were chosen to allow the breakthrough of hydrogen peroxide solution in the columns. Undisturbed soil taken from soil cores was placed inside the experimental column. Duplication of column studies was not possible because natural undisturbed soil has a heterogeneous character and it was not possible to set-up two columns with identical soil conditions.

The chemical feed system consisted of a glass bottle for H<sub>2</sub>O<sub>2</sub> stock solution, a Tedlar<sup>®</sup> bag containing TCE solution or TCE and Fe<sup>2+</sup> stock solution, Teflon<sup>®</sup> tubing for the delivery of TCE and H<sub>2</sub>O<sub>2</sub>, and a peristaltic pump. All chemicals used were of reagent grade.

The soil column was prepared by inserting a 43 mm i.d. × 76 mm long stainless steel pipe into an aluminum core (minimizing soil disturbance) containing uncontaminated soil that was taken from a site located in North Haven, Connecticut (Table 2).

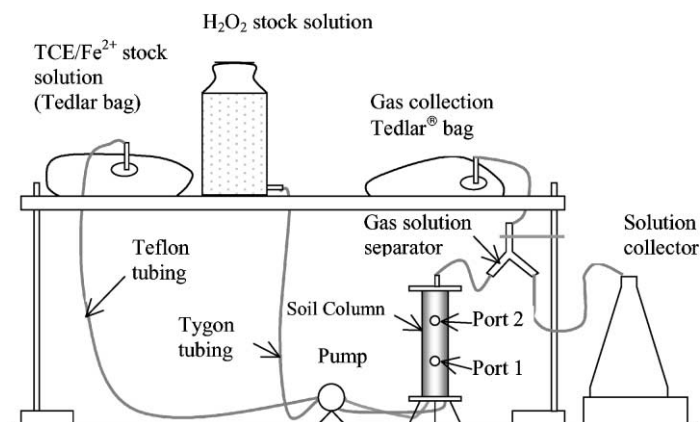


Fig. 2. Schematic of the 76 mm column set-up.

Table 2  
Characteristics of the sandy soil used in the experiments

Parameter	Value
Moisture content <sup>a</sup> (saturated conditions) (%)	17–27
Porosity	~0.3
Organic carbon (%)	~0.02
Chromium (Cr) ( $\mu\text{g/g}$ )	24–40
Copper (Cu) ( $\mu\text{g/g}$ )	17–27
Iron (Fe) ( $\mu\text{g/g}$ )	11049–22111
Magnesium (Mg) ( $\mu\text{g/g}$ )	501–1603
Manganese (Mn) ( $\mu\text{g/g}$ )	281–541

<sup>a</sup> Weight of moisture/weight of dry soil.

Soil was tested according to USEPA method-8260B for analysis of volatile organic compounds in soil and water samples to ensure that there was no trace of chlorinated solvents or any of the other 60 target VOCs listed in that method was present in the study soil [16]. The stainless steel column was then mounted on a tripod (Fig. 2). At each end of the soil column, a stainless steel screen and a thin layer of glass beads were added to retain soil in the column under flow conditions. Two small holes (ports 1 and 2) were drilled through the side of the column to facilitate the mounting of the sample collection fittings. Samples were collected periodically from the inlet, port 1, port 2, and the outlet using a 5 ml airtight syringe (Hamilton part # 81520).

The effluent collection system consisted of a Y-shaped connector serving as a water-gas separator, a piece of Teflon<sup>®</sup> tubing bent into a U-shape form to maintain the water level in the Y-shaped connector, a Tedlar<sup>®</sup> bag to collect the gas, and a volumetric flask to collect the effluent (Fig. 2).

Three sets of experiments were conducted with the column apparatus. The first experiment was designed to assess the soil oxidant demand under continuous flow conditions. The decomposition of  $\text{H}_2\text{O}_2$  solutions was studied at concentrations of 0.1, 1, and 10 g/l. The pH level of influent groundwater without adjustment was measured to be  $7 \pm 0.05$ . The groundwater used for the experiments had a good buffering capacity and no pH adjustment was needed to attain a pH of 7. For  $\text{H}_2\text{O}_2$  concentration measurements, samples were taken from sampling ports 1, 2, and the outlet.

In the second experiment, the possibility of oxidizing TCE with soil-induced decomposition of  $\text{H}_2\text{O}_2$  (a Fenton-type reaction) was evaluated. A TCE solution at 250 mg/l and an  $\text{H}_2\text{O}_2$  solution at 10 g/l were simultaneously pumped into the column at a flow rate of 0.15 ml/min. In order to maintain the natural soil conditions, the pH levels of the two solutions were not lowered. The concentrations of TCE,  $\text{H}_2\text{O}_2$ , and  $\text{Cl}^-$  from two sampling ports and from the effluent were measured over time. The generated gas was collected in a Tedlar<sup>®</sup> bag, and TCE concentrations were measured at the end of the experiment.

The third experiment was designed to study the oxidation of TCE in a mixture of TCE-contaminated groundwater and Fenton's reagent in a soil column. Two solutions, one containing 30 g/l  $\text{H}_2\text{O}_2$  and the other containing 900 mg/l  $\text{Fe}^{2+}$  in groundwater, were pumped continuously into the column at a flow rate of 0.15 ml/min. A 5 ml aqueous

solution saturated with TCE was then injected into the  $\text{Fe}^{2+}$  solution line within 10 mm of the column inlet port. The pH level of the solution was lowered to about 3 with addition of appropriate quantities of 5 M sulfuric acid solution. The concentrations of TCE,  $\text{Cl}^-$ , and  $\text{H}_2\text{O}_2$  in the effluent were measured over time (Fig. 2).

## 4. Chemical analysis

### 4.1. Volatile organic compounds (VOCs)

A gas chromatograph (Model HP-5890, Series II Plus) connected to a mass selective detector (HP-MSD 5971A) was used for the analysis of VOCs in the aqueous solution. A HP-3365 Series II (Chem-Station software version A.02.12) was used for quantification of VOCs. The column used was a capillary column, 60 m-long (two interconnected 30 m columns), 0.319 mm i.d., 0.50  $\mu\text{m}$  (film thickness) DB-1, J&W Scientific. The initial oven temperature was set at 35°C for 1 min and raised to 180°C at 8°C/min, then held at 180°C for 15.48 min. The total run time was 34.6 min. Samples were introduced into the GC/MSD through a Tekmar LSC-2016 connected to a Tekmar-LSC-2000 automated purge and trap system. Samples were purged with high purity grade helium for 12 min.

### 4.2. Chloride ( $\text{Cl}^-$ )

Chloride concentrations were determined by a DIONEX series 4000 ion chromatograph (HPIC) equipped with a DIONEX Ionpac AS12A 4 mm column, an anion micro membrane suppressor, and a conductivity detector. The eluent used was 2.1 mM sodium carbonate ( $\text{Na}_2\text{CO}_3$ )/0.8 mM sodium bicarbonate ( $\text{NaHCO}_3$ ). The flow rate of the eluent was set at 1.5 ml/min, the typical pressure was between 12400 and 13800 kPa (1800 and 2000 psi), and the background conductivity was about 24  $\mu\text{S}$ . The area integration method was used to quantify the concentration of  $\text{Cl}^-$ .

### 4.3. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ )

The  $\text{H}_2\text{O}_2$  solution was prepared from a 30% stock solution and standardized using a titration method with potassium permanganate [17]. The standardized  $\text{H}_2\text{O}_2$  solution was used to produce a standard curve of  $\text{H}_2\text{O}_2$  with a spectrophotometric method using cobalt ( $\text{Co}^{2+}$ ) and bicarbonate [14]. The  $\text{H}_2\text{O}_2$  concentrations were analyzed with the spectrophotometric method. The detection limit of the method was  $\pm 0.01$  mg/l of  $\text{H}_2\text{O}_2$ . The concentration range measured was between 0 and 1 mg/l, at a wavelength of 260 nm. The spectrophotometer used was a Milton Roy Spectronic 601.

### 4.4. Ferrous Iron ( $\text{Fe}^{2+}$ )

Ferrous iron was analyzed by the standard 3500-Fe D-Phenanthroline method, at a wavelength of 510 nm. The same Milton Roy Spectronic 601, spectrophotometer used for  $\text{H}_2\text{O}_2$  analysis was used for the analysis of  $\text{Fe}^{2+}$ .

#### 4.5. Quality control/quality assurance

All analytical instrumentations were calibrated prior to sample analysis based on the instrument's standard operating procedure used at the Environmental Research Institute. Calibration verification (CV), blanks, duplicates, and spikes were used during the system operation to control the precision of the instruments. A CV is a standard prepared from a source which is different than the source used for the initial calibration. The acceptance criterion for CV was 70 to 130% recovery and all CV recoveries were within the acceptable range [18].

### 5. Results and discussion

#### 5.1. Batch experiments

During the batch experiments, Fenton's reagent was able to completely dechlorinate aqueous-phase TCE with and without the presence of soil. About 90–100% of TCE was degraded in 5 h (Fig. 3), and 93–102% of the stoichiometric releases of  $\text{Cl}^-$  were detected (Table 3). During each experimental run, the pH of the solutions decreased from 3 to as low as 2.43 (Table 3). Decreasing pH values may have been caused by the generation of  $\text{CO}_2$  or  $\text{H}^+$ . This is in accordance with the findings of Weeks et al. [5] and Gates et al. [19]. The  $\text{H}_2\text{O}_2$  solutions are acidic, and if Fenton-type reactions occur, production of  $\text{H}^+$  due to reduction of  $\text{Fe}^{3+}$  may result into lower pH values [19]. No VOC intermediates or by-products were found in the oxidation process. The only peak observed in the generated

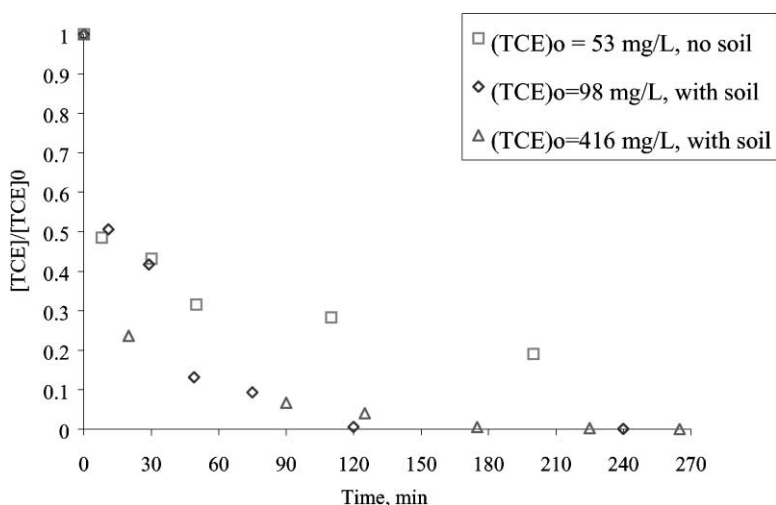


Fig. 3. TCE degradation in groundwater and soil slurries. Experimental conditions: zero-headspace reactors;  $(\text{pH})_0 = 3$ ; for the experiment without soil,  $(\text{H}_2\text{O}_2)_0 = 520 \text{ mg/l}$ ,  $(\text{Fe}^{2+})_0 = 15 \text{ mg/l}$ ; for experiments with soil,  $(\text{H}_2\text{O}_2)_0 = 1000 \text{ mg/l}$ ,  $(\text{Fe}^{2+})_0 = 30 \text{ mg/l}$ , soil:solution = 1:10 (g/g).



Table 3  
Recovery rate of chloride and pH changes in the experiments on oxidation of TCE in groundwater and soil slurries<sup>a</sup>

Experiment	Initial pH	Final pH	Cl <sup>-</sup> generated (mg/l)	Cl <sup>-</sup> predicted (mg/l)	Recovery rate (%)
FTG-B	3.01	2.77	44	43	102
FTS-B1	~7	6.5	N.A.	N.A.	N.A.
FTS-B2	3.0	2.71	73.7	79.3	93
FTS-B3	3.0	2.43	329	336.8	97.7

<sup>a</sup> F: Fenton's reagent; T: TCE; G: groundwater; S: soil; B: batch experiment.

chromatograms of the GC/MSD chromatographic analysis was the TCE peak. Near the end of the first experiment (FTG-B), one sample was analyzed for total organic carbon (TOC). The concentration was lower than the detection limit, indicating no organic acid by-products were formed at high concentrations. Therefore, it is most likely that TCE was mineralized to CO<sub>2</sub>, Cl<sup>-</sup>, and H<sup>+</sup>.

The soil iron content may have induced a Fenton-type reaction leading to the production of hydroxyl radicals. Therefore, in the presence of soil, TCE may have successfully competed for •OH against soil and other species (such as H<sub>2</sub>O<sub>2</sub>, Fe<sup>2+</sup>, and Fe<sup>3+</sup>) in the solution and was preferentially degraded.

In all of the three experiments, Fe<sup>2+</sup> concentrations decreased to <0.1 mg/l within the first 30 min of the experiment. Oxidation of TCE continued afterward and was likely catalyzed by Fe<sup>3+</sup> or regenerated Fe<sup>2+</sup> (Eqs. (5) and (6)). The reaction rates were rapid in the first 100 min of the experiments and followed a slower trend afterwards. More than 56% of the TCE was destroyed within the first 30 min (Fig. 3). The observed overall degradation rate constant of TCE in soil slurries followed a pseudo first-order kinetic and ranged from 0.0283 to 0.033 min<sup>-1</sup> for aqueous TCE concentrations of 98 and 416 mg/l, respectively (Table 4).

Weeks et al. [6] found that the first-order model provided the best fit for change of concentrations of H<sub>2</sub>O<sub>2</sub> and TCE as a function of time in their experimental studies. They also noted that the actual processes involved in the degradation of H<sub>2</sub>O<sub>2</sub> and TCE are more complex than first-order model predictions. Degradation rate constants of TCE obtained in the batch experiments depended on the experimental conditions, such as the initial [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>2+</sup>] ratio and the initial H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> concentrations. Reactions in the later stages may have been catalyzed by regenerated Fe<sup>2+</sup> and possibly Fe<sup>3+</sup>. The degradation rate constants of H<sub>2</sub>O<sub>2</sub> and TCE during the batch experiments are presented in Table 4. In

Table 4  
Hydrogen peroxide and TCE degradation in aqueous and soil slurries

Experiment	Soil:water (w:w)	Initial H <sub>2</sub> O <sub>2</sub> (mg/l)	Initial Fe <sup>2+</sup> (mg/l)	Initial TCE (mg/l)	Initial pH	Final pH	KH <sub>2</sub> O <sub>2</sub> (min <sup>-1</sup> )	KTCE (min <sup>-1</sup> )
FTG-B	N.A.	520	15	53	3.010	2.77	N.A.	0.0057
FTS-B1 (control)	1:10	1000	30	0	3.000	2.72	0.0147	N.A.
FTS-B2	1:10	1000	30	98	3.000	2.71	0.0068	0.033
FTS-B3	1:10	1000	30	416	3.000	2.43	0.00378	0.0283

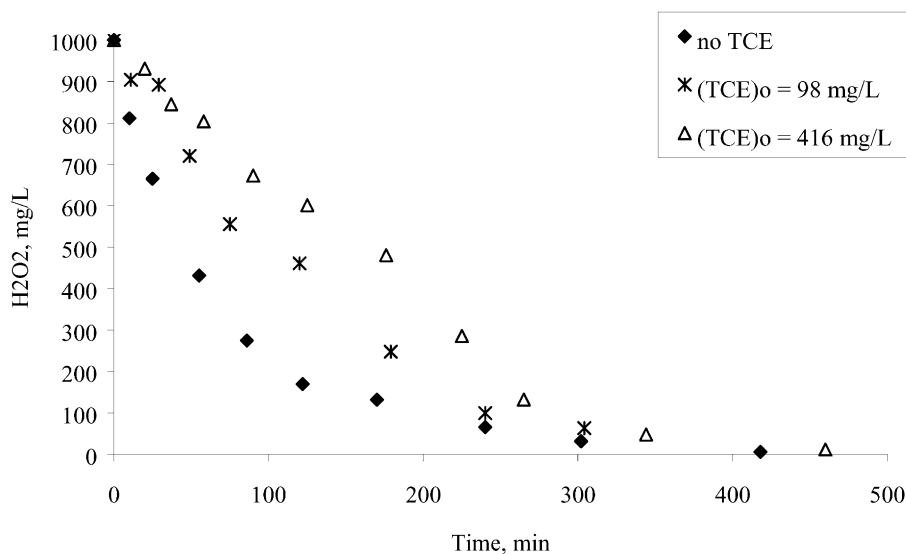


Fig. 4. The effect of TCE on H<sub>2</sub>O<sub>2</sub> degradation in soil slurries. Experimental conditions: (H<sub>2</sub>O<sub>2</sub>)<sub>0</sub> = 1000 mg/l; (Fe<sup>2+</sup>)<sub>0</sub> = 30 mg/l; soil:solution = 1:10; total volume = 100 ml.

the experiments, oxidizing TCE in soil slurries (Fig. 4), higher initial TCE concentrations lowered the H<sub>2</sub>O<sub>2</sub> degradation rates. At initial TCE concentrations of 0, 98, and 416 mg/l, the half-lives of H<sub>2</sub>O<sub>2</sub> were 47, 102, and 165 min, respectively. In the experiment, oxidizing TCE in groundwater with no soil slurry (Fig. 5), the concentration of H<sub>2</sub>O<sub>2</sub> only

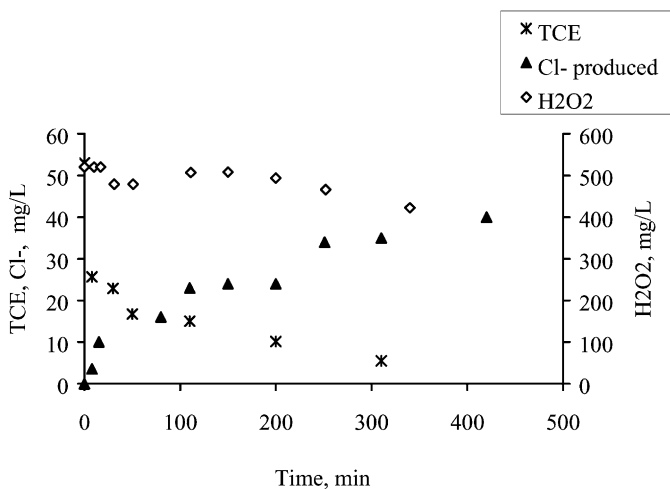
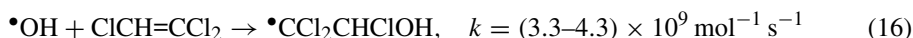
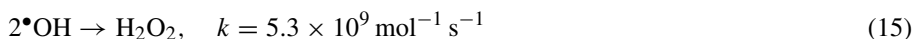
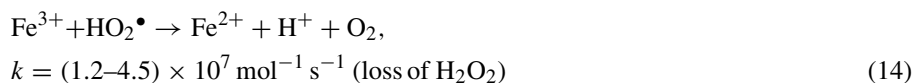
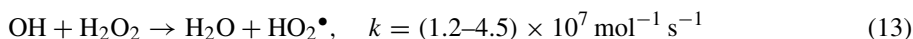


Fig. 5. Oxidation of TCE by Fenton's reagent in groundwater. Experimental conditions: (H<sub>2</sub>O<sub>2</sub>)<sub>0</sub> = 520 mg/l; (Fe<sup>2+</sup>)<sub>0</sub> = 15 mg/l; (TCE)<sub>0</sub> = 53 mg/l; total volume = 100 ml.

decreased by 10% throughout the experiment. Leung et al. [20] studied the oxidation of PCE, which has chemical properties very similar to those of TCE, with Fenton's reagent. They used the same method for H<sub>2</sub>O<sub>2</sub> analysis; however, they did not run a control to compare the rates of H<sub>2</sub>O<sub>2</sub> degradation with and without PCE. In the literature, many studies have mainly focused on the degradation of target compounds and have not provided data on H<sub>2</sub>O<sub>2</sub> degradation. A control experiment (FTS-B1) was conducted to compare H<sub>2</sub>O<sub>2</sub> degradation rates with and without the presence of TCE. The degradation rate constant of H<sub>2</sub>O<sub>2</sub> decreased from 0.0147 (control-no TCE) to 0.00378 min<sup>-1</sup> (initial TCE concentration = 416 mg/l).

The decomposition rate of H<sub>2</sub>O<sub>2</sub> was slowed by TCE, and it appears that TCE competed better than other species in the mixture for •OH radicals. Walling [14] noted that various organic substrates could retard the decomposition of H<sub>2</sub>O<sub>2</sub> by acting as •OH scavengers, so that less •OH reacts with H<sub>2</sub>O<sub>2</sub>. The reaction rate constants [21], show that hydroxyl radicals prefer TCE to H<sub>2</sub>O<sub>2</sub>; therefore, when TCE is present, less H<sub>2</sub>O<sub>2</sub> is consumed (Eqs. (13)–(16)).



This is an encouraging finding and implies that once Fenton's reagent is mixed with the TCE contaminated groundwater in the subsurface, H<sub>2</sub>O<sub>2</sub> may persist until TCE is oxidized to a very low concentration. Scavenging of hydroxyl radicals by TCE is the first step of the oxidation process and it is possible that the intermediates will also scavenge the •OH radicals in the aqueous phase [6].

## 5.2. Column experiments

### 5.2.1. Soil oxidant demand

The results of H<sub>2</sub>O<sub>2</sub> decomposition in a 76 mm column are given in Table 5. H<sub>2</sub>O<sub>2</sub> had a very short life span in the sandy soil column. After 50 pore volumes, 10 g/l H<sub>2</sub>O<sub>2</sub> groundwater solution could not break through 25 mm of sandy soil. Throughout the experiments, the H<sub>2</sub>O<sub>2</sub> concentration was less than the detection limit (5 mg/l) at sampling ports 1, 2 and the effluent. The retention time in 25 mm of the soil column was 34 min (porosity = 0.3), implying that the life span of H<sub>2</sub>O<sub>2</sub> was <34 min.

Iron and manganese contents of soil have been considered as potential causes of H<sub>2</sub>O<sub>2</sub> decomposition [11, 15, 22]. For the soil studied, the iron and manganese contents were 12,950 and 306 mg/kg, respectively. High concentrations of iron and manganese in soil may explain the rapid H<sub>2</sub>O<sub>2</sub> decomposition process.

Reducing the pH of the soil medium could decelerate the decomposition rate of H<sub>2</sub>O<sub>2</sub> in the soil column. With influent H<sub>2</sub>O<sub>2</sub> concentration of 15 g/l and a pH of 2.2, the effluent

Table 5  
Decomposition of H<sub>2</sub>O<sub>2</sub> in 76 mm soil column

Variables	Experiment		
	HC-1	HC-2	HC-3
Inlet H <sub>2</sub> O <sub>2</sub> (mg/l)	100	1000	10000
Running time (day)	3.86	4.9	3
Effluent pH	7.4	7.4	7.4
Effluent Fe <sup>2+</sup> (μg/l)	30	35	99
Retention time of port 1 (min)	34	34	34
H <sub>2</sub> O <sub>2</sub> in port 1 (mg/l)	<5	<5	<5
H <sub>2</sub> O <sub>2</sub> in port 2 (mg/l)	<5	<5	<5
H <sub>2</sub> O <sub>2</sub> in effluent (mg/l)	<0.2	<0.2	<0.2

H<sub>2</sub>O<sub>2</sub> concentration was about 150 mg/l after 10 days of steady flow through the column.

The sandy soil used in this experiment was a typical silica-based sandy soil found in Connecticut (Table 2). High oxidant demand was not expected for this type of soil, and the extremely rapid decomposition of H<sub>2</sub>O<sub>2</sub> in this soil indicates that the decomposition of H<sub>2</sub>O<sub>2</sub> in the subsurface could be a common problem for in situ application of Fenton's reagent.

The decomposition of H<sub>2</sub>O<sub>2</sub> generates oxygen (O<sub>2</sub>) [13]. The generation of gas was not observed when the inlet H<sub>2</sub>O<sub>2</sub> concentration was 0.1 g/l, but gas started to form as the influent H<sub>2</sub>O<sub>2</sub> concentration increased.

Overall, the fast decomposition of H<sub>2</sub>O<sub>2</sub> in soils with high SOD causes two major concerns: first, a great portion of H<sub>2</sub>O<sub>2</sub> may be consumed on the soil surface and the effectiveness of spreading H<sub>2</sub>O<sub>2</sub> in the subsurface may require closer injection wells or higher injection H<sub>2</sub>O<sub>2</sub> concentrations, and second, the gas generated in the subsurface may alter the flow path of groundwater or even the soil structure, especially when high H<sub>2</sub>O<sub>2</sub> concentrations are applied. In a field study by Roberts and Bauer [5], 50% (by weight) H<sub>2</sub>O<sub>2</sub> was injected under a pressure of 345 kpa (~50 psi) and caused soil fractures through the oxidation process. Therefore, relatively low H<sub>2</sub>O<sub>2</sub> concentration and closer injection well may be a better choice for field applications.

### 5.2.2. Oxidation of TCE with soil-induced decomposition of H<sub>2</sub>O<sub>2</sub>

Although the decomposition of H<sub>2</sub>O<sub>2</sub> was very rapid in the test soil, TCE was not degraded by the soil-induced decomposition of H<sub>2</sub>O<sub>2</sub>. The total mass of TCE that eluted from the column was 103.85% of the total mass pumped into the column (Fig. 6), and throughout the experiment, the effluent and background Cl<sup>-</sup> concentrations were the same. The mass balance of TCE shows that nearly 70% of the TCE was stripped into the gaseous phase (Table 6). Therefore, the decomposition of H<sub>2</sub>O<sub>2</sub> induced by the test soil did not degrade TCE, and H<sub>2</sub>O<sub>2</sub> degradation had a gas-sparging effect on the TCE-contaminated groundwater.

The gas-sparging effect of soil-induced decomposition of H<sub>2</sub>O<sub>2</sub> on TCE can change the fundamental concept of in situ oxidation with Fenton's chemistry. The original purpose of

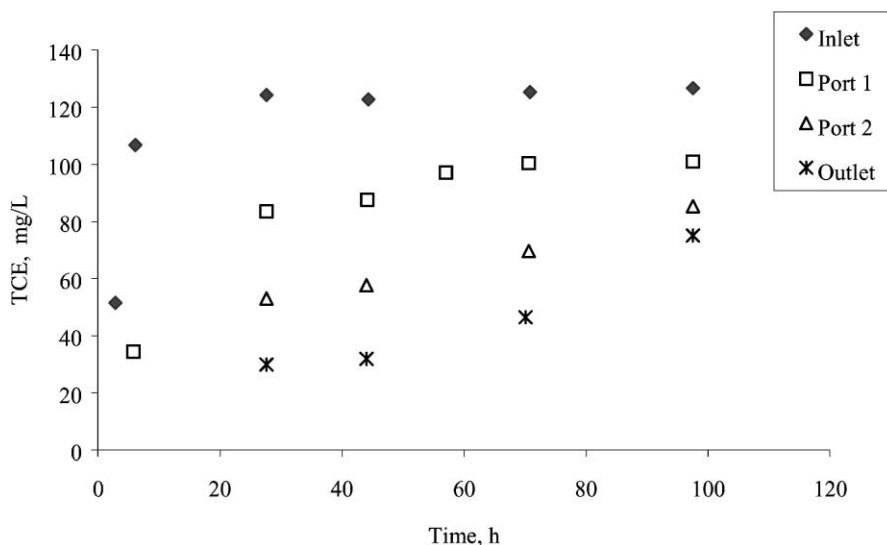


Fig. 6. Oxidation of TCE with  $H_2O_2$  in 76 mm column. Experimental conditions:  $(H_2O_2)_{in} = 10$  g/l at a flow rate of 0.15 ml/min,  $(TCE)_{in} = 250$  mg/l at a flow rate of 0.15 ml/min. The pH of both solutions was approximately 6.7.

using in situ Fenton's oxidation is to destroy the contaminants in the subsurface, instead it may act as a gas-sparging device for stripping of VOCs, especially in areas where ferrous ion does not reach the contaminated zone. Since, ferrous iron is not stable, after addition it will change to ferric iron relatively fast and may precipitate out of groundwater as  $Fe(OH)_3$  [5]. Therefore, the radius of influence of  $H_2O_2$  from an injection well may not be the radius of influence of the Fenton's reagent. This gas-stripping effect on VOCs may also spread VOCs by vapor transport. Therefore, monitoring the possible pathway of vapor transport in the vadose zone may be necessary during the implementation of in situ oxidation technology with Fenton's reagent.

In some works related to pilot scale and full-scale in situ oxidation with Fenton's chemistry, an increase of VOC concentrations in monitoring wells was observed, but no calculations in regard to the total VOC mass in the vapor phase was presented and the radius of influences of ferrous iron was not reported either [23,5].

Table 6  
TCE mass balance during the experiment "oxidation of TCE by  $H_2O_2$ "

		Total TCE out (%)	Error (%)
TCE inflow to the column	207.35 mg		
TCE outflow in liquid phase	64.86 mg	30.12	
TCE outflow in gaseous phase	150.48 mg	69.88	
Total TCE out of column	215.34 mg		3.85

### 5.2.3. Oxidation of pulse-source TCE with Fenton's reagent

A solution of 30 g/l  $\text{H}_2\text{O}_2$  at a flow rate of 0.15 ml/min and a solution of 900 mg/l  $\text{Fe}^{2+}$  ions at a flow rate of 0.15 ml/min were fed continuously and simultaneously into the 76 mm soil column from the two inlets located on the bottom of the column (the center of two inlets were 22 mm apart). The pH value of both influents was about 3. When the effluent concentration of  $\text{H}_2\text{O}_2$  became stable, 5 ml of a TCE saturated aqueous solution ( $\sim 1100$  mg/l) was injected into the column through the Teflon<sup>®</sup> tubing at the ferrous iron solution line, (within  $\sim 10$  mm of the column inlet) (Fig. 2). The effluent concentrations of TCE,  $\text{Cl}^-$ , and  $\text{H}_2\text{O}_2$  were measured over time (Fig. 7). Results of oxidizing the pulse source TCE showed that TCE was completely oxidized in the column. The total  $\text{Cl}^-$  generated was 104.5% of the predicted amount. The difference could have resulted from the  $\text{Cl}^-$  analysis on the HPIC and in the measurement of the effluent volume. The results of this experiment indicated that TCE reacted with Fenton's reagent instantaneously as both solutions mixed in the sandy soil column. The generated gas was collected in a Tedlar<sup>®</sup> bag and analyzed for presence of any VOCs. Based on the GC-MS analysis of the gas, neither TCE nor the possible transformed TCE intermediates were stripped into the gaseous phase.

The results of this experiment indicated that Fenton's reagent was able to oxidize TCE even in high SOD soil. The lack of any TCE or other VOCs in the generated gas may point to the fact that Fenton's reagent was well mixed with the TCE-contaminated groundwater leading to a complete oxidation process. Pinpointing the location of TCE sources in the saturated zone can be an important factor in efficient application of Fenton's reagent because groundwater around the contamination source has the highest TCE concentration and delivering Fenton's reagent directly to the zone of highest contamination in high SOD soils can produce more efficient results.

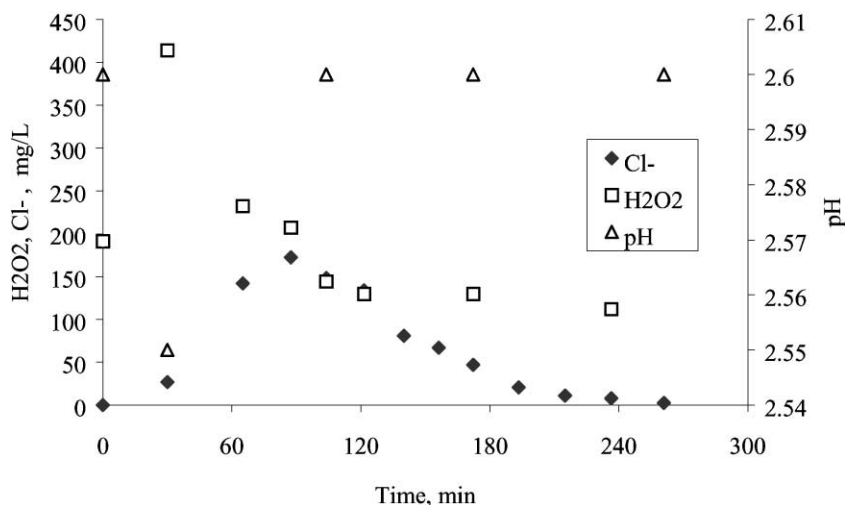


Fig. 7. Oxidation of a pulse source TCE in a 76 mm column. Experimental conditions:  $(\text{H}_2\text{O}_2)_{\text{in}} = 30$  g/l at a flow rate of 0.15 ml/min;  $(\text{Fe}^{2+})_{\text{in}} = 940$  mg/l at a flow rate of 0.15 ml/min. The pH level of both solutions was 3.

## 6. Conclusions

Rapid decomposition of  $\text{H}_2\text{O}_2$  in some soils may limit the application of Fenton's reagent for in situ remediation of sites contaminated with chlorinated solvents. Prior to field application of Fenton's reagent, bench-scale column experiments may be performed to help in better understanding the decomposition patterns of  $\text{H}_2\text{O}_2$  and the contaminants in the target soil. Determining the zone of influence of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  from the injection well is among the critical factors that need to be considered in real world field application of Fenton's reagent.

The soil-induced decomposition of  $\text{H}_2\text{O}_2$  may not be capable of degrading VOCs, such as TCE. Delivering  $\text{H}_2\text{O}_2$  and the ferrous salt solution to the zone of highest contaminant concentration and lowering the pH of the soil medium are important factors for successful in situ application of Fenton's reagent.

The use of high concentrations of  $\text{H}_2\text{O}_2$  can generate a large amount of gas in a short period. In addition, Fenton's reagent produces an exothermic reaction that generates heat. The increased temperature of groundwater and the large amount of gas released from the reactions can strip VOCs into soil gas, creating new preferential pathways in the subsurface. Therefore, in field applications a relatively low  $\text{H}_2\text{O}_2$  concentration and closer injection wells may produce better oxidation results than high concentration  $\text{H}_2\text{O}_2$  and injection wells located further apart. Moreover, a careful chemical delivery and monitoring system should be established prior to the field application of Fenton's reagent.

## Acknowledgements

This research was supported by the United Technologies Research Center in Connecticut. The authors gratefully acknowledge the technical assistance of Dr. Kun-Chang Huang, Dr. Shili Liu, Dr. Jian-Shi Kang, and Mr. Sharavan V. Govindan of the Environmental Research Institute at the University of Connecticut.

## References

- [1] P.H. Howard, G.W. Sage, W.F. Jarvis, D.A. Gray, Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Vol. II, Lewis Publishers Inc., Chelsea, Michigan, 1991.
- [2] Y.Y. Yin, H.E. Allen, In situ chemical treatment, Groundwater Remediation Technologies Analysis Center, Technology Evaluation Report, TE-99-01, Pittsburgh, PA, 82 pp., 1999, <http://www.gwrtac.org/html/topics/inchemox.htm>.
- [3] K.M. Jerome, B.B. Looney, J. Wilson, Field demonstration of in situ Fenton's destruction of DNAPLs. In: G.B. Wickramanayake, R.E. Hincsee (Eds.), Proceedings of The First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, 1998, pp. 353–358.
- [4] R. Levin, E. Kellar, J. Wilson, L. Ware, J. Findley, J. Baehr, Full-scale soil remediation of chlorinated solvents by in situ chemical oxidation, In: G.B. Wickramanayake, A.R. Gavaskar, A.S.C. Chen (Eds.), Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, 2000, pp. 153–159.
- [5] E.P. Roberts, N. Bauer, In situ chemical oxidation limited by site conditions — a case study, In: G.B. Wickramanayake, A.R. Gavaskar, A.S.C. Chen (Eds.), Proceedings of The Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, 2000, pp. 169–176.

- [6] K.R. Weeks, C.J. Bruell, N.R. Mohanty, Use of Fenton's reagent for the degradation of TCE in aqueous systems and soil slurries, *J. Soil Sediment Contamination* 9 (4) (2000) 331.
- [7] C.W. Fetter, *Contaminant Hydrogeology*, Macmillan, New York, 1999.
- [8] D.L. Sedlak, A.W. Andren, Oxidation of chlorobenzene with Fenton's reagent, *Environ. Sci. Technol.* 25 (4) (1991) 777.
- [9] A.P. Vella, B. Beronda, Oxidation of trichloroethylene: a comparison of potassium permanganate and Fenton's reagent, in: *Proceedings of the Presentation at the third International Symposium on Chemical Oxidation Technology for the Nineties*, Vanderbilt University, Nashville, TN, 1993.
- [10] R.J. Watts, M.D. Udell, S.W. Leung, Treatment of contaminated soils using catalyzed hydrogen peroxide, in: *Proceedings of the First International Symposium on Chemical Oxidation Technology for the Nineties*, Vanderbilt University, Nashville, TN, 1992, p. 37.
- [11] J.X. Ravikumar, M.D. Guroi, Chemical oxidation of chlorinated organics by hydrogen peroxide in the presence of sand, *Environ. Sci. Technol.* 28 (3) (1994) 394.
- [12] D.D. Gates, L.R. Siegrist, *Chemical Oxidation of Volatile and Semi-Volatile Organic Compounds in Soil*. Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1995.
- [13] J.H. Mertz, W.A. Waters, The mechanism of oxidation of alcohols with Fenton's reagent discussion, *Faraday Soc.* 2 (1947) 179.
- [14] C. Walling, Fenton's reagent revisited, *Acc. Chem. Res.* 8 (1975) 125.
- [15] C.M. Miller, R.L. Valentine, Oxidation behavior of aqueous contaminants in the presence of hydrogen peroxide and filter media, *J. Hazardous Mater.* 41 (1995) 105–116.
- [16] United States Environmental Protection Agency (USEPA), *Test Methods for Evaluating Solid Waste, Method 8260B, for Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MSD)*, SW-846, 3rd Edition, 1996.
- [17] W. Masschelein, M. Denis, R. Ledent, *Spectrophotometric Determination of Residual Hydrogen Peroxide*, Water & Sewage Works, August 1977, p. 69.
- [18] Environmental Research Institute, The University of Connecticut, *Laboratory Methods for the Determination of Volatile Organic Compounds in Summa Canister Ambient Air Samples by Cryogenic Preconcentration and Gas Chromatography/Mass Spectrometry (GC/MS)*, Standard Operating Procedure, Storrs, Connecticut, 2000.
- [19] D.D. Gates, R.L. Siegert, In situ chemical oxidation of trichloroethylene using hydrogen peroxide, *J. Environ. Eng. (ASCE)* (1995) 639–644.
- [20] W.S. Leung, R.J. Watts, G.C. Miller, Degradation of perchloroethylene by Fenton's reagent: speciation and pathway, *J. Environ. Qual.* 21 (1992) 377.
- [21] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ( $\text{OH}/\text{O}^-$ ) in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (2) (1988) 513.
- [22] B.C. Lawes, Soil-induced decomposition of hydrogen peroxide, in: R.D. Hinchee, R.F. Olfenbottle (Eds.), *In Situ Bioreclamation: Applications and Investigations for Hydrocarbon and Contaminated Site Remediation*, Butterworth, Boston, 1991, pp. 143–56.
- [23] K.M. Jerome, B. Riha, B.B. Looney, Final report for the demonstration of in situ oxidation of DNAPL using the Geo-Cleanse technology, WSRC-TR-97-00283, Westinghouse Savannah River Company, Aiken, South Carolina, 1997, <http://www.envnet.org/scfa/prodlines/dnapl/factsheets/tms2161.pdf>.