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X-231B Technology Demonstration for In Situ Treatment of Contaminated Soil: *Laboratory Evaluation of Chemical Oxidation Using Hydrogen Peroxide*

D. D. Gates
R. L. Siegrist

Environmental Sciences Division
Publication No. 4106

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Date Published: September 1993

Prepared for
U.S. Department of Energy Portsmouth Gaseous Diffusion Plant
Piketon, Ohio
(64 70 36 00 1)

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
managed by
MARTIN MARIETTA ENERGY SYSTEMS
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U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

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ACRONYMS AND ABBREVIATIONS

DI	deionized
EPA	U.S. Environmental Protection Agency
Fe^{2+}	ferrous iron
GC	gas chromatograph
H_2O_2	hydrogen peroxide
OCDD	octachlorodibenzo-*p*-dioxin
OD	outer diameter
ORNL	Oak Ridge National Laboratory
PCE	perchloroethylene
PCP	pentachlorophenol
RCRA	Resource Conservation and Recovery Act
RPM	revolutions per minute
TCE	trichloroethylene
TCLP	toxic characteristic leaching procedure
TOC	total organic carbon
DOE	U.S. Department of Energy
VOA	volatile organic analysis
VOCs	volatile organic compounds
ZHE	zero headspace extraction

PREFACE

Fine-textured soil and sediments contaminated by trichloroethylene (TCE) and other chlorinated organics present a serious environmental restoration challenge at U.S. Department of Energy (DOE) sites. Although in situ processes such as bioremediation and soil vapor extraction are feasible at sites with permeable soils (e.g., $K > 10^{-3}$ cm/s), their application is normally infeasible in wet, clay soils, and sediments. Environmental restoration of these sites has normally consisted of either (1) excavation and on-site storage, off-site land filling, or thermal treatment; or (2) in-place containment by capping and slurry wall emplacement.

In November 1990, DOE and Martin Marietta Energy Systems, Inc., initiated a research and demonstration project at Oak Ridge National Laboratory (ORNL). The goal of the project was to demonstrate a feasible and cost-effective process for closure and environmental restoration of the X-231B Solid Waste Management Unit at the DOE Portsmouth Gaseous Diffusion Plant located in southern Ohio. Silt and clay deposits ($K < 10^{-6}$ cm/s) beneath the unit were contaminated with volatile organic compounds (VOCs) such as TCE (approximately 1-100 ppm range) and low levels of radioactive substances. The shallow groundwater (water table at approximately 12-14 ft depth) was also contaminated, and some contaminants were at levels well above drinking water standards.

After an initial technology evaluation and screening phase, the X-231B project focused on research and demonstration of in situ vapor stripping, chemical oxidation, and solidification; and reagent delivery to the subsurface was achieved by soil mixing techniques. The primary objectives of the project were to develop processes as necessary and appropriate and to characterize the operation and performance of each process with regard to in situ treatment of VOCs in clay soils. Secondary objectives were to determine the treatment process zone of influence; the treatment process effects on air emissions, soil chemistry, and microbiology properties; and the fate of heavy metal and radioactive materials. Soil homogenization and translocation were also studied.

Since July 1991 varied research activities have been conducted. Site characterization and contaminant modeling work has included use of a hydraulic probe for collection of nearly 200 soil samples with on-site laboratory analysis for target VOCs. These data were used for statistical simulation and 3-dimensional modeling of contaminant distribution. A series of laboratory experiments were completed using bench-scale apparatus as well as a pilot-scale soil mixing system in which soil cores from the site were treated. A full-scale field demonstration was completed at the X-231B site in June 1992. Replicated tests of in situ vapor stripping, peroxidation, and solidification were made in soil columns measuring 10 ft. in diameter and 15 to 22 ft. deep. A computerized data acquisition system linked to approximately 60 sensors enabled near-continuous monitoring of process operation and performance (e.g., recording intervals of 0.2 to 2 min. for auger position, off-gas air flow rate and VOC content, soil vapor pressure and temperature). In addition, nearly 500 soil and gas samples were collected before, during, and after soil

treatment, for analyses of physical, chemical, and biological parameters. Soil matrix, soil vapor, and off-gas VOC measurements were made by multiple methods.

The X-231B project has been a multidisciplinary and multi-institutional, fast-track, applied research and demonstration effort. Directed by ORNL, the project has benefitted from the significant contributions of research staff from six divisions at ORNL, technical and management staff at Portsmouth and Energy Systems, and principal collaborators from two universities (The University of Tennessee and Michigan Technological University) and several private industries (e.g., Chemical Waste Management, Millgard Environmental, Envirosurv, and NovaTerra).

Results of the project have been very insightful regarding in situ environmental restoration of contaminated clay soils. For example, the use of a hydraulic probe for soil sampling with on-site VOC analyses, followed by 3-D visualization, provided enhanced information compared with conventional sampling, off-site analyses, and routine data treatment. In situ treatment of VOCs in clay soils was effectively (e.g., >85% reduction) and rapidly accomplished (e.g., >15 yd^3/h) and the fate of VOCs and radioactive substances was controlled. Moreover, in situ treatment costs were acceptably low. Operation and performance did vary for the different processes evaluated, and there were advantages and disadvantages associated with each. Ancillary study results indicated interesting changes in soil properties following treatment. For example, soil bacteria levels were increased by several orders of magnitude following ambient air stripping. The favorable project results are being used to design and implement a cost-effective in situ treatment process for full-scale closure of the X-231B Unit.

This report describes the methods and results of one part of the X-231B project. Details regarding other aspects of the work are available in other project publications. Information regarding these publications may be obtained by contacting Dr. Robert L. Siegrist, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6038; (615) 574-7286.

ACKNOWLEDGMENTS

Many individuals and organizations have contributed to the successful completion of this research project. Technical staff at ORNL provided outstanding support in completing laboratory work in a timely and effective manner. Significant contributions were also made by university research collaborators. The following individuals are recognized for their contributions:

Oak Ridge National Laboratory

O. M. West	Environmental Sciences Division
C. M. Morrissey	Environmental Sciences Division
D. S. Marshall	Environmental Sciences Division
H. L. Jennings	Chemical Technology Division
A. J. Lucero	Chemical Technology Division
D. W. Greene	Health and Safety Research Division
R. A. Jenkins	Analytical Chemistry Division
M. P. Maskarinec	Analytical Chemistry Division
R. Eiger	Analytical Chemistry Division
C. Rogers	Analytical Chemistry Division
N. M. Ferguson	Analytical Chemistry Division

Universities

D. Hurst	University of Tennessee, Knoxville
K. G. Robinson	University of Tennessee, Knoxville
S. Schmunk	Michigan Technological University

ABSTRACT

Treatability studies were conducted as part of a comprehensive research project initiated to demonstrate as well as evaluate in situ treatment technologies for volatile organic compounds (VOCs) and radioactive substances in wet, slowly permeable soils. The site of interest for this project was the X-231B Oil Biodegradation Unit at the Portsmouth Gaseous Diffusion Plant, a U.S. Department of Energy (DOE) facility in southern Ohio. This report describes the treatability studies that investigated the feasibility of the application of low-strength hydrogen peroxide (H_2O_2) solutions to treat trichloroethylene (TCE)-contaminated soil.

The processes investigated in this research included the oxidative destruction of VOCs and a combination of deep soil mixing and chemical oxidation. Upon introduction of a weak peroxide solution (<5%) to a contaminated soil, the peroxide nonselectively oxidizes any available oxidizable matter, including the target contaminants (in these studies, TCE). Two types of laboratory studies were conducted to evaluate peroxidation: bench-scale studies conducted in 300-mL zero headspace extraction (ZHE) vessels and pilot-scale treatability studies conducted using ~7.5-L soil columns. All laboratory studies were conducted using soils retrieved from the Portsmouth X-231B site and artificially contaminated with TCE at concentrations comparable to the level of contamination found at the X-231B site.

The bench-scale studies demonstrated that TCE reductions as great as 98% of initial concentration could be achieved when H_2O_2 is added to TCE-contaminated slurries prepared from Portsmouth soil. Evaluation of reaction by-products by gas chromatograph analysis revealed that no TCE daughter products were formed, which supports the conclusion that complete destruction of TCE resulted from the addition of H_2O_2 to the contaminated soils. These studies also indicated that peroxidation is a rapidly occurring reaction (2 h or less), and process efficiency appears to be independent of initial TCE concentration. The studies also demonstrated that TCE degradation efficiency increased with increasing peroxide strength.

The pilot-scale studies demonstrated that Portsmouth soil physical properties would not be adversely impacted by the addition of a weak peroxide (5%) solution at a level equal to 10% of the pretreated soil volume. The off-gas generation rate and composition were also monitored during the pilot-scale studies. It was observed during the pilot studies that most of the off-gas that was generated (>90%) evolved within 10 min of H_2O_2 addition, giving further evidence of the rapid rate of peroxidation reactions. A decrease in TCE destruction efficiency was noted when decreasing volumes of equal strength H_2O_2 solutions were used to treat contaminated soils, which suggests that the process may be mass transfer limited.

On the basis of the results of this investigation, peroxidation of contaminated soils at the Portsmouth X-231B site appears to be a viable treatment technology. Further experimentation and field demonstration will be required to optimize the process.

1. INTRODUCTION

Bench-, pilot- and field-scale studies were conducted to determine the technical feasibility of in situ soil mixing combined with hydrogen peroxide (H_2O_2) injection as an environmental restoration technique for slowly permeable soil contaminated with trichloroethylene (TCE) and other volatile organic compounds (VOCs). This report describes the processes investigated and summarizes the findings of the laboratory studies completed to support the design and conduct of the field demonstration.

1.1 PROCESS DESCRIPTION

1.1.1 Chemical Oxidation Processes

Chemical oxidation processes have been used to effectively treat many compounds that are refractory, toxic, or inhibitory to conventional wastewater treatment processes. Oxidants commonly applied for this purpose include H_2O_2, ozone (O_3) and chlorine dioxide (ClO_2). Hydrogen peroxide is often selected as an oxidant because of its ease of application (at low concentrations), availability and reasonable cost, and its ability to oxidize a wide variety of compounds (Weber 1972). Although H_2O_2 itself is only a moderate oxidant, it has been demonstrated that in the presence of ferrous iron (Fe^{2+}), Fenton's reagent, which has proved to be a very powerful and effective oxidizing agent, is formed. *Fenton's reagent* refers to the catalytic decomposition of H_2O_2 in the presence of Fe^{2+} with the generation of hydroxyl radicals. A widely accepted mechanism for this reaction is given below:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\bullet \quad (1)$$
$$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^- \quad (2)$$
$$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O \quad (3)$$
$$Fe^{2+} + HO_2\bullet \rightarrow Fe^{3+} + HO_2^- \leftrightarrow H_2O_2 \quad (4)$$
$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + H^+ + O_2 \quad (5)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+ \quad (6)$$

The oxidation of organic compounds by Fenton's reagent can proceed by both chain and nonchain mechanisms. The rate limiting step is the formation of the hydroxyl radicals.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\bullet \quad \text{chain initiation} \quad (7)$$
$$R\text{-}H + HO\bullet \rightarrow R\bullet + H_2O \quad \text{chain propagation} \quad (8)$$
$$R\bullet + H_2O_2 \rightarrow ROH + HO\bullet \quad \text{chain propagation} \quad (9)$$
$$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^- \quad \text{chain termination} \quad (10)$$
$$R\bullet + Ho\bullet \rightarrow ROH \quad \text{non-chain termination} \quad (11)$$
$$2R\bullet \rightarrow Products \quad \text{non-chain termination} \quad (12)$$

The previous series of equations describe the reactions that conceivably occur during peroxidation. The following empirical reaction describes the complete oxidation of TCE to CO_2 and H_2O and is also useful when discussing the process application addressed by this research.

$$C_2HCl_3 + 4.5\ H_2O_2 \rightarrow 2\ CO_2 + 5\ H_2O + 3\ Cl^- \tag{13}$$

1.1.2 Application of Chemical Oxidation with H_2O_2

1.1.2.1 Use of H_2O_2 in Aqueous Systems

Hydrogen peroxide has been used to oxidize a variety of compounds in several aqueous matrices including drinking water, municipal and industrial wastewaters, and contaminated groundwaters. Experimental studies have focused on either the use of H_2O_2 to achieve complete oxidation of target contaminants or the use of H_2O_2 to enhance bioremediation by partial oxidation of recalcitrant compounds.

Glaze and Kang (1988) investigated the oxidative treatment of TCE- and pentachlorphenol (PCE)-contaminated groundwaters with H_2O_2 and combinations of H_2O_2 and ozone. Using a 70-L bench scale reactor operated in the batch mode, the authors studied the impact of operating conditions on the rate of reaction. The authors noted that pH had little impact on reaction rate in the range 4 to 10, and bicarbonate (and theoretically other impurities) had a negative effective on the process by scavenging free radicals responsible for target contaminant oxidation. Bellamy et al. (1991) conducted studies in a manner similar to Glaze and Kang's using TCE- and PCE-spiked groundwater and suggested that the rate of the oxidation reactions should be independent of substrate concentration. Murphy et al. (1989) observed that when 30% (weight) H_2O_2 was used to oxidize formaldehyde-containing wastewaters, 95% oxidation of the target contaminant occurred within 90 min of oxidant delivery. Murphy et al. also observed that the reaction rate increased with increasing temperature and oxidant concentration.

Bowers et al. (1989) investigated the applicability of H_2O_2 as a bioremediation enhancer for an industrial wastewater contaminated with 2,4 dichlorophenol and dinitro-ortho-cresol. Bowers et al. defined the contaminants as being "non-biocompatible" because they are known to be toxic, inhibitory, or refractory to common microorganisms. H_2O_2 was added to the wastewater in batch reactors over a period of 4 h. The authors used batch-fed reactors seeded with waste activated sludge to evaluate the biodegradability of the reaction products and noted that the peroxide-treated wastewater was significantly more biodegradable than the untreated wastewater.

1.1.2.2 Use of H_2O_2 in Soil Systems

Recent works have begun to focus on the use of chemical oxidation as a soil/sediment remediation process. Ravikumar and Gurol (1991) percolated H_2O_2 through

sand columns pre-contaminated with pentachlorophenol (PCP) and TCE and observed a 98% reduction in contaminant concentration following treatment with H_2O_2. Gurol and Ravikumar (1991) further explored the application of Fe(II) in conjunction with H_2O_2 to sand columns precontaminated with PCE and TCE to determine if the addition of Fe(II) would increase process efficiency by supporting the production of Fenton's reagent. The authors concluded that the addition of Fe(II) did indeed enhance the chemical oxidation of PCP and TCE in the test sand columns. Watts et al. (1990) in column studies similar to those of Gurol and Ravikumar did not observe any increase in PCP oxidation when Fe(II) amendments were made to natural soils spiked with PCP. Both Gurol and Ravikumar and Watts et al. measured stoichiometric increase in chloride concentration following H_2O_2 addition and used this finding to support their conclusions that chemical oxidation was the mechanism of contaminant destruction.

Leung et al. (1992) and Watts et al. (1991) conducted laboratory studies of peroxidation of soils contaminated with PCP and octachlorodibenzo-*p*--dioxin (OCDD), respectively. In the Leung et al. studies, silica sand and two natural soils were artificially contaminated with PCP. In batch test, 2.5 g of contaminated soil were treated with 12.5 mL of 6.5% H_2O_2 (H_2O_2 load = 327 g/kg soil) followed by the addition of 1 mL of $FeSO_4$. More than 99.9% of the initial PCP was degraded in 24 h. Leung also noted a decrease in total organic carbon (TOC) accompanied PCP destruction, and the oxidative processes proceeded without iron amendments in natural soils. Watts et al. treated 1 g aliquots of either natural soils or silica sand contaminated to 200 μg OCDD/kg with 1 mL of $FeSO_4$ and 2 mL of 12% H_2O_2. Reactant addition was repeated four times for each soil sample. Watts also conducted studies in which the H_2O_2 concentration was varied to either 3.5% or 35%, and temperatures of 20, 40, 60, and 80° C were evaluated. Watts observed that OCDD destruction was inversely related to soil organic carbon content, which the researchers concluded reflected the competition of soil organic carbon and OCDD for oxidants. The maximum OCDD removal by peroxidation found in their studies was 96%. Peroxidation of contaminant material was found to increase with increasing temperature but to be independent of H_2O_2 concentration for the natural soils studied. It should be noted that ferrous iron amendments were used in all of the studies conducted by Watts et al.

Watts (1992) reported the field application of peroxidation of contaminated soil at an equipment storage yard in Reno, Nevada. This work included the excavation and batch treatment of soil contaminated with petroleum hydrocarbons (ex situ treatment). Excavated soil was treated in the batch mode at pH 3 with no soluble iron addition and the addition of H_2O_2 of either 2 or 7% strength (weight) to the reactors at a volume equal to four times the field capacity of the untreated soil. After two H_2O_2 additions the target contaminant level was reduced to below detection limits [2000 mg/kg TPH (total petroleum hydrocarbons) reduced to <100 mg/kg TPH].

1.2 EXPERIMENTAL STUDIES

Prior research has demonstrated that chemical oxidation using H_2O_2s and Fenton's like chemistry can yield significant treatment of organically contaminated soils. However, research to date has focused on process application and control in either (1) flow through saturated systems or (2) ex situ slurry reactors. There has been no research into in situ treatment of fine-textured soils. The purpose of the research conducted at Oak Ridge National Laboratory (ORNL) and described here was to evaluate the effectiveness of in situ peroxidation in clay soils contaminated with TCE and other chlorinated aliphatic compounds. This research was needed to support the design and conduct of the full-scale field test at the X-231B site at the U.S. Department of Energy (DOE) Portsmouth Gaseous Diffusion Plant.

To enable in situ treatment in dense, clay soils, H_2O_2 solutions were injected and mixed into clay soils using in situ soil-mixing technologies. In this way, a thoroughly mixed subsurface reactor could be created within which in situ peroxidation could occur. The objectives of this research were to develop the in situ process to yield relatively high destruction efficiencies (>70% mass removal) under acceptable operating conditions (e.g., H_2O_2 dose, reaction time).

Three types of studies were conducted to evaluate the applicability of in situ mixing and peroxidation to the Portsmouth X-231B site: (1)bench-scale zero head space extraction (ZHE) vessel studie, (2) pilot-scale treatability studies, and (3) a field-scale demonstration of the process. In parallel with this research, experiments were conducted by collaborating researchers at the University of Tennessee, Knoxville, to provide insight into the mobilization of metals during in situ peroxidation (Robinson 1992). These studies are summarized and compared in Table 1.

Table 1. Comparison of peroxidation experiments

Experiment type/ research organization	Scale	Scope	Approach
ZHE[a] (ORNL)	Bench	Effect of reaction time and peroxide strength	Peroxide added to soil slurries and crumbs
Treatability studies (ORNL[b])	Pilot	Impact on soil properties	Peroxide injected and mixed into soil cores
TCE fate studies (UTK[c])	Bench	Fate of TCE	Soil minicolumns spiked with radiolabeled TCE
Metals mobilization studies (UTK)	Bench	Mobilization of metals	Adsorption isotherms developed using soil slurries
Demonstration (ORNL)	Field		In situ injection and mixing of peroxide in contaminated soils

[a]ZHE = zero headspace extraction vessel.
[b]ORNL is Oak Ridge National Laboratory.
[c]UTK is the University of Tennessee, Knoxville.

2. BENCH-SCALE STUDIES

Although peroxidation of VOCs has been shown to be effective in aqueous solutions and some sand systems, the application of this process to low permeability, clayey soil, or in combination with soil mixing has not been discussed in the literature. Bench-scale studies were first conducted to determine if peroxidation of VOCs would proceed in high clay soil systems. The bench-scale studies used ZHE vessels that held either TCE-contaminated soil slurries or soil aggregates. H_2O_2 solution was injected into the ZHE vessels and TCE reduction assessed. Soil slurries, prepared with Portsmouth X-231B soil, were used for the majority of the ZHE studies. This was done to minimize mass transfer limitation by promoting intimate and complete mixing between the H_2O_2 solutions and the TCE-contaminated media.

2.1 OBJECTIVES AND SCOPE

The bench-scale peroxidation ZHE studies were conducted to meet the following objectives:

1. To determine if H_2O_2 could oxidize TCE in a clay soil matrix without the addition of Fe(II).

2. To evaluate the impact of reaction (contact) time on TCE removal by peroxidation.

3. To determine the effect of initial TCE concentration on removal efficiency.

Two series of ZHE experiments were conducted over a period of 3 weeks (March 11-30, 1992). The first series included experiments were H_2O_2 solution ranging in strength from 0.015% to 7.3% (by weight) was added to TCE contaminated soil slurries prepared from Portsmouth soil. Each treatment was evaluated in duplicate. The second series was similar to the first except soil aggregates (~ 1.5 cm diameter aggregates) prepared from Portsmouth soil were used instead of slurries for some of the treatments. In the second series of experiments, the level of TCE-contamination varied, only one H_2O_2 solution strength (1.5%) was used and the peroxidation reaction time was decreased.

In summary, H_2O_2 solutions with concentrations in the range of 0.015 to 7.3% (by weight) were used to treat soils with initial TCE loadings in the range 1.9 to 34.0 mg TCE/kg soil. Process reaction times of 24 and 2 h were investigated. A summary of the methods employed during the bench-scale experiments and the target contaminant loadings and H_2O_2 dose concentrations are given in Fig. 1 and Tables 2 and 3.

ORNL-DWG 93-11974

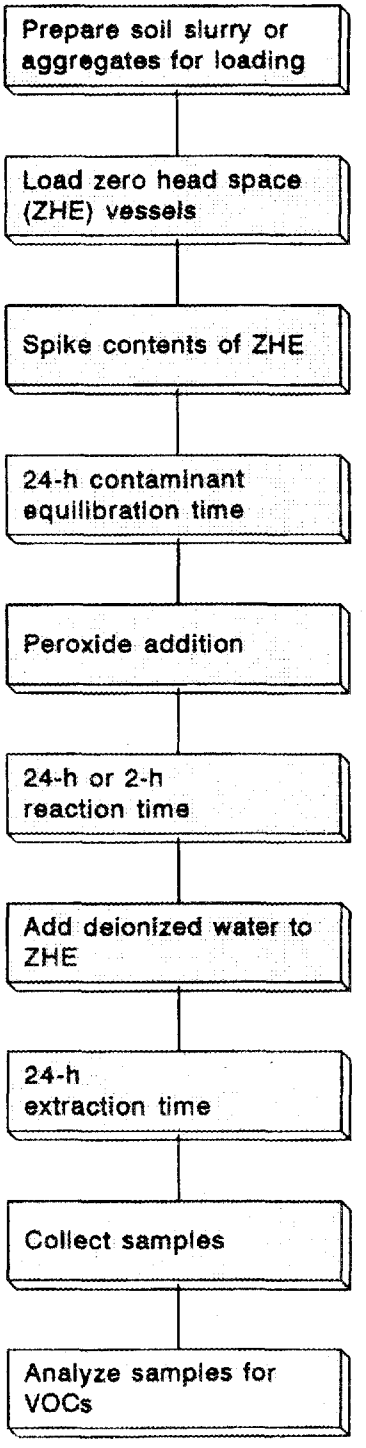

Fig. 1. Bench-scale experimental method summary.

Table 2. Design experimental conditions for bench-scale series No. 1—Peroxide added to soil slurries, 24 h reaction time

Treatment No.[a]	Matrix	Target TCE loading[b] (mg/kg)	H_2O_2 concentration[c] (%)
1	Slurry[d]	5.0	0.015
2	Slurry	5.0	0.15
3	Slurry	5.0	1.5
4	Slurry	5.0	7.3
Controls	Slurry	5.0	0.0
	Slurry	0.0	0.0
	Slurry	0.0	0.0

[a]Each treatment evaluated in duplicate.
[b]10 mL of spiking solution added to each zero headspace extraction (ZHE) vessel.
[c]10 mL of H_2O_2 solution added to each ZHE vessel.
[d]1:1 soil:water slurry.

Table 3. Design experimental conditions for bench-scale series No. 2—Peroxide added to soil slurries or aggregates, 2 h reaction time

Treatment No.[a]	Matrix	Target TCE loading[b] (mg/kg)	H_2O_2 concentration[c] (%)
3R[d]	Slurry[e]	5.0	1.5
5	Slurry	50.0	1.5
	Slurry	5.0	0.0
Controls	Slurry	50.0	0.0
6	Aggregates	5.0	1.5
	Aggregates	0.0	0.0
Controls	Aggregates	0.0	0.0

[a]Treatments 3R and 5 conducted in duplicate, treatment 6 conducted in triplicate.
[b]10 mL of spiking solution added to each zero headspace extraction (ZHE) vessel.
[c]10 mL of H_2O_2 solution added to each ZHE vessel.
[d]Repeat of treatment 3 from Series No. 1.
[e]1:1 soil:water slurry.

2.2 MATERIALS AND METHODS

2.2.1 Experimental Apparatus

The bench studies were conducted using 1-L gas-tight stainless steel reactors identical to those used for TCLP [U.S. Environmental Protection Agency (EPA) Method SW846] analysis manufactured by Associated Design and Manufacturing Company (Figs. 2 and 3). The apparatus included the following parts:

- 1-L stainless steel evacuation chamber (Part No. 3);
- stainless steel piston (Part No. 5) which can be moved within the evacuation chamber to change the dimension of the open space in the evacuation chamber and eliminate head space if desired;
- end cap (Part No. 1) through which air can be introduced to move the piston within the evacuation chamber;
- a filtration assembly (Parts No. 7 and 20), consisting of one 0.7 micron glass fiber filter placed between 2 stainless steel 90-mm mesh screens;
- top cap (Part No. 2) with Luer-Lok® fitting, which allowed the introduction and extraction of fluids from the ZHE vessel;
- pressure gage (Part No. 18) used to indicate the pressure exerted on the piston within the evacuation chamber;
- rotating rack (not shown), which could accommodate 12 assembled ZHE vessels and rotate them end over end at the rate of 30 revolutions per minute (rpm) and;
- assorted viton O-rings (Parts No. 11 and 13) were used to maintain gas-tight conditions within the evacuation chamber.

2.2.2 Soil Sample Collection

Soils were collected from the X-231B unit during January 1992 using conventional drilling and sampling methods. Soil cores were collected from multiple depths using a split-barrel sampler lined with stainless steel sleeves 2.5 in. wide and 6 in. long. The cores were sealed with aluminum foil and plastic end caps and stored in coolers filled with "blue-ice" during transportation back to ORNL laboratories. At ORNL the cores were refrigerated at 4°C until the start of the laboratory experiments.

For the bench-scale experiments two soil cores were selected that had negligible concentrations of the target VOCs (nondetectable, $<15\mu g/kg$). This was done so that controlled experiments could be conducted using actual material from the X-231B site; TCE, the principal target VOC, would be added to each experimental treatment at a known concentration. The soils used were collected from a depth zone of 9.5 to 10.5 ft

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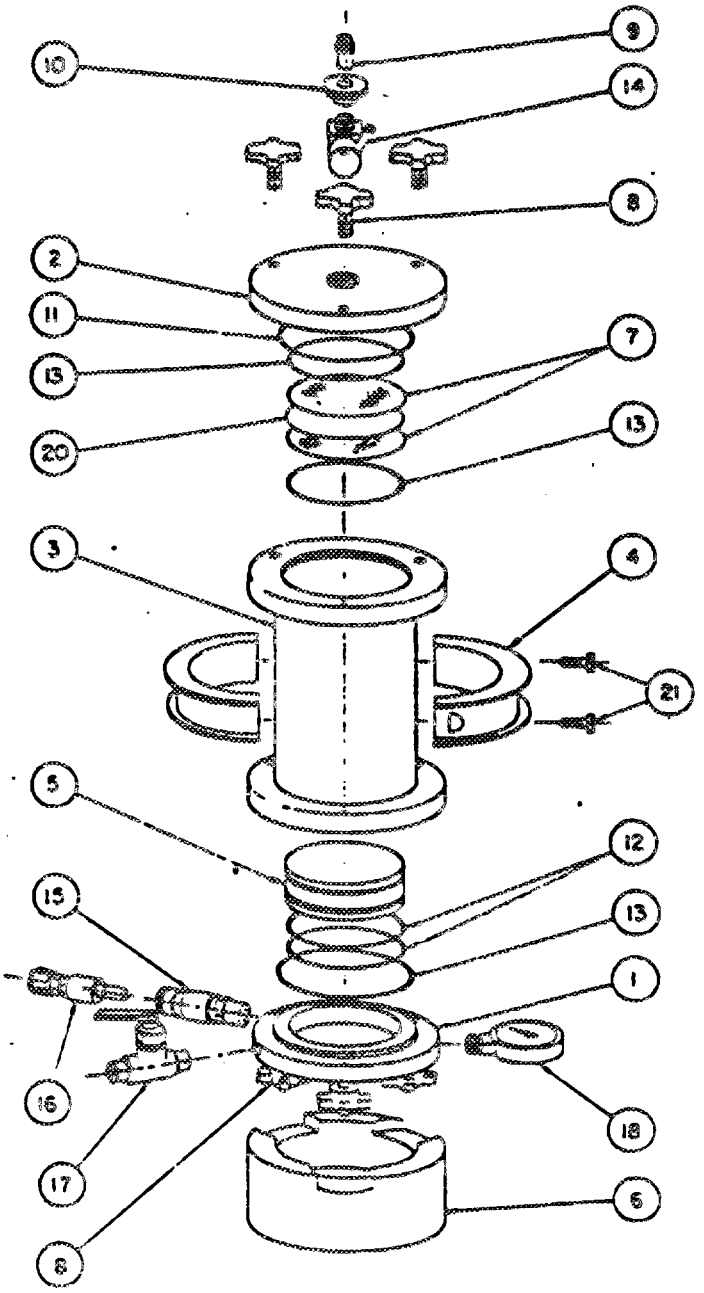

MODEL #3745-ZHE

Fig. 2. Zero head space extraction (ZHE) vessel.

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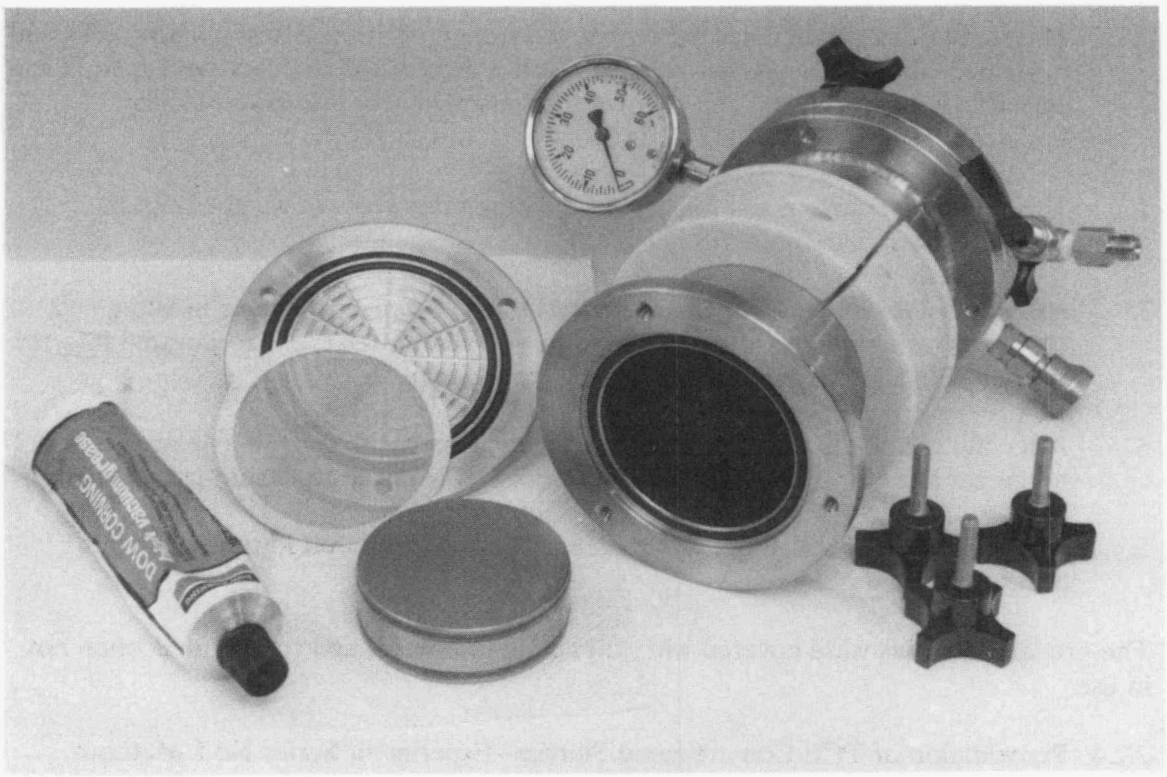

Fig. 3. Photograph of a disassembled zero headspace extraction (ZHE) vessel.

at the site. Representative soil properties are summarized in Table 4. Detailed information about the characteristics of the X-231B site is contained in other project reports (Siegrist et al. 1992a).

2.2.3 Soil Slurry Preparation

Soil slurries were prepared using a blender (SoilTest model 936 Mechanical Analysis Stirrer) with a stainless steel dispersion cup. The following procedures were used:

1. The stainless steel soil cores were removed from cold storage and opened. The soil contained within the core was removed with a precleaned stainless steel spatula and placed in a mixing bowl. The soil was then manually cut into small, blocky fragments, typically 0.5 to 1.0 cm in length.

2. The desired amount of soil for the slurry being prepared was weighed out in 100-g portions (see Table 5).

3. Soil and deionized (DI) water were added to the blender container in 100-g and 100- or 50-mL aliquots, respectively. New soil additions were incorporated into the slurry by blending at medium-high speed for ~3 min.

4. After the slurry was prepared, the blender container with slurry was placed in a hot-water bath for 3 h. The slurry was periodically mixed to ensure homogeneity.

5. After heating, the soil slurry was reblended and then poured into a large glass beaker.

The prepared slurries were covered with foil and plastic wrap, and refrigerated when not in use.

2.2.4 Peroxidation of TCE-Contaminated Slurries--Experiment Series No.1 Methods

1. Eleven ZHE vessels were assembled with their pistons positioned to leave a reaction chamber of ~1 cm-depth in each vessel. This depth provided a reaction volume of ~45 mL. This volume was sufficient to accommodate the initial soil slurry and solutions added to the vessels.

2. Sixty grams of soil slurry were weighed out and carefully transferred to the reaction chamber of each vessel.

3. Aqueous stock solutions containing TCE were prepared using reagent grade neat TCE and DI water. The solutions were prepared in either 250-mL Teflon Tedlar bags or 100-mL plastic bottles covered with Teflon-lined septum caps. The stock TCE solution concentration of 12.5 mg/L was selected for the first series of bench experiments.

Table 4. Soil properties typical of the X-231B site (Siegrist et al. 1992)

Parameter	Units	Representative properties
Texture	—	Silty clay loam 10% Sand 60% Silt 20-25% Clay
pH	—	5.5–6.0
TOC	Dry wt%	0.06–0.12
Fe (acid extract)	Dry wt%	2.5–3.5
Fe (free iron oxide)	Dry wt%	1.5–2.0
Mn (acid extract)	Dry wt%	0.01–0.1

Table 5. Soil slurry composition

Slurry	Soil core[a]	Soil water content (%)	Mass of soil[a] (grams)	Volume of water added (mL)	Soil conc.[b] (g/mL)
1	1037	16.8%	500	450	0.8
2	1035	18.8%	600	600	0.7

[a]Soil cores were collected using a split-barrell sampler during a full investigation conducted in January 1992.

[b]Dry weight basis.

4. Ten mL of TCE stock solution were injected in selected vessels using a 10-mL plastic syringe fitted with a stainless steel needle. The filtration assembly was placed on top of the ZHE chamber over the syringe needle and held in place while the TCE solution was distributed directly into the soil slurry. The ZHE vessels that were not spiked with TCE had a volume of DI water added to the soil slurry equivalent to that of the TCE solution.

5. After TCE spiking, the ZHE vessels were sealed, and a pressure of ~10 pound per square inch (psi) was applied to the piston to ensure that the vessel was gas tight.

6. The loaded and pressurized ZHE vessels were placed in a rotating rack and tumbled at 30 rpm for a period of 24 h. This "contaminant equilibration time" was included to allow the TCE to sorb to the soil particles. The pressure gages on the ZHE vessels were read and recorded before and after tumbling to determine if any leaks in the vessels developed during mixing.

7. After the contaminant equilibration time, the ZHE vessels were removed from the mixing racks and depressurized in preparation for H_2O_2 addition.

8. H_2O_2 solutions were prepared by serial dilutions using a reagent grade 30% H_2O_2 solution and distilled water supplied by a Milli Q Water System.

9. Ten mLs of H_2O_2 solution were injected into selected ZHE vessels through a gas-tight glass syringe attached to the Luer-Lok® fitting on the top cap of the ZHE vessel (Fig. 4). The sides of the vessels were gently tapped during H_2O_2 addition to prevent sudden, jerking movement of the piston within the chamber. The vessels that were not injected with H_2O_2 were injected with 10 mLs of DI water.

10. After the addition of H_2O_2, the ZHE vessels were pressurized to 10 psi and mixed for a period of ~24 hours. This "reaction time" was selected to allow sufficient time for the expected reactions to go to completion.

11. After the reaction time had elapsed, the ZHE vessels were removed from the rotating rack and depressurized in preparation for water addition.

12. One-hundred mLs of distilled water were added to each ZHE to solubilize and extract any TCE remaining. The water was added in a manner identical to the addition of H_2O_2. The DI water was added in two 50-mL injections.

13. After the addition DI water, the ZHE vessels were again pressurized to 10 psi and mixed for 24 h. This "extraction time" was selected to allow the TCE in the ZHE vessels to solubilize.

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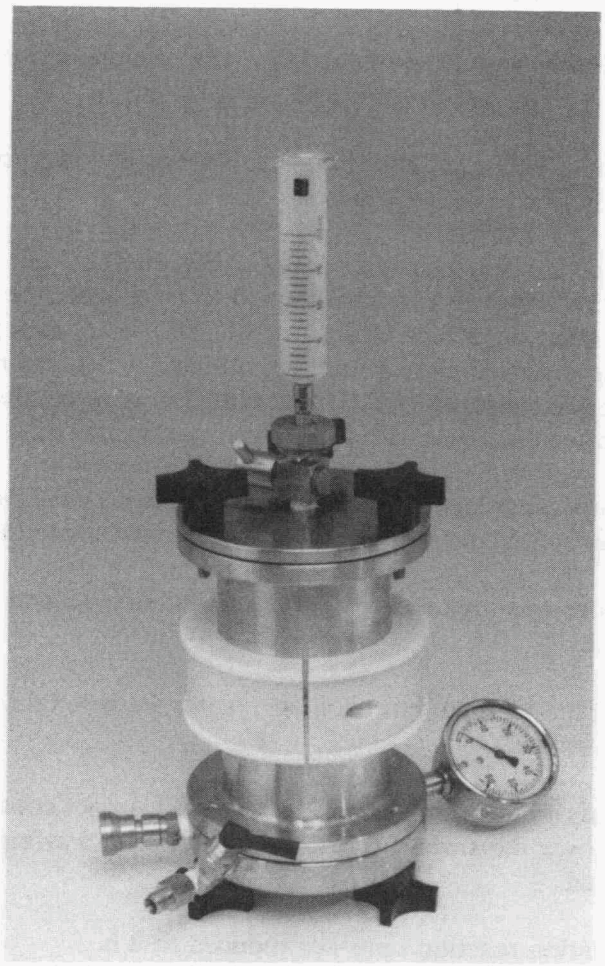

Fig. 4. Injection of fluid into a zero headspace extraction (ZHE) vessel.

14. Posttreatment solution samples were collected after the extraction time had elapsed. Samples were collected by applying pressure (as much as 50 psi) to the bottom of the piston in the ZHE chamber which forced the solution in the ZHE vessel through the filter assembly and into 7-mL glass volatile organic analysis (VOA) vials (Fig. 5). All vials of posttreatment extract were capped with Teflon-lined septum caps and stored at 4°C prior to analysis.

15. The ZHE vessels were then opened, and the remaining contents were transferred to glass jars, which were covered and refrigerated.

2.2.5 Peroxidation of TCE-Contaminated Soil Slurries and Aggregates–Experiment Series No. 2 Methods

The second series of bench-scale peroxidation studies were conducted to confirm the results of the first series of experiments and to investigate the effect of reaction time and TCE concentration on process efficiency. This series of experiments was also designed to provide insight into mass transfer effects (i.e., soil slurry vs soil aggregates) on peroxidation. The second series of ZHE experiments were conducted in a manner similar to the first series of experiments with the following exceptions:

1. Soil aggregates were treated in five of the available ZHE vessels instead of soil slurries. The aggregates were prepared and contaminated as follows:

   a. A soil core was removed from refrigerated storage and broken into 1-cm-diam aggregates.

   b. Thirty grams of field-moist soil aggregates were weighed and placed in each ZHE chamber.

   c. Three mL of TCE solution (125 mg TCE/L target concentration) were rapidly trickled over the surface of the aggregates with a syringe, and the ZHE vessel was closed.

2. The peroxidation reaction time was reduced to 2 h.

3. The amount of DI water added to the ZHE vessels containing soil aggregates was increased to 137 mL during the extraction step (No. 12).

2.2.6 Analysis

ZHE posttreatment aqueous extract samples (Step No. 14) and samples of the TCE spiking solutions were analyzed for TCE content by gas chromatography in accordance with EPA method SW8240. Samples of the stock H_2O_2 solutions were stored in 40-mL glass vials and analyzed by idometric titration. The posttreatment slurry mixtures were

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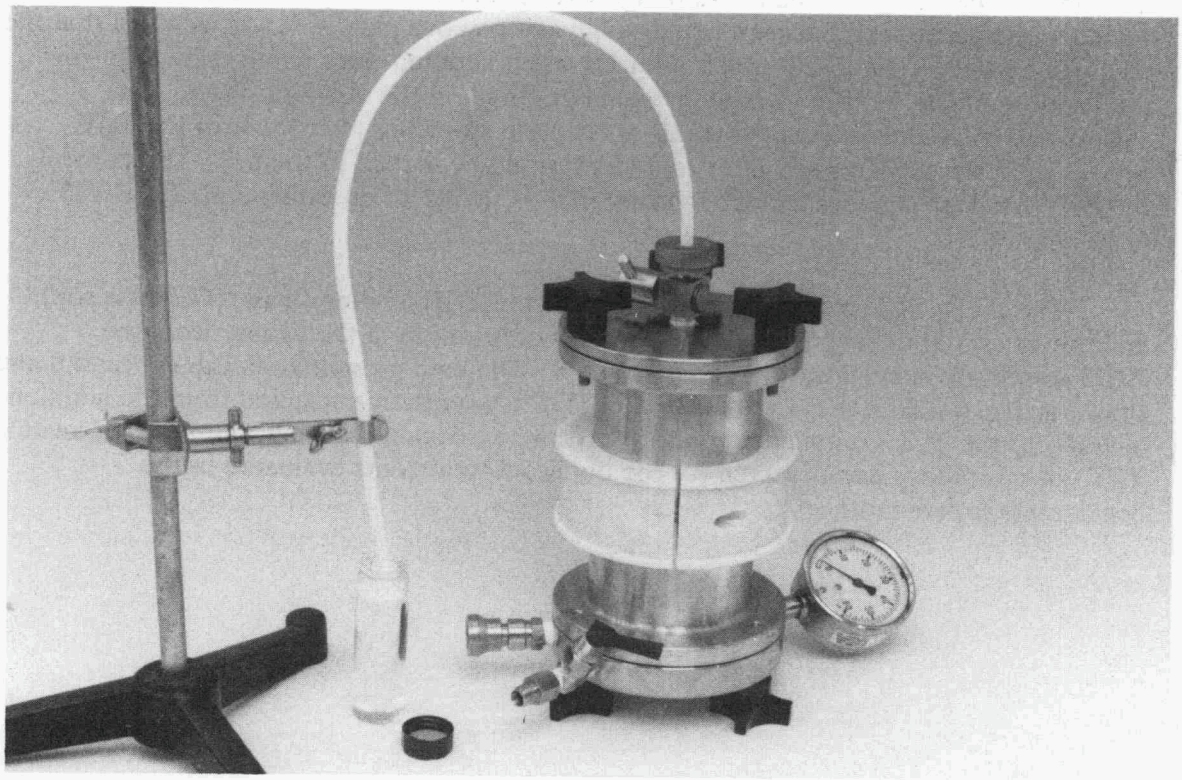

Fig. 5. Photograph of extraction of aqueous samples from zero headspace extraction (ZHE) vessel.

placed in 50-mL centrifuge tubes and spun for ~ 4-6 h at 2000 rpm. The centrate was then decanted and analyzed for iron, TOC, and pH. Sample handling and analysis are summarized in Table 6.

2.3 BENCH-SCALE STUDY RESULTS

2.3.1 TCE Destruction Efficiency

The destruction of TCE after the addition of H_2O_2 was inferred by comparing the TCE levels in the ZHE vessels treated with H_2O_2 with the TCE levels in the untreated (control) vessels. TCE concentrations were measured in the aqueous extracts withdrawn from the vessels after treatment. Although it is reasonable to expect the TCE in the vessels to be partitioned between liquid, solid, and gaseous phases, it was assumed that the mixtures formed in the ZHE vessels after DI water addition were dilute enough so that the majority of the TCE in the system would be found in the aqueous phase. The calculations in Appendix A support this assumption revealing that <1% of the TCE remaining in the ZHE vessels after treatment would be sorbed to the soil. The percent removal based on aqueous extract concentration is therefore an estimation of the TCE mass removal.

The initial TCE concentration, the calculated TCE loading (mass TCE/mass soil), and the measured final (posttreatment) TCE concentration in the filtrate from the ZHE vessels are summarized in Tables 7 and 8. The data presented in Tables 7 and 8 and shown in Fig. 6 indicate that a reduction in TCE concentration resulted from the addition of H_2O_2 to the TCE-contaminated slurries. Close agreement between the posttreatment TCE concentrations was observed for the duplicate treatments evaluated in the bench-scale experiments.

Table 6. Methods of analysis for peroxide bench-scale studies

Medium/ sample type	Container	Preserva- tion	Holding time	Parameter measured	Method
Soil	6 in. Stainless steel sleeve	4°C	>60 d	Moisture content	Methods of soil analysis
Post-treatment aqueous extract	7-mL Glass VOA vials	4°C	<7 d	TCE	SW 8240[a]
TCE spiking solution	25-mL Glass VOA vials	4°C	<7 d	TCE	SW 8240
Dilution water	40-mL Glass vial	4°C	<7 d	TCE	SW 8240
Peroxide stock solution	40-mL amber glass vial	4°C	n/a	H_2O_2	Idometric titration[b]
Post-treatment slurry (centrate)	50-mL Plastic beakers	4°C	n/a	pH TOC Fe	EPA 150.1 9060 236.1

[a]Test methods for the evaluation of solid waste, Physical/Chemical Methods, SW-846, 3rd edition. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, D.C. November 1986.

[b]Kolthoff et al. 1969. Quantitative Chemical Analysis. The Macmillan Company, Toronto. p. 854.

Table 7. Bench-scale study results with peroxide added to TCE-contaminated soil slurries —24 h reaction time

Treatment No./ matrix		Predicted pretreatment TCE mass loading[a] (mg/kg)	Predicted pretreatment TCE concentration[b] μg/L	H_2O_2 Dosed solution strength (wt%)	Posttreatment TCE concentration[c] μg/L
1 Slurry	1a	1.87	313.7	0.015 %	168.5
	1b	1.88	313.9		180
2 Slurry	2a	1.87	313.7	0.15%	62.9
	2b	1.85	312.8		52.8
3 Slurry	3a	1.86	313.3	1.5%	15.5
	3b	1.87	313.5		17.8
4 Slurry	4a	1.86	313.2	7.3%	<5
	4b	1.86	313.3		<5
Control Slurry	C1	1.86	313.4	0	209.3
	C2	1.87	313.5		224.4
	C3	0	0	0	0

[a]Calculated on the basis of measured TCE spiking solution concentration and mass of soil in slurry.

[b]Calculated on the basis of total volume of fluid in vessel (includes slurry, TCE solution, peroxide solution and DI water added for extraction) using measured stock TCE solution concentration and assuming all TCE in aqueous phase.

[c]Measured value in posttreatment extract.

Table 8. Bench-scale study results with peroxide added to TCE-contaminated soil slurries or aggregates—2 h reaction time

Treatment No./ matrix		Predicted pretreatment TCE mass loading[a] mg/kg	Predicted pretreatment TCE concentration[b] μg/L	H_2O_2 Dosed solution strength (wt%)	Posttreatment TCE concentration[c] μg/L
3R Slurry	3Ra	4.0	605.6	1.5 %	23
	3Rb	3.9	602.9		37
5 Slurry	5a	33.8	5237.6	1.5%	151
	5b	33.7	5233.6		64
Controls slurry	CS1	3.9	603.5	0	1035
	CS2	34.1	5247.6		10271
6 Aggregates	6a	1.1	1682	1.5	534
	6b	1.1	1682	1.5	518
	6c	1.1	1682	1.5	250
Controls aggregates	CA1	1.1	1682	0	423
	CA2	1.1	1682		709

[a]Calculated on the basis of TCE spiking solution concentration and mass of soil in slurry.

[b]Calculated on the basis of total volume of fluid in vessel (includes slurry, TCE solution, peroxide solution and DI water added for extraction) using measured stock TCE solution concentration and assuming all TCE in aqueous phase.

[c]Measured value in posttreatment extract.

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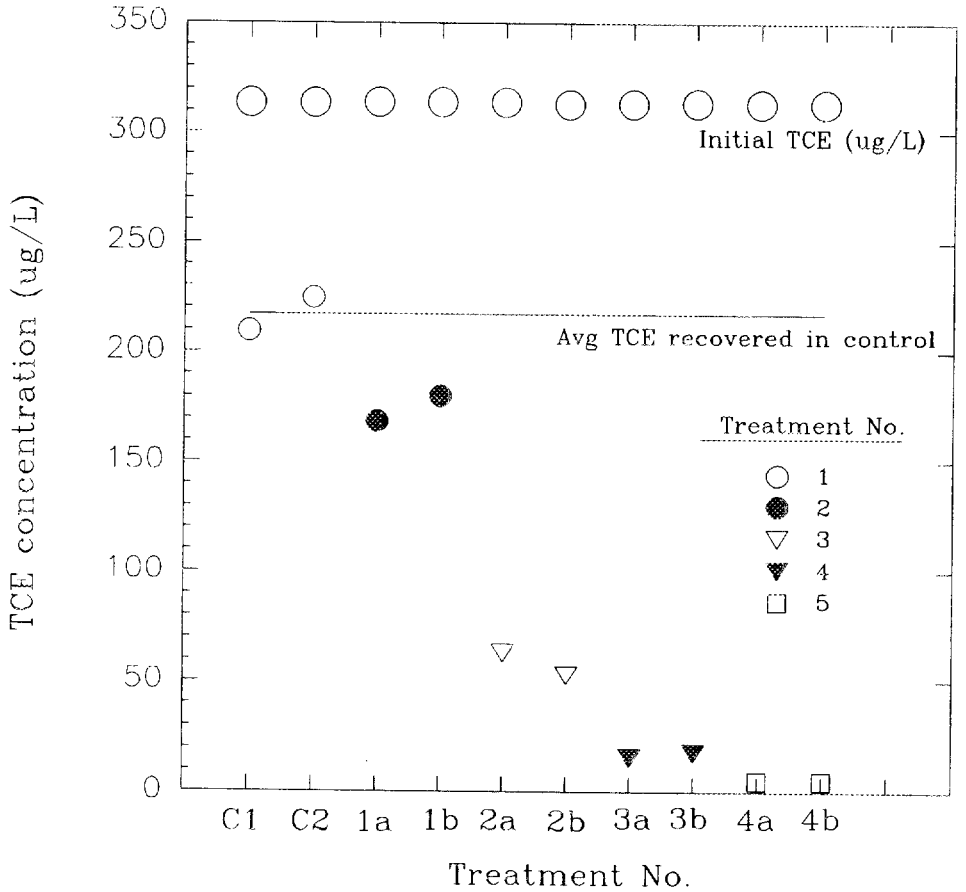

Fig. 6. TCE concentration reduction in bench-scale experiment No. 1.

The percentage of TCE removed from the soil slurries in the ZHE vessels was calculated relative to the level of TCE recovered in the control vessel using the following equations:

$$TCE_{remv} = \left[\frac{(TCE_{initial} - TCE_{adjust}) - TCE_{final}}{(TCE_{initial} - TCE_{adjust})} \right] \times 100 \quad (14)$$

where

TCE_{remv} = percent TCE removed due to peroxidation (%),

$TCE_{initial}$ = the initial concentration of TCE in the ZHE vessel based on the measured TCE concentration of the stock solution used for spiking and the measured volume of water within the ZHE (μg/L),

TCE_{final} = the measured concentration of TCE in the ZHE vessels based on post-treatment sampling and analyses (μg/L),

TCE_{adjust} = an adjusted concentration based on the change in TCE within the control ZHEs which accounts for changes in TCE concentration associated with the experimental and analytical procedures (μg/L):

$$TCE_{adjust} = (TCE_{C\text{-}initial} - TCE_{C\text{-}final}) \quad (15)$$

with

$TCE_{C\text{-}initial}$ = the initial concentration of TCE in the control ZHE vessel based on measured TCE concentration of the stock solution used for spiking and the measured volume of water within the control ZHE vessel (μg/L)

$TCE_{C\text{-}final}$ = the measured concentration of TCE in the control ZHE vessels based on post-treatment sampling and analyses (μg/L).

The control experiments in ZHE series No. 1 yielded a 69% recovery of the dosed TCE while the control experiments in ZHE series No. 2 slurries yielded TCE recoveries >100% (Table 9). In the case where the calculated TCE_{adjust} was negative (series No. 2 control experiments with slurries), TCE_{adjust} was assigned a value of 0.0 in Equation 14. The TCE recoveries observed in most of the control experiements were within the range of recoveries found to be acceptable when working with volatile organic compounds (Siegrist 1992).

In Fig. 7 the percentage of TCE removed in bench-scale experiment No. 1 is shown as a function of the concentration of the H_2O_2 solution used for treatment when the same volume (10 mL) of H_2O_2 solution was added in each vessel. TCE removal percentages in the first series of experiments increased as the H_2O_2 concentration increased from an average of 19.6% removed with 1.5% H_2O_2 to 97.7% removal with 7.3% H_2O_2.

Table 9. TCE recovery in control studies[a]

Series No.	Control No.	Matrix	Predicted pretreatment TCE concentration[b] μg/L	Measured posttreatment TCE concentration[c] μg/L	Percent TCE recovery
1	C1	Slurry	313.4	209.3	66.8
1	C2	Slurry	313.5	224.3	71.6
2	CS1	Slurry	603.5	1035	170
2	CS2	Slurry	5247.6	10271	195
2	CA1	Aggregates	1682	423	25
2	CA2	Aggregates	1682	709	42

[a]TCE-contaminated soil slurries and aggregates with no peroxide added.

[b]Calculated on the basis of total volume of fluid in vessel (includes slurry, TCE solution, peroxide solution and DI water added for extraction) using measured stock TCE solution concentration and assuming all TCE in aqueous phase.

[c]Measured value in posttreatment extract.

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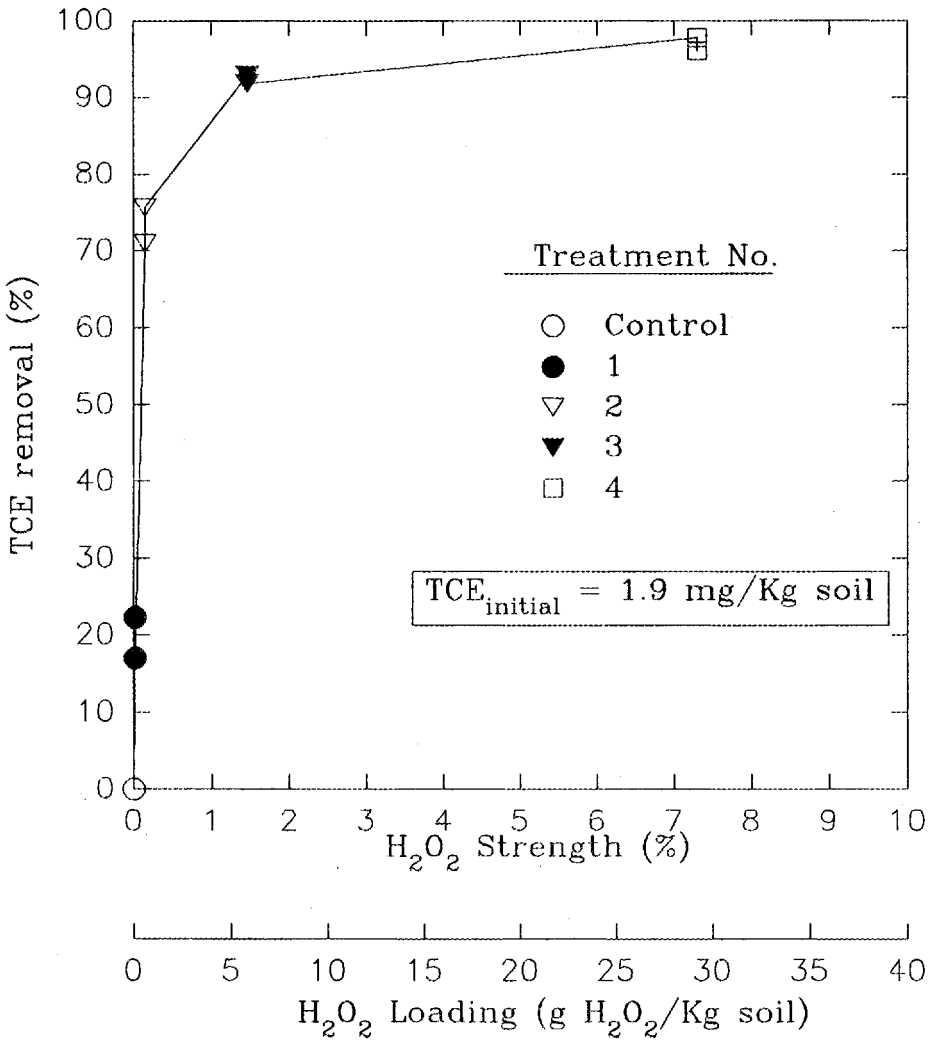

Fig. 7. TCE removal in bench-scale study No. 1.

Figure 8 shows the TCE reductions observed during the second series of experiments, which indicate that significant TCE reduction occurred in the vessels filled with slurry, while minimal TCE reduction took place in the vessels loaded with TCE-contaminated soil aggregates. TCE removals observed during the bench-scale experiments are summarized in Table 10.

2.3.2 Effects on System Chemistry

An increase in pressure in the ZHE vessels after H_2O_2 addition was the first indication that some type of reaction had occurred in the ZHE experiments. It should be noted that the pressure gages on the apparatus were not designed to measure small changes in pressure but were able to confirm the generation of gas if a sufficient amount were formed. The greatest increase in pressure occurred with the addition of the 7.3% H_2O_2 solution in the ZHE series No. 1 experiments (Fig. 9). Although the increases in pressure observed were interpreted as indicating that some type of gas-evolving reaction had taken place (chemical oxidation), no attempt was made to capture or analyze the off-gas generated.

The pH, TOC, and iron levels in the posttreatment slurry centrates are shown in Figs. 10-14. Similar trends were observed during both series of ZHE experiments. It should be noted that the posttreatment slurries were stored for several days prior to analysis. It was observed that the pH of the slurry centrate decreased with respect to the pH of the control at H_2O_2 concentrations $>1.5\%$. This result is not unexpected, since the H_2O_2 solutions are acidic, and if Fenton's-type reactions did occur, this would also result in the release of H^+ upon the reduction of Fe^{3+} as detailed in Equation 6. No significant changes in pH were observed at the lower ($<1.5\%$) H_2O_2 concentrations.

Iron levels in the posttreatment slurry centrates differed from the control iron levels with an increase in iron concentration observed at lower H_2O_2 concentration and a decrease in iron concentration observed at higher H_2O_2 concentrations. In the absence of data detailing iron speciation, little can be inferred from the level of iron measured in the posttreatment slurry centrate.

The TOC concentration in the posttreatment slurry centrates increased at the higher H_2O_2 concentrations. This suggests that at the higher H_2O_2 concentrations the soil organic matter is partially oxidized, which results in solubilization of organic carbon.

2.4 BENCH-SCALE STUDY DISCUSSION

TCE removals as high as 98% were obtained when H_2O_2 was added to TCE-contaminated slurries. Although TCE reduction was observed at all H_2O_2 concentrations, the maximum TCE removals ($>70\%$) were observed when H_2O_2 concentrations $>1.5\%$ were used. The trends in pH, TOC, and iron concentrations all suggest that it is possible that Fenton's-like chemical reactions may be occurring and yielding TCE oxidation.

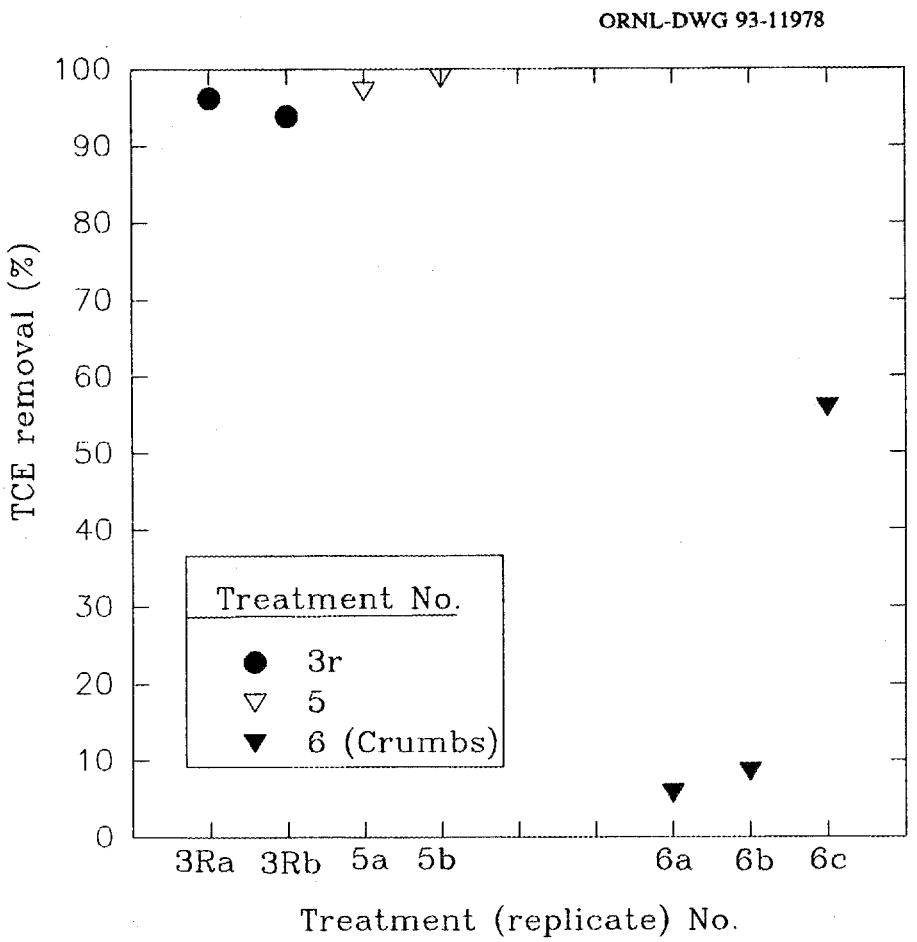

Fig. 8. TCE removal efficiency in bench-scale study No. 2.

Table 10. Bench-scale study summary of peroxidation of TCE-contaminated soil slurries

Treatment No.	Pretreatment TCE loading (mg/kg)	H_2O_2 dose solution strength (wt %)	Reaction time (h)	Avg. TCE removal
1	1.9	0 .015	24	20
2	1.9	0 .15	24	73
3	1.9	1.5	24	92
4	1.9	7.3	24	98
3R	4.0	1.5	2	95
5	34.0	1.5	2	98

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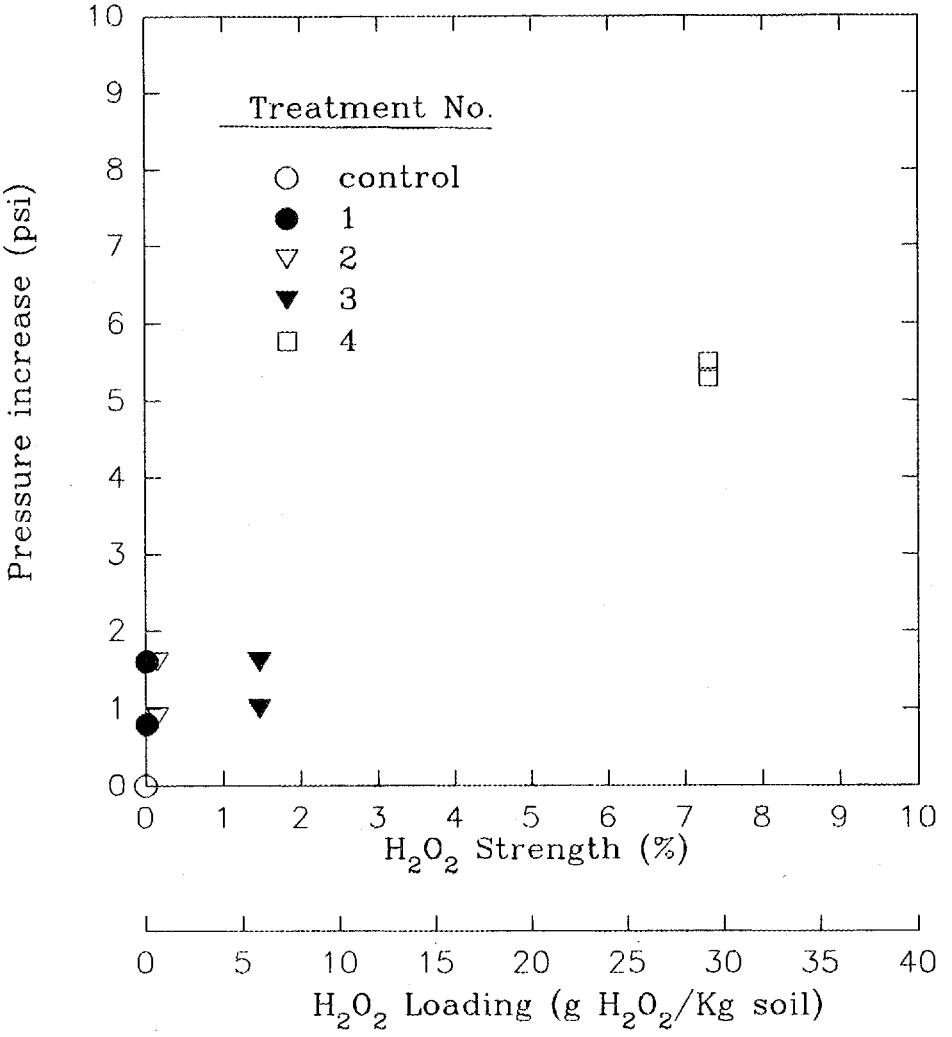

Fig. 9. Pressure changes following hydrogen peroxide addition to TCE-contaminated soil slurries in bench scale study No. 1.

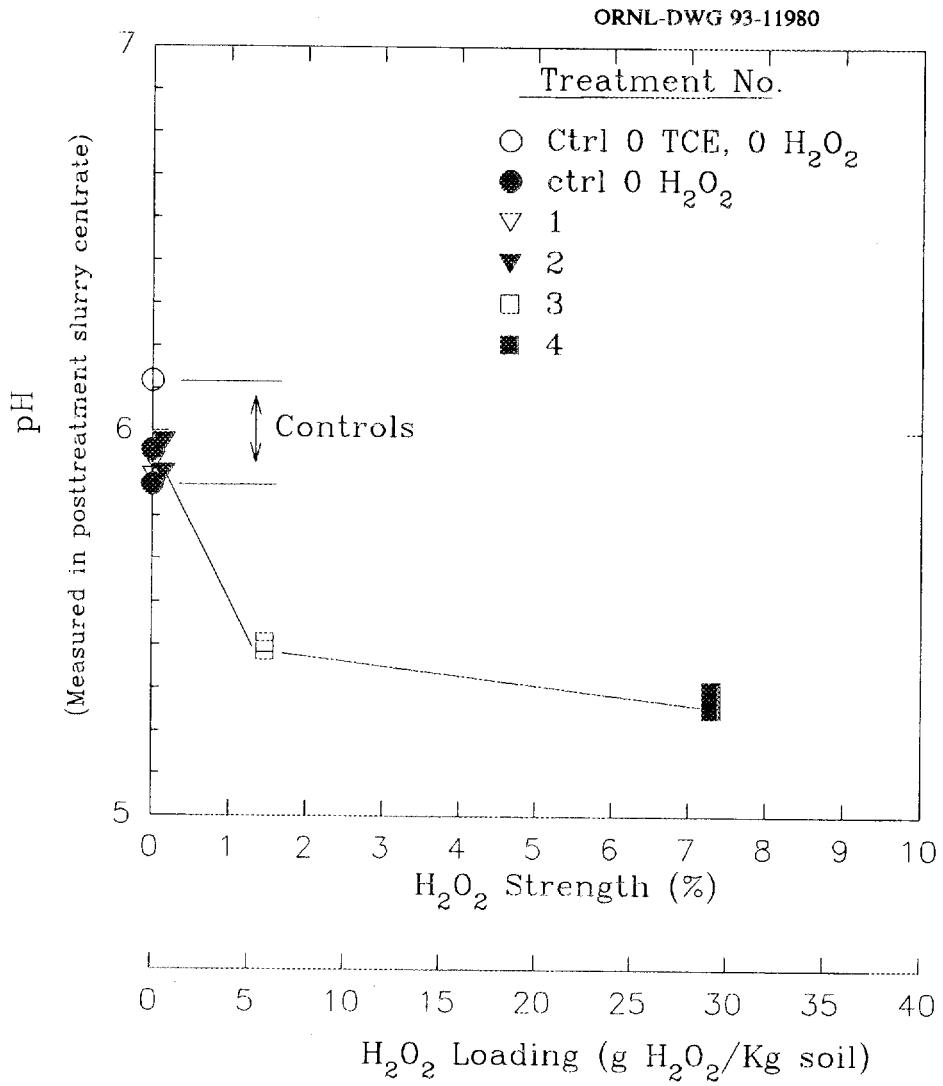

Fig. 10. pH changes following hydrogen peroxide addition to TCE-contaminated soil slurries in bench scale study No. 1.

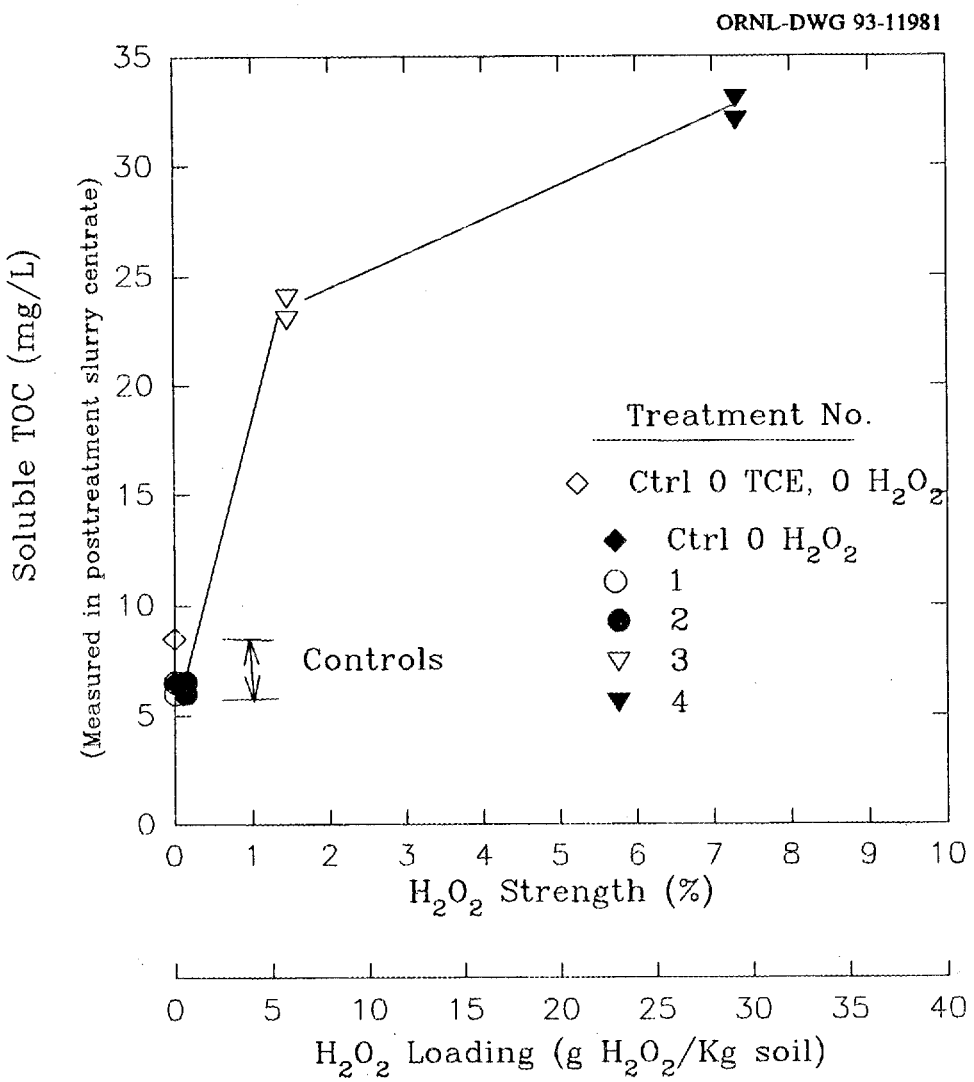

Fig. 11. Total organic carbon (TOC) changes following hydrogen peroxide addition to TCE-contaminated soil slurries in bench scale study No. 1.

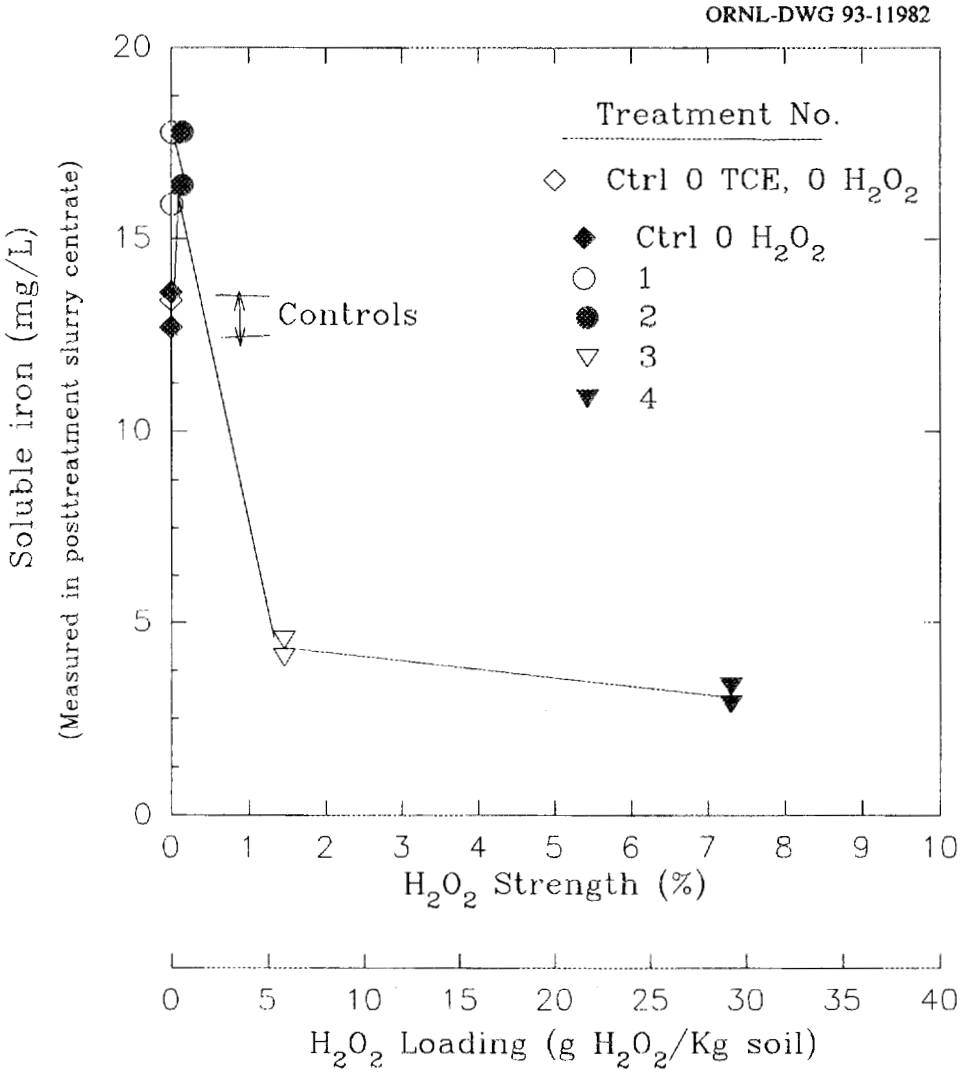

Fig. 12. Iron changes following hydrogen peroxide addition to TCE-contaminated soil slurries in bench scale study No. 1.

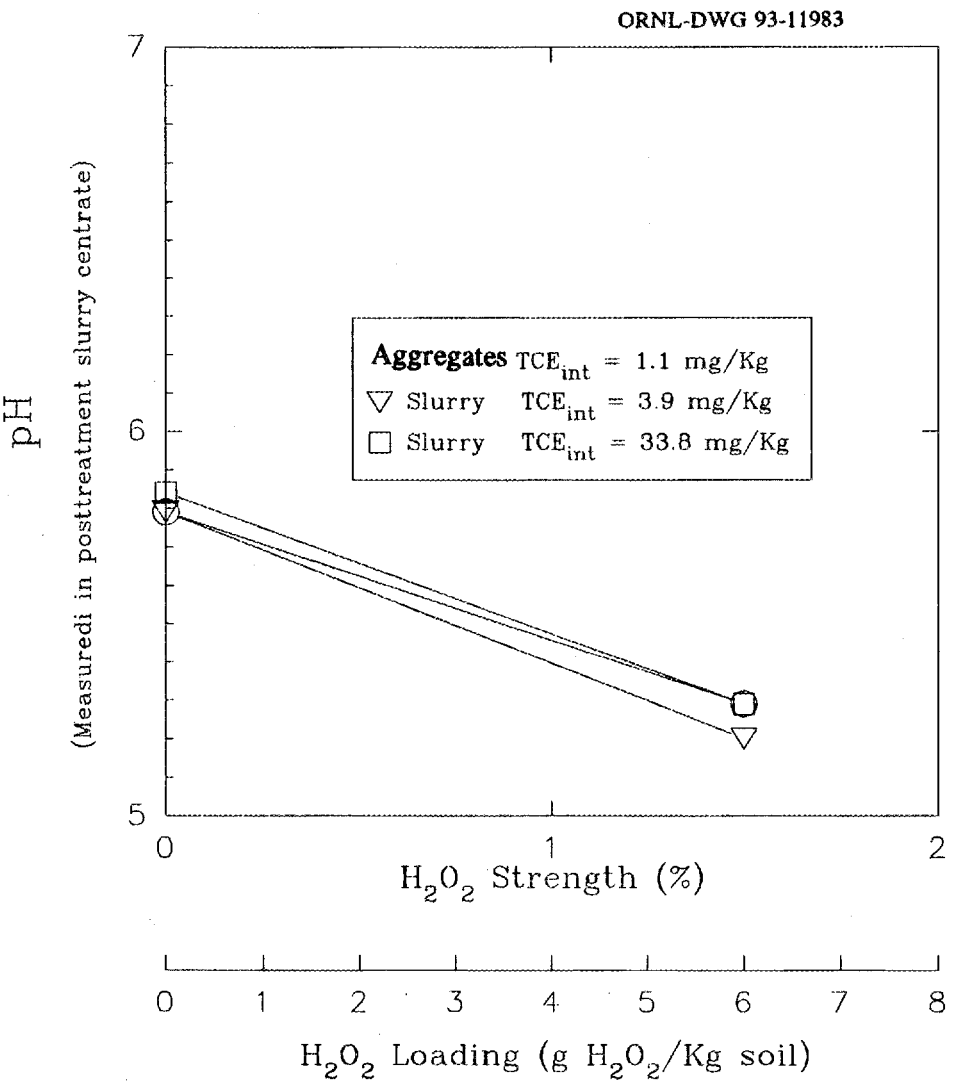

Fig. 13. pH changes following hydrogen peroxide addition to TCE-contaminated soil slurries and aggregates in bench scale study No. 2.

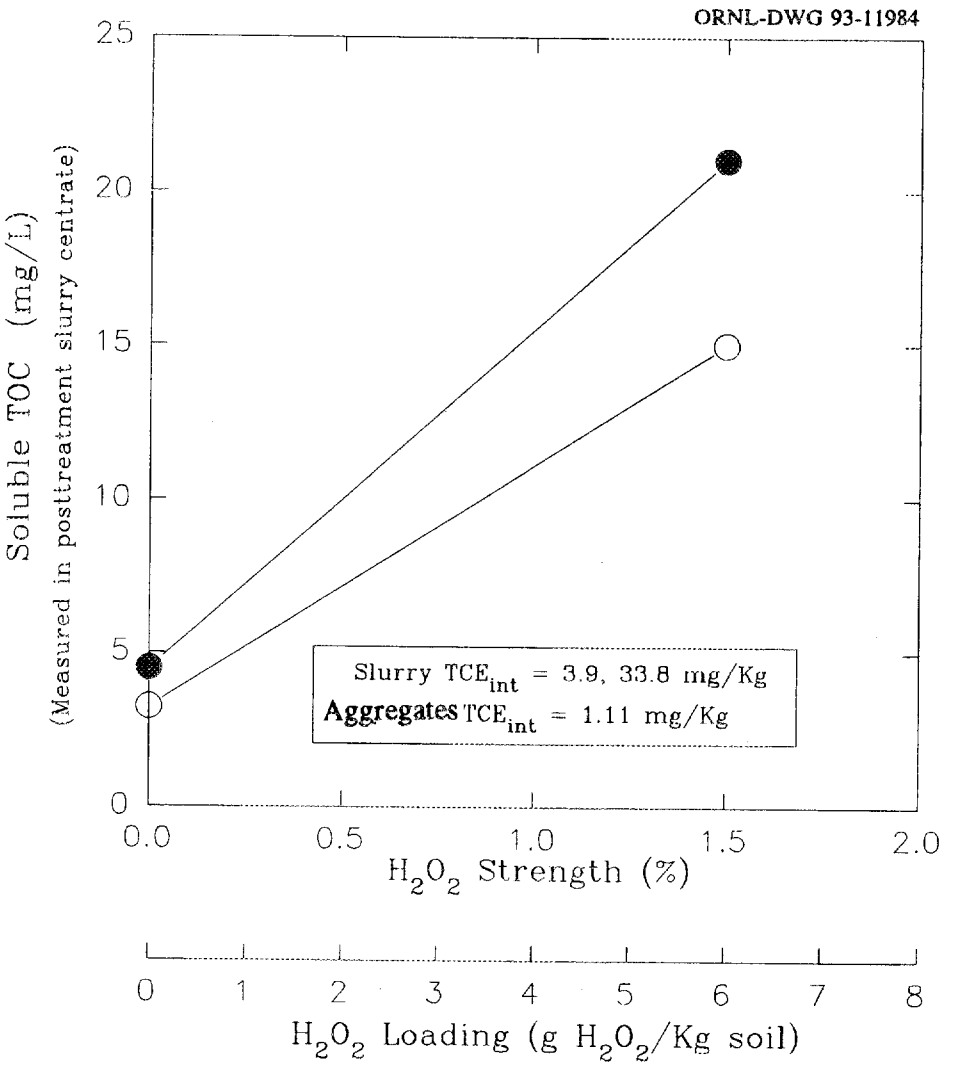

Fig. 14. Total organic carbon (TOC) changes following hydrogen peroxide addition to TCE-contaminated soil slurries and aggregates in bench scale study No. 2.

Limited data from the experiment suggest TCE reduction due to peroxidation may be independent of initial TCE concentration (see Fig. 15). TCE reductions >90% were reached in experiments with initial TCE concentrations of 4.0 and 34.0 mg/kg soil at equivalent H_2O_2 doses.

Peroxide concentrations far greater than the theoretical (or stoichiometric) amount needed for complete TCE destruction (Equation 13) were used in the bench-scale studies. In Fig. 16 the TCE removal percentage is shown as a function of the H_2O_2 molar loading (mole H_2O_2/mole TCE). The data shown in Fig. 16 suggest that the peroxidation process requires a H_2O_2 dose sufficient to oxidize the target contaminant in addition to that consumed by simple decomposition and the oxidation of nontarget material. In soil systems the predominant nontarget oxidizable material is most probably soil organic matter. In fact, it is possible that TCE degradation is merely incidental to soil TOC degradation, considering the predominance of soil organic matter relative to the number of contaminant molecules in the matrix evaluated in this study. The increase in soluble TOC in the posttreatment slurry centrate was presumed to be indicative of partial soil organic matter oxidation. A comparison of soluble TOC increases at different TCE loading and the same H_2O_2 dose (Fig. 17) revealed nearly identical increases in soluble TOC. These preliminary findings suggest that soil composition, particularly TOC content, may impact the effectiveness of peroxidation. Therefore, soil TOC levels need to be taken into consideration when the H_2O_2 dose required to achieve a desired level of VOC reduction is being determined—perhaps the TOC content is even more important than the initial TCE concentration.

Similar TCE reductions were found in experiments with reaction times of 24 h and 2 h (Figs. 18 and 19). These findings support the conclusion that the principal peroxidation process is very rapid, possibly occurring within minutes of the introduction of H_2O_2 into the contaminated media.

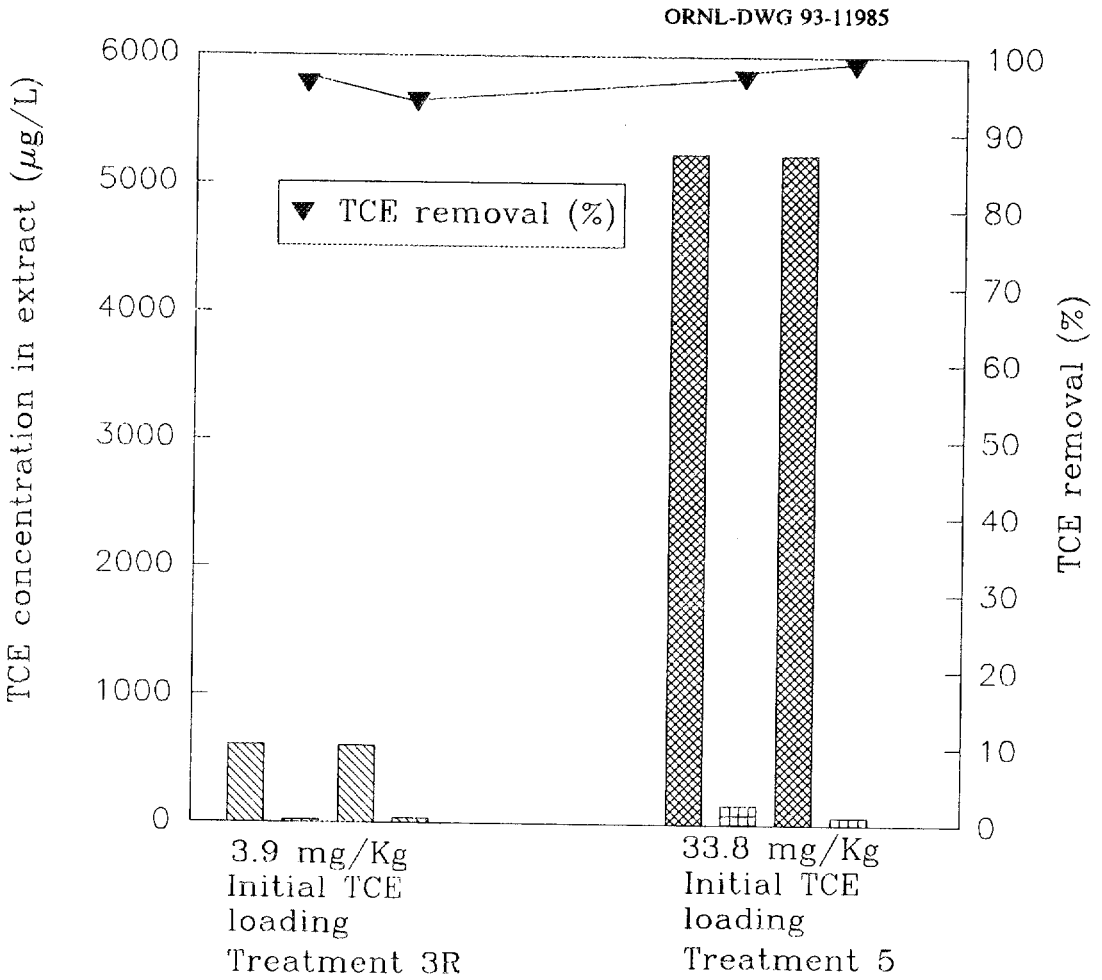

Fig. 15. TCE removal with peroxide addition at different initial TCE loading levels.

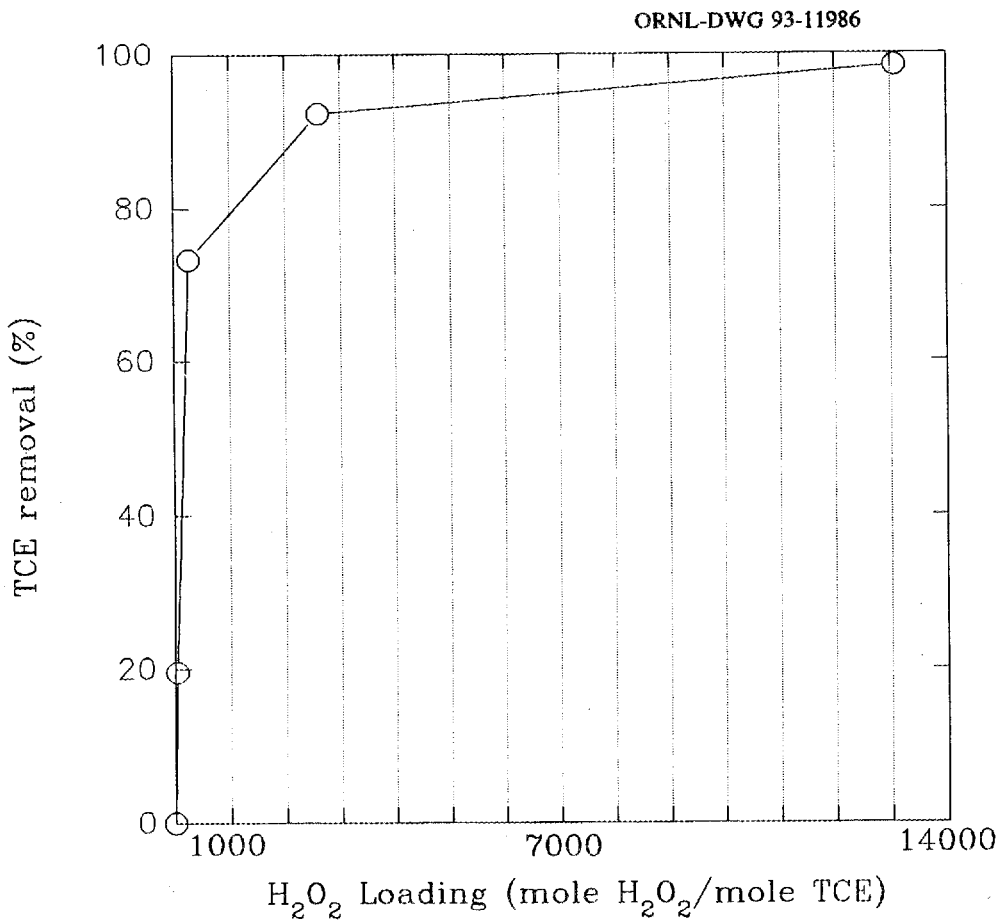

Fig. 16. TCE removal as a function of peroxide loading.

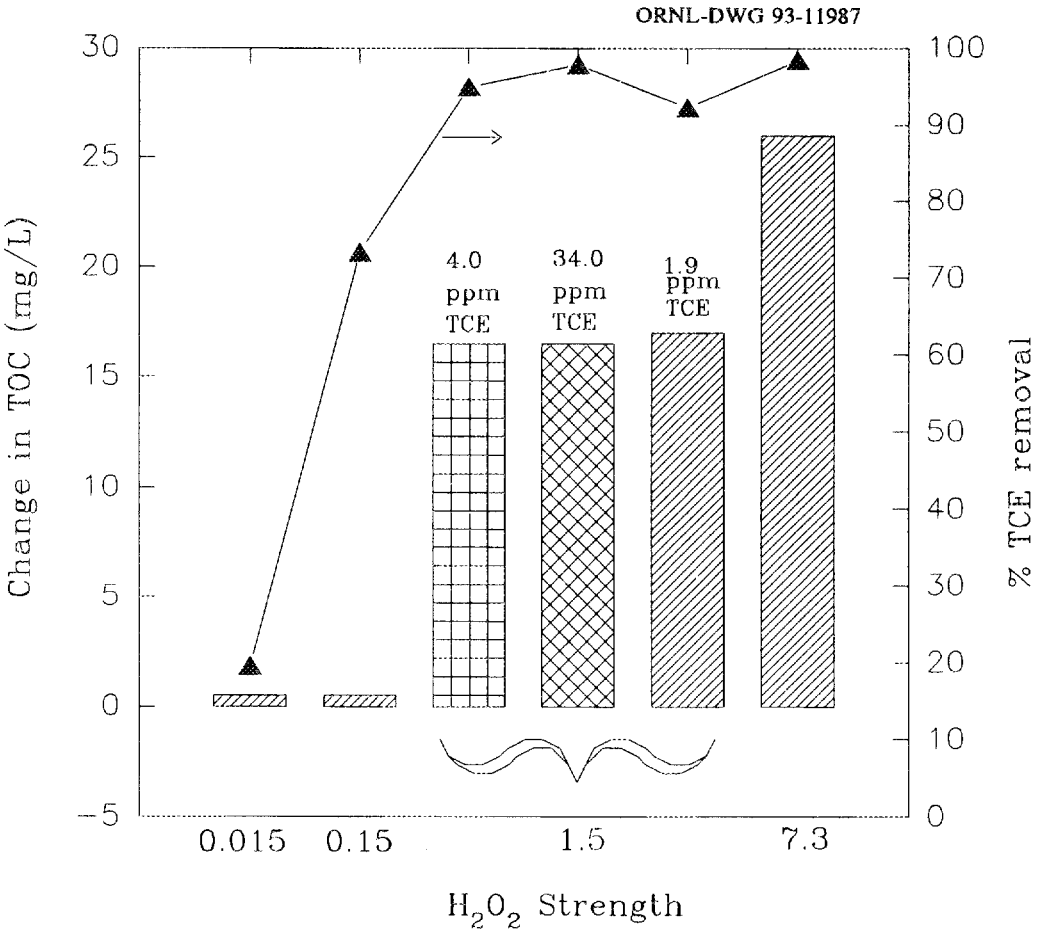

Fig. 17. Increase in soluble total organic carbon (TOC) after the addition of peroxide.

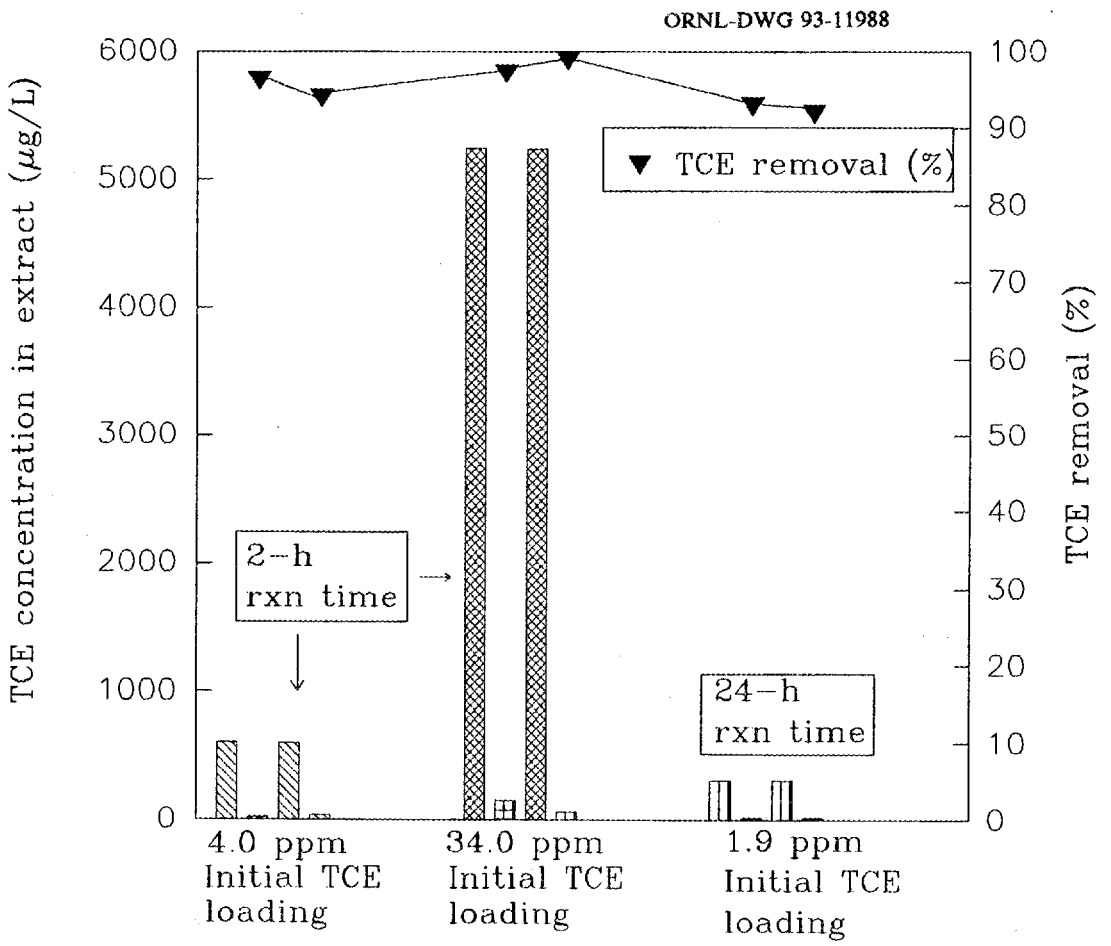

Fig. 18. TCE removal with the addition of peroxide at different initial TCE concentrations and reaction (rxn) times.

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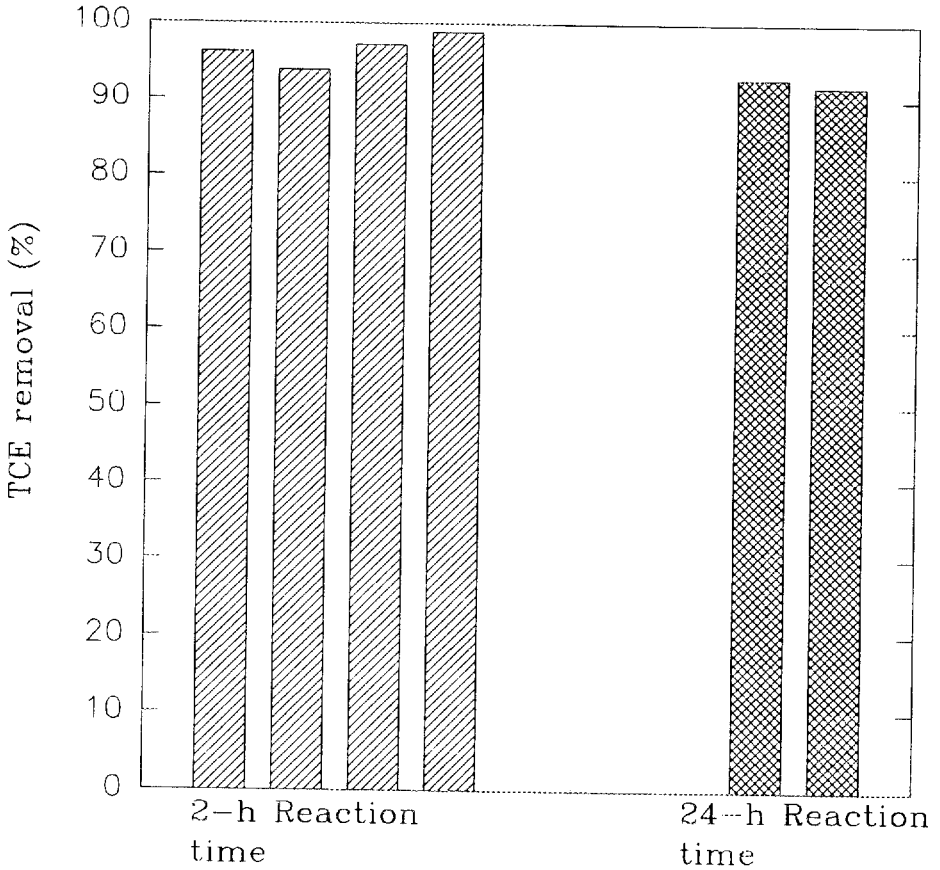

Fig. 19. TCE removal as a function of reaction time (peroxide strength constant at 1.5%).

3. PILOT-SCALE TREATABILITY STUDIES

Pilot-scale treatability studies were conducted after the completion of the bench-scale studies to further investigate peroxidation of TCE-contaminated soils. This series of experiments was conducted with the use of an 8-in. outside diameter (OD), 9-in.-long reaction lysimeter packed with Portsmouth soil. The soil in the reaction lysimeter was mixed and injected with a H_2O_2 solution using a modified core drill assembly. This type of experiment was needed to study the process for in situ peroxidation of clay soils.

3.1 OBJECTIVES AND SCOPE

The objective of the treatability studies was to further investigate peroxidation with the use of a soil-mixing system to deliver H_2O_2 solutions into a zone of contaminated soil. This system is more closely related to field conditions than the bench-scale studies and was expected to provide data to aid in the design of a full-scale field demonstration of peroxidation. The following specific objectives were established for the treatability studies:

1. To evaluate the extent of TCE reduction possible by peroxidation conducted with a soil-mixing and oxidant delivery system.

2. To investigate the effect of H_2O_2 loading volume on TCE reduction.

3. To evaluate the amount and characteristic of the off-gas generated during the course of peroxidation of TCE.

4. To determine the effect of H_2O_2 addition on soil properties.

Three treatability experiments were conducted to generate sufficient data to meet the objectives previously set forth. The first series was conducted using clean soil from the Portsmouth site, whereas the second and third series were conducted using Portsmouth soil that was artificially contaminated with TCE prior to H_2O_2 treatment. In all cases the soils were mixed and H_2O_2 was injected as part of the treatment process. The experimental conditions maintained during the treatability study are summarized in Table 11.

Table 11. Peroxide treatability study design experimental conditions

Series	Treatment No.	H_2O_2[a] volume added	H_2O_2 loading g/kg soil	Reaction time (h)	TCE target contamination level (mg/kg)
1	1a	80 mL	2.5	2	None
	1b	0 mL	0		
2	2a	80 mL	2.5	2	5
	2b	80 mL	2.5		
3	3a	40 mL	1.2	2	5
	3b	40 mL	1.2		

[a]Five percent peroxide solution used for all treatments except 1b which had 80 mL of deionized water added.

3.2 MATERIALS AND METHOD

3.2.1 Experimental Apparatus

The main components of the apparatus used for the treatability studies are as follows (see Figs. 20–22):

- A stainless steel 8-in-OD, 9-on.-long reaction lysimeter which could be packed with soil requiring treatment. The reaction lysimeter was sealed using viton gaskets to minimize the loss of VOC during treatment as a result of leakage from the system.

- A core drill equipped with a swivel joint to allow H_2O_2 injection into the rotating hollow shaft during the mixing process. The core drill was manually lowered during the course of a treatability experiment.

- A perforated mixing blade through which H_2O_2 solution was injected into the soil mixing zone

Further details of the design and operation of the treatability apparatus can be found elsewhere (West et al. 1992).

3.2.2 Experimental Methods

The treatability studies consisted of the following steps:

1. Preparation of a soil core by packing soil into the reaction lysimeter and spiking the soil with TCE solution (no TCE spiking for experiment No. 1). The soil cores used in the treatability studies were collected and handled in a manner similiar to that given in Section 2.2.2 with the exception that sleeves 8 in. in diam by 24 in. in length were used to collect larger soil samples. Field soil core #SBO8, from a depth of 11 to 13 ft with a field-screening VOC level of 49 μg/kg was used for the peroxidation treatability studies. Spiking was done as follows:

    a. A preweighed mass of field moist soil was packed into the soil core treatment zone and compacted into an even layer ~1.5 cm thick.

    b. The upper surface of the packed soil was scored in a crosshatch pattern using the blade of a screwdriver.

    c. TCE solution (10 mL) was quickly and evenly distributed over the scored soil surface using a glass syringe fitted with a metal needle.

    d. Another preweighed layer of soil was placed in the treatment zone and steps b and c were repeated until a total of 4 layers of soil had been placed in the treatment zone and contaminated with TCE.

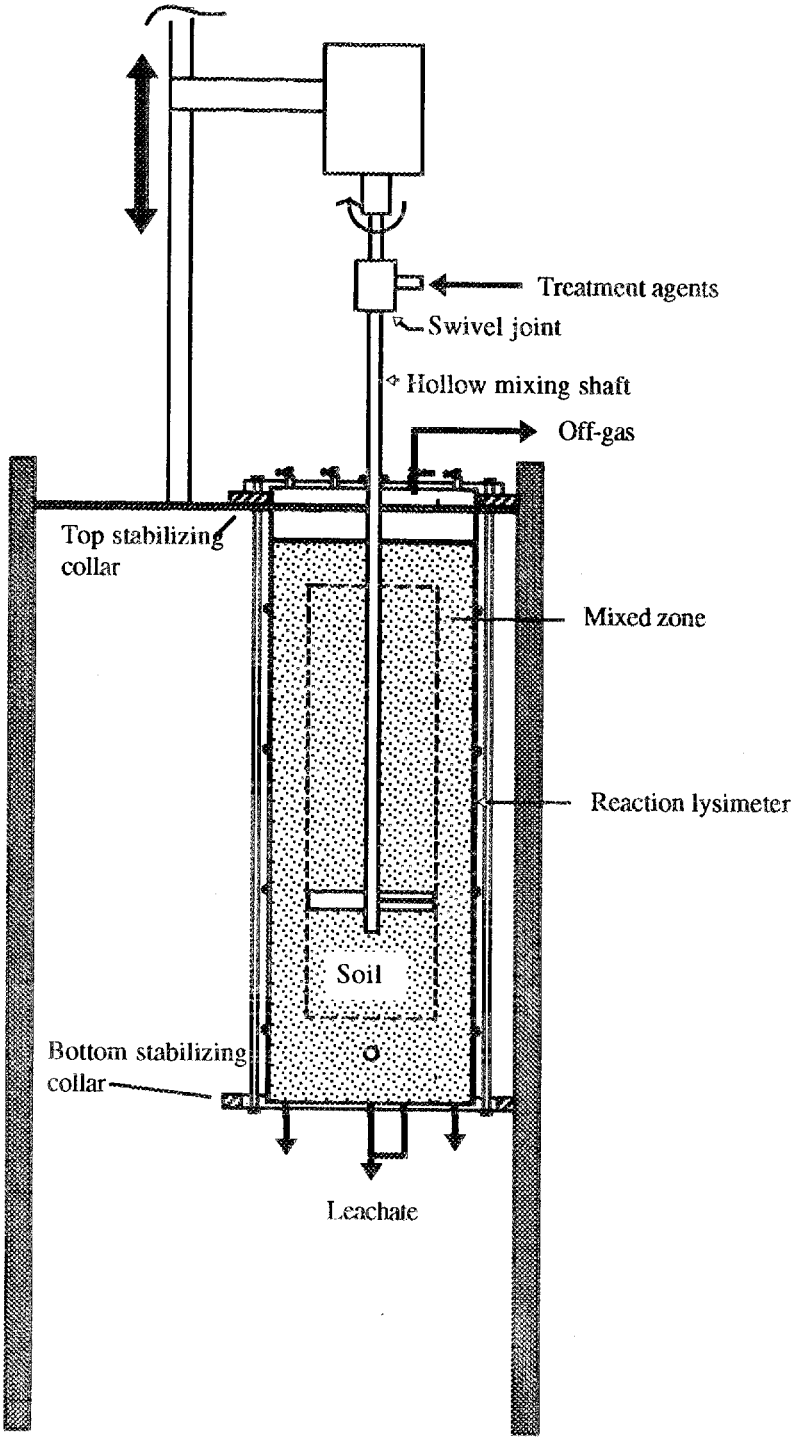

Fig. 20. ORNL soil-core mixing apparatus (West, O.M., et al. 1992).

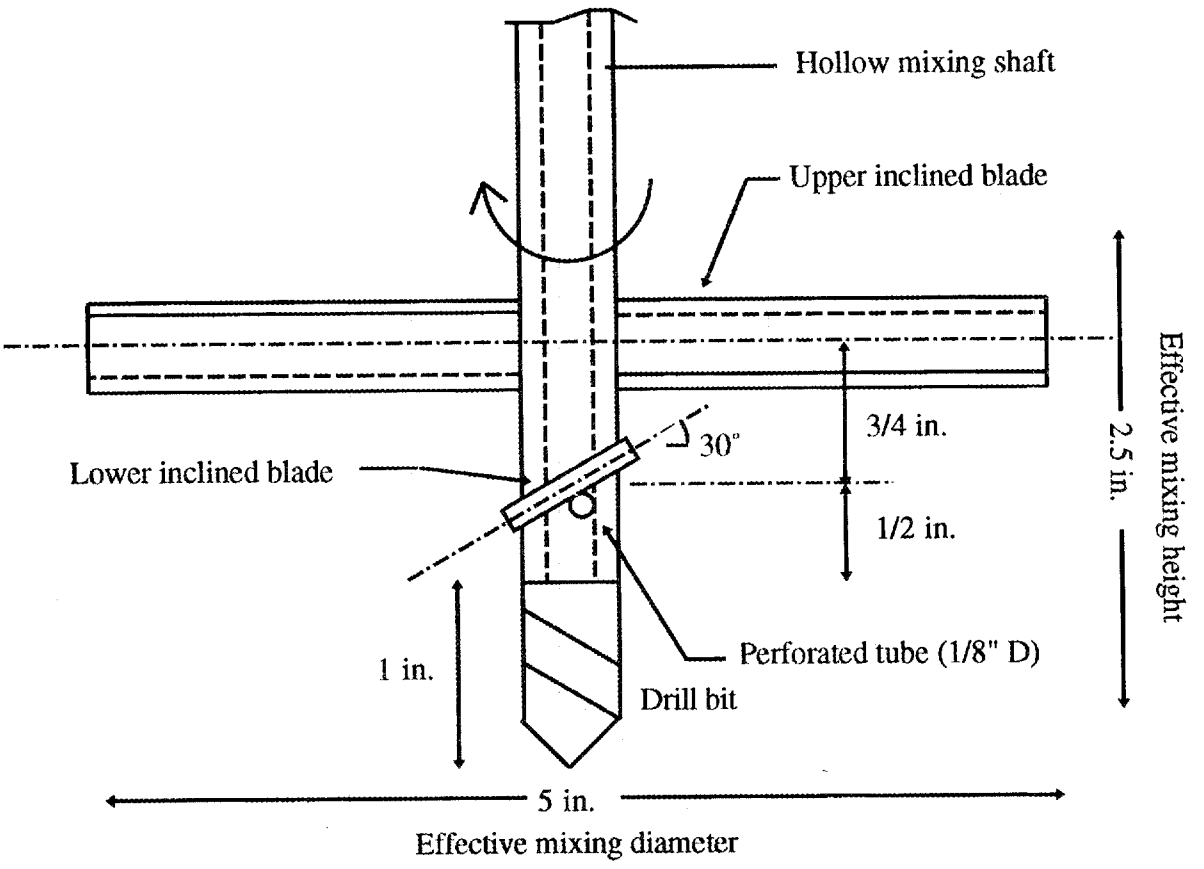

Fig. 21. Mixing blade design used during peroxidation treatability studies (West, O.M., et al. 1992).

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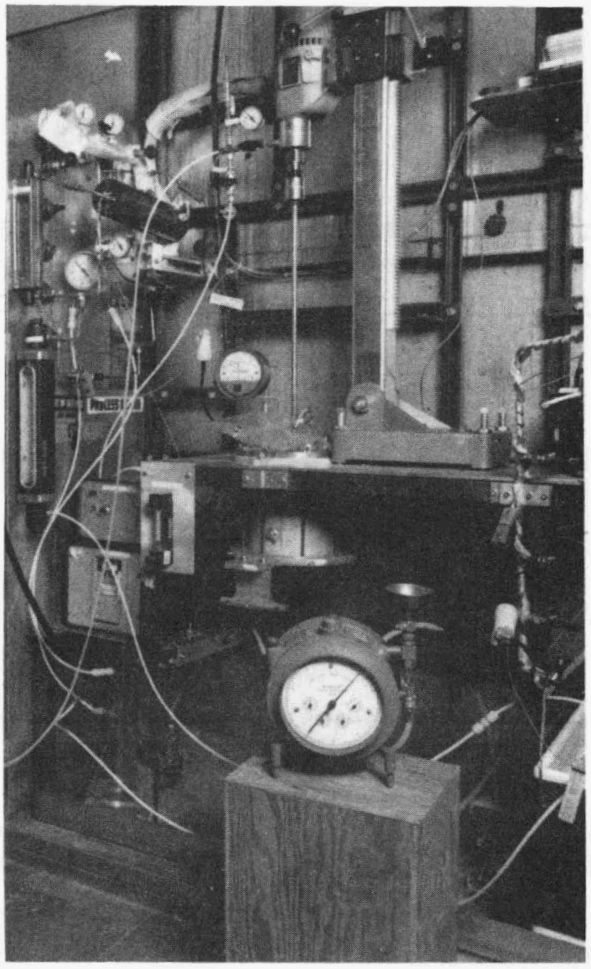

Fig. 22. Apparatus used during peroxidation treatability studies (West, O.M., et al. 1992).

e. A final layer of soil was placed in the treatment zone and compacted in place but was not contaminated with TCE.

f. The reaction lysimeter was capped and sealed and then allowed to sit undisturbed for at least 2 hours before H_2O_2 treatment was initiated.

2. The lysimeter was opened and pretreatment soil samples were collected. A total of two pretreatment samples were taken at separate locations for each experiment, using a 3/4-in. diam stainless steel soil probe. After the soil probes were withdrawn, the contents were divided into three equal portions which were then placed in preweighed amber VOA vials. The vials were closed using Teflon-lined septum caps and then refrigerated at 4°C prior to analysis.

3. Mixing of soil cores and injection of H_2O_2 were accomplished as follows: The soil treatment zone was premixed with one pass of the mixing blades prior to H_2O_2 injection. The mixing blade was operated at the rate of ~3 in. per min. Following premixing, the soil core drill was manually lowered and raised while H_2O_2 was injected at the rate of 40 mL/min. Injection of the H_2O_2 solution was complete in under 3 min. The H_2O_2 solution was prepared daily and supplied to the swivel joint by a masterflex pump. After H_2O_2 addition was completed, two additional passes of the mixing blade were made to promote thorough mixing.

4. H_2O_2 addition and soil mixing were followed by a 2 h reaction time in which each treated core was allowed to sit undisturbed, and off-gas generation was monitored.

5. Withdrawal of posttreatment samples. (see Step No. 2)

Peroxidation is an exothermic reaction that can proceed with the generation of gas. The off-gas generated during peroxidation would be expected to consist of mostly O_2 and CO_2 and possibly some gaseous TCE. The rates of off-gas generation and total off-gas volume were measured during treatability runs No. 1 and 3 (10% and 5% H_2O_2 addition by volume, respectively). In addition, during treatability run No. 3 the off-gas was collected in a Tedlar bag and analyzed for TCE.

Thermocouples were installed in the reaction lysimeter, but they did not register any appreciable increase in temperature during peroxidation. It should be noted that the thermocouples measured the temperature of the annular region of soil surrounding the mixed treatment zone and not the temperature within the treatment zone.

3.2.3 Analysis

During the peroxidation treatability studies, the TCE concentration in the soil samples was measured directly using a heated head space gas injection into a gas chromatograph. The procedure followed was similar to EPA Field Screening Method FM-5, with the exception that ~6 g soil samples were placed in 40-ml reaction vials for analysis, and an autosampler was not used. Samples were heated for 1 h at 60°C before analysis.

A Perkin Elmer Sigma 2000 GC with a VOCOL column measuring 30 m x 0.53 mm was used. N_2 was used as the carrier and make-up gas. The detection and injection temperature were 300 and 200°C respectively. Treatability study sample analysis is summarized in Table 12.

3.3 TREATABILITY STUDY RESULTS

The percentage of TCE removed during the treatability experiment was calculated using the following equation:

$$TCE_{remvt} = \frac{(TCE_{initial} - TCE_{final})}{TCE_{initial}} \times 100 \qquad (16)$$

where

TCE_{remvt} = percent TCE removed during treatability experiment,

$TCE_{initial}$ = average pre-treatment sample TCE concentration (mg/kg dry soil basis),

TCE_{final} = average posttreatment sample TCE concentration (mg/kg dry soil basis).

The TCE removals observed during the treatability studies are summarized in Table 13 and shown in Fig. 23. TCE reductions >70% were observed at both H_2O_2-loading volumes investigated.

Treatability run No. 1 (uncontaminated soil) was conducted to determine the impact of in situ mixing with H_2O_2 injection on bulk soil properties. The changes in moisture content observed after the addition of equal volumes of water (run 1a) or H_2O_2 (run 1b) (10% of total volume of soil) are summarized in Fig. 24. Photographs of soil before and after in situ mixing and H_2O_2 addition (10% of total volume of soil) are shown in Figs. 25 and 26.

The rate of off-gas generation during treatability runs 2a and 3b is shown in Fig. 27. During treatability run 2b, the off-gas was collected in a Tedlar bag and analyzed. This analysis did not measure any significant quantities of CO_2 in the off-gas but did detect a small quantity of TCE in the off-gas.

3.4 TREATABILITY STUDY DISCUSSION

A decrease in TCE removed was noted when the level of H_2O_2 added to treat the soil was decreased. The measured initial TCE concentration was somewhat higher for the runs receiving the lower volume of H_2O_2. On the basis of the results of the bench-scale studies, in which it was shown that initial TCE concentration did not have an apparent

Table 12. Methods of analysis for the peroxide treatability study

Medium/ sample type	Container	Preservation	Holding time	Parameter measured	Method
Soil	40-ml Glass vial	None	N/A	Moisture	Methods of soil analysis
TCE spiking solution	40-ml Glass vial	None	<3 h	TCE	8240
Soil	40-ml Glass vial	None	<3 h	TCE	EPA field method FM-5
Off-gas	1-L Tedlar bag	None	<3 h	TCE CO_2 O_2	

Table 13. Peroxidation treatability study results summary

			TCE Concentration (mg/kg)		
Series	Treat-ment No.	H_2O_2 loading g/kg soil	Pre-treatment	Post-treatment	% TCE removal
2	2a	2.5	1.5 ± 0.3 (n = 4)	0.15 ± 0.02 (n = 3)	90.2
	2b	2.5	1.1 ± 0.3 (n = 5)	0.17 ± 0.03 (n = 4)	84.7
3	3a	1.2	2.0 ± 0.3 (n = 3)	0.48 ± 0.08 (n = 5)	76.1
	3b	1.2	2.3 ± 0.2 (n = 2)	0.62 ± 0.04 (n = 4)	73.7

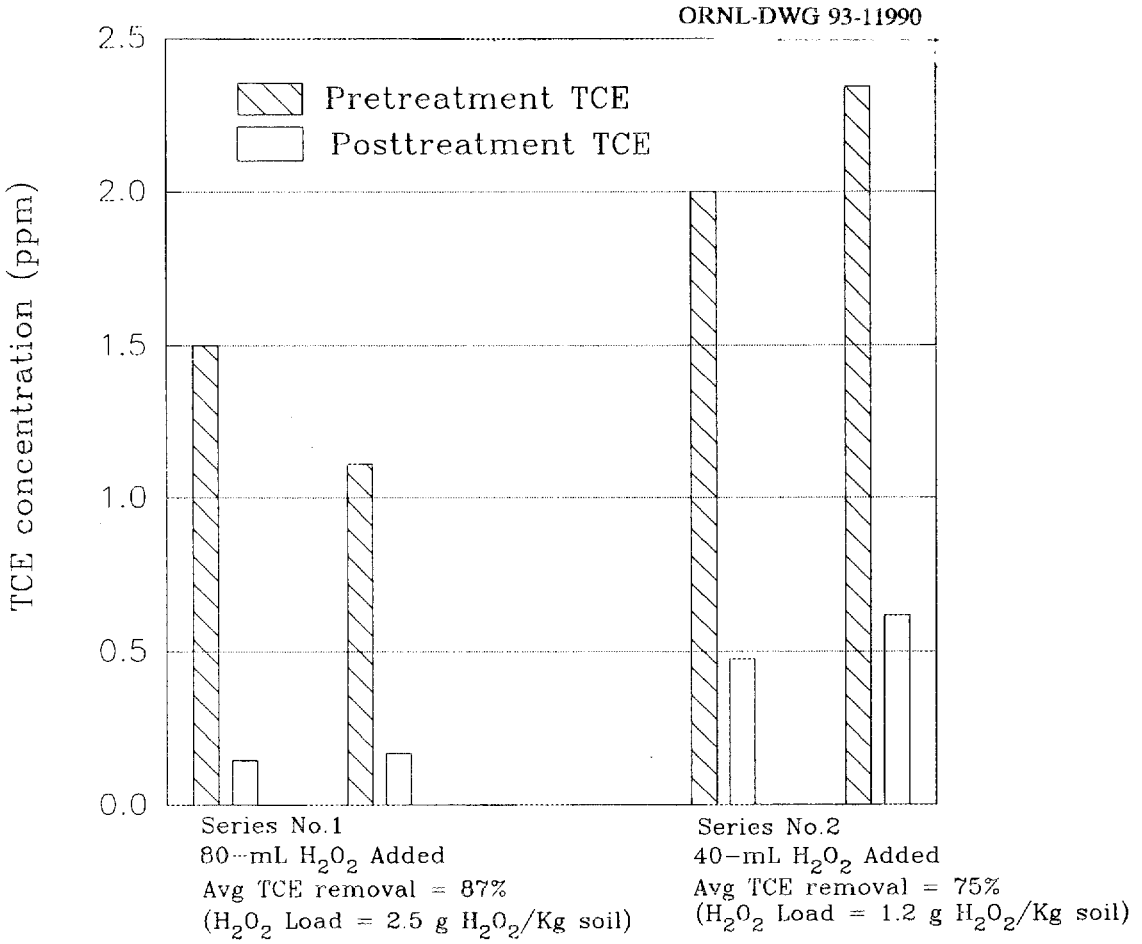

Fig. 23. Peroxidation treatability study results.

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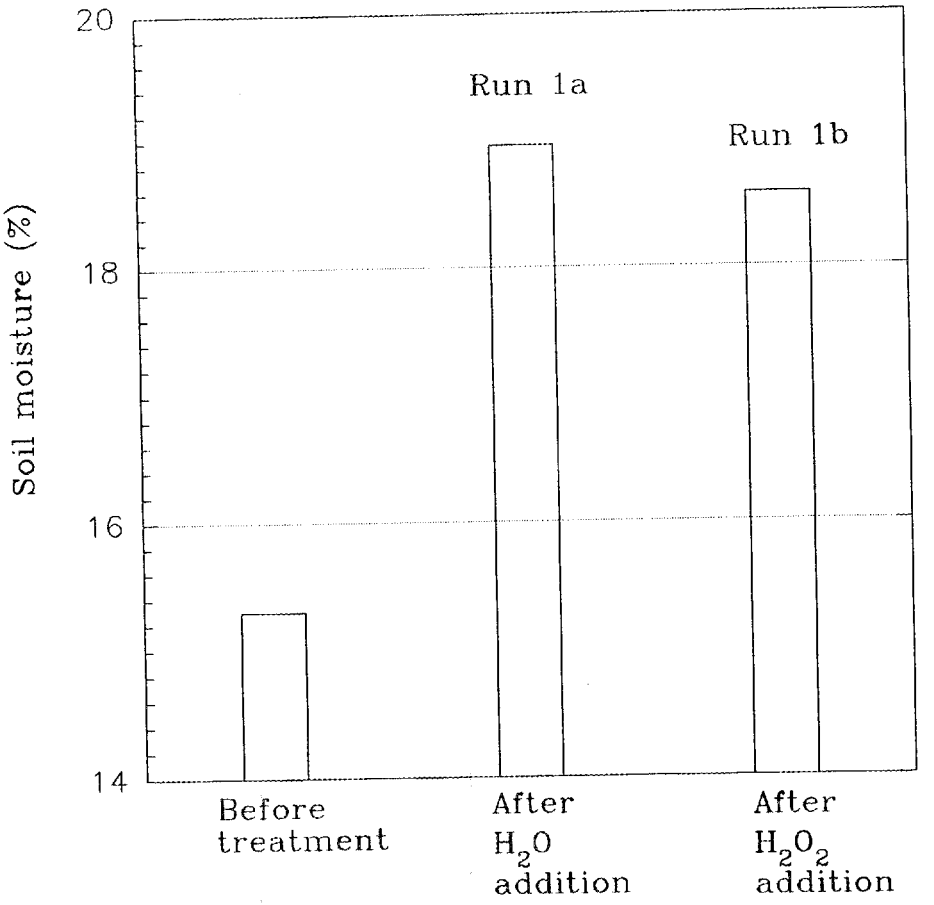

Fig. 24. Change in soil moisture content with fluid addition.

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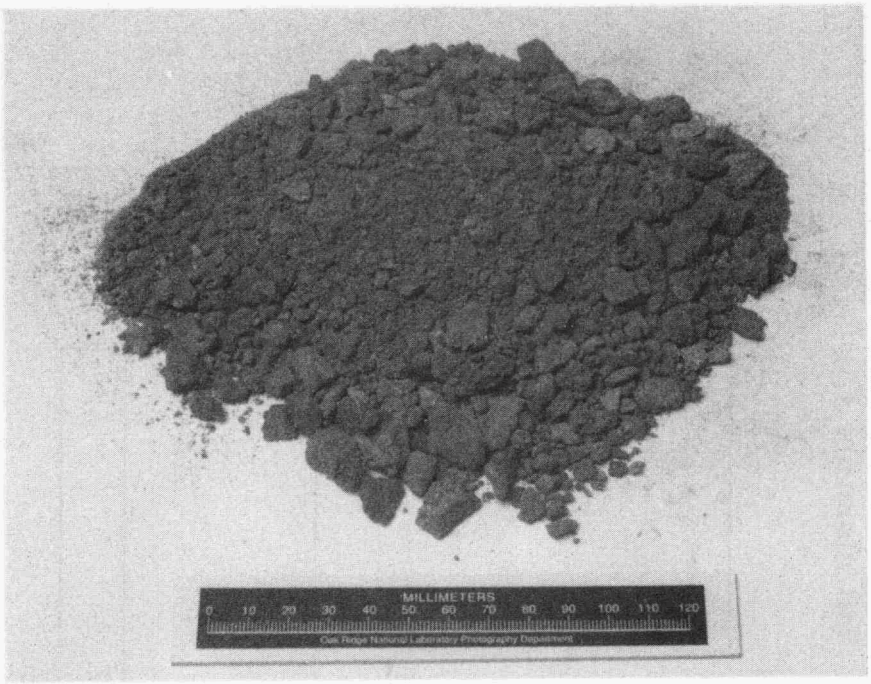

Fig. 25. Portsmouth soil before treatment.

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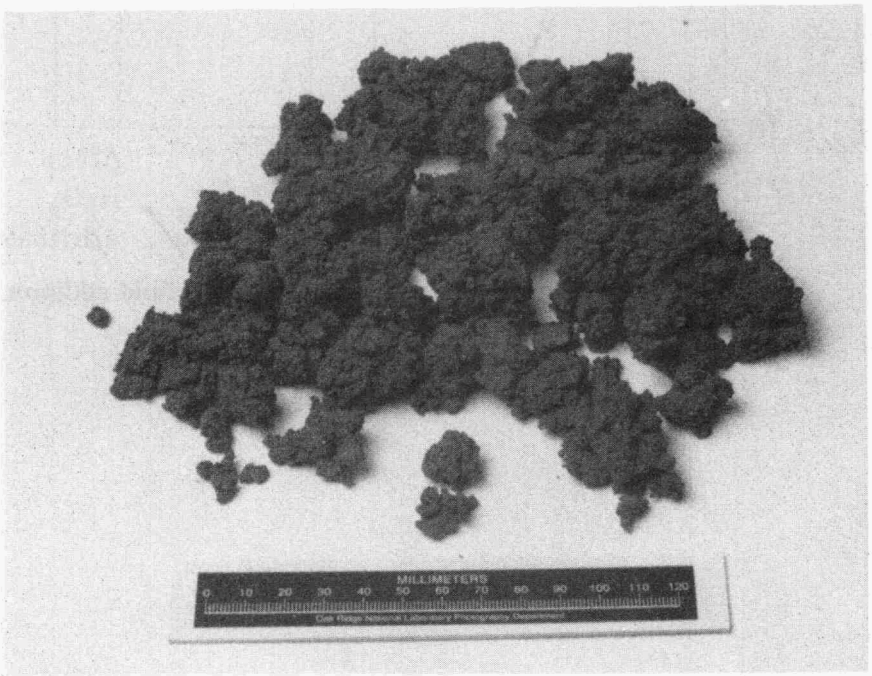

Fig. 26. Portsmouth soil after treatment.

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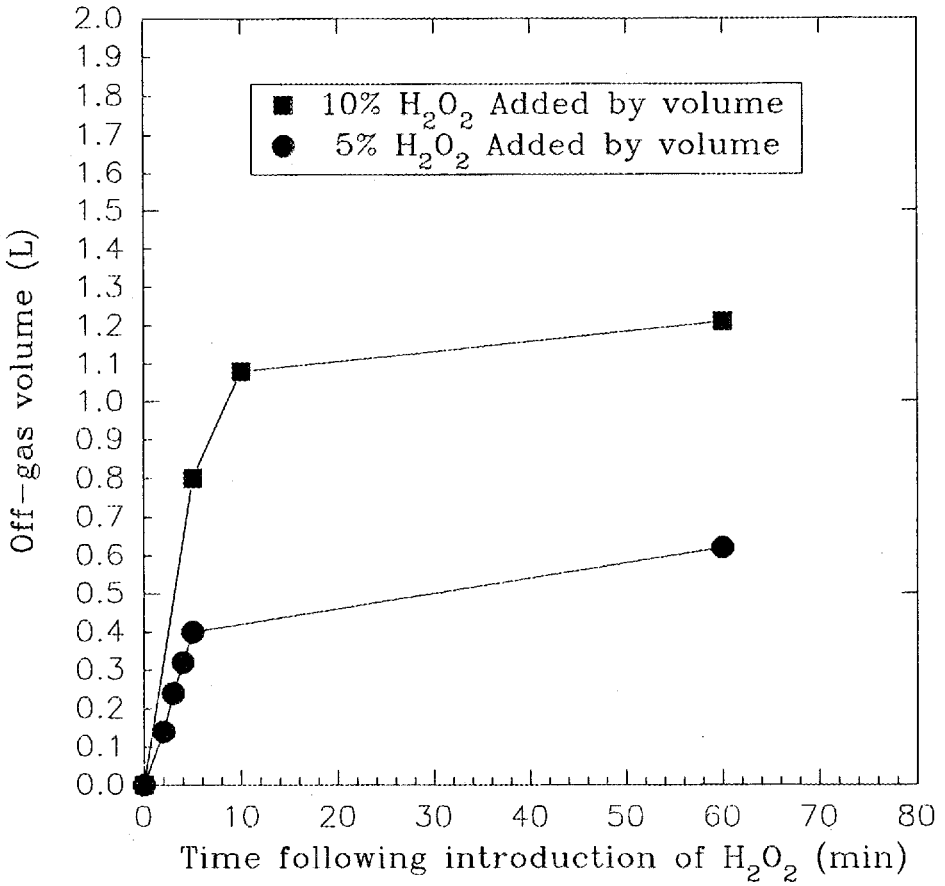

Fig. 27. Off-gas generation after peroxide addition.

effect on TCE destruction efficiency, it was concluded that the decrease in efficiency observed was not due to the increased TCE concentration. The results observed were not unexpected and suggest that the process of interest may be mass transfer limited.

At both H_2O_2 addition levels, more than 90% of the total off-gas generated was evolved within 10 min of H_2O_2 addition. This was interpreted as being indicative of the rapid rate of peroxidation reactions. As expected, a decrease in the total amount of off-gas generated was observed when the level of H_2O_2 added was decreased. The TCE measured in the off-gas was assumed to be carried over from TCE volatilized in the head-space of the reaction lysimeter prior to H_2O_2 addition and not to be indicative of in-complete TCE degradation.

In both treatability runs, in which 10% by volume of either water or H_2O_2 was mixed with Portsmouth soil, the posttreatment soil was considerably more moist than the untreated soil, but no freestanding moisture was observed. After treatment, the soil could be formed into a ball that held together after compaction. It was observed that the peroxide-treated soil formed smaller, more finely divided clumps than the DI water-treated soil.

4. DISCUSSION

In Figs. 28 and 29 the combined results of the bench-scale and pilot-scale studies are shown. Fig. 29 gives more detail of peroxidation at lower H_2O_2 loadings (corresponding to H_2O_2 strengths <3% in the slurry studies and 5% in the treatability studies). The same trends are observed for both types of studies with the exception of the bench-scale studies using soil aggregates. The data shown in Fig. 29 demonstrate that removal efficiency is dependent on H_2O_2 loading and apparently independent of initial TCE concentration. Peroxide loadings >3 g H_2O_2/kg soil appear to be required to achieve TCE removal efficiencies >90% for the soils used in these studies, which had TOCs in the range 0.05 to 0.1%. Rapid reaction times (<2 hr) were also observed in both the bench and pilot-scale studies.

The experimental methods used in the laboratory studies conducted during the X-231B project differed in several significant ways from the studies reported in the literature review. This study used exclusively a fine-textured clayey soil, whereas many of the other studies used quartz sand as their soil material. The laboratory studies also used lower H_2O_2 loadings with only one treatment of H_2O_2 as opposed to repeated treatments with H_2O_2 used by Watts (1991) and Leung (1991).

There were, however, several areas in which the findings of this study agreed with those published in the literature. The maximum destruction efficiencies observed in this study were similar to those reported by other investigators using TCE-contaminated soils [TCE reductions as high as 98% were reported in this study and by Gurol and Ravikumar (1991)]. Similarly high destruction efficiencies were reported by several authors for other contaminants in either soil or aqueous systems. An increase in peroxidation efficiency as the H_2O_2 dose increased was observed in this and many of the other studies previously reviewed. Iron amendments were not required to reach high removal efficiencies, which suggests that sufficient iron is present in native soils to support the formation of Fenton's-like reagents if they are indeed responsible for peroxidative destruction of contaminants. Watts et al. (1991) found peroxidation to be independent of initial contaminant concentration but dependent on soil organic carbon content. The effect of soil organic carbon was not evaluated in this study because only one soil source was used. However, in the laboratory studies, several initial TCE concentrations were studied, and the independence of removal efficiency on contaminant concentration was demonstrated.

The laboratory studies conducted at ORNL were one component of a series of studies designed to evaluate the peroxidation of clay soils contaminated with VOCs. These activities were conducted to support a field demonstration of this process at the Portsmouth X-231B site. Researchers at the University of Tennessee, Knoxville, led by Dr. Kevin Robinson, evaluated the fate of radiolabled TCE during peroxidation and the impact of peroxidation on the mobilization of metals. These studies are described in detail

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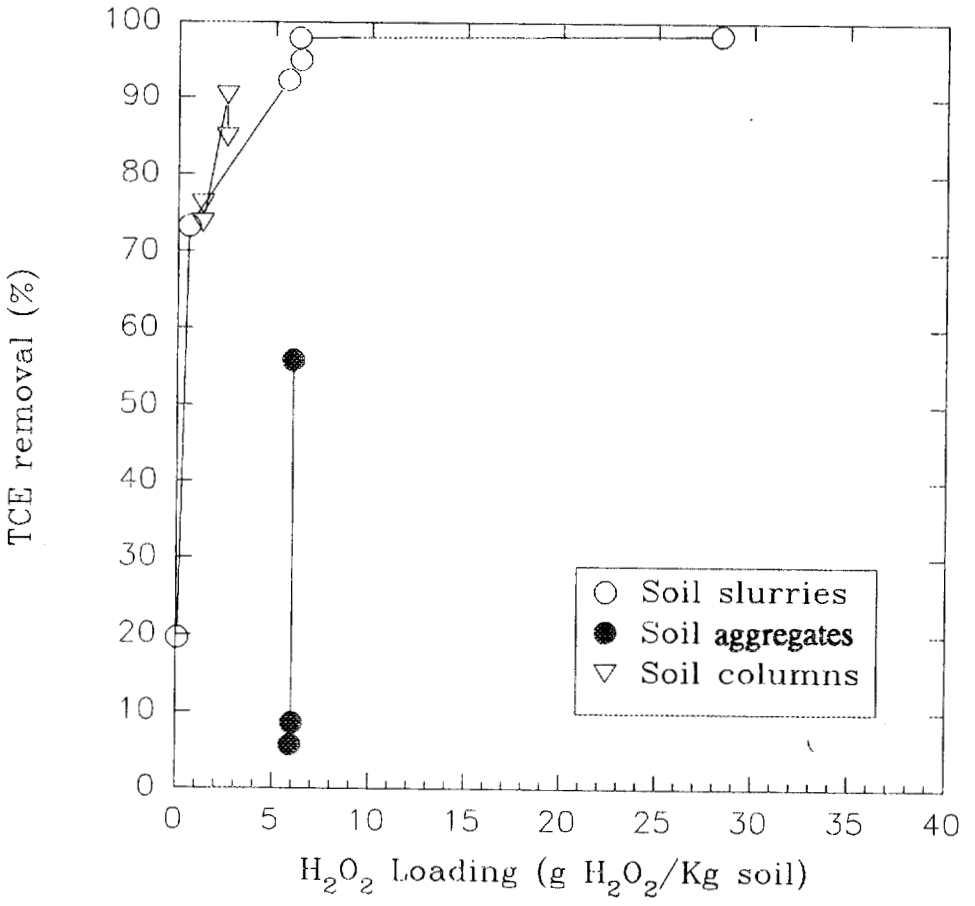

Fig. 28. TCE removal in bench- and pilot-scale studies.

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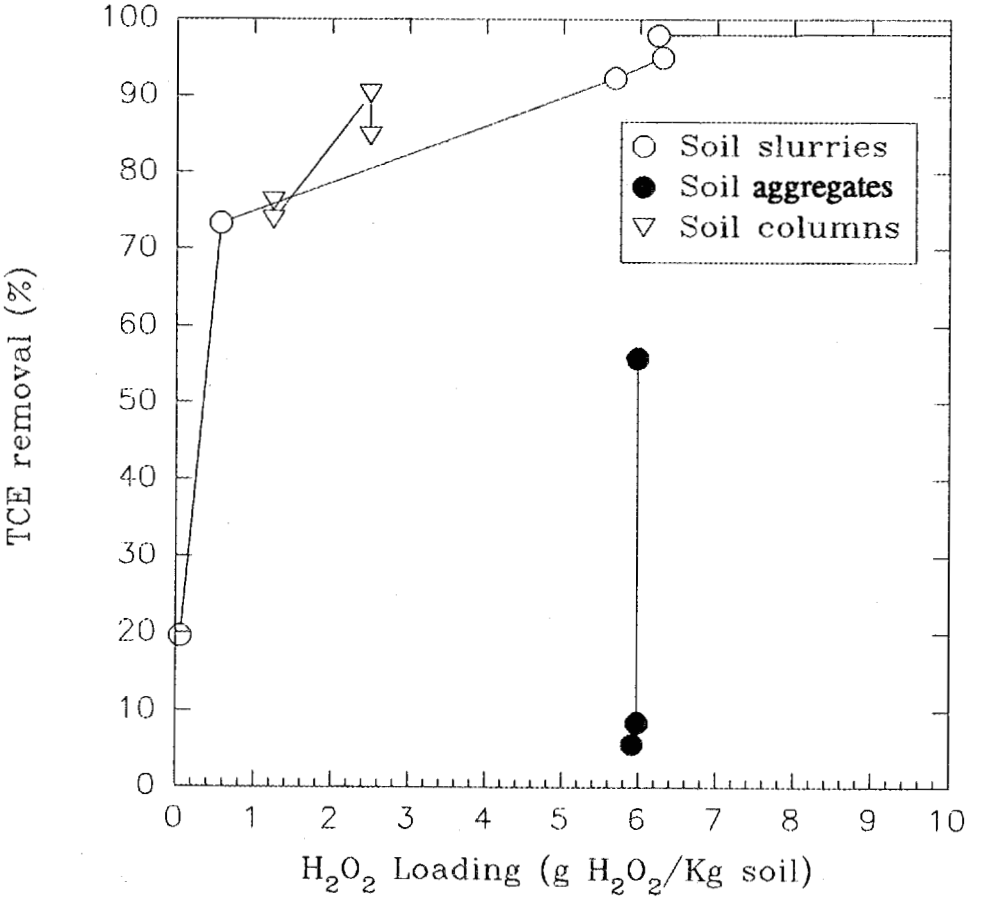

Fig. 29. TCE removal in bench- and pilot-scale studies.

in a separate report (Robinson 1992). A brief discussion of this research is presented in the following paragraph.

TCE destruction due to peroxidation was studied in batch experiments performed using 40-mL VOA vials and in minicolumn (60-mL, 1-in. diam syringes) experiments in which soils were contaminated with radiolabeled (C-14) TCE prior to peroxidation. Due to logistical concerns regarding the handling of X-231B soil, the soil used in the university studies was not from the X-231B site. The objective of these studies was to account for TCE and its oxidation by-products during and after peroxidation. A loam soil with an organic carbon content of ~0.3% was used. Robinson observed TCE reductions as great as 60% and a significant (as much as 60%) volumetric expansion of soils after peroxidation. The radiolabeled TCE studies showed an increase in activity in both carbon and alkaline vapor traps as the H_2O_2 loading was increased from 0 to 25 g H_2O_2/kg. The maximum TCE reduction observed in the radiolabeled TCE studies was 40%. Metals mobilization studies indicated that with repeated peroxidations treatments, some leaching of metals will occur. However, at the H_2O_2 loading levels determined to be effective in the ORNL studies (<5% H_2O_2 strength; <20 g H_2O_2/kg soil), metals mobilization did not appear to occur in the experiments conducted by Robinson.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The bench- and pilot-scale peroxidation studies described herein were conducted to assess the potential for peroxidation as an environmental restoration technique for VOC-contaminated, low permeability, clayey soils such as those found at the Portsmouth 231-B site. The laboratory studies were conducted using a limited number of operating conditions. Only those parameters that could be easily and economically varied in the field were evaluated. As a result of the laboratory investigations, the following conclusions have been reached:

1. H_2O_2 degrades TCE under the conditions maintained during the laboratory studies, with removal rates as high as 98%.

2. TCE degradation efficiency increases with increasing H_2O_2 strength.

3. Peroxidation treatment effeciencies appear to be independent of initial TCE concentration for the range of conditions tested. Treatment efficiency may be more dependent on soil mineralogy and TOC content than initial TCE.

4. Peroxidation is a rapid reaction and is near completion within 2 after H_2O_2 addition.

5. In soil matrices, peroxidation efficiency may be limited by the ability to deliver oxidant to the site of the target contaminant.

6. Soil does not appear to be adversely affected by the addition of a weak H_2O_2 solution (5% strength) at a volumetric level equal to 10% of the pre-treated soil volume.

5.2 RECOMMENDATIONS

On the basis of the results of this investigation, peroxidation of Portsmouth soil contaminated with VOCs appears to be a viable environmental restoration technique. Further experimentation and field demonstration are required to determine the design and operating conditions under which treatment would be optimal.

The ORNL laboratory studies described herein provide information regarding the peroxidation of Portsmouth soil contaminated with TCE under a limited number of operating conditions. Future laboratory studies should be broadened to include more than one soil source and target contaminant.

Specific areas that should be included in future laboratory studies include the following:

1. Evaluate the effects of soil mineralogy and TOC content on peroxidation treatment efficiency.

2. Evaluate effects of temperature and pH on peroxidation treatment efficiency.

3. Evaluate effects of peroxidation on microbial activity.

4. Evaluate effects of peroxidation on metals mobilization.

5. Evaluate effects of peroxidation on other chlorinated and nonchlorinated organics.

6. Investigate alternative methods to deliver H_2O_2 to contaminated soil.

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APPENDIX A

CALCULATION OF TCE DISTRIBUTION IN CONTROL BENCH EXPERIMENT

Question: After water has been added to the contents of a ZHE vessel (posttreatment) how much of the remaining TCE is sorbed onto soil and how much TCE remains in solution (i.e., what percentage of the TCE remaining after treatment can be found in the aqeous phase)?

$$C_T = \alpha C_v \rho_b + \frac{\theta C_L}{\rho_b} + C_s \qquad (1)$$

where

C_T = Total VOC concentration per unit weight dry soil (μg/g)

C_v = Soil vapor phase VOC concentration (μg/cm^3)

C_L = Soil solution VOC concentration (μg/cm^3)

C_S = Soil sorbed VOC concentration (μg/g)

ρ_b = soil bulk density (g/cm^3)

θ = Soil water content (cm^3/cm^3)

α = Soil air content (cm^3/cm^3)

Freundlich isotherm relationships can be used to describe the amount of VOCs (in this case TCE) sorbed from aqueous solutions onto soils:

$$C_S = KC_L^{\frac{1}{n}} \qquad (2)$$

where:
n = empirical constant
K = partition coefficient (mL/g)

For dilute aqueous solutions of VOCs, K is often referred to as the distribution coefficient, K_D, a parameter strongly related to soil organic matter content, f_{OM} and the organic matter/water partition coefficient, K_{OM}

$$K_D = f_{OM} K_{OM} \qquad (3)$$

For TCE K_{OM} = 27.4 mL/g

and the average percent TOC in the soil used to prepare slurries was 0.09 wt%

Thus:

$$K_D = 27.4 \times \frac{0.09}{100} = 0.025 mL/g$$

The following information pertaining to the control study No. 1 is needed to determine the percentage of TCE sorbed to soil particles:

C_L = 216.8 μg/l

m_s = mass of soil in slurry = 25.7 g

C_T = total mass of TCE spiked to slurry = 0.048 mg

V = final volume of fluid in ZHE vessel = 153 mL

Using the experimentally determined value of C_L and assuming that n is equal to 1 (a valid assumption for dilute aqueous TCE solutions), substituting into equation (2) yields:

$$C_S = 0.025 \frac{mL}{g} \times 216.8 \frac{\mu g}{l} \times \frac{1 l}{1000} mL = 0.0054 \frac{\mu g}{g}$$

Calculate mass of TCE sorbed onto known mass of soil in slurry.

$$TCE_{sorbed} = 0.0054 \frac{\mu g}{g} \times 25.7 g = 0.14 \mu g$$

Calculate mass of TCE in aqueous phase in ZHE vessel.

$$TCE_{soln} = 216.8 \frac{\mu g}{l} \times 153 ml \times \frac{1 l}{1000} mL = 33.2 \mu g$$

$$C_{T_{rem}} = 0.14 \mu g + 33.2 \mu g = 33.3 \mu g$$

Percentage of total TCE remaining sorbed to soil can now be calculated:

$$\%TCE_S = \frac{0.14\mu g}{33.3} x\ 100 = 0.42\%$$

This series of calculations reveals that less than 1% of the TCE remaining in the ZHE vessel after extraction with large volumes of deionized water would be expected to be sorbed to soil surfaces. Therefore, it is reasonable to assume that the all (>99%) of the TCE remaining after treatment will be found in the posttreatment aqueous extract.

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