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Hydrogen peroxide decomposition in model subsurface systems

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Abstract

Rates of hydrogen peroxide decomposition, hydroxyl radical production, and oxygen evolution were investigated in silica sand–goethite slurries using unstabilized and stabilized hydrogen peroxide formulations. The goethite-catalyzed decomposition of unstabilized hydrogen peroxide formulations resulted in more rapid hydrogen peroxide loss and oxygen evolution relative to systems containing a highly stabilized hydrogen peroxide formulation. Systems at neutral pH and those containing higher goethite concentrations were characterized by higher rates of hydrogen peroxide decomposition and by more oxygen evolution. The stabilized hydrogen peroxide formulation showed greater hydroxyl radical production relative to the unstabilized formulations. Furthermore, hydroxyl radical production rates were greater at neutral pH than at the acidic pH regimes. The results suggest that when stabilized hydrogen peroxide is injected into the subsurface during in situ bioremediation, naturally occurring minerals such as goethite may initiate Fenton-like reactions. While these reactions may prove to be toxic to microorganisms, they have the potential to chemically oxidize contaminants in soils and groundwater.

Keywords: Goethite; Fenton-like reactions; Hydrogen peroxide; Hydroxyl radicals; Stabilized hydrogen peroxide

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1. Introduction

The contamination of groundwater and subsurface soils remains a significant problem, even after decades of remediation research and implementation. The US EPA, in a survey of 466 public water supply wells, found that one or more volatile organic compounds (VOCs) were detected in 16.8% of small water systems and 28% of large water systems. The VOCs found most often were trichloroethylene (TCE) and perchloroethylene (PCE) [1]. In addition, a survey of 7000 wells in California showed that approximately 1500 contained detectable concentrations of organic chemicals [2]. The most common chemicals detected were PCE, TCE, chloroform, 1,1,1-trichloroethane and carbon tetrachloride.

Many groundwater restoration processes have been ineffective, including pump and treat systems, because they are limited by contaminant desorption from subsurface solids and dissolution from nonaqueous phase liquids (NAPLs) [3]. However, in situ remediation processes have been demonstrated to be viable methods of groundwater decontamination. Both biotic and abiotic processes have been used for subsurface restoration. In situ bioremediation has been commonly promoted through the use of indigenous microorganisms with addition of the most effective electron acceptor and cometabolite. The most common application of in situ chemical oxidation has been the injection of hydrogen peroxide and catalysts to promote Fenton-like reactions.

In situ bioremediation has been used extensively with wide-ranging conditions of oxidation–reduction potential, electron acceptors, cometabolites, etc. Aerobic bioremediation has been used to degrade a wide range of reduced organic compounds such as alkylbenzenes, polycyclic aromatic hydrocarbons, heterocyclic organic compounds, and some chlorinated solvents with a low degree of chlorine substitution [4]. To enhance aerobic microbial growth during bioremediation, oxygen is often supplied to the groundwater. Several methods have been used to supply and maintain dissolved oxygen including air sparging, ozone addition, liquid or gaseous oxygen addition, and hydrogen peroxide injection [5]. Of these methods, the use of hydrogen peroxide was once popular because it is relatively inexpensive, is nonpersistent, and is unlikely to be a health hazard if used properly [6,7]. It is more than seven orders of magnitude more soluble in water than molecular oxygen and has more potential for supplying dissolved oxygen downgradient [8]. However, Spain et al. [9] found that hydrogen peroxide decomposed rapidly in biofilms surrounding injection wells; as a result, the use of hydrogen peroxide as an oxygen source has decreased dramatically.

The most common application of an abiotic transformation in subsurface remediation has been the injection of hydrogen peroxide and catalysts, such as iron (II) sulfate, to promote the generation of hydroxyl radicals ($OH\cdot$) through so-called Fenton-like reactions:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH\cdot \quad (1)$$

Hydroxyl radicals react with many organic compounds with rate constants of 10^9–10^{10} $M^{-1}\ s^{-1}$, which is near the diffusion-controlled rate in water; they are effective in oxidizing TCE, PCE, aromatic hydrocarbons and other halogenated alkenes and aromat-

ics [10]. Recent studies by Ravikumar and Gurol [11], Miller and Valentine [12] and Watts et al. [13] have shown that naturally occurring iron minerals in soils are also capable of promoting Fenton-like reactions when hydrogen peroxide is added to a soil slurry. In situ application of Fenton-like reactions has recently been implemented at full scale in treating gasoline-contaminated groundwater [14]. Hydrogen peroxide and iron catalysts are injected upgradient from the plume with cleanup usually complete within weeks [15].

Whether hydrogen peroxide is added to the subsurface for in situ bioremediation or in situ chemical oxidation, it decomposes through several mechanisms, including enzymatic decomposition through catalase and reactions with soluble iron or iron oxides, which may affect both biological and chemical treatments that use hydrogen peroxide. Several formulations have been developed to stabilize hydrogen peroxide because of its rapid decomposition in the presence of transition elements, metal oxyhydroxides, and soil surfaces. Phosphate is most commonly used in bioremediation formulations because it is not only an inorganic stabilizer, but also a bacterial nutrient. Phosphate inhibits hydrogen peroxide decomposition by lowering the dissolved metal concentrations through either precipitation reactions or, in the presence of excess phosphate, conversion to relatively stable complexes [6]. Once the iron is complexed, it is considered nonreactive with hydrogen peroxide. Phosphate also functions as a radical scavenger because it quenches hydroxyl radicals and terminates chain decomposition reactions [16]. However, phosphate does not inhibit biological decomposition of hydrogen peroxide by the bacterial enzyme catalase [17].

Although mineral-catalyzed hydrogen peroxide decomposition has been studied for the degradation of contaminants such as PCE [18], quinoline [19] and chlorobenzenes [20], a detailed investigation of oxygen species formed during mineral-catalyzed hydrogen peroxide decomposition, including molecular oxygen and hydroxyl radicals, has not been reported. Mineral-catalyzed hydrogen peroxide decomposition may provide sufficient molecular oxygen to promote microbial growth during lag growth phases, or, alternatively, produce a sufficient flux of hydroxyl radicals to destroy contaminants in the system or inhibit microbial growth. The purpose of this research was to quantify the rates of mineral-catalyzed hydrogen peroxide decomposition, oxygen evolution and hydroxyl radical production using extremes of hydrogen peroxide stabilization. Sensitivity to other parameters such as pH and iron mineral concentration was also evaluated.

2. Materials and methods

2.1. Materials

Nitrobenzene was obtained from Aldrich (Milwaukee, WI) and hexane was purchased from Fisher Scientific (Fair Lawn, NJ). Hydrogen peroxide (50%, technical grade) was provided gratis by Solvay Interox (Deer Park, TX). The double deionized water (> 18 mΩ cm) used in all reactions was purified with a Barnstead Nanopure II Ultrapure system.

2.2. Model subsurface materials

A combination of silica sand and goethite (α-FeOOH) was used as a model subsurface material. Washed silica sand (80–100 mesh; 0.15–0.18 mm) was obtained from J.T. Baker (Phillipsburg, NJ). Goethite (100–200 mesh; 0.075–0.15 mm) was obtained from D.J. Minerals (Butte, MT). The purity of the goethite and silica sand was qualitatively examined with a Cameca electron microprobe [21]. Silica sand characteristics are summarized in Table 1. Less than 1% of the goethite was silica (SiO_2), sulfur, phosphorous, or manganese.

2.3. General procedures

The model subsurface material used for hydrogen peroxide decomposition and hydroxyl radical production experiments consisted of 10 g of 7% goethite in silica sand (w/w). Because goethite is 71% Fe, the 7% goethite mixture contained 5% iron in the sand/mineral system, which is within the range of typical iron oxyhydroxide concentrations of subsurface materials [22]. Silica sand alone was used as a control. Experiments were conducted in 40 ml borosilicate vials fitted with PTFE septum caps at room temperature (20 ± 2°C) without agitation. These conditions are representative of groundwater systems with a low hydraulic conductivity.

2.4. Hydrogen peroxide decomposition

Separate experimental units conducted in triplicate vials were used to monitor hydrogen peroxide decomposition at a minimum of five time periods over 6 days. The

Table 1
Concentrations of trace elements in the silica sand

Element	Concentration (mg kg^{-1})
Na	20
Mg	40
Al	150
Ti	3
Mn	2
Fe	40
Sr	2
Y	< 1
Zr	< 1
Ba	10
La	1
Ce	< 1
Pr	< 1
Gd	< 1
Pb	3
Th	< 1
U	< 1

pH was monitored daily and adjusted accordingly. The reactions were stopped by filtering the sand slurry through a 0.45 μm membrane filter. An aliquot of the filtrate was analyzed for residual hydrogen peroxide while the remainder of the sample was analyzed for soluble iron. Two hydrogen peroxide formulations of widely differing stabilities were used: unstabilized hydrogen peroxide (100 mg l^{-1}), and the highly stabilized hydrogen peroxide formulation used by Raymond et al. [23]. The latter consisted of 100 mg l^{-1} hydrogen peroxide containing 27.3 g l^{-1} of ammonium sulfate $[(NH_4)_2SO_4]$ and 28.6 g l^{-1} of monobasic sodium phosphate $(NaH_2PO_4 \cdot 7H_2O)$. Experiments investigating the effect of varying goethite concentration on hydrogen peroxide stability used goethite mixtures containing 2.5%, 5%, 7.5% and 10% iron, and were conducted with unstabilized hydrogen peroxide at pH 7.

2.5. Oxygen evolution

The rate of goethite-catalyzed oxygen generation was determined in 300 ml biochemical oxygen demand (BOD) bottles using the same proportion of solids and hydrogen peroxide as in the hydrogen peroxide stability experiments. Separate samples containing 100 mg l^{-1} hydrogen peroxide (unstabilized or stabilized) were adjusted to pH 4, 5, 6, or 7 using H_2SO_4 or NaOH and added to the BOD bottle. Nitrogen gas was then sparged through the solution for 10 min to remove the dissolved oxygen. The sparger was removed and additional hydrogen peroxide solution was added to bring the concentration back to 100 mg l^{-1}. The solutions were then mixed by inverting the BOD bottle repeatedly for 1 min after which the first dissolved oxygen reading was taken. Using a dissolved oxygen meter, readings were taken at 1 h intervals over a 6 h period. The effect of varying goethite mineral concentrations (2.5%, 5%, 7.5% and 10% as iron) on oxygen evolution was also evaluated using unstabilized hydrogen peroxide at pH 7.

2.6. Hydroxyl radical production

Nitrobenzene was used as a hydroxyl radical probe because it reacts rapidly with hydroxyl radicals ($k_{OH\cdot} = 3.9 \times 10^9$ M^{-1} s^{-1}) [24]. For the hydroxyl radical production assays, a solution containing 1.5 μmol l^{-1} nitrobenzene and 30 μmol l^{-1} 1-octanol (a hydroxyl radical scavenger) in 100 mg l^{-1} of stabilized or unstabilized hydrogen peroxide was added to each 40 ml vial. Separate experiments were adjusted to pH 4, 5, 6, or 7. The pH was monitored daily and adjusted as necessary. Nitrobenzene was analyzed at 0, 12, 24, 36, 48, and 72 h by extracting each vial with 5 ml of hexane. The vials were then placed on a wrist shaker for 24 h followed by centrifugation for 5 min. The hexane supernatant fluid was then analyzed for nitrobenzene by gas chromatography.

2.7. Analysis

Hydrogen peroxide concentrations were measured using a Bausch and Lomb Spectronic 70 spectrophotometer after color development with titanium sulfate [25]. Soluble iron concentrations were analyzed using flame methodology on a Perkin-Elmer 3100

atomic absorption spectrophotometer. Dissolved oxygen was determined using a YSI model 50B dissolved oxygen meter. Residual nitrobenzene extracted into hexane was analyzed using a Hewlett-Packard 5890A gas chromatograph with electron capture detector and a Supelco PTE-5 glass capillary column (0.32 mm i.d. × 15 m length). The chromatographic conditions were initial oven temperature 100°C, final oven temperature 250°C, program rate 5°C min^{-1}, injector temperature 225°C, detector temperature 300°C, and nitrogen carrier gas flow rate 3.5 ml min^{-1}.

3. Results and discussion

3.1. Hydrogen peroxide decomposition

Hydrogen peroxide decomposition in the unstabilized goethite–sand system at the four pH regimes investigated is shown in Fig. 1. Hydrogen peroxide decomposition rates were rapid in the first few days and decreased with time. The rates were approximately an order of magnitude greater than in the sand-only controls. The data were modeled empirically using pseudo first-order kinetics, consistent with other studies that have shown a pseudo first-order rate for decomposition of hydrogen peroxide by aquifer solids [5,26]. Using the integral method of rate analysis, plots of the natural log of concentration as a function of time were linear, with $r^2 \geq 0.9$. Hydrogen peroxide decomposition data followed pseudo first-order kinetics for all of the conditions employed, and the first-order rate constants for the four pH regimes are also shown in

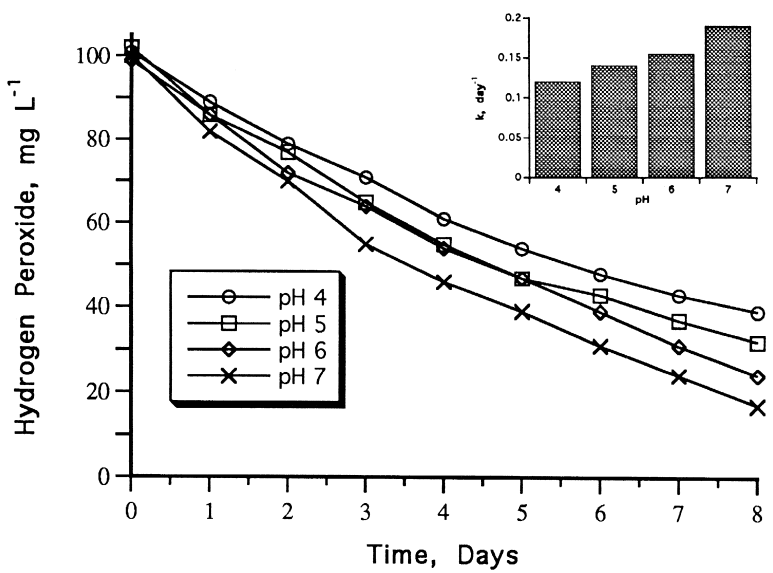

Fig. 1. Decomposition of unstabilized hydrogen peroxide at four pH regimes with the corresponding first-order rates of hydrogen peroxide decomposition.

Fig. 1. The decomposition of the stabilized hydrogen peroxide formulation over a pH range of 4 to 7 is shown in Fig. 2. The results of Figs. 1 and 2 indicate that the rates of hydrogen peroxide decomposition for both the stabilized and unstabilized formulations increased as the pH increased. These results agree with the information of Schumb et al. [25] that hydrogen peroxide is more stable at low pH. However, the stabilized formulation containing phosphate decomposed more slowly than the unstabilized hydrogen peroxide at each pH. Phosphate appears to inhibit the hydrogen peroxide decomposition reactions that are catalyzed by mineral surfaces, possibly by affecting the surface charge or redox potential at the mineral surface. Therefore, both low pH and the presence of phosphate promoted the stability of hydrogen peroxide and slowed its decomposition.

The effect of goethite concentration (as % iron) on unstabilized hydrogen peroxide decomposition at pH 7 is shown in Fig. 3. The data show that the hydrogen peroxide decomposition rate increased with the mass of goethite in the system and that, in the absence of other catalysts, goethite controlled the rate of hydrogen peroxide decomposition.

Soluble iron was measured in the goethite and control systems to determine whether it was present in sufficient concentration to catalyze hydrogen peroxide decomposition. Concentrations of soluble iron in the goethite and sand control systems at pH 4 over the course of a typical experiment are listed in Table 2. These results show that the concentration of soluble iron in the goethite–sand system was no greater than in the

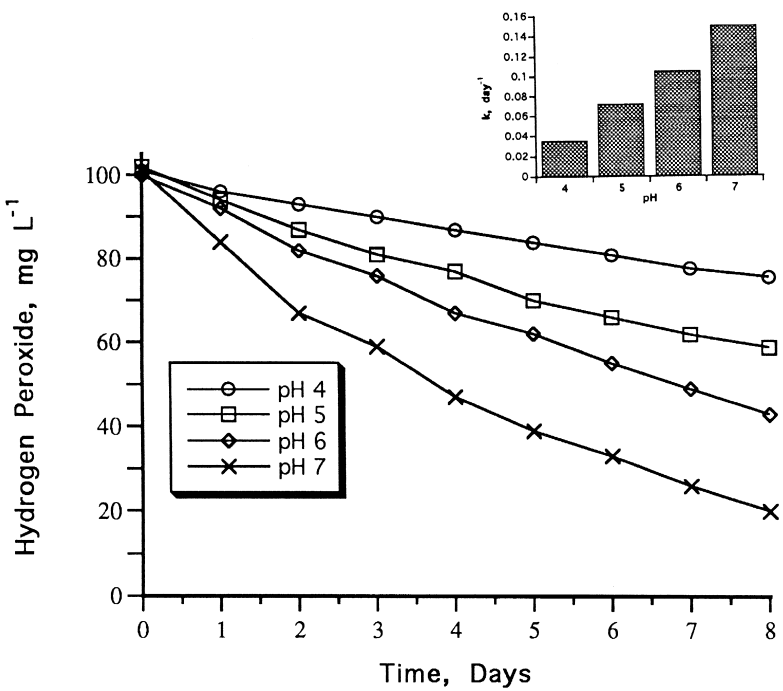

Fig. 2. Decomposition of stabilized hydrogen peroxide at four pH regimes with the corresponding first-order rates of hydrogen peroxide decomposition.

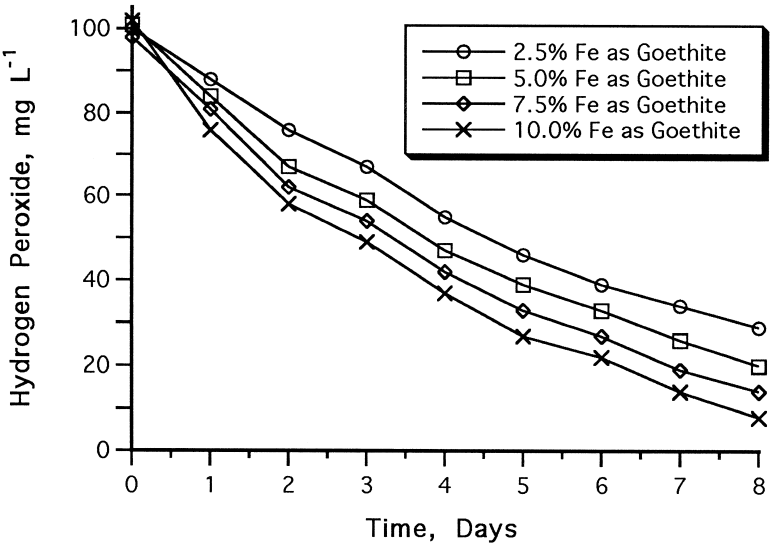

Fig. 3. Effect of goethite concentration on hydrogen peroxide decomposition rates for unstabilized hydrogen peroxide at pH 7.

sand control, although goethite–sand systems catalyzed hydrogen peroxide decomposition at a rate approximately an order of magnitude greater than the sand controls. Because the only difference between the controls and goethite systems was the presence of goethite, the additional hydrogen peroxide decomposition in the goethite systems was the result of heterogeneous catalysis by the mineral.

3.2. Oxygen evolution

Oxygen evolution at pH regimes of 4, 5, 6 and 7 for the unstabilized and stabilized hydrogen peroxide formulations are shown in Figs. 4 and 5, respectively. The rate of

Table 2
Concentrations of soluble iron in goethite and sand control systems at pH 4

Time (day)	Soluble iron (mg l^{-1})	
	Sand control	Sand–goethite system
0	0.051	0.048
1	0.050	0.053
2	0.052	0.050
3	0.050	0.055
4	0.058	0.056
5	0.053	0.047
6	0.058	0.056
7	0.051	0.046
8	0.053	0.055

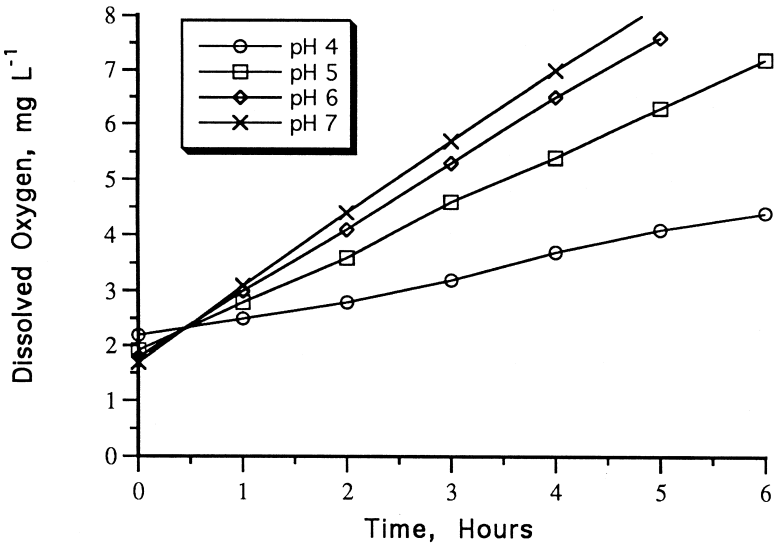

Fig. 4. Oxygen evolution for unstabilized hydrogen peroxide in the goethite–silica sand system at four pH regimes.

oxygen evolution was linear for all pH regimes and hydrogen peroxide formulations, with $r^2 \geq 0.9$, indicating zero-order kinetics. For both formulations, the rate of oxygen production increased as a function of pH, which is in agreement with previous work that

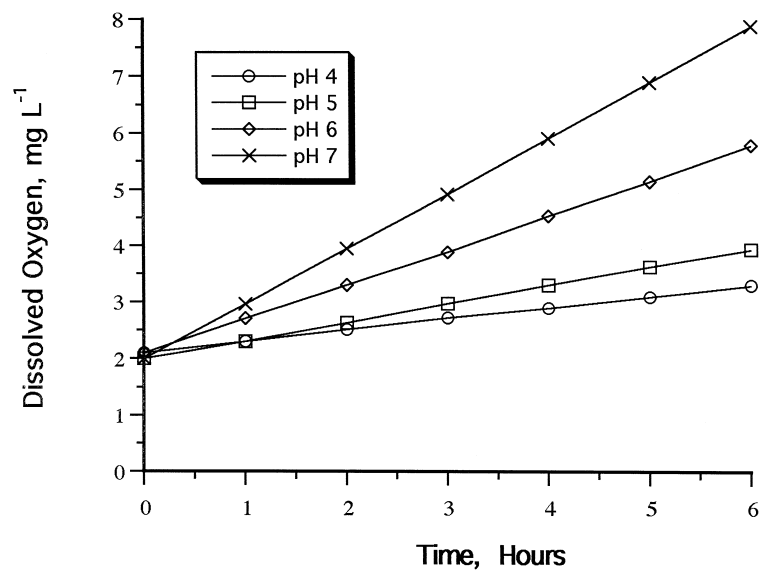

Fig. 5. Oxygen evolution for stabilized hydrogen peroxide in the goethite–silica sand system at four pH regimes.

showed that oxygen evolution is the predominant route of hydrogen peroxide decomposition at neutral pH [24]. For each pH regime, the rates of oxygen production were also higher with unstabilized hydrogen peroxide than with stabilized hydrogen peroxide.

A comparison of zero-order oxygen evolution rates for unstabilized hydrogen peroxide at pH 7 with varying goethite mineral concentrations is shown in Fig. 6. The rate of oxygen evolution increased with the iron oxide concentration. Because the soluble iron concentrations of the sand controls were not significantly different than that of the goethite sand systems, these data indicate that molecular oxygen evolution was a result of heterogeneous catalysis of hydrogen peroxide on mineral surfaces rather than catalysis by soluble iron.

3.3. Hydroxyl radical production

To measure OH· production, nitrobenzene was used as a probe compound in reactions under pH regimes from 4 to 7. Typical nitrobenzene decomposition at pH 7 in the presence of unstabilized and stabilized hydrogen peroxide is shown in Figs. 7 and 8, respectively. In both cases, nitrobenzene decomposition followed a typical first-order reaction with $r^2 > 0.95$. The stabilized hydrogen peroxide system was characterized by a more rapid rate of nitrobenzene degradation relative to the unstabilized hydrogen peroxide system.

Steady-state hydroxyl radical production rates for different conditions were calculated based on the kinetic approach and mechanism outlined by Zepp et al. [27]:

$$v_{\mathrm{OH}\cdot} = k_{\mathrm{expt}}(\Sigma k_{\mathrm{OH}\cdot}[S_i])/k_{\mathrm{OH}\cdot,\mathrm{P}} \quad (2)$$

where k_{expt} = experimentally determined first order rate constant for nitrobenzene loss (s^{-1}); $v_{\mathrm{OH}\cdot}$ = rate of hydroxyl radical production (M s^{-1}); $k_{\mathrm{OH}\cdot}$ = second-order rate

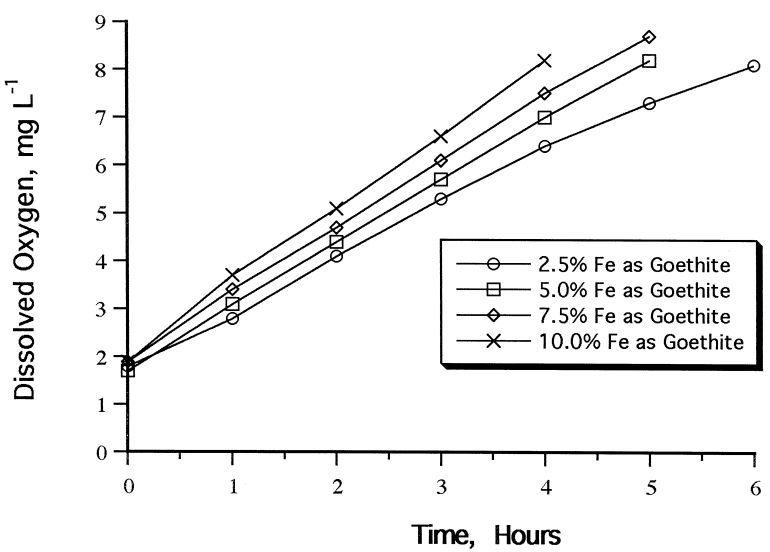

Fig. 6. Effect of goethite concentration on the rate of oxygen evolution for unstabilized hydrogen peroxide at pH 7.

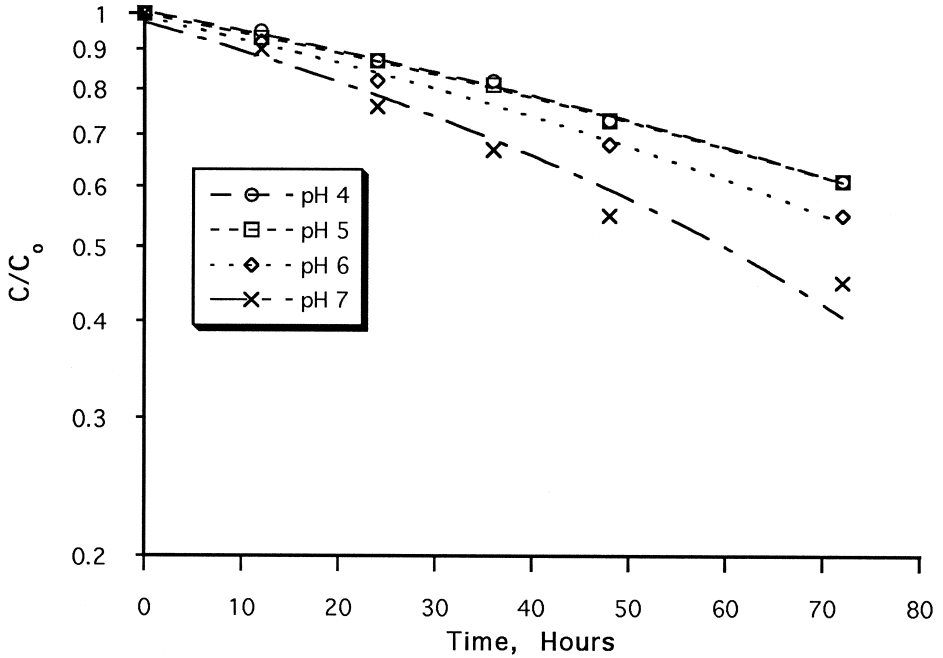

Fig. 7. Decomposition of nitrobenzene in goethite–silica sand systems with unstabilized hydrogen peroxide at pH 4, 5, 6 and 7 (1.5 μmol l^{-1} of nitrobenzene, 30 μmol l^{-1} of 1-octanol and 100 mg l^{-1} hydrogen peroxide).

constant (M^{-1} s^{-1}); $[S_i]$ = hydroxyl radical scavenger concentration (M); $k_{OH\cdot,P}$ = second-order rate constant for reaction of OH· with the probe P (M^{-1} s^{-1}).

Hydroxyl radical production rates for both unstabilized and stabilized hydrogen peroxide under different pH regimes are listed in Table 3. Hydroxyl radical production rates for the conditions studied ranged from 1.77×10^{-8} to 2.94×10^{-8} M s^{-1}. For each pH regime, stabilized hydrogen peroxide showed a higher rate of hydroxyl radical production than did the unstabilized system, in spite of the lower hydrogen peroxide decomposition rates in the stabilized systems. Such a phenomenon may be due to accumulation of $H_2PO_4^-$ and HPO_4^{2-} at the mineral surface that may have resulted in a mineral–phosphate surface complex or charge neutralization at the mineral surface, providing enhanced hydroxyl radical production or electron transfer processes [28].

The relatively high rates of hydroxyl radical production in goethite-catalyzed hydrogen peroxide systems have important implications for both chemical and biological remediation of contaminated soils and groundwater. Because of the limited water solubility of molecular oxygen, stabilized and unstabilized hydrogen peroxide formulations have been used to provide a mechanism for introducing dissolved oxygen downgradient in groundwater systems to enhance biodegradation reactions:

$$H_2O_2 \xrightarrow{Fe^{3+}} \frac{1}{2}O_2 + H_2O \quad (3)$$

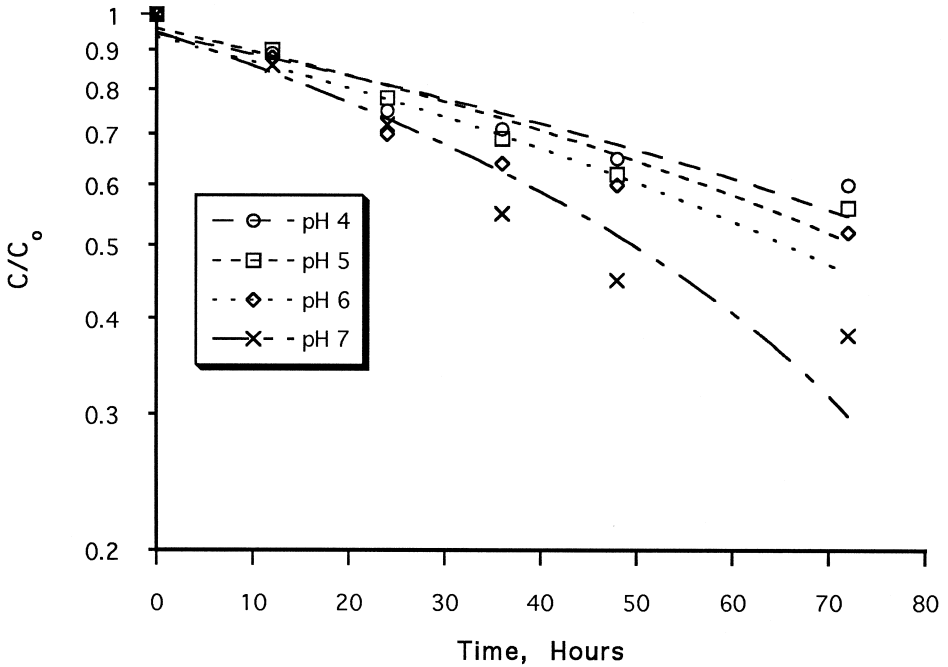

Fig. 8. Decomposition of nitrobenzene in goethite–silica sand systems with stabilized hydrogen peroxide at pH 4, 5, 6, and 7 (1.5 μmol l^{-1} of nitrobenzene, 30 μmol l^{-1} of 1-octanol and 100 mg l^{-1} hydrogen peroxide).

Phosphate is commonly used as a stabilizer in these systems because it complexes and precipitates soluble iron, which was thought to be the only significant Fenton's catalyst in contaminated groundwater systems. However, because mineral-catalyzed hydrogen peroxide decomposition generates hydroxyl radicals, microbial viability in these systems may be affected. Generation of hydroxyl radicals catalyzed by soil minerals may result in toxicity to the microorganisms that are responsible for contaminant remediation [29]. Several studies have shown that uncatalyzed hydrogen peroxide is toxic to microorganisms, with toxicity to mixed cultures of bacteria reported at concentrations of 3.2 to 500 mg l^{-1} [8]. In many of these toxicity assays, the presence of soluble iron and iron oxyhydroxides was not documented, and the occurrence of Fenton-like reactions may be

Table 3
Hydroxyl radical production rates with stabilized and unstabilized H_2O_2 under different pH regimes

	$OH\cdot$ production rates $\times 10^{-8}$ (M s^{-1})	
	Stabilized H_2O_2	Unstabilized H_2O_2
pH 4	1.79	1.77
pH 5	2.05	1.80
pH 6	2.15	2.04
pH 7	2.94	2.58

a reason for the widely ranging toxicity of hydrogen peroxide formulations. Therefore, hydroxyl radicals generated by mineral-catalyzed hydrogen peroxide decomposition may be toxic to existing microbial populations at cleanup sites.

In the past, Fenton's reactions have almost always been conducted under acidic pH regimes to maintain the solubility of the iron catalyst [10]. One of the concerns in using Fenton's processes for soil and groundwater remediation has been the need to pH adjust large volumes of soils or groundwater [30]. However, because mineral-catalyzed Fenton-like reactions are not dependent upon maintaining soluble iron, hydroxyl radicals are generated at neutral pH regimes. If such reactions can be promoted in soils of varying mineralogy and textural classes, the Fenton's process could be implemented more effectively and economically.

Spain et al. [9] found that stabilized hydrogen peroxide decomposed rapidly in biofilms surrounding injection wells when used as an oxygen source, and subsequently its use for in situ bioremediation of groundwater decreased substantially. However, our results indicate that Fenton-like transformations can be catalyzed by naturally occurring iron minerals in the absence of soluble iron, and that the use of stabilized hydrogen peroxide for such reactions can result in effective stoichiometry of contaminant oxidation. Khan and Watts [18] also documented the oxidation of PCE in model groundwater systems using mineral-catalyzed reactions with hydrogen peroxide concentrations as low as 0.1 mM. Therefore, the use of stabilized hydrogen peroxide for in situ abiotic oxidation of contaminants deserves further investigation at full scale. Such a system has the potential for oxidizing biorefractory and sorbed contaminants [13], and could yield a high degree of chemical process control through varying degrees of chemical stabilization combined with physical process control through a matrix of injection networks.

4. Conclusions

Sand slurries containing the iron mineral goethite and unstabilized or highly stabilized hydrogen peroxide were investigated for hydrogen peroxide decomposition, oxygen evolution, and hydroxyl radical generation. The rate of hydrogen peroxide decomposition was decreased by the addition of the stabilizer monobasic sodium phosphate. Decomposition was most rapid at neutral pH for both unstabilized and stabilized hydrogen peroxide formulations. Hydrogen peroxide decomposition rates and oxygen evolution rates increased with increasing iron mineral content of the systems. Because of the minimal presence of soluble iron in the iron mineral systems, hydrogen peroxide decomposition and oxygen evolution resulted from reactions involving the iron oxyhydroxide surfaces. As the concentration of iron mineral increased in these systems, so did the reaction rates, suggesting that the rate limiting factor for these reactions is the availability of iron mineral surfaces.

The steady state hydroxyl radical production rates were higher in the phosphate-stabilized system than in the unstabilized system, even though the rates of hydrogen peroxide decomposition and oxygen production were greater with the unstabilized system. These results indicate that iron minerals can serve as catalysts for Fenton-like reactions in place of soluble iron, raising the possibility of in situ Fenton-like treatment

of contaminated soils and groundwater using naturally occurring soil minerals. However, a high rate of production of hydroxyl radicals may result in toxicity to bacteria being used to promote bioremediation. Future studies will further optimize conditions for in situ Fenton-like reactions in soils, and investigate the effect of such reactions on commonly used bioremediation microbes.

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