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Use of hydrogen peroxide as an oxygen source for *in situ* biodegradation
Part I. Field studies

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Abstract

Hydrogen peroxide, which is commonly used as an oxygen source for *in situ* biodegradation, tends to decompose into water and oxygen gas. The rate of this decomposition relative to the oxygen demand of the contaminated aquifer is important to the success of an *in situ* process. The objective of this study, which was performed at Eglin Air Force Base in northwest Florida, was to evaluate *in situ* hydrogen peroxide stability and biological oxygen utilization for the biodegradation of JP-4 jet fuel. Hydrogen peroxide was injected into the subsurface, concentrations of hydrogen peroxide and oxygen were measured in monitoring wells, and *in situ* tests were conducted to determine hydrogen peroxide decomposition and oxygen use rates at the well locations. Because the rates of hydrogen peroxide decomposition were consistently found to be much higher than the rates of oxygen utilization, it is unlikely that any significant part of the oxygen from the hydrogen peroxide in excess of that initially required to saturate the groundwater was used to degrade jet fuel.

Introduction

Most hydrocarbons are biodegradable by soil microorganisms under aerobic conditions. In field applications of *in situ* bioremediation to treat petroleum hydrocarbon-contaminated soil and groundwater, the limiting factor is generally oxygen. Because of the low aqueous solubility of oxygen, hydrogen peroxide is commonly used as an oxygen source for saturated zone applications. Hydrogen peroxide is miscible in water and decomposes to release water and oxygen:

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2 \quad (1)$$

However, if the rate of oxygen generation by peroxide decomposition exceeds

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the rate of oxygen utilization, oxygen may escape in gaseous form because of its limited solubility in water. Gaseous oxygen may form bubbles which may not be transported in groundwater and the result may be inefficient oxygen delivery in the contaminated zone.

Phosphate is commonly used in nutrient formulations in an effort to decrease the rate of peroxide decomposition in groundwater applications [1]. The effectiveness of phosphate in stabilizing peroxide injected into an aquifer has not been well established and conflicting results have been reported by different workers [2–5].

In 1986, the United States Air Force Engineering and Services Center initiated a demonstration of the enhanced *in situ* bioreclamation process using phosphate as the peroxide stabilizer [4,6]. Early in this study, rapid decomposition of peroxide was observed and no peroxide was detected in monitoring wells as little as 2 feet (0.6 m) downgradient from the injection points. To investigate further the stability of hydrogen peroxide, the present study was designed and conducted in 1988 on a small portion of the contaminated site. The objectives of this study were to evaluate *in situ* hydrogen peroxide stability and biological oxygen utilization.

Site description

A portion of the contaminated site at Eglin Air Force Base in northwest Florida was chosen for the present study. The site is underlain by poorly consolidated sediments to a depth of approximately 40 feet (12 m). The sediments, which consist mainly of fine- to coarse-grained quartz sand, overlie the relatively impermeable Pensacola Clay Formation. The surficial aquifer is unconfined and found at a depth of 2 to 6 feet (0.6 to 1.8 m) below land surface.

The Air Force first detected a 20,000- to 40,000-gallon (80,000- to 150,000-£) JP-4 jet fuel spill in 1984. Nonaqueous phase liquid (NAPL) fuel was found to be present on the water table. In monitoring wells NAPL thicknesses of 1 to 2 feet (0.3 to 0.6 m) were observed [7]. Initial skimming operations recovered an estimated 7,400 gallons (28,000 l) of NAPL.

At the time of the present study, no NAPL was observed; however, the site was still hydrocarbon-contaminated. A typical profile of concentrations of organic and inorganic constituents of soils from the study area is presented in Table 1; the location from which this sample was collected is illustrated in Fig. 1. The sample was collected shortly before this field study was initiated.

Experimental design

As a part of the Downey et al. [4] and Hinchee et al. [6] studies, hydrogen peroxide was injected at concentrations of up to 500 mg/L into injection wells, injection galleries, and a spray area. Bench-scale treatability testing was con-

TABLE 1

Chemical decomposition of soils collected from the vicinity of the hydrogen peroxide test (location indicated on Fig. 1) at the Eglin Air Force Base site (mg/kg)

Sample depth below surface (feet)[a]	Total petroleum hydrocarbons (EPA Method 418.1)	Calcium	Iron	Hydraulic condition
1 (0.3)	14	1.8	590	Unsaturated
2 (0.6)	1800	0.77	400	Unsaturated
3 (0.9)	3600	1.1	500	Unsaturated
4 (1.2)	1300	0.45	25	Saturated
5 (1.5)	2100	0.48	25	Saturated
6 (1.8)	1700	0.56	32	Saturated
7 (2.1)	24	0.35	37	Saturated

[a]The values in parentheses give the sample depth in meters.

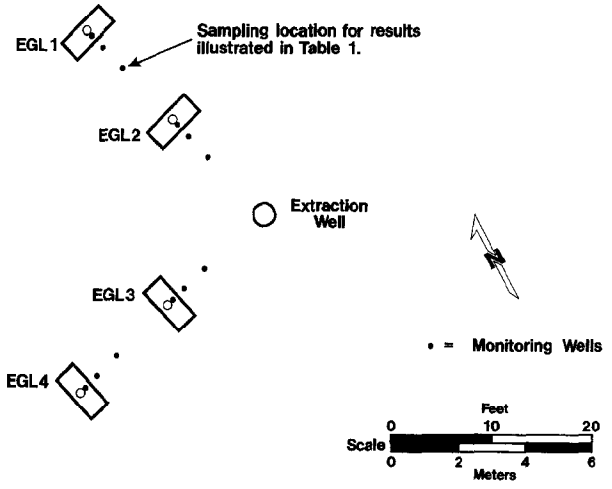

Fig. 1. Layout of the hydrogen peroxide study site (sampling location for results illustrated in Table 1).

ducted by the hydrogen peroxide supplier prior to the field effort. This testing indicated that in untreated soils, the hydrogen peroxide first order half-life was 370 minutes, increasing to 780 minutes upon repeated exposure to hydrogen peroxide. In the laboratory this could be increased to 2,400 min by pretreatment with Restore® 375, a phosphate-containing nutrient mixture [6]. However, after several months of injection, no hydrogen peroxide was observed in any of the monitoring wells, some as close as 2 feet (0.6 m) to the point of injection. During exploratory excavation of the infiltration galleries, bubbles were observed in the hydrogen peroxide-laden injection water. Analysis of soil gas samples collected from three locations immediately above the injection

TABLE 2

Composition of gas samples collected immediately above the full scale injection galleries (%)

Compound	Sample			Background air
	1	2	3	
Oxygen	82	83	36	21
Nitrogen	16	16	59	78
Carbon dioxide	1.5	1.0	5.4	<1.0
Methane	<0.2	<0.2	<0.2	<1.0

TABLE 3

Chemical characteristics of injection waters[a] (mg/L)

Compound	Tap water	System water
Iron	<0.03	2.8
Aluminum	0.09	<0.1
Magnesium	15.4	2.3
Manganese	<0.02	0.079
Sodium	14	49
Calcium	24	19
Alkalinity	120	28
Chloride	5.1	75
Fluoride	0.3	<0.1
Inorganic carbon	30.7	10.8
Filterable residue	150	220
Total organic carbon	<1	15

[a]Tap water was injected into EGL-1 and EGL-2; System water was injected into EGL-3 and EGL-4.

galleries indicated oxygen concentrations well above atmospheric levels (Table 2). These injection galleries were constructed as part of the full-scale *in situ* biodegradation study, and were installed at a different location and prior to the injection galleries installed for this study.

After the apparent failure of hydrogen peroxide to move into the aquifer because of its rapid decomposition, as evidenced by elevated oxygen concentration in soil gas above the infiltration galleries, a smaller-scale system of injection galleries and monitoring wells was installed. Four treatments were used to evaluate the effect of various operating parameters on peroxide stability and oxygen utilization:

Injection gallery	Treatment
EGL1	Tap water
EGL2	Tap water, soils pretreatment with Restore® 375

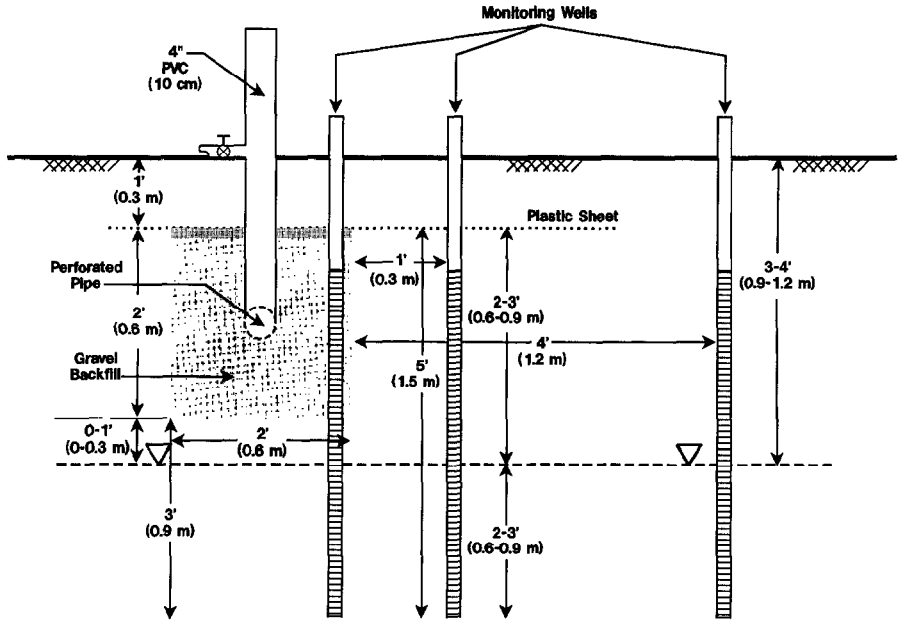

Fig. 2. Detail of the infiltration gallery construction.

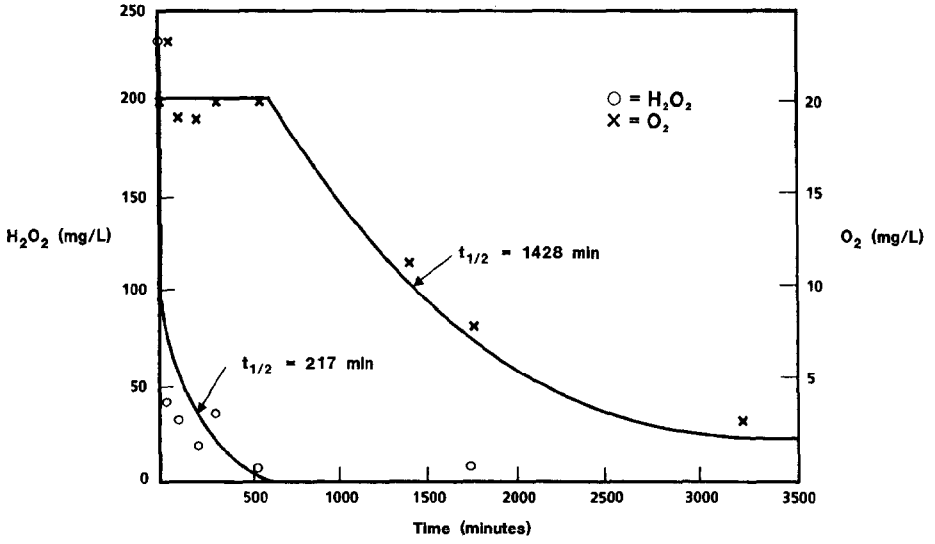

Fig. 3. Results of a June 15, 1988, *in situ* test at EGL1.

EGL3 System water, soils pretreatment with Restore® 375
EGL4 System water.

Tap water consisted of Eglin Air Force Base potable water passed through a 55-gallon (210-L) activated carbon cylinder. System water was groundwater

extracted from the site and aerated at a 25:1 air-to-water ratio in a basin with a 66-minute retention time. The partially clarified groundwater was filtered before use. The two different water supplies are compared in Table 3. The flow to enter each gallery was 2 gallons per minute (gpm) (7.6 L/min). Water was withdrawn from the extraction well at 10 gpm (38 L/min). Soil pretreatment consisted of injecting Restore® 375 (a commercial nutrient formulation of 50% ammonium chloride and a blend of 20% disodium phosphate, 17.5% sodium tripolyphosphate and 12.5% monosodium phosphate) at each gallery before initiating peroxide injection. The system configuration is shown in Fig. 1 and the details of gallery construction is portrayed in Fig. 2. Monitoring wells were installed by hand using a gentle jetting action and no backfill material was used so that aquifer materials were in direct contact with the screens.

Nutrients were added on a batch basis three times per week at a concentration of 1,000 mg/L during each batch application. Each injection gallery received 10 pounds (4.5 kg) of Restore® 375 per week. Pretreatment of EGL2 and EGL3 consisted of water and nutrient injection for 2 weeks of operation prior to hydrogen peroxide injection. Hydrogen peroxide injection was initiated on April 4, 1988, at 300 mg/L. Actual hydrogen peroxide concentration measured in the injection piping over the 105 days of operation varied from 240 to 350 mg/L. Injection continued at this level with the exception of a single 24-hour slug at 5,000 mg/L initiated on June 22, 1988.

To evaluate hydrogen peroxide and oxygen behavior, dissolved concentrations were measured in the monitoring well. During active pumping, water collected from monitoring wells installed in the injection galleries was similar to the injected water. Water collected from the other downgradient wells was representative of shallow groundwater.

Oxygen concentrations were measured with a YSI-Model 58 portable dissolved oxygen meter. Water samples were collected in a bottom-filling bailer and carefully transferred to a beaker for contact with the probe. Hydrogen peroxide was measured in the field by a rapid titanium sulfate colorimetric method. Samples were collected in bailers, rapidly transferred to a test tube, mixed with the titanium sulfate reagent, allowed to react for 2 minutes, and then quantified visually against a calibrated color chart. These rapid field measurements allow real-time determination of the relatively unstable oxygen and hydrogen peroxide concentrations.

In situ tests were conducted to determine hydrogen peroxide decomposition and oxygen utilization rates at the well locations. These tests consisted of shutting down all flow into the galleries and out of the extraction well and measuring changes in concentration over time. During these shutdown periods, water rapidly drained from the galleries and water collected from the wells installed in the galleries was representative of groundwater immediately below the gravel backfill. Prior to sampling, a minimum of three casing volumes were purged from each well. Fig. 3 illustrates the results typical of one such *in situ* test

conducted in the well installed through EGL1. Half-lives and decay constants are calculated as first order with respect to hydrogen peroxide or oxygen. Oxygen utilization rates were calculated based on data collected after no hydrogen peroxide was detected in the water.

Results and discussion

Hydrogen peroxide concentrations measured in the injection galleries ranged from below detection to 340 mg/L during steady-state operating conditions. Average hydrogen peroxide concentrations in EGL1, EGL2, and EGL3 were 210 mg/L, 227 mg/L, and 192 mg/L, respectively. These are somewhat below the average injection concentration of 300 mg/L, indicating some loss of hydrogen peroxide in the galleries. The average of 94 mg/L in EGL4 indicates a loss of more than two-thirds. At the conclusion of the 5,000 mg/L shock test, hydrogen peroxide concentrations of 4,500 mg/L, 4,500 mg/L, 340 mg/L, and 35 mg/L were measured in EGL1, EGL2, EGL3, and EGL4, respectively. Despite periodic measurements at approximately 15 times during the 105-day study, hydrogen peroxide was not detected 1 or 4 feet (0.3 or 1.2 m) downgradient from any gallery, except at the conclusion of the shock test when hydrogen peroxide concentrations of 260 mg/L and 2,500 mg/L were measured 1 foot (0.3 m) downgradient of EGL1 and EGL2, respectively.

Oxygen concentrations detected in groundwater in the infiltration galleries and in water containing hydrogen peroxide were typically 15 to 30 mg/L, with an average of approximately 20 mg/L. An exception was during the 5,000 mg/L hydrogen peroxide shock test, when oxygen concentrations of up to 67 mg/

TABLE 4

Oxygen concentrations observed in monitoring wells (mg/L)[a]

Distance downgradient (feet)[b]		EGL1	EGL2	EGL3	EGL4
0 (0)	Average[c]	21	20	22	21
	Shock[d]	67	32	29	29
1 (0.3)	Average	7.1	11.5	8.8	3.5
	Shock	34	50	25	3.7
4 (1.2)	Average	2.1	4.4	3.8	2.5
	Shock	5.0	12	8.2	3.0

[a]Oxygen concentrations above 20 mg/L were determined using rapid dilution; concentrations above 40 ± mg/L are likely due to the presence of bubbles.
[b]The values in parentheses are in meters.
[c]Average denotes the average of all oxygen measurements at steady-state operating conditions.
[d]Shock refers to the oxygen concentrations measured on June 23, 1988, at the conclusion of the 5,000 mg/L hydrogen peroxide shock load.

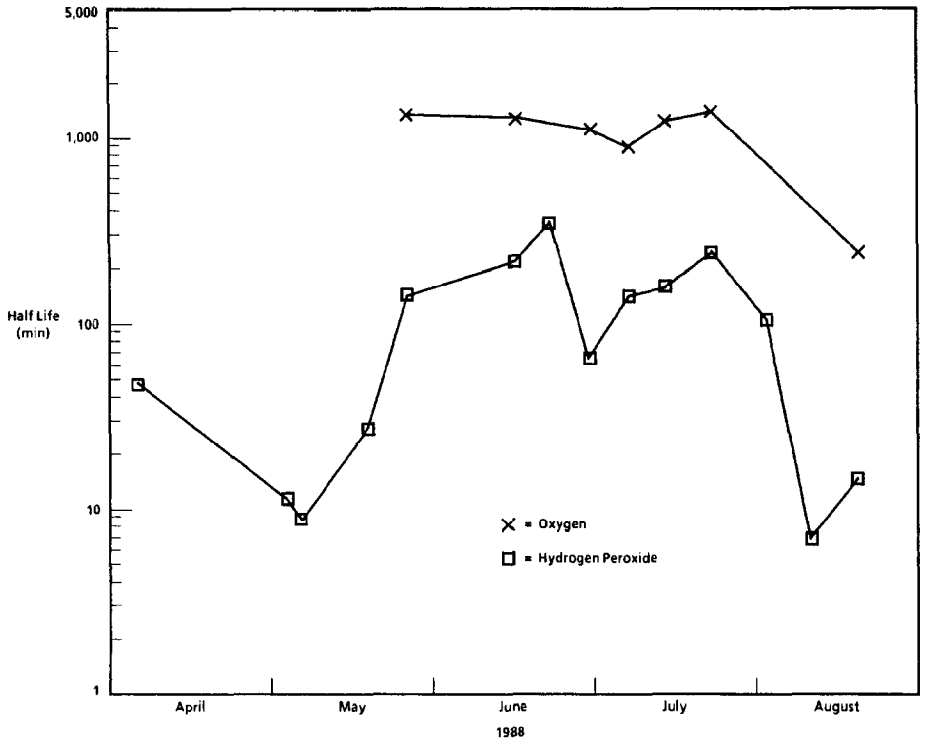

Fig. 4. First order half-lives of hydrogen peroxide and oxygen determined in soil immediately adjacent to EGL1.

L were measured in groundwater with 4,500 mg/L of hydrogen peroxide. Note that oxygen concentrations greater than 20 mg/L were measured using a rapid dilution technique. Measured oxygen concentrations greater than 40 mg/L are likely due to oxygen bubbles in the presence of rapidly decomposing hydrogen peroxide. The accuracy of oxygen measurements in the presence of high hydrogen peroxide concentrations is questionable. Table 4 illustrates the average oxygen concentrations observed in the monitoring wells at steady-state flow conditions and the oxygen measurements made at the end of the 5,000 mg/L hydrogen peroxide shock.

These compare with an average background oxygen concentration of 1.4 mg/L at a nearby monitoring well, of similar construction, in the contaminated zone not impacted by this test. Oxygen levels in all the injection galleries, and 1 foot (0.3 m) downgradient of all but EGL4, were substantially increased. The monitoring well 1 foot (0.3 m) downgradient from EGL4 had an average oxygen content of only 3.7 mg/L. The wells 4 feet (1.2 m) downgradient appeared to show slight increases over background levels; however, using the Student's "*t*" test, the differences were not significant at the 95-percent level.

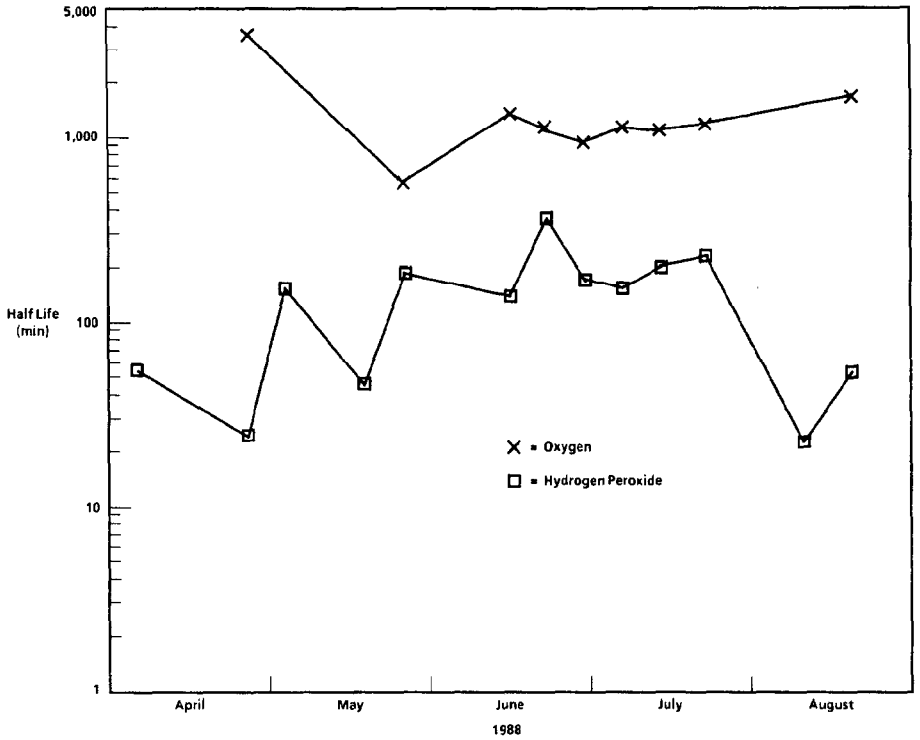

Fig. 5. First order half-lives of hydrogen peroxide and oxygen determined in soil immediately adjacent to EGL2.

It is possible that a difference exists, but the sample size was too small to show statistical significance. Although some noise was present in the data, none of the concentrations showed a significant change with time over the course of the test. The 5,000 mg/L hydrogen peroxide shock increased oxygen levels in the injection galleries and downgradient of EGL1, EGL2, and EGL3, but EGL4 appeared unaffected.

Hydrogen peroxide decomposition and oxygen utilization half-lives in the saturated soil immediately below the injection galleries are shown in Figs. 4, 5, 6, and 7. These half-lives are based on first-order decay constants relative to hydrogen peroxide and oxygen concentrations. The oxygen decay rates were calculated from data collected after all hydrogen peroxide had decayed. There is considerable variability in the data; however, hydrogen peroxide half-lives are typically an order of magnitude or more lower than the oxygen utilization rates. The 5,000 mg/L hydrogen peroxide shock had no observed effect on either hydrogen peroxide stability or oxygen utilization rates. The shock did temporarily increase hydrogen peroxide stability within the gallery gravel backfill at EGL1 and EGL2, resulting in some hydrogen peroxide transport to

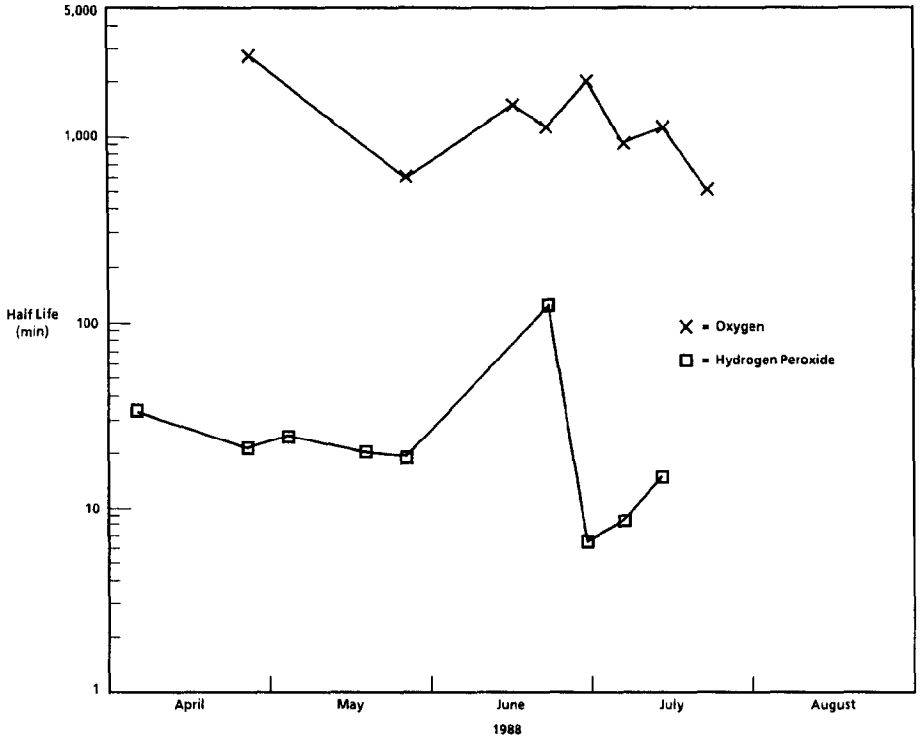

Fig. 6. First order half-lives of hydrogen peroxide and oxygen determined in soil immediately adjacent to EGL3.

the 1-foot (0.3-m) downgradient monitoring wells. No difference between treatments is apparent. A more limited number of oxygen utilization rates were calculated for the 1-foot (0.3-m) downgradient locations. The mean oxygen half-life in the gallery wells was 1,262 min, and 1 foot (0.3 m) downgradient the mean half-life was 1,246 min. This indicates that exposure to hydrogen peroxide had no measurable toxic effect in the soils immediately below the injection galleries.

Available data are insufficient to develop a precise mass balance to calculate what fraction of the hydrogen peroxide was used to satisfy the oxygen demand, and what portion was lost to off-gasing. Given the consistently much higher rates of hydrogen peroxide decomposition than oxygen utilization, it is unlikely that any significant part of the hydrogen peroxide generated oxygen in excess of that required to increase water concentrations from air saturated to approximately 20 mg/L was utilized to biodegrade jet fuel.

Hydrogen peroxide did succeed in supplying dissolved oxygen at concentrations above air saturation levels in the immediate vicinity of the injection galleries, and much of this dissolved oxygen was presumably used to degrade the

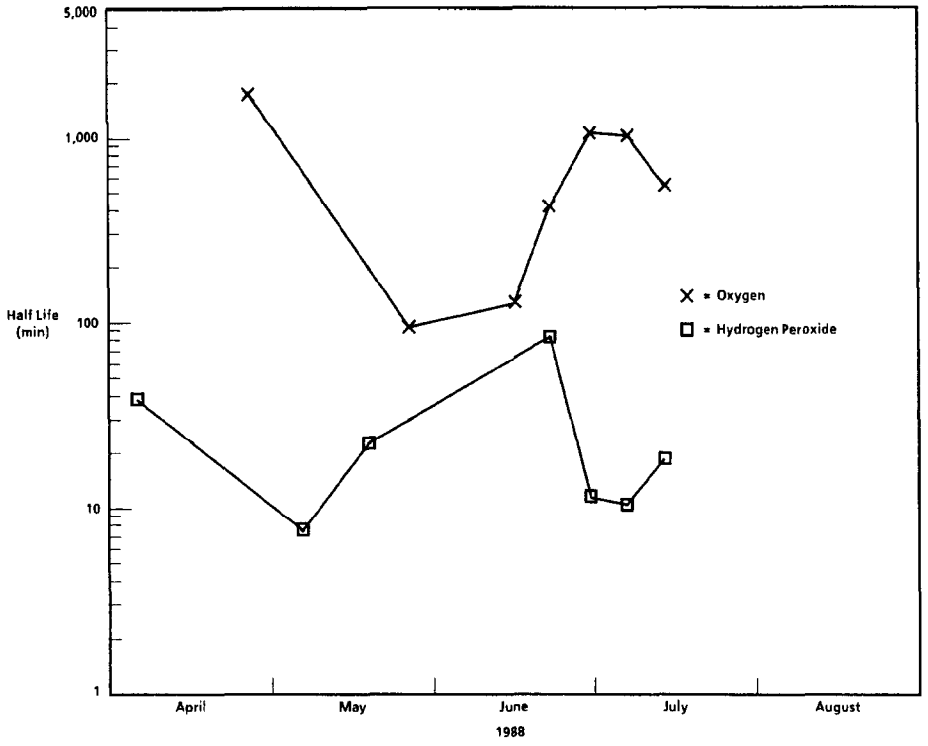

Fig. 7. First order half-lives of hydrogen peroxide and oxygen determined in soil immediately adjacent to EGL4.

TABLE 5

Catalytic activity of several ferric-centered catalysts in the decomposition of hydrogen peroxide (from Nicholls and Schonbaum [9])

Catalyst	Activity (turnover number)[a]
Catalase	9×10^4 (pH 7, 20 °C, 0.01 *M* peroxide)
Peroxidase	4.0 (pH 7, 20 °C, 0.01 *M* peroxide)
Fe(III)-TETA	22.0 (pH 7, 25 °C, 0.15 *M* peroxide)
Fe(II) or Fe(III) ion	1.0 (pH 5, 0 °C)

[a]Turnover number = number of peroxide molecules decomposed per second by each mole of the catalyst.

JP-4 jet fuel hydrocarbons. Other sources of oxygen demand, such as oxidation of ferrous iron, may also have been responsible for some of the oxygen utilization observed. Oxygen concentrations observed in the presence of hydrogen peroxide were typically about 20 mg/L, approximately half the pure oxygen saturation level. The hydrogen peroxide was not sufficiently stable to move significantly into the formation. Most, if not all, of the hydrogen peroxide de-

composed either in the injection galleries or within a few inches of entering the formation. The use of the different treatments did not have a sufficient effect to allow efficient hydrogen peroxide use. The injection galleries receiving tap water did have somewhat improved hydrogen peroxide stability during the 5,000 mg/L shock; however, the impact of the shock was limited, and no lasting effect was measured. Although the gallery EGL4 receiving system water without pretreatment exhibited the most rapid hydrogen peroxide decomposition within the gallery, decomposition in the soils immediately underlying the gallery was similar to the other treatments.

Data presented in this paper demonstrate that hydrogen peroxide decomposes at a rapid rate in groundwater applications. Many substances commonly present in groundwater and soils act as catalysts for the decomposition of peroxide. Important among these are aqueous species of iron and copper and the enzyme catalase [8]. Although inorganic catalysts contribute to the decomposition of peroxide *in situ*, the most important catalyst may be catalase. The strong effect of the enzyme catalase is indicated by the data in Table 5, which lists the activity of several catalysts of peroxide decomposition.

Several inorganic and organic compounds are known to reduce the catalytic decomposition of hydrogen peroxide. Phosphate, which is commonly used as peroxide stabilizer in groundwater applications, apparently [10] deactivates only the inorganic catalysts and does not react with catalase. Because the activity of catalase is highly significant in groundwater [11], phosphate stabilization may not prove adequate to allow efficient use of hydrogen peroxide as an oxygen source for *in situ* bioremediation. A detailed laboratory investigation of the performance of several peroxide stabilizing additives has been conducted, and the results are presented in the companion paper [10].

All field measurements of hydrogen peroxide decomposition indicated rates significantly more rapid than indicated by the laboratory treatability tests. In addition, the field data did not support the laboratory conclusions regarding the effectiveness of soil pretreatment with Restore® 375. The reasons for this are unclear. In the bench-scale studies described by Hinchee et al. [6], a 33% soil slurry was used, and this may not have adequately represented field conditions. It is also possible that if the hydrogen peroxide decomposition in the field was primarily the result of the microbially produced catalyse, whereas in the relatively short-term laboratory bench-scale tests the microorganisms were not acclimated to hydrogen peroxide and were producing less catalyse. In any case, this study indicates that care must be taken in the design and interpretation of laboratory bench-scale tests, and in their subsequent application to field design.

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