

ON SITE TREATMENT OF CONTAMINATED SOILS USING CATALYZED PEROXIDE

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16. ABSTRACT <p>Treatment of contaminated water, timbers, and soils was investigated using catalyzed hydrogen peroxide, a procedure based on Fenton's reagent [hydrogen peroxide and iron (II)]. The process produces hydroxyl radicals which oxidize essentially all organic contaminants. Fenton's methodology was used to treat total petroleum hydrocarbons (TPH) in an oil-water separator effluent from the WSDOT White Pass maintenance station. Results indicated that the presence of surfactants affected treatment efficiency. Although surfactants lowered the effectiveness of the process, 25% of the TPH was removed.</p> <p>Wood posts contaminated with pentachlorophenol (PCP) and creosote were treated using the catalyzed peroxide process, resulting in 84% degradation of PCP and 74% degradation of creosote with 6% hydrogen peroxide and 56 mg/l Fe. Estimated chemical cost for treatment was \$1.00/kg of wood.</p> <p>A central composite rotatable design was used to investigate the interactions between hydrogen peroxide concentration, slurry volume, initial contaminant concentration, and soil organic carbon content in the catalyzed hydrogen peroxide remediation of diesel-contaminated soil to develop design criteria for soil remediation. Two separate experimental matrices were investigated: 1) high slurry volumes and low peroxide concentrations, and 2) low slurry volumes with high peroxide concentrations. Time required for high volume/low concentration system to proceed to completion was approximately three weeks; low volume/high concentration reactions were complete within three days.</p> <p>The results showed that soil organic carbon content was an insignificant variable in the catalyzed peroxide treatment of diesel-contaminated soils. However, significant interactions were found for the remaining three variables. Data were analyzed for total petroleum hydrocarbon (TPH) degradation and treatment stoichiometry. Although both systems could achieve equal levels of treatment, stoichiometry of the high volume/low concentration system was significantly more efficient; therefore, high volume/low concentration was the most economical system for the remediation of diesel-contaminated soils.</p>			
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**ON SITE TREATMENT OF CONTAMINATED SOILS
USING CATALYZED PEROXIDE**

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ON SITE TREATMENT OF CONTAMINATED SOILS USING CATALYZED PEROXIDE

STUDY SUMMARY

The treatment of contaminated water, timbers, and soils was investigated using catalyzed hydrogen peroxide, a procedure based on Fenton's reagent [hydrogen peroxide and iron (II)]. The process produces hydroxyl radicals which oxidize essentially all organic contaminants. The Fenton's methodology was used to treat total petroleum hydrocarbons (TPH) in an oil-water separator effluent from the Washington State Department of Transportation (WSDOT) White Pass maintenance station. Results indicated that the presence of surfactants affected the treatment efficiency. Although surfactants lowered the effectiveness of the process, 25% of the TPH was removed.

Wood posts contaminated with pentachlorophenol (PCP) and creosote were treated using the catalyzed peroxide process, resulting in 84% degradation of the PCP and 74% degradation of the creosote with 6% hydrogen peroxide and 56 mg/l Fe. The estimated chemical cost for treatment was \$1.00/kg of wood.

A central composite rotatable design was used to investigate the interactions between hydrogen peroxide concentration, slurry volume, initial contaminant concentration, and soil organic carbon content in the catalyzed hydrogen peroxide remediation of diesel-contaminated soil to develop design criteria for soil remediation. Two separate experimental matrices were investigated: 1) large volume of low peroxide concentration, and 2) small volume of high peroxide concentration. The time required for the high volume/low concentration system to proceed to completion was approximately three weeks; the low volume/high concentration reactions were complete within three days.

The results showed that the soil organic carbon content was an insignificant variable in the catalyzed peroxide treatment of diesel-contaminated soils. However, significant interactions were found for the remaining three variables. The data were analyzed for total

petroleum hydrocarbon (TPH) degradation and treatment efficiency. Although both systems could achieve equal levels of treatment, the efficiency of the high volume/low concentration system was significantly more efficient; therefore, the high volume/low concentration was the most economical system for the remediation of diesel-contaminated soils.

CONCLUSIONS AND RECOMMENDATIONS

The results of this experimental investigation showed that catalyzed hydrogen peroxide effectively treated a variety of contaminated wastes. Although the peroxide treatment did achieve degradation of the TPH in an oil-water separator effluent, a more cost effective approach was to adjust the pH and allow settling with entrapment of the TPH contaminants. Contaminated timbers were effectively treated to remove 84% PCP and 77% of total contaminants by cutting the timber into small pieces followed by catalyzed hydrogen peroxide treatment. A possible alternative to overcome these mass transfer limitations would be the use of a pressure reactor, which may allow penetration of the peroxide and iron solution into the wood. Diesel contaminated soil was effectively treated using catalyzed hydrogen peroxide.

A four dimensional central composite rotatable experimental design (5 contaminant concentrations x 5 organic carbon concentrations x 5 peroxide concentrations x 5 slurry volumes) was used to investigate the remediation of a Palouse loess soil contaminated with diesel fuel as the basis for assessing soil remediation design criteria. The design was used at two process extremes: 1) low hydrogen peroxide concentrations and high slurry volumes, and; 2) high hydrogen peroxide concentrations and low volumes. The time required for the completion of the high volume/low concentration was 24 days, while the low concentration/high volume systems reacted within 3 days. Initial TPH concentrations were compared to residuals after the reactions were complete as the basis for statistical comparisons.

The results showed that catalyzed hydrogen peroxide remediation of the diesel-contaminated Palouse loess was unaffected by organic carbon content, but significant interactions were found between hydrogen peroxide concentration, slurry volume, and initial diesel concentration. Equal masses of TPH were degraded by either the low concentration/high volume system or the high concentration/low volume system; however, the treatment efficiency and subsequent costs were greater in the low volume/high

concentration system. Greater than 80% TPH loss was found in the high volume/low concentration system at a chemical cost of \$29 per 909 kg (1 U.S. ton). For approximately the same cost (\$38 per 909 kg), the high concentration/low volume system degraded only 60% of the diesel and, in order to achieve 80% reduction the cost increased to \$285 per 909 kg. The costs of the low concentration/high volume system are lower, but the process requires a longer reaction time. Each of the systems may have value depending on site and logistic considerations. The low volume/high concentration system would be more applicable for use under emergency response or *in situ* conditions. However, the high volume/low concentration system would be most effective in a lined on site reactor when the time required for treatment is not a significant factor and when reagent costs are a primary concern.

We recommend the use of catalyzed hydrogen peroxide to remediate soils contaminated with petroleum hydrocarbons based on time constraints and logistics. If a rapid clean up is desired and/or space at the site is a constraint, a small volume of high concentration peroxide is the best process option. If such an approach is taken, peroxide treatment can be achieved in less than a day.

If site area constraints are not a problem and time is not a major factor, the batch treatment of soils containing a large volume of dilute peroxide is the most efficient and economical treatment. This procedure, which costs in the range of \$20-\$40/yd of soil depending on the level of contamination, requires two-to-three weeks to treat the soil.

The use of chemical oxidants to treat contaminated soils is extremely complex and, unfortunately, *hydrogen peroxide dosages cannot be predicted based solely on contaminant levels*. The important variables in the treatment of contaminated soils include contaminant concentration, soil organic carbon content, slurry volume (i.e., the volume of aqueous peroxide solution per mass of soil), and the hydrogen peroxide concentration. The algorithm developed for hydrogen peroxide requirements was based on these four variables. Because soil organic carbon was not a significant variable, only three variables

(hydrogen peroxide concentration, slurry volume, and contaminant concentration) were used in the response equations.

Based on the data and equations developed in this study, we have recommended two procedures for assessing treatment conditions for contaminated soils: 1) A procedure based on response equations that would be used by engineers and scientists, and; 2) a recipe technique that would be used by field and maintenance personnel. Although the process engineering of catalyzed peroxide soil treatment is extremely complex, the guidelines provided in this report provide an approximate procedure for determining peroxide requirements.

INTRODUCTION

RESEARCH OBJECTIVES

The objective of this research was:

To investigate the effectiveness and cost of the treatment of various WSDOT samples with Fenton's reagent.

THE PROBLEM

Technological advances over the last century have increased the standard of living in the United States. With these advances came the demand for faster and more accessible transportation, which has improved to meet these demands. For example, passenger cars, once a luxury for only the rich, number over 110 million today. In order to accommodate these vehicles, over 4 million miles of streets, roads, and highways have been constructed. Slightly over half of all petroleum is consumed through transportation (1).

The high demand for petroleum results in many possible sources of contamination, including accidental releases associated with highway maintenance, spills during transport, accumulation on roadways from improperly maintained cars, and leaking underground storage tanks (USTs). Out of the several million USTs located in the United States it is estimated that 10 to 25% of them may be leaking (2), which means that approximately 500,000 of the existing USTs may leak before they are replaced with new tanks that have corrosion protection and leak detection systems. As a direct result of these releases, surface soils become contaminated with petroleum hydrocarbons which may result in groundwater contamination and possible exposure to the public.

The remediation of petroleum-contaminated soils is a significant problem for the Washington State Department of Transportation (WSDOT) and others involved in the transportation industry. Current remediation practices include landfilling the material,

bioremediation, and incineration. All of these processes have limitations. Landfilling has costs associated with both transportation of the soil to the landfill and tipping fees with costs ranging from \$20-\$50 per ton depending on transportation distances.(3) Incineration is also costly (\$80-\$150 per ton depending on the fuel content of the soil) but has the advantage of rapid treatment.(4) Bioremediation has the potential for inexpensively treating large quantities of soil, but has lengthy time requirements, sometimes up to two years to treat a soil if the soil temperature is low.(5) Therefore, ultimate disposal is still a challenge, so a processes that could be conducted *ex situ* or *in situ* and promote contaminant destruction in a short time period would provide a number of benefits.

The use of catalyzed hydrogen peroxide has many of the positive attributes of all of the remedial options described above. It has the potential to remediate soils in a time period of hours to days with costs that may approach the price of bioremediation. Therefore, contaminated soils may potentially be treated to the 200 ppm TPH cleanup standard of Washington State Department of Ecology. Also of concern to the Department of Ecology and the U.S. Environmental Protection Agency is the possible presence of degradation products during soil remediation. The results of a companion document "Process Conditions for the Total Oxidation of Hydrocarbons" (T9234-08) has documented that catalyzed hydrogen peroxide oxidizes hydrocarbons to the harmless end products of carbon dioxide and water. Therefore, the regulatory constraints should not be a problem in the catalyzed peroxide treatment of hydrocarbon-contaminated soils.

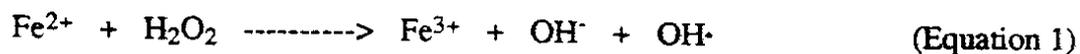
The U.S. Environmental Protection Agency (EPA) is continually searching for new soil remediation technologies that provide contaminant destruction with lower operational costs. Section 121(b) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) requires the EPA to seek permanent solutions and alternative treatment technologies (6). The *in situ* or on site treatment of contaminated soils has recently gained widespread attention, and will become more commonplace as the landfill disposal of toxic residuals becomes more restricted (3). The introduction of a strong

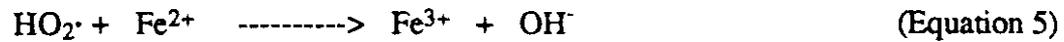
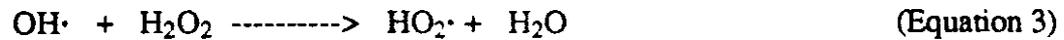
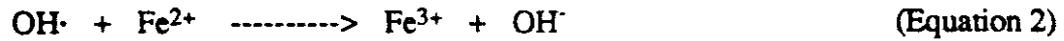
oxidant, such as the hydroxyl radical, is one possible method for destroying hazardous contaminants. A remediation technique that has gained recent attention for rapidly oxidizing even biorefractory compounds is the catalyzed decomposition of hydrogen peroxide by iron (II) to form highly reactive oxygen radicals.

Research to date has documented chemical reactions that oxidize contaminants in the aqueous phase using Fenton's reagent and has provided initial data on what variables control the efficiency of treatment with contaminated soils. The treatment of TPH contaminated soils at the pilot scale has shown promising results. However, minimal research has focused on real world samples. The first segment of this research was to investigate the effectiveness and cost of treating a variety of samples including oil-water separator wastes, timber samples, and a natural soil system contaminated with diesel fuel. Furthermore, for the development of catalyzed peroxide soil remediation systems, an algorithm that describes hydrogen peroxide requirements based on site conditions would aid in system design. Recent research has provided conceptual results on variables that control the effectiveness of catalyzed peroxide soil remediation, including contaminant concentration, soil organic carbon content, peroxide concentration, and slurry volume (7-9). Therefore the second objective of this research was to develop design equations to optimize the peroxide requirements for the remediation of a soil contaminated with diesel fuel as a function of initial diesel concentration and soil organic carbon content.

REVIEW OF CURRENT PRACTICE

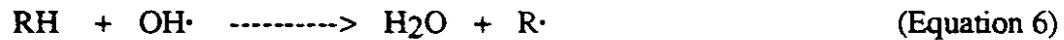
Catalyzed hydrogen peroxide, commonly known as Fenton's reagent, is well documented in the fundamental chemistry literature (10-13). Haber and Weiss (14) first proposed that hydroxyl radical is the oxidant in the peroxide-iron (II) system, and Barb *et al.* (15) suggested the following reactions to describe the Fenton's process:





where $\text{OH}\cdot$ is hydroxyl radical and $\text{HO}_2\cdot$ is perhydroxyl radical.

If an organic compound is present in the system, the reactions include:



In waste treatment, Fenton's chemistry was first applied to the oxidation of a number of aqueous wastes. Barbeni *et al.* (16) investigated the degradation of chlorophenols, and documented their transformation to carbon dioxide, water, and chloride. A Fenton-like reaction using iron (II) was also shown to oxidize a formaldehyde waste stream (17). Catalyzed hydrogen peroxide was also used as a pretreatment process for industrial wastewaters that contain organic compounds, such as chlorophenols, which are toxic to microorganisms (18). The degradation of organic and inorganic compounds in waste streams by chemical oxidation is a viable alternative to biological methods, especially when the contaminants are biorefractory, toxic, or present at high concentrations.

Based on fundamental chemical oxidations and the positive results obtained in aqueous treatment, catalyzed hydrogen peroxide has recently been applied to the remediation of contaminated soils. Watts *et al.* (7) documented the mineralization of pentachlorophenol (PCP) and showed that optimum treatment in both silica sand and natural soils occurred at pH 2 to 3. Tyre *et al.* (8) found that the ratios of the first-order rate constants for contaminant degradation to hydrogen peroxide decomposition varied depending on the iron (II) amendment and organic carbon content of the soil. The ratios

were more efficient for low soil organic carbon content and no iron addition, but were most sensitive to iron addition. They proposed that naturally occurring iron minerals in soils may catalyze the decomposition of hydrogen peroxide and promote Fenton-like reactions. Watts *et al.* (9) compared the standard Fenton procedure, the sequential addition of iron (II) and hydrogen peroxide, and peroxide catalyzed by the iron mineral goethite to treat silica sand contaminated by PCP. Although slower, the most efficient process for PCP degradation was the mineral system.

One concern in the use of Fenton's reagent for the treatment of contaminated soils is the nature and potential toxicity of the intermediate products. Leung *et al.* (19) reported mineralization of perchloroethylene (PCE) in silica sand and further analysis revealed that dichloroacetic acid (DCAA) was the only significant intermediate generated that was limiting mineralization. Formic acid was the final product before PCE was mineralized.

Although modified Fenton's reagent has proven successful for treating contaminated soils in bench scale studies, there is always concern in scaling up a new treatment process. Watts (20) conducted a pilot study where the soil was excavated and treated in fifty-five gallon polyethylene drums. It was found that by adding 2% hydrogen peroxide at a volume of four times the water-holding capacity of the soil, the total petroleum hydrocarbon (TPH) concentration could be reduced from 200 mg/kg to below the action level of 100 mg/kg within two days.

EXPERIMENTAL METHODOLOGY

MATERIALS

Hydrogen peroxide was supplied by Solvay Interlox (Deer Park, TX), and H_2SO_4 was purchased from Fisher Scientific. Diesel, obtained from Cenex (St. Paul, MN), was selected as a model contaminant because of its widespread use in transportation and common occurrence as a soil and groundwater pollutant. Diesel is the fraction of petroleum with a distillation range of 200-400 °C and a hydrocarbon composition (consisting of

alkanes, isoalkanes, cycloalkenes, and polycyclic aromatic hydrocarbons) ranging from C₁₅ to C₂₅ (21).

The soil used was a Palouse Loess, a silty loam that was collected from a wheat field near Pullman, WA. The soil was sampled from successive horizons to provide a gradient of organic carbon contents. Particle-size analysis was determined by the pipette method (22). Organic carbon was determined by combustion at 900 °C with evolved CO₂ trapped in KOH and measured by back titration of nonreacted KOH (23). Amorphous and crystalline iron and manganese oxyhydroxides were determined by citrate-bicarbonate-dithionite extraction (24). Cation exchange capacity was established by saturation with sodium acetate at pH 8.2 (25). The soil characteristics are listed in Table 1. Because the soil is of low development, the samples were relatively uniform in particle size distribution, cation exchange capacity, mineralogy, pH, and field capacity, but organic carbon varied from 0.11% to 1.28%.

OIL-WATER SEPARATOR EFFLUENT TREATMENT

A sample of oil-water separator effluent from White Pass, WA was obtained from the Washington State Department of Transportation in order to assess its potential for catalyzed hydrogen peroxide treatment. The concentration of hydrocarbons present in the sample was first determined by gas chromatography. Based on these concentrations, various experiments were conducted using catalyzed hydrogen peroxide to determine treatment conditions. In order to compare the degradation of the contaminants in the sample to the degradation of diesel fuel, an experiment was conducted using the effluent sample as well as a parallel experiment using 30 mg/l diesel fuel in water. One ml of hydrogen peroxide was added to obtain concentrations of 400 and 800 mg/l followed by one ml of FeSO₄ to provide a concentration of 100 mg/l Fe. One-half ml of 0.1N thiosulfate was also added to the solution in order to sustain the reaction (Stanton and Watts, unpublished data). These additions were added sequentially every 24 hours over a

period of four days. The experiment was conducted at a pH of 3.0 (Z) and extracted using 3 ml of ethyl acetate. Deionized water controls were also run in parallel.

A subsequent experiment was conducted to observe the effect of pH adjustment on the settling of solids containing TPH. The pH of the 30 ml samples were adjusted to 2.0 and allowed to settle for 18 hours. The liquid was decanted from the settled solids and both phases were extracted using 3 ml of ethyl acetate. Control experiments were conducted in parallel for total TPH concentration as well as with no pH adjustment.

Table 1. Characteristics of the five Palouse soils.

Characteristic	Soil I	Soil II	Soil III	Soil IV	Soil V
Organic Carbon (%)	0.11	0.33	0.50	0.83	1.28
Sand (%)	20.4	18.4	19.6	22.4	22.4
Silt (%)	60.8	58.8	57.4	54.6	58.8
Clay (%)	18.8	22.8	22.8	22.8	20.8
Cation Exchange Capacity (centimoles/kg)	22.5	19.1	20.1	22.0	21.0
Crystalline Fe (mg/kg)	33540	30390	30846	31730	30880
Crystalline Mn (mg/kg)	539	690	686	679	613
Amorphous Fe (mg/kg)	22.5	38.3	38.6	39.2	74.7
Amorphous Mn (mg/kg)	35.5	30.4	33.6	39.8	40.2
pH	6.4	6.2	6.2	6.1	5.7
Field Capacity (mL/g)	0.356	0.318	0.325	0.339	0.336

TIMBER TREATMENT

Contaminated posts supplied by WSDOT were first analyzed by gas chromatography to determine primary contaminants and their respective concentrations. Prior to starting the experiments, timber pieces were chipped from the outside of the posts to approximately 2 cm in length and 2 mm in diameter. A variety of treatment conditions were tested using 0.1 g of wood at pH 3.0, along with deionized water controls. Subsequent optimization was conducted using a 2:1 molar ratio of thiosulfate to FeSO_4 with volumes of 5, 10, and 20 ml hydrogen peroxide. The consumption of hydrogen peroxide was monitored daily over a two day period.

The use of a Parr pressure reactor was also employed to enhance the reaction of the catalyzed hydrogen peroxide with the wood. The pressure was applied in order to force the peroxide and iron solution into the interior of the wood. Half of a gram of wood was completely submerged into 50 ml of 1% hydrogen peroxide that contained 1000 mg/l of iron (II) as FeSO_4 . The experiment was kept under pressure (200 psi) for two days. A deionized water control was also performed following the same procedure.

SOIL TREATMENT

A central composite rotatable experimental design was used to investigate the interactions between four treatment parameters (26). The four dimensional matrix consisted of five hydrogen peroxide concentrations x five volumes of hydrogen peroxide x five contaminant concentrations x five soils with varying organic carbon contents. Two separate experimental matrices were investigated: 1) high slurry volumes but low concentrations of hydrogen peroxide (Table 2), and; 2) low slurry volumes but high concentrations of hydrogen peroxide (Table 3). The ranges of organic carbon content and contaminant concentrations remained the same for the two experimental systems. The ranges of hydrogen peroxide volume and concentration were based on preliminary experiments.

Table 2. Treatment conditions for the high volume/low concentration matrix.

Condition	Range of Values				
Hydrogen Peroxide Conc. (mg/L)	1000	3250	5500	7750	10000
Hydrogen Peroxide Vol. (x field capacity)	10	20	30	40	50
Contaminant Conc. (mg/kg)	500	875	1250	1625	2000
Organic Carbon Content (%)	0.11	0.33	0.50	0.83	1.28

Table 3. Treatment conditions for the low volume/high concentration matrix.

Condition	Range of Values				
Hydrogen Peroxide Conc. (mg/L)	100000	150000	200000	250000	300000
Hydrogen Peroxide Vol. (x field capacity)	0.2	0.9	1.6	2.3	3.0
Contaminant Conc. (mg/kg)	500	875	1250	1625	2000
Organic Carbon Content (%)	0.11	0.33	0.50	0.83	1.28

The soil was spiked by adding diesel fuel to 200 g of soil, and 2.5 g aliquots were weighed into 40 mL borosilicate glass vials. Experiments were initiated by adding hydrogen peroxide to the vials followed by adjusting the pH to 3 using 0.1N H₂SO₄. Each matrix consisted of 31 combinations of the four parameters and all 31 points were conducted in triplicate. Control experiments using deionized water were performed in parallel. For the high volume/low concentration matrix, the peroxide and pH were monitored every two days and the slurries were adjusted to pH 3 when necessary. When the peroxide concentration was below detection (at approximately 24 days), the matrix was shake-extracted for 24 hours with 8 mL of ethyl acetate and analyzed by gas chromatography. For the low volume/high concentration matrix, the reactions were completed after 3 days; at this time, the matrix was shake-extracted for 24 hours with 5 mL deionized water and 8 mL ethyl acetate followed by gas chromatographic analysis.

ANALYSIS

Hydrogen peroxide consumption was monitored by iodate titration for concentrations > 0.1% (27) and by TiSO₄ spectrophotometry for concentrations ≤ 0.1% (28). The contaminant concentration was determined using a shake extraction followed by gas chromatographic analysis (8). The solvent was added to the samples using a volumetric glass pipette, then the vials were placed on a wrist shaker for 24 hours. The extracts were then analyzed by a modified EPA Method 8015 using a Hewlett Packard 5890A gas chromatograph with flame ionization detector and a 10 m x 0.18 mm (i.d.) DB-5 capillary column. The wood samples were analyzed under the following conditions: initial oven temperature 140 °C, program rate 7 °C per minute, final oven temperature 220 °C, injector temperature 260 °C, and detector temperature 350 °C. The oil water separator and diesel contaminated soil samples were analyzed under the following conditions: initial oven temperature 80 °C, program rate 5 °C per minute, final oven temperature 250 °C, injector temperature 260 °C, and detector temperature 350 °C.

RESULTS AND DISCUSSION

OIL-WATER SEPARATOR EFFLUENT TREATMENT

Analysis of the oil-water separator effluent sample showed that there was a total petroleum hydrocarbon (TPH) concentration of approximately 3 mg/l. Aliquots of the sample were then treated using a variety of oxidation conditions and degradation was minimal. To evaluate if catalyzed peroxide is capable of oxidizing TPH a solution of 30 mg/l diesel in deionized water was treated. Results showed that there was 60% degradation of the diesel compared to the 25% degradation of the oil-water separator waste (Figure 1). These data suggest that the degradation was inhibited by the presence of surfactants or other materials used in the oil-water separation process.

During the oxidation treatment considerable settling of solids occurred in the samples. By reducing the initial pH from 7.4 to 2.0 and allowing the sample to settle for 18 hours, the clear supernatant could be decanted with a solid layer remaining at the bottom. In a 30 ml sample, 28 ml of clear liquid was decanted leaving 2 ml of a settled solids. Analysis of both the liquid supernatant and the settled material showed that 94% of the TPH was in the sludge and 6% remained in solution. A sample that was not adjusted to pH 2.0 was used as a control and 32% of the TPH settled in the solids with 68% remaining in solution (Figure 2). Assuming linear scale up to a 500 gallon waste tank, 0.21 gallons of 93% sulfuric acid would be required to reduce the pH from 7.4 to 2.0. The treatment would have an estimated cost of \$2.50 based on a unit price of \$8.25 for a 2.5 liter of 93% technical grade sulfuric acid. Based on a 90% reduction in concentration and 3 mg/l initial concentration of TPH, the final concentration of the decanted liquid would be 0.3 mg/l, which would meet Washington State effluent standards.

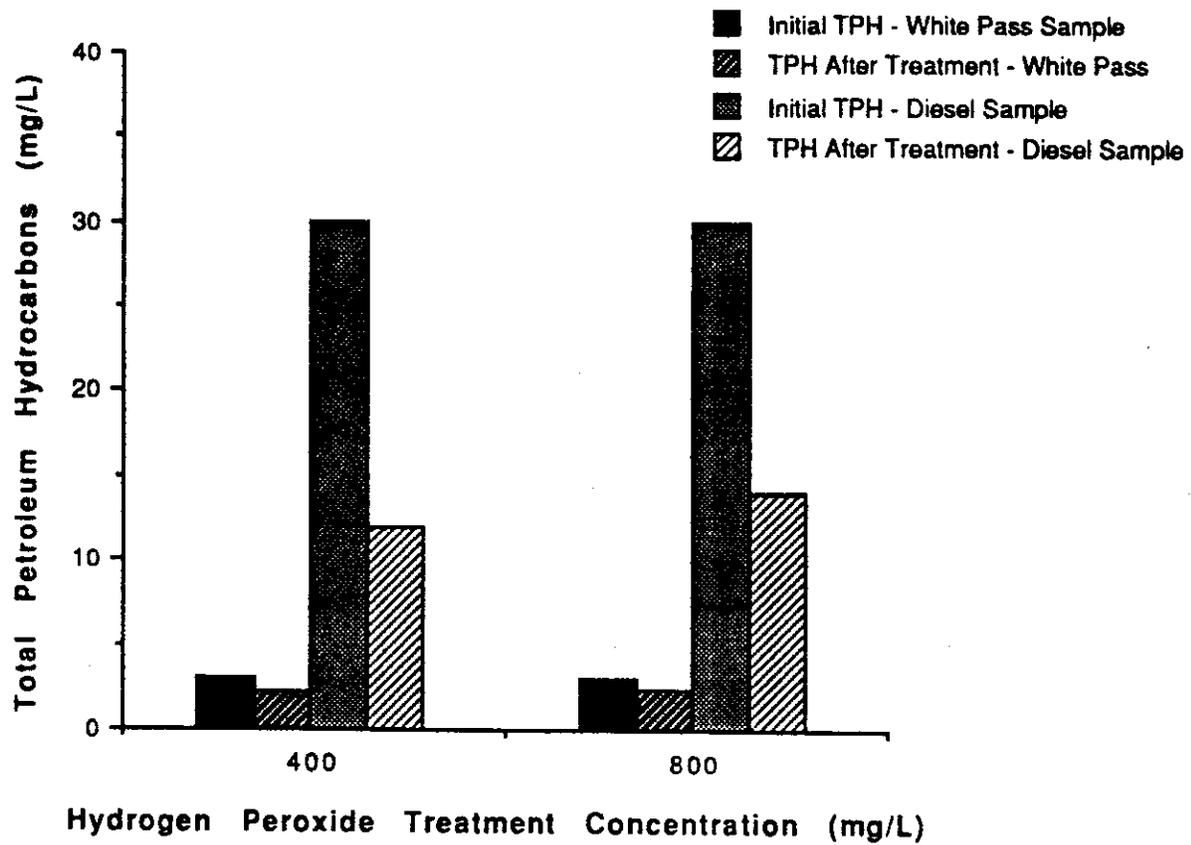


Figure 1. Degradation of oil-water separator effluent and diesel using catalyzed hydrogen peroxide treatment.

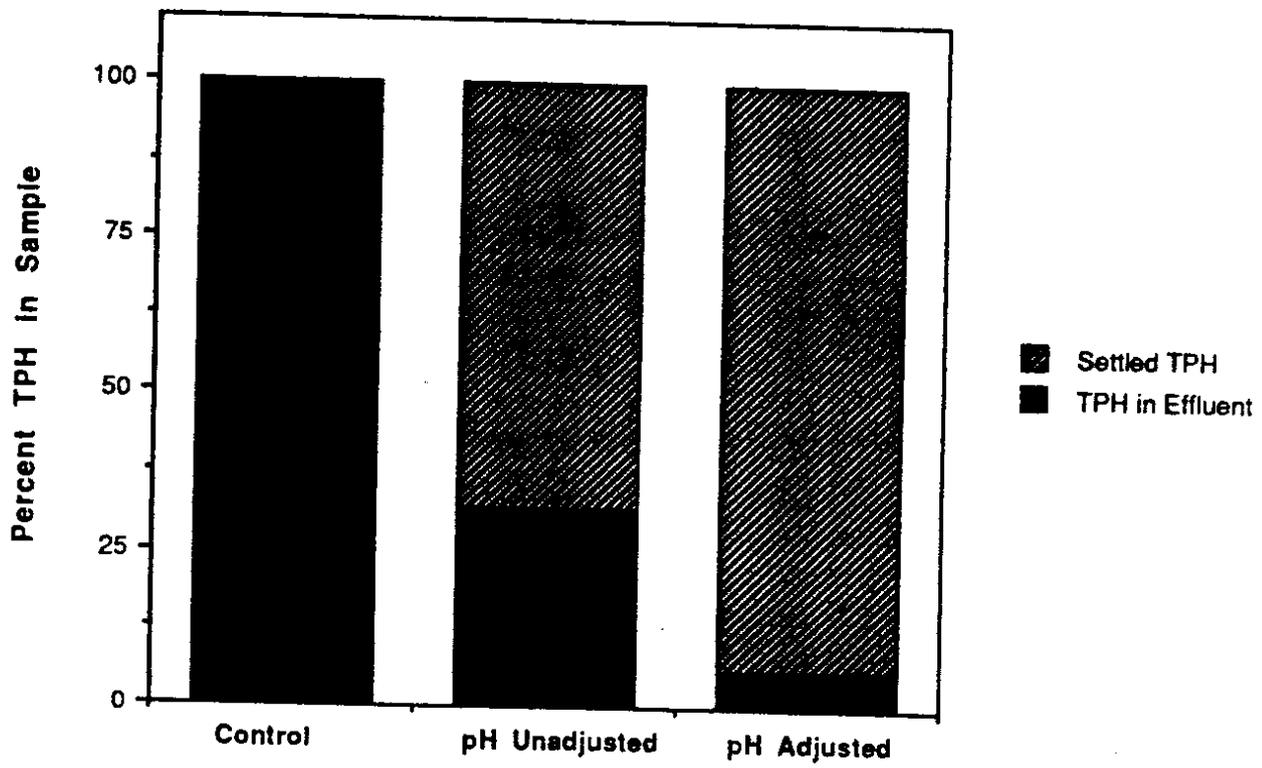


Figure 2. TPH concentration of oil-water separator effluent after settling.

TIMBER TREATMENT

Gas chromatographic analysis showed that the primary contaminant in the wood posts was pentachlorophenol, which made up approximately 30% of the total contamination. The remaining compounds were assumed to be creosote. The concentration of pentachlorophenol in the outside cm of the post was approximately 3000 mg/kg and the total contaminant concentration was approximately 10000 mg/kg. Initially, 73% of the total contaminants were degraded using 20 ml of 6% hydrogen peroxide and 56 mg/l Fe over a two day period, as shown in Figure 3. A subsequent experiment using the same peroxide and iron concentrations was conducted, but the volume was varied to see the effect on the ratio of peroxide consumed to wood treated. Also, thiosulfate was added to the reaction to determine if the reactions could be made more efficient. Figure 4 shows the hydrogen peroxide consumption for the three volumes. These data show that after two days the majority of the peroxide is gone. The data of Figures 5 and 6 show that 20 ml of 6% peroxide per 0.1 g wood (i.e., 12,000 mg H₂O₂/g wood) remains the optimum volume with 77% degradation of total contaminants and 84% removal of pentachlorophenol, respectively. Based on these conditions, only limited increases in degradation occurred by increasing the dosage, which may be due to mass transfer limitations. This treatment would reduce the pentachlorophenol concentration from 3000 mg/kg to 480 mg/kg and the total contaminant concentration from 10000 mg/kg to 2300 mg/kg at a ratio of approximately 12000 mg hydrogen peroxide per gram of wood. The estimated cost of hydrogen peroxide for this treatment would be \$1.00 to treat 1 kg of wood. The treatment of contaminated wood can be achieved using catalyzed hydrogen peroxide. However, the wood posts would most likely have to be cut into small pieces to provide the necessary surface exposure for oxidative treatment.

A pressure reactor was used to investigate treatment without cutting the wood posts into small pieces. Under pressure of 200 psi, 74% of the total contaminants and 67% of

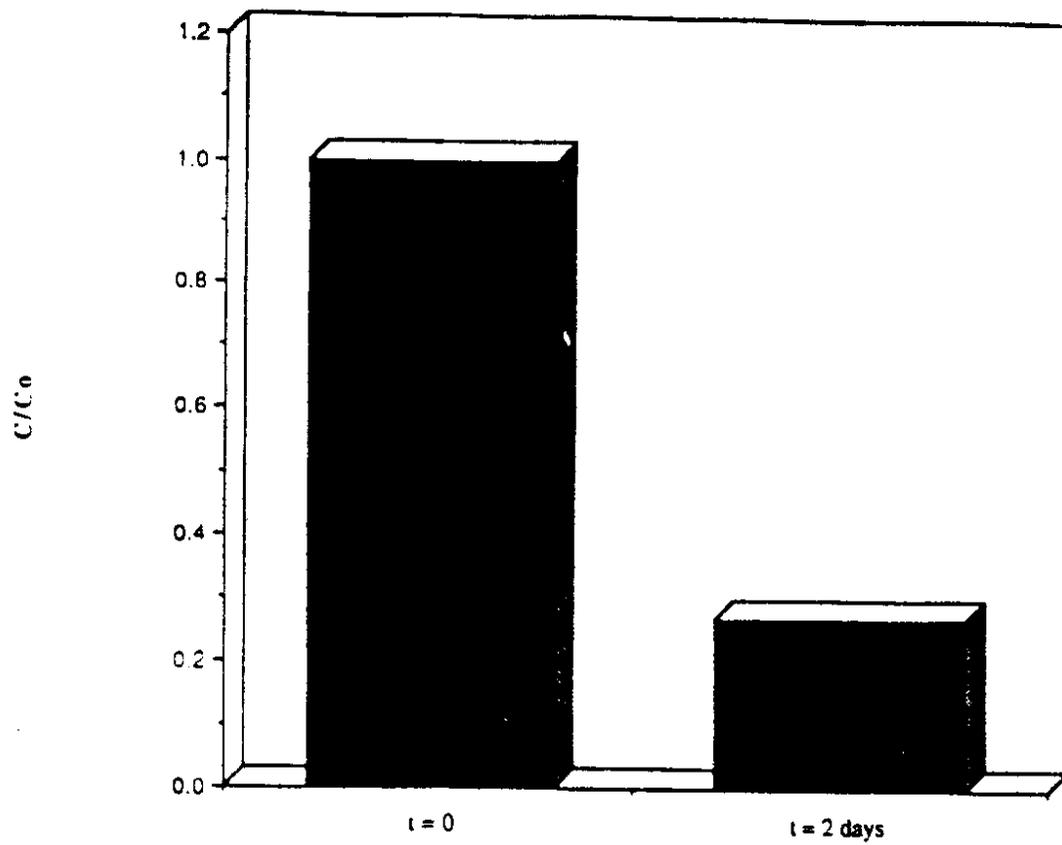


Figure 3. Degradation of wood contaminants using catalyzed hydrogen peroxide treatment.

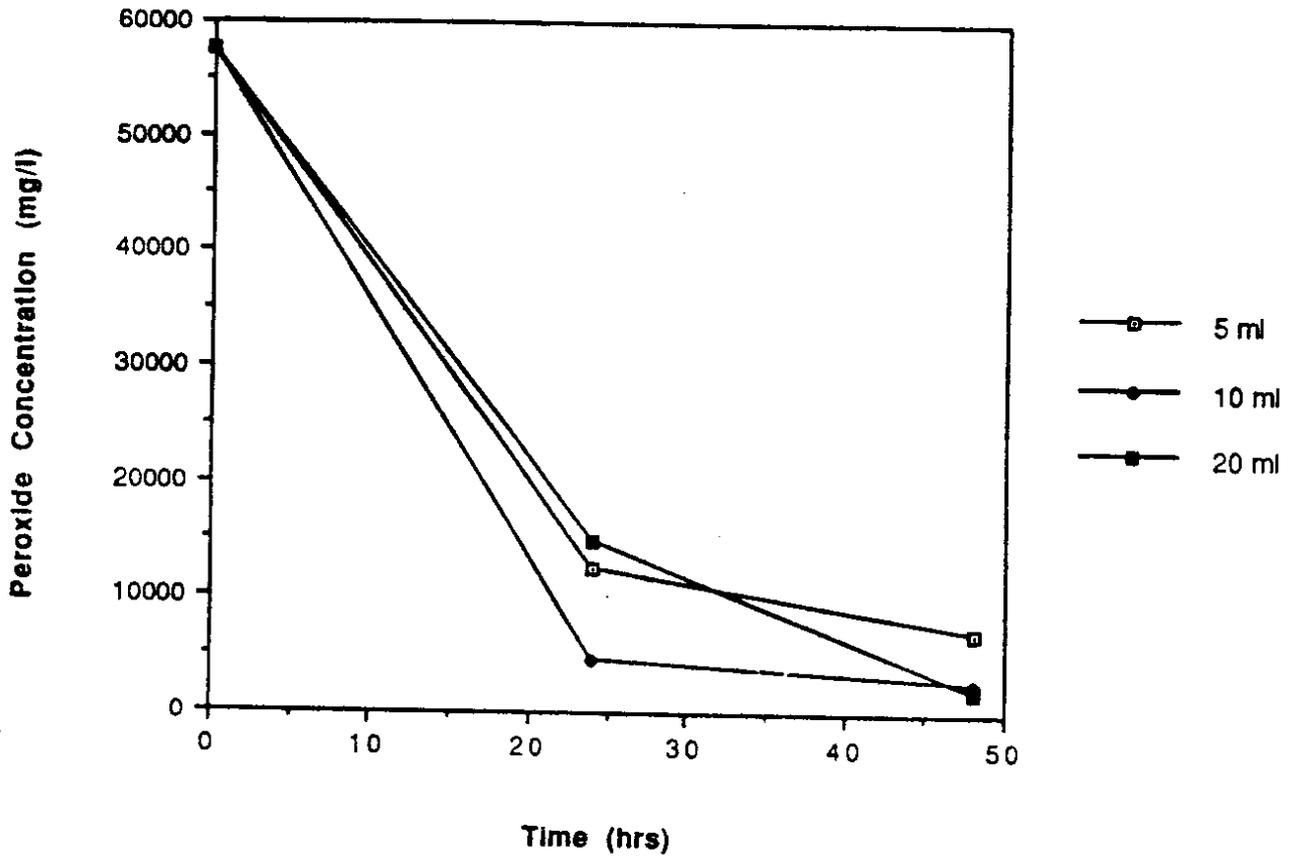


Figure 4. Hydrogen peroxide consumption during wood treatment.

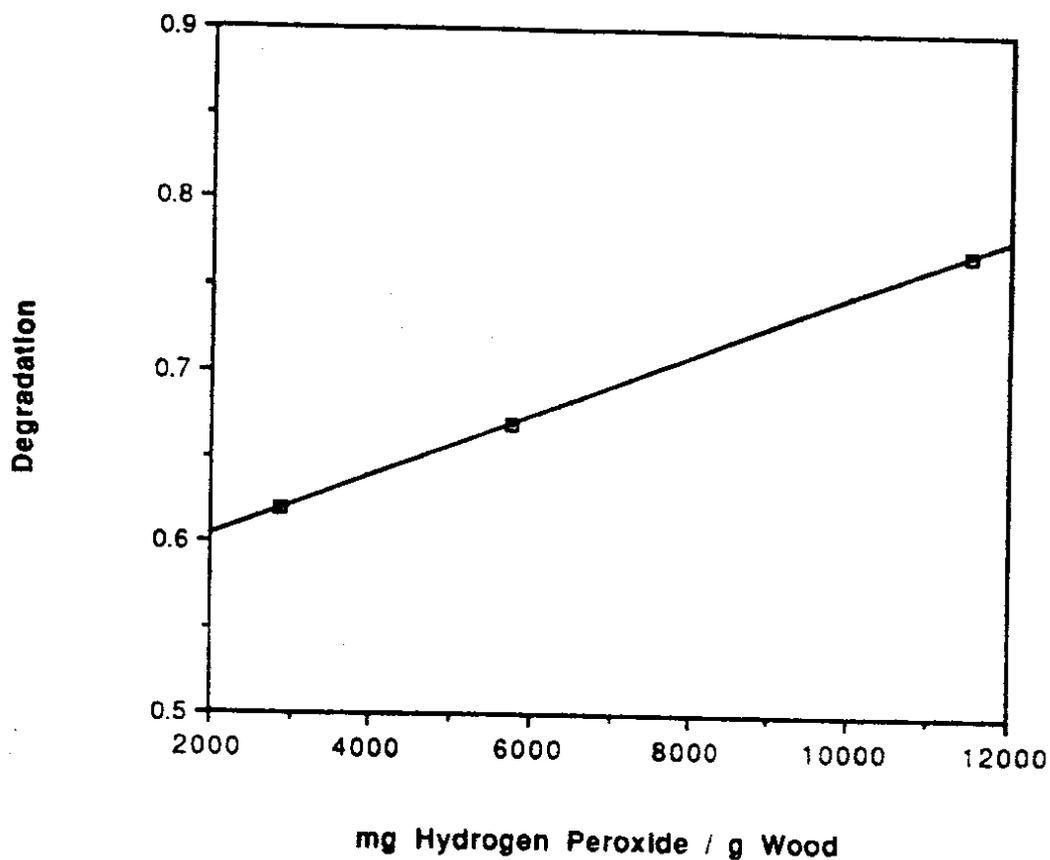


Figure 5. Degradation as a function of efficiency for wood contaminants using catalyzed hydrogen peroxide.

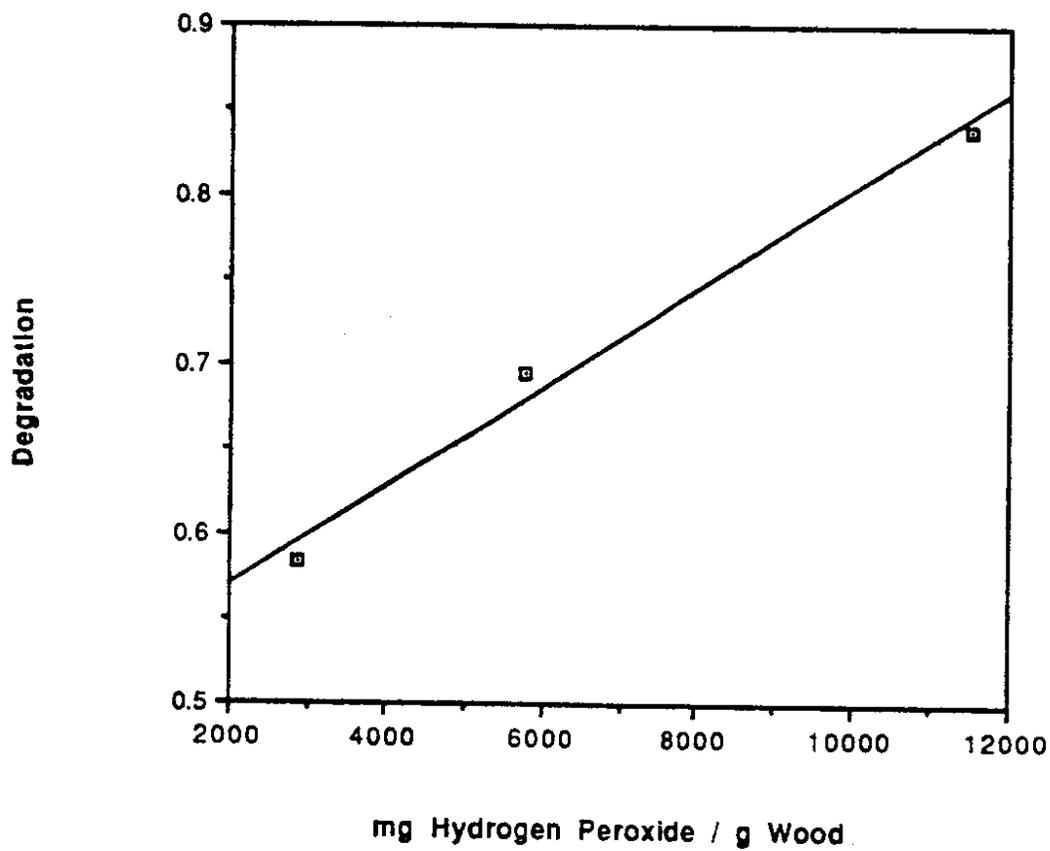


Figure 6. Degradation as a function of efficiency for PCP on wood samples using catalyzed hydrogen peroxide.

the pentachlorophenol were degraded. While this procedure would be more expensive and more complex, it offers promise for the treatment of contaminated timbers.

SOIL TREATMENT

The approach most commonly used in experimental research is to hold all variables constant except one, which is varied until the desired result is found. Using this point, the procedure is repeated for a second variable until its result is determined. The process is then repeated until the information under consideration is found for each of the variables. Such a method for either the optimization or mechanistic experimental investigation of several variables is inefficient and time consuming. More importantly, it negates the possibility of detecting interactions among variables.

The central composite rotatable design is a multivariable, multilevel experimental procedure that analyzes the interactions between the variables and produces a response equation. If only two dimensions are considered, the results may be described by a surface response, a planar description of experimental data including the maxima, minima, and interactions, which may be visualized by folds and shifts in the surface plane. Although only two dimensions may be represented graphically, a multidimensional response equation may be generated that describes the response of all variables and interactions.

The results of both the high volume/low concentration and low volume/high concentration matrices were evaluated for the concentration of diesel degraded and for treatment efficiency (mg of H₂O₂ consumed/mg of diesel degraded). The data were first analyzed to determine the response surface equation by using all four variables as well as all second, third, and fourth order interactions regardless of their level of significance. The resulting equations were characterized by low R² values (approximately 0.50). The data were then analyzed by a stepwise variable selection linear regression algorithm. In other words, the variables and interactions were analyzed in a step-wise fashion to assess their effect and importance on the response surface. The stepwise analysis showed that the effect of soil organic carbon was insignificant in the treatment of diesel fuel in the Palouse

loess soil; therefore, organic carbon was omitted in subsequent response surface development.

Similar results were noted by Tyre *et al.* (8) in the catalyzed hydrogen peroxide soil treatment of hexadecane and dieldrin. In treating four sandy soils with organic carbon contents ranging from 0.4% to 1.7%, they found that soil organic carbon had no effect on the pseudo first-order rates of hexadecane and dieldrin degradation. Although hydroxyl radical is a strong, nonspecific oxidant, it appears that, especially when the reactions are catalyzed by minerals, the oxidation of some contaminants is not affected by soil organic carbon. This minimal competition is likely related to the physical characteristics of soil organic matter, because much of it is in particulate state or bound to inorganic soil fractions (7,8). Therefore, mass transfer limitations, and the low rate at which hydroxyl radical crosses the liquid-solid interface, may provide a mechanism for minimal interference of soil organic carbon in catalyzed hydrogen peroxide soil remediation.

Total Petroleum Hydrocarbon Removal

The experimental data were first analyzed for total petroleum hydrocarbon (TPH) destruction, and the following equations were developed to describe the surface responses of the two systems without organic carbon as a significant variable.

High Volume/Low Peroxide Concentration:

$$\text{TPH degraded} = -28.8 + (1.88 \times 10^{-2})(C_{H_2O_2}) + (0.669)(C_{cont}) + (2.64 \times 10^{-2})(V)^2 + (2.50 \times 10^{-5})(C_{cont})^2 \quad R^2 = 0.99 \quad (\text{Equation 8})$$

Low Volume/High Peroxide Concentration:

$$\text{TPH degraded} = 567.49 - (1.69 \times 10^{-3})(C_{H_2O_2}) - (36.8)(V)^2 + (9.86 \times 10^{-4})(C_{H_2O_2})(V) + (1.79 \times 10^{-6})(C_{H_2O_2})(C_{cont}) \quad R^2 = 0.89 \quad (\text{Equation 9})$$

where $C_{H_2O_2}$ = Hydrogen Peroxide Concentration (mg/L)
 C_{cont} = Contaminant Concentration (mg/kg)
 V = Slurry Volume (multiples of field capacity)

In order to interpret Equations (8) and (9), hydrogen peroxide concentration as a function of slurry volume was plotted at low, medium, and high contaminant concentrations. The plots for the high volume/low peroxide concentration systems are shown in Figure 7a-c.

The response surfaces are read by drawing an imaginary vertical line up from any point on the x axis to meet a line drawn horizontally from the y axis. These conditions of slurry volume and hydrogen peroxide concentration will produce a specific amount of TPH degradation, which is noted on the isoconcentration lines running across the plots. For example, in Figure 7a, a treatment system using a peroxide volume of 30 times the soil field capacity at a concentration of 6000 mg/l will treat 450 ppm of TPH. By analogy on Figure 7b, a liquid peroxide volume of 25 times the soil field capacity of 10,000 mg/l hydrogen peroxide will degrade 1,050 ppm TPH.

The trends are the same for the three initial TPH concentrations; more contaminant was degraded with higher volumes and higher concentrations of peroxide. These data also show greater TPH destruction with increased hydrogen peroxide concentration compared to increased volume. The effect may be related to the dynamics of the high volume system in which desorption is the rate-limiting step that requires a long-lasting peroxide residual, a system characteristic enhanced by high peroxide volume and concentration.

The results of the low volume/high peroxide concentration system are shown in Figure 8a-c. The trend is the same for the three contaminant levels; i.e., the amount of TPH degraded increased with higher slurry volumes and higher peroxide concentrations. However, unlike the data of Figure 7, slurry volume had a significant effect, especially at the lower slurry volumes and the high peroxide concentrations.

The data of Figures 7 and 8 also show that the higher the initial TPH concentration, the greater the mass of TPH destroyed. This trend may be due to a greater number of collisions between hydroxyl radicals and hydrocarbon molecules as a function of the initial TPH concentration. Both systems were able to meet the common state regulatory criteria of

High Volume/Low Concentration

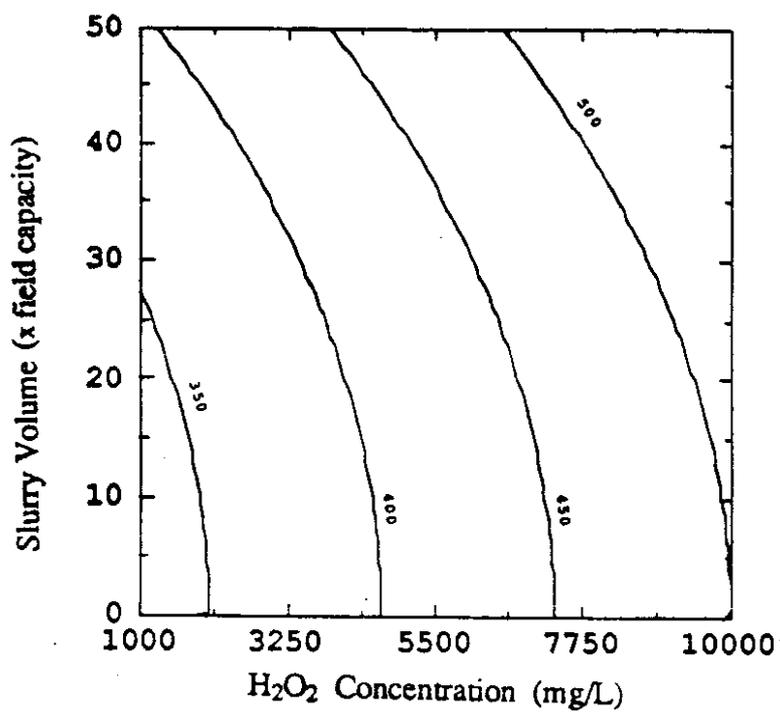


Figure 7a. Mg diesel degraded as a function of hydrogen peroxide and slurry volume with initial diesel concentrations of 500 mg/kg.

High Volume/Low Concentration

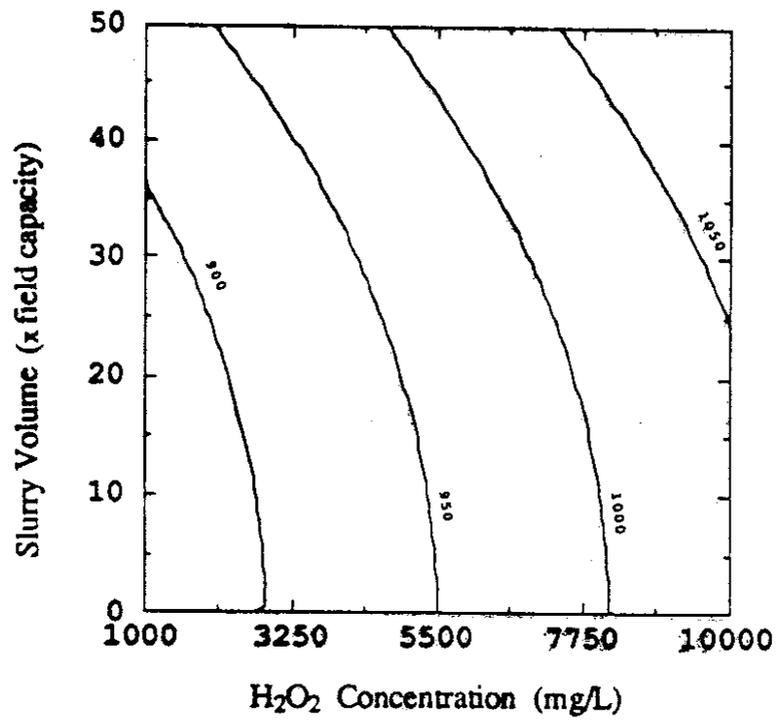


Figure 7b. Mg diesel degraded as a function of hydrogen peroxide and slurry volume with initial diesel concentrations of 1,250 mg/kg.

High Volume/Low Concentration

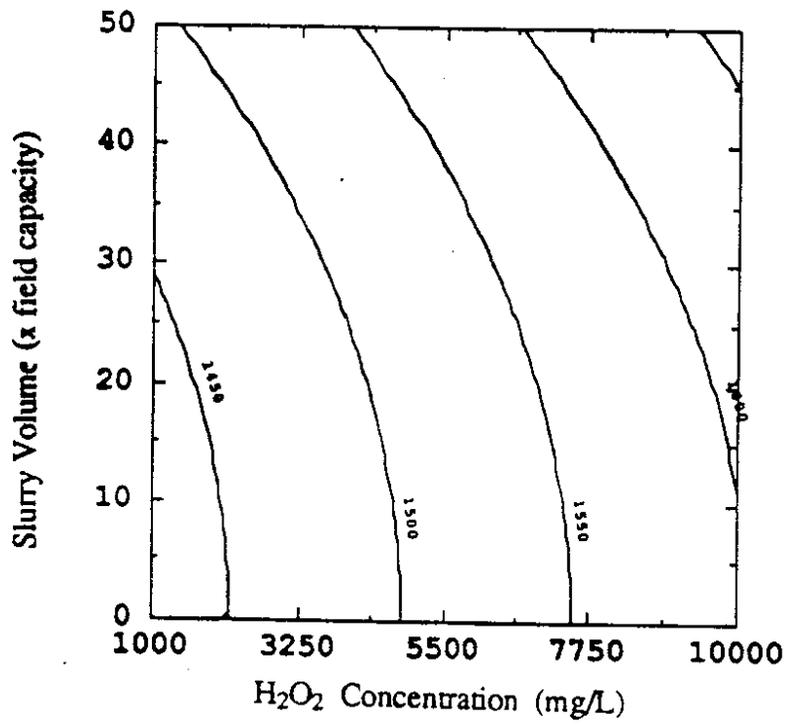


Figure 7c. Mg diesel degraded as a function of hydrogen peroxide and slurry volume with initial diesel concentrations of 2,000 mg/kg.

Low Volume/High Concentration

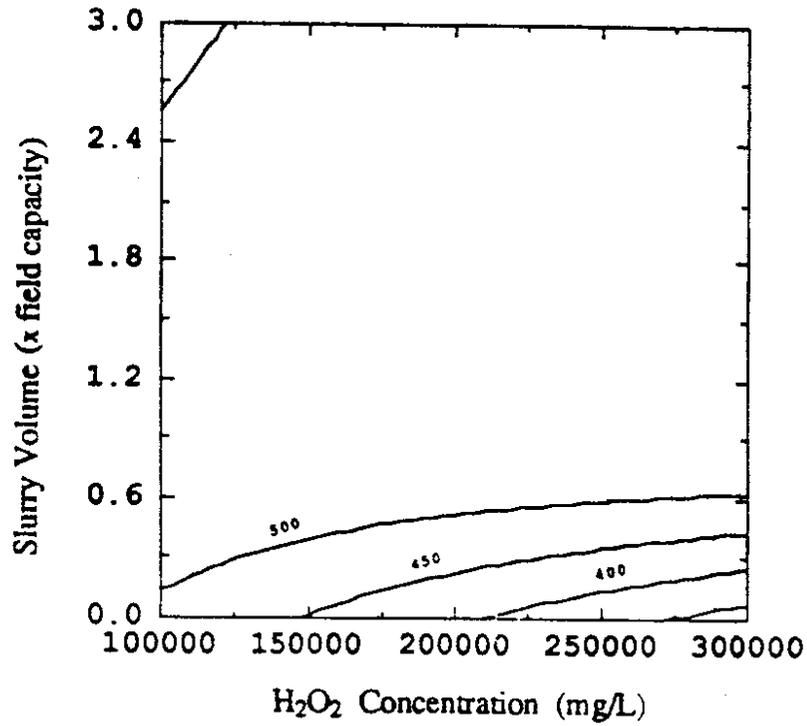


Figure 8a. Mg diesel degraded as a function of hydrogen peroxide and slurry volume with initial diesel concentrations of 500 mg/kg.

Low Volume/High Concentration

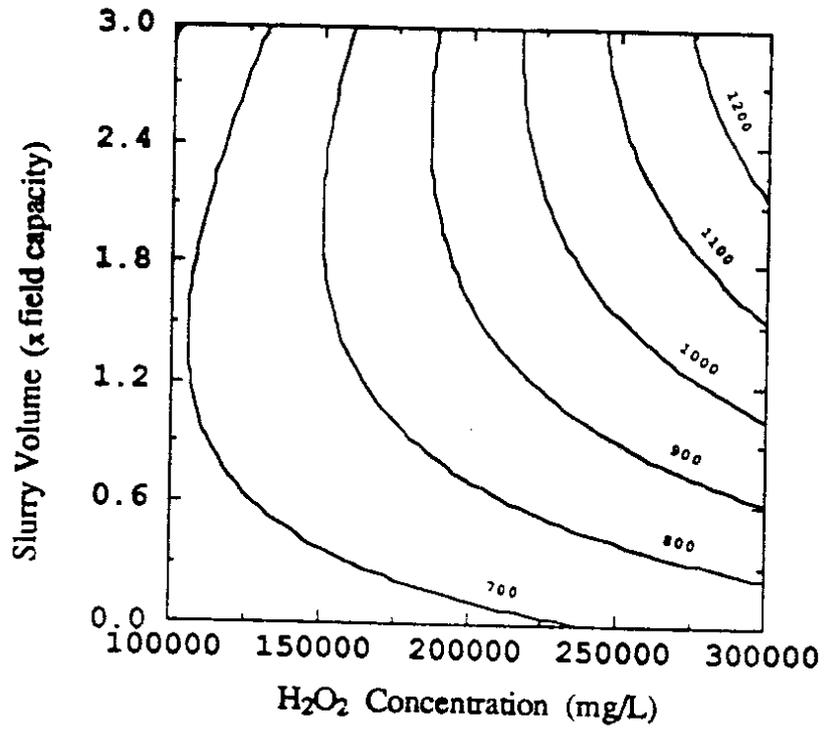


Figure 8b. Mg diesel degraded as a function of hydrogen peroxide and slurry volume with initial diesel concentrations of 1,250 mg/kg.

Low Volume/High Concentration

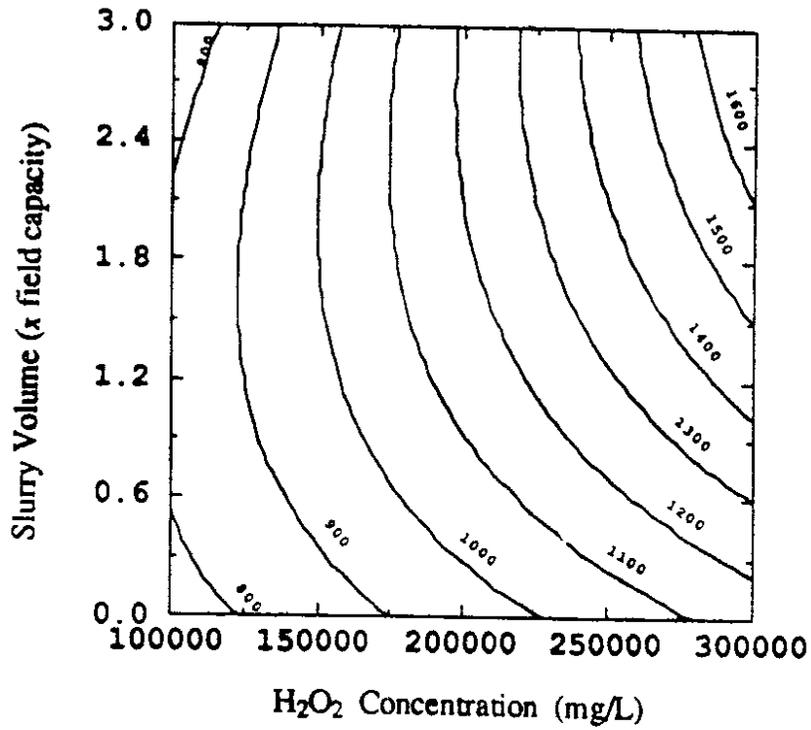


Figure 8c. Mg diesel degraded as a function of hydrogen peroxide and slurry volume with initial diesel concentrations of 2,000 mg/kg.

200 mg/kg TPH for diesel under the experimental treatment conditions, except at the initial TPH concentration of 2000 mg/kg. At this higher initial TPH concentration, a sufficient amount of hydrogen peroxide may not have been available to drive the reaction below the 200 mg/kg action level. Although soil characteristics may vary, equations (8) and (9) serve as a basis to assess the peroxide requirements for required TPH destruction. By using the response equations or the response surfaces, peroxide dosages and slurry volumes may be determined for a range of initial TPH concentrations.

Treatment Efficiency

Not only is the effective treatment of TPH or other contaminants important in soil remediation, but also the cost of the process. The primary cost for catalyzed peroxide treatment is hydrogen peroxide. Therefore, the most efficient treatment efficiency (i.e., minimal peroxide consumed/contaminant degraded) is necessary in order to provide cost-effective remediation. Treatment efficiency is most commonly reported as moles of peroxide consumed/mole substrate degraded. However, diesel is composed of hundreds of hydrocarbons of varying molecular weights, and an analysis of molar efficiency is impossible. Therefore, treatment efficiency was calculated on a mass basis (i.e., mg peroxide consumed/mg TPH destroyed). The following response surface equations were then developed to describe the treatment efficiency of both systems.

High Volume/Low Concentration:

$$\text{Efficiency} = 148 - (0.186)(C_{cont}) + (5.30 \times 10^{-5})(C_{cont})^2 + (3.34 \times 10^{-4})(C_{H_2O_2})(V) \quad R^2 = 0.93 \quad (\text{Equation 10})$$

Low Volume/High Concentration:

$$\begin{aligned} \text{Efficiency} = & -145 + (1.054 \times 10^{-3})(C_{H_2O_2}) + (150)(V) \\ & + (7.10 \times 10^{-5})(C_{cont})^2 \\ & + (2.64 \times 10^{-4})(C_{H_2O_2})(V) \\ & - (7.70 \times 10^{-7})(C_{H_2O_2})(C_{cont}) \\ & - (9.00 \times 10^{-2})(C_{cont})(V) \end{aligned} \quad R^2 = 0.98 \quad (\text{Equation 11})$$

where $C_{H_2O_2}$ = Hydrogen Peroxide Concentration (mg/L)
 C_{cont} = Contaminant Concentration (mg/kg)
 V = Slurry Volume (multiples of field capacity)

Equations (10) and (11) were interpreted by plotting response surfaces for hydrogen peroxide concentration as a function of slurry volume at low, medium, and high contaminant concentrations. The efficiency of the high volume/low concentration matrix is shown in Figure 9a-c. The trends of the three figures are similar, which show that the system is more efficient with low slurry volumes and low peroxide concentrations. Both variables (slurry volume and peroxide concentration) affect the system efficiency; therefore, at low contaminant levels most of the hydrogen peroxide is in excess and decomposes with no beneficial effect. At low slurry volumes, the peroxide is in closer contact with the contaminant and the mineral surfaces where Fenton-like reactions are likely occurring (7). Furthermore, the treatment efficiency becomes increasingly efficient as a function of initial TPH concentration. In summary, reducing the slurry volume likely increases the potential of hydroxyl radical collisions with the contaminant, and by analogy, hydroxyl radical collisions are also enhanced in soils containing higher concentrations of hydrocarbons.

The treatment stoichiometries shown in Figures 9 and 10 become more efficient at lower peroxide concentrations due to decreased quenching. Equations (2) and (3) are the predominant quenching reactions in Fenton's systems; however, the reaction described by Equation (2) is probably not important because soluble iron concentrations are negligible in these mineral-catalyzed soil systems. The most efficient Fenton's systems use dilute hydrogen peroxide to minimize quenching (11); based on the data shown in Figure 7a-c, the same trend is evident for mineral-catalyzed Fenton-like reactions in soils.

The trends in the efficiency of the low volume/high concentration system (Figure 10a-c) are similar to the high volume/low concentration system. However, with the initial TPH concentration of 2000 mg/kg, there was an anomalous trend in that more efficient efficiency was achieved at high peroxide concentrations and small volumes. In

High Volume/Low Concentration

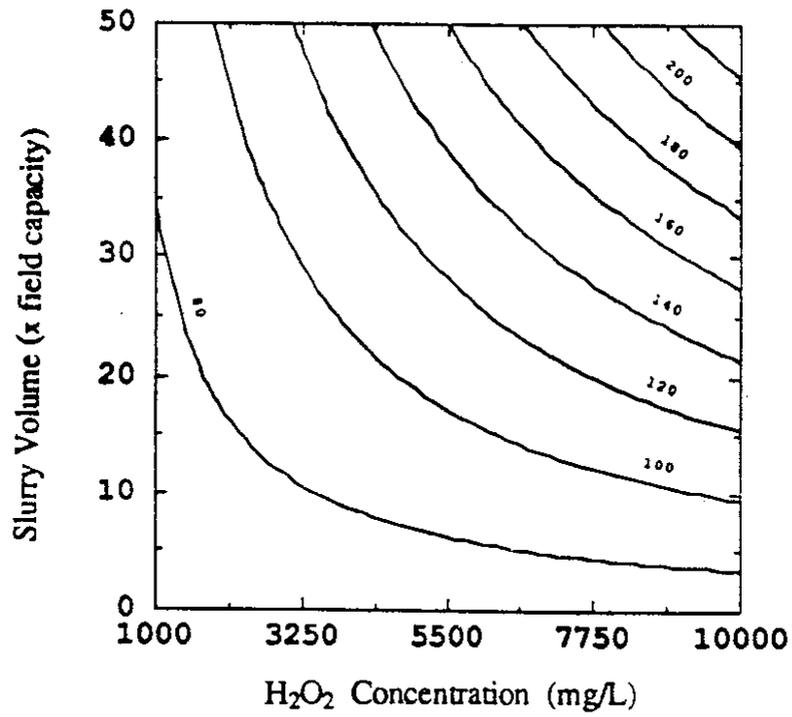


Figure 9a. Mg peroxide consumed/mg of diesel degraded as a function of hydrogen peroxide and slurry volume with initial diesel concentrations of 500 mg/kg.

High Volume/Low Concentration

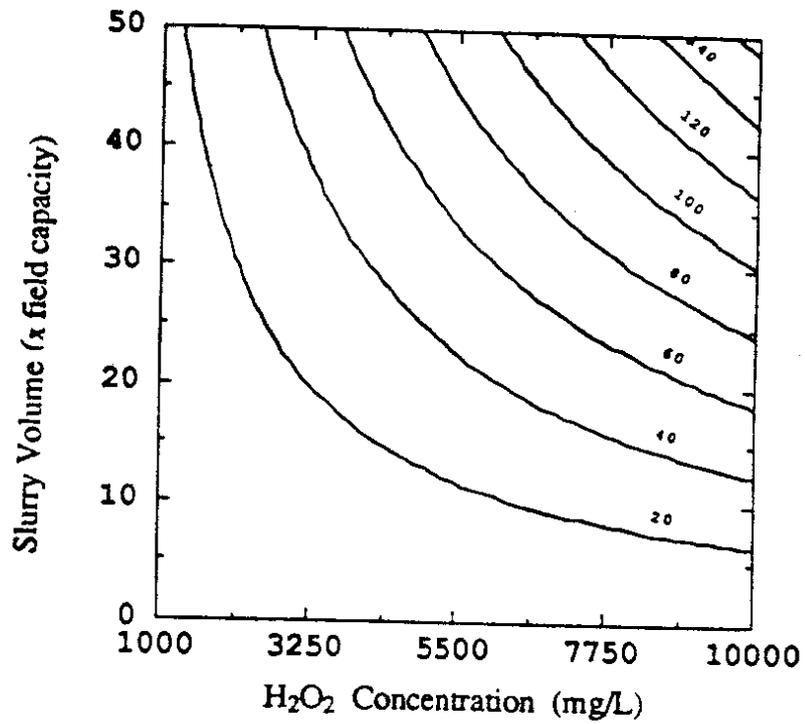


Figure 9b. Mg peroxide consumed/mg of diesel degraded as a function of hydrogen peroxide and slurry volume with initial diesel concentrations of 1250 mg/kg.

High Volume/Low Concentration

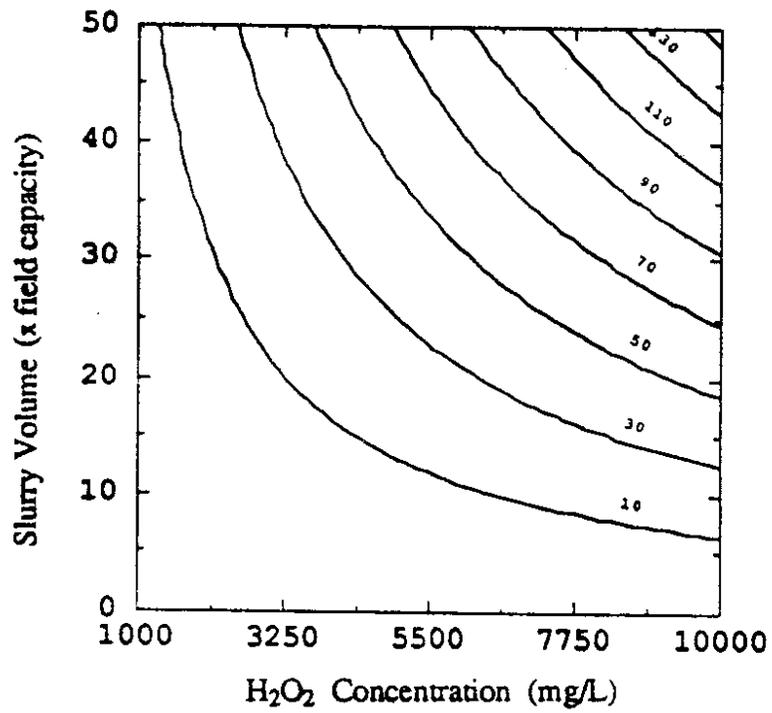


Figure 9c. Mg peroxide consumed/mg of diesel degraded as a function of hydrogen peroxide and slurry volume with initial diesel concentrations of 2000 mg/kg.

Low Volume/High Concentration

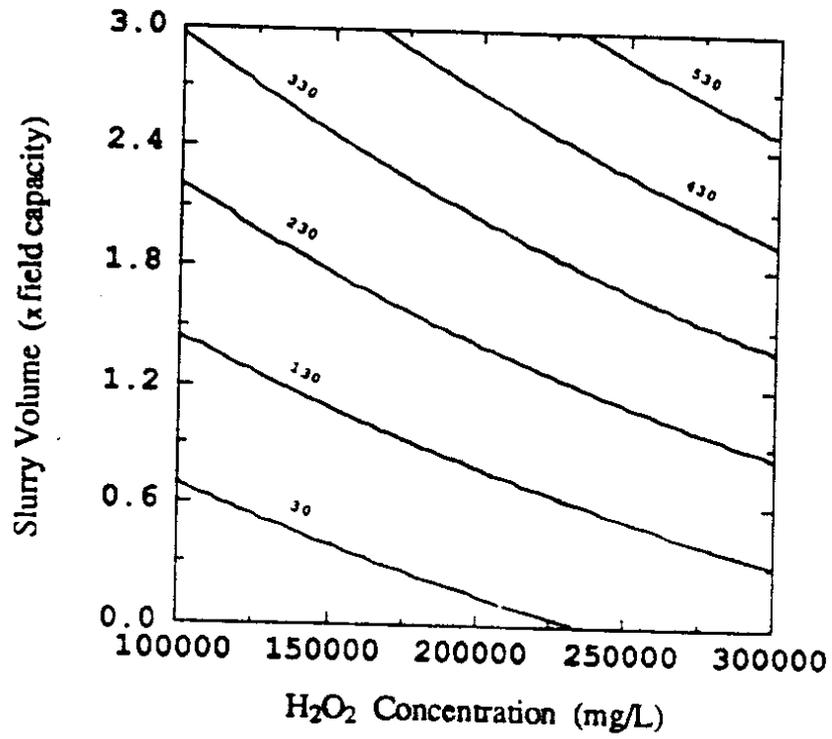


Figure 10a. Mg peroxide consumed/mg of diesel degraded as a function of hydrogen peroxide and slurry volume with initial diesel concentrations of 500 mg/kg.

Low Volume/High Concentration

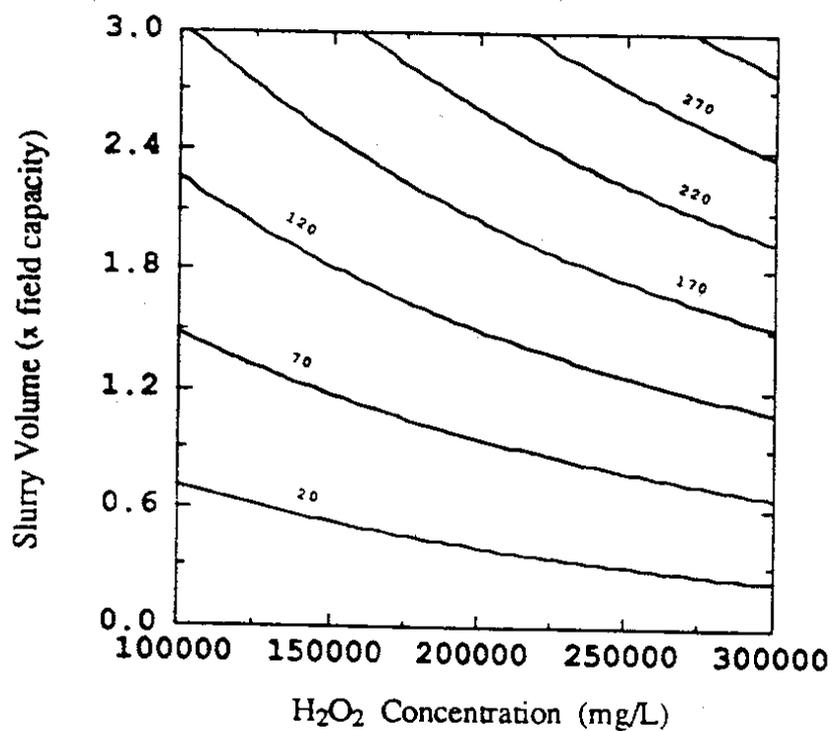


Figure 10b. Mg peroxide consumed/mg of diesel degraded as a function of hydrogen peroxide and slurry volume with initial diesel concentrations of 1250 mg/kg.

Low Volume/High Concentration

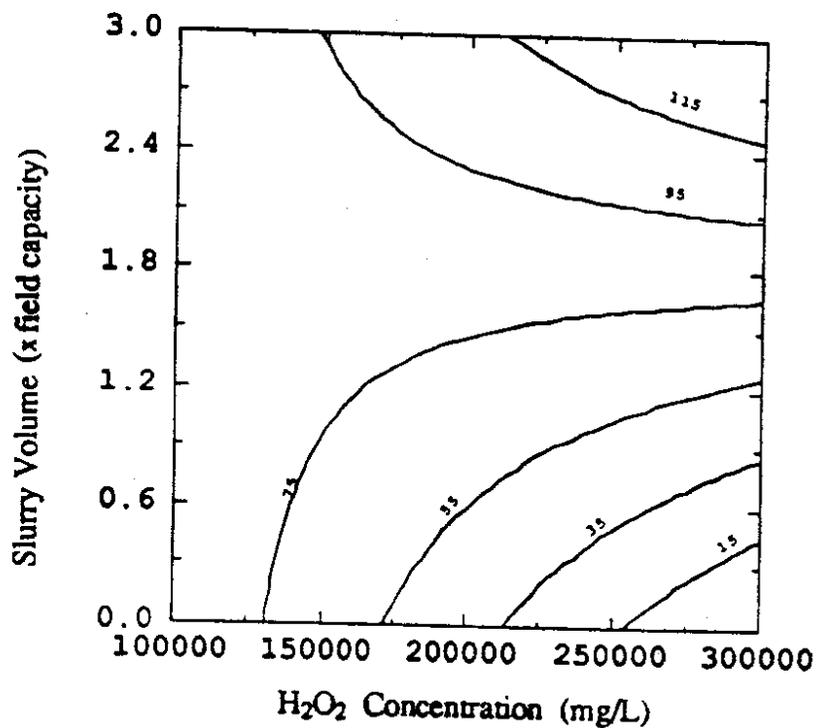


Figure 10c. Mg peroxide consumed/mg of diesel degraded as a function of hydrogen peroxide and slurry volume with initial diesel concentrations of 2000 mg/kg.

this system, the volumes may have been so much smaller that there was optimum contact between the hydrocarbons and the oxidants with resulting efficient efficiency.

Molar efficiency for the catalyzed peroxide treatment of aqueous waste streams usually ranges from 4-13 moles of peroxide/mole of substrate (18). In applying catalyzed hydrogen peroxide to the treatment of soils under aggressive conditions, molar stoichiometries of 600 - 3000 moles of peroxide/mole of substrate have been required (7, 9). In this study, efficiency was calculated on a mass basis because of the complex composition of diesel fuel. However, by assuming a mean hydrocarbon size of C_{20} , the average molecular weight for diesel would be 282 g/mole, and the most effective efficiency of 10 mg peroxide/mg diesel (achieved at initial diesel concentration of 2000 mg/kg and 10,000 mg/L of peroxide at 6.5 x field capacity in the high volume/low concentration system) would be equivalent to 83 moles of peroxide/mole of diesel. Considering the complexity of soil systems and the associated quenching reactions, 83 moles peroxide/mole diesel is significantly more efficient than previously reported results.

Cost Considerations

The application of the response surfaces to the remediation of contaminated soils requires treating to regulated or negotiated levels, while doing so under the most economical conditions. By using Figure 7 in conjunction with Figure 9, and Figure 8 combined with Figure 10, respectively, the process conditions that provide effective treatment with the most efficient efficiency may be assessed. For example, by transposing Figures 7c and 9c (high volume/low concentration), the optimum treatment may be achieved with 1600 mg of TPH destroyed and efficiency of 10 mg peroxide/mg TPH degraded (Figure 11). The process conditions for this system include 10,000 mg/L hydrogen peroxide at 6.5 times the soil field capacity. Based on a unit price of \$0.343/lb for 50% peroxide, the peroxide cost is \$29 per 909 kg of soil treated (1 U.S. ton).

By overlaying Figure 8c with Figure 10c, (low volume/high concentration), the optimum treatment is found at 1200 mg of TPH destroyed and efficiency of 15 mg peroxide/mg TPH degraded as shown in Figure 12. The process conditions for this system are 282,000 mg/L hydrogen peroxide at a volume of 0.3 times field capacity with a cost of \$38 per 909 kg of soil. These process conditions provide only 60% reduction of TPH; however, 80% TPH reduction may be achieved with a significantly higher cost. Using efficiency of 95 mg peroxide/mg TPH degraded and 1600 mg of TPH destroyed, the process conditions are 300,000 mg/L hydrogen peroxide and a slurry volume of 2.1 times field capacity. The cost of this more aggressive system increases to \$285 per 909 kg of soil. Therefore, if a short time is required to complete the remediation, the most economical application of the low volume/high concentration system would be to add sequential doses at the more efficient process condition. The high volume/low concentration process conditions are the most economical, but require approximately three weeks for treatment. The chemical costs for the low volume/high concentration system are substantially higher, but the reactions are completed within three days. Therefore, the high concentration/low volume system may find more use for spills and emergency response efforts that require rapid treatment based on regulations or site logistics.

DESIGN PROCEDURE

Fenton's systems, particularly in soils, are extremely complex. Some of the reactions that may occur include quenching of hydroxyl radicals by hydrogen peroxide, perhydroxyl, iron, bicarbonate, and organic matter. In addition, sorption of the contaminants greatly controls treatment effectiveness and the hydroxyl radical generation rates are proportional to the iron oxide content of the soil. Because of the extreme degree of complexity and competing reactions, prediction of hydrogen peroxide dosages based on simple linear relationships (e.g. hydrogen peroxide concentration as a function of TPH to be treated) is nearly impossible. However, two procedures for process design may be

used: 1) a more accurate approach based on the response surface procedures and 2) an estimation technique based on the surface response combined with engineering judgement. The first approach would best be used by WSDOT scientists and engineers who could perform the necessary calculations and provide a more accurate process design for clean up. The second method is more applicable for use by maintenance and field personnel, and would be more of a "recipe" approach involving specified volumes and weights of each of the reagents used.

The procedure for the first (response surface procedure) is:

1. Determine the mean contaminant concentration of the soil and the mass or volume of soil to be treated (On the average, 1 yd³ weighs 3800 lbs).
2. Using the high volume/low concentration surface response equation (Equation 8) and a volume of 10 x the field capacity, solve for the required concentration of hydrogen peroxide.

Note: field capacity is a measure of the water-holding ability of the soil, and is the best indicator of the hydrogen peroxide volume requirement. Typical values of field capacity are 0.3 to 0.5 ml/gram of soil or 72 to 120 gallons/ton of soil. The field capacity can be estimated by placing 1 lb of soil in a flower pot and adding water until it drips out the bottom. The volume added is the field capacity per lb of soil. If you do not measure the field capacity of the soil, use a value of 80 gallons/ton of soil.

3. Repeat the calculation at volumes of 15, 20, 25, and 30 times field capacity.
4. Determine the cost of hydrogen peroxide associated with each volume (10, 15, 20, 25, 30 times field capacity) and use the volume with the least cost.

The second method for determining hydrogen peroxide requirements is based on data developed from the response surfaces, but simplified into tabular form for use by field personnel. The procedure is based simply on knowing the initial TPH concentration and reading the hydrogen peroxide concentration and volume from Table 4.

Table 4. Field estimation of catalyzed peroxide treatment using low peroxide concentrations and high volumes.

Initial TPH Concentration	Hydrogen Peroxide Concentration	Volume per ton of soil
300 - 800	0.5%	800 gallons
800 - 1300	1%	2000 gallons
1300 - 1800	1%	2400 gallons
1800 - 2300	1%	3200 gallons

Desorption (the release of weakly bonded hydrocarbons from soil particles into the water phase of a soil-water slurry) is the process that controls the effectiveness of hydrogen peroxide treatment, and is the reason for the time requirement of two-to-three weeks for the high volume/low concentration systems. Use of low volume/high concentration peroxide has advantages of oxidizing adsorbed contaminants (i.e., it is not necessary to wait for the contaminants to desorb before they are oxidized); therefore, remediation can be achieved in a short time period of a few hours. The low volume/high concentration process modification is best suited for compounds that do not readily desorb. The class of waste materials of concern to WSDOT that falls into this category include motor oil, hydraulic oil, and other heavy petroleum fractions. In addition, the low volume/high concentration system can be used on lighter fractions (e.g., gasoline, diesel) if rapid (2-3 hr) clean up is warranted.

The response surface procedure (i.e., the engineering/scientific basis) for determining hydrogen peroxide requirements for the low volume/high concentration system are as follows:

1. Determine the mean contaminant concentration of the soil and the mass or volume of soil to be treated.
2. Using the low volume/high concentration surface response equation (Equation 9), and a volume of 0.5 times the soil field capacity, solve for the required concentration of hydrogen peroxide.
3. Repeat the calculation at volumes of 1, 1.5, 2, and 2.5 times the soil field capacity.
4. Determine the cost of hydrogen peroxide for each volume and use the volume with the volume with the least cost.

To implement the low volume/high concentration system without the engineering analysis, the guidelines of Table 5 can be followed to estimate peroxide dosage.

Sample	Percent H ₂ O ₂	Volume
Gasoline or diesel 200 - 1000 mg/kg	25%	48 gal
Gasoline or diesel 1000 - 2000 mg/kg	35%	48 gal
Motor oil or hydraulic oil 200 - 1000 mg/kg	50%	96 gal
Motor oil or hydraulic oil 1000 - 2000 mg/kg	50%	192 gal

Example 1. Ten tons of soil contaminated with 800 mg/kg diesel are to be treated to the 200 mg/kg level using catalyzed hydrogen peroxide. The soil field capacity is 0.35 ml/g. Using the response surface equation (Equation 8) for high volume/low peroxide concentration, determine the hydrogen peroxide requirements.

Solution: Using a multiple of field capacity of 10, Equation 8 becomes:

$$600 \text{ mg/kg} = -28.8 + (1.88 \times 10^{-2}) (\text{CH}_2\text{O}_2) + 0.669 (800) = (2.64 \times 10^{-2}) (10)^2 + 2.50 \times 10^{-5} (800)^2$$

$$\text{CH}_2\text{O}_2 = 4000 \text{ mg/l.}$$

Using 15 times the field capacity, $\text{CH}_2\text{O}_2 = 3800 \text{ mg/l}$.

$$V = 1,260 \text{ gallons}$$

$$\text{Cost} = \$29/\text{ton}$$

Using Vol = 20 times field capacity:

$$\text{CH}_2\text{O}_2 = 3,570 \text{ mg/l.}$$

$$V = 1,677 \text{ gallons}$$

$$\text{Cost} = \$36/\text{ton}$$

The most inexpensive process design is $\text{CH}_2\text{O}_2 = 4000 \text{ mg/l}$ and Volume = 10 times the soil field capacity.

Example 2. Repeat Example 1 using the field approximation technique.

Solution: From Table 4, use 0.5% H_2O_2 and 800 gallons of liquid. This treatment provides a slightly lower volume of H_2O_2 , but higher concentration, resulting in about the same dosage.

SITE AND SAFETY FACTORS

Fenton's reactions in soils are extremely complex, but some trends are emerging as research progresses. Soil moisture content has little effect on the remediation process because it is conducted under saturation conditions. Because iron oxides are the primary Fenton's catalysts in soil systems, catalysis rates are proportional to the crystalline iron

oxide content of the soil. The effect of soil particle size distribution requires further study; the data collected to date suggest that the process is more effective in sandy soils.

The effect of catalyzed hydrogen peroxide reactions on metals in soils has not been studied, the process will likely have no effect because metals are conservative and not highly mobile in their oxidized state (which is promoted by the high oxidizing conditions of catalyzed peroxide).

Although transition metals (e.g. iron, copper, zinc cadmium) have been shown to catalyze hydrogen peroxide, nontransition elements (e.g., calcium, magnesium, sodium, potassium) do not catalyze Fenton's reactions. The most important metal fraction for catalyzing the decomposition of hydrogen peroxide are naturally occurring iron oxides such as goethite and hematite (8,9).

The oxidation-reduction processes of Fenton's reactions produce trace quantities of sulfur dioxide, but these reactions can be controlled by minimizing the use of sulfuric acid.

ENGINEERING APPLICATIONS

On site soil remediation can be conducted under either *in situ* or *ex situ* conditions. *In situ* treatment involves treating the soil while it is still in place. *Ex situ* treatment consists of excavation of the soil and treating it in an on site reactor. During *in situ* treatment, the hydrogen peroxide would be applied directly to the contaminated soil. Possible applications include intermittent spraying, a continuous sprinkler system, or by nozzle injection. *Ex situ* treatment applications would involve placing the excavated soil and peroxide solution into a batch reactor. The reactor may consist of a polyethylene tank, a shallow earth basin lined with a high-density polyethylene liner, or a concrete mixer.

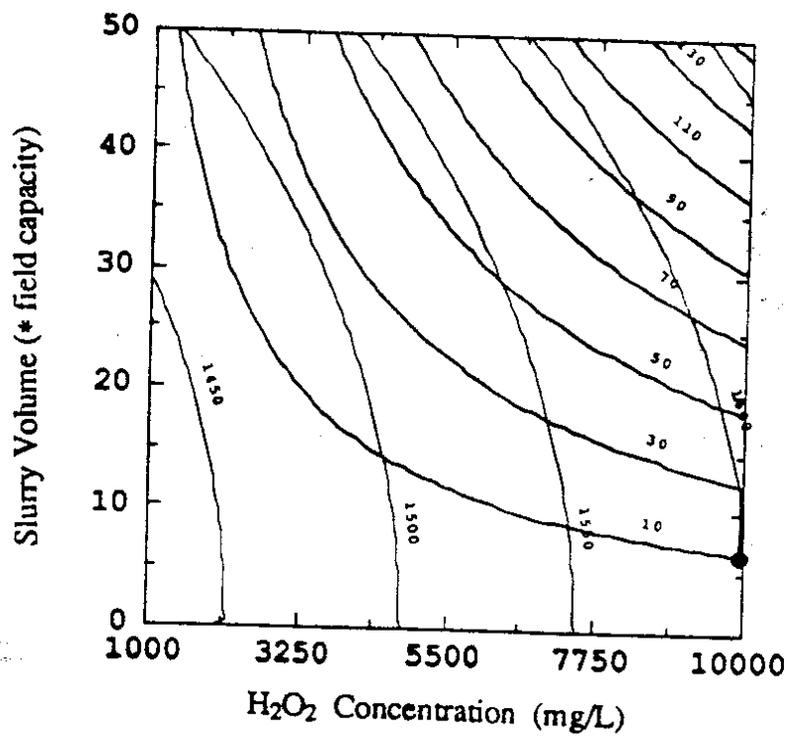


Figure 11. Efficiency and TPH removal for the high volume/low concentration at an initial diesel concentration of 2000 mg/kg.

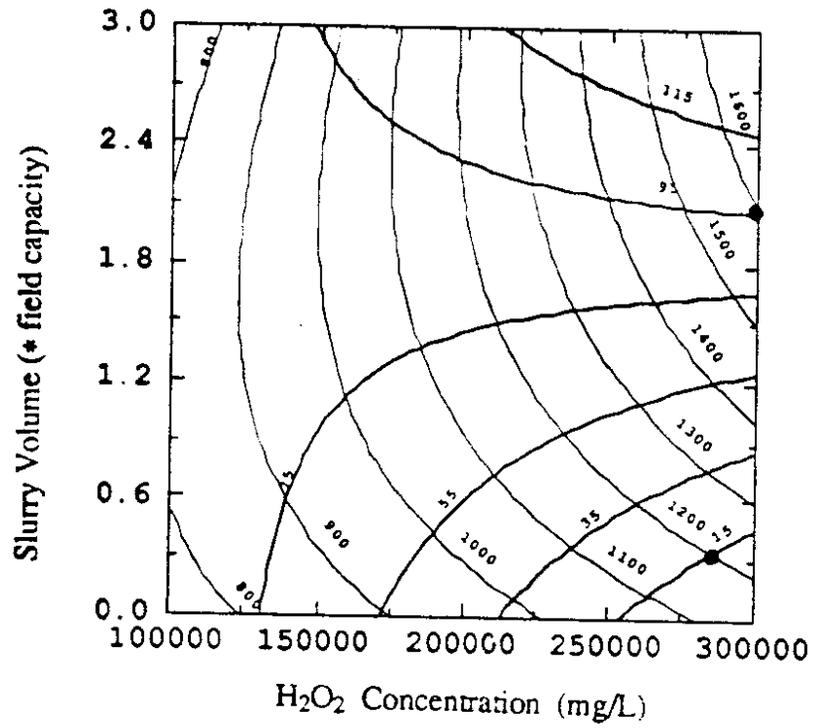


Figure 12. Efficiency and TPH removal for the low volume/high concentration at an initial diesel concentration of 2000 mg/kg.

The mixing action that would be provided by the concrete mixer may enhance mass transfer and reduce the time required for the reaction to take place. Another possibility for *ex situ* treatment would be to create a leach system, where the excavated soil is piled onto a concrete barrier that has a collection system installed. The peroxide solution could then be applied with a sprinkler system, allowing the solution to leach through the soil. Different soil and contaminant characteristics affect treatment conditions, such as the concentration and volume of hydrogen peroxide and the reaction time required. Therefore, pilot studies may be needed to evaluate the scale-up effectiveness of different reactor configurations.

With *in situ* treatment more risks are involved because of the potential for leaching contaminants or degradation products. *Ex situ* treatment is more conservative because there is more control over the process and the system is contained. As research continues, emphasis will first be placed on *ex situ* treatment before developing *in situ* application processes. The required peroxide may be applied in one dose, sequential doses or continuously. If the peroxide is added in one dose, it will require a higher concentration and a larger volume. Alternatively, if the peroxide is added continuously, the constant conditions will keep the peroxide concentration at a steady state. This may be more efficient and cost effective. Another possible application of the catalyzed hydrogen peroxide treatment is to use it in combination with other soil treatment technologies. For example, in combination with the soil washing process or bioremediation.

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REFERENCES

1. Khisty, C.J. *Transportation Engineering An Introduction*. Prentice Hall, Englewood Cliffs, New Jersey, 1990.
2. Maresca Jr., J.W.; Roach, R.D.; Sibel, M.; Star, J.W. *Volumetric Leak Detection Methods for Underground Fuel Storage Tanks* Pollution Technology Review No. 180. Noyes Data Corp., Park Ridge, New Jersey, 1990.
3. U.S. Environmental Protection Agency "Remedial Actions at Waste Disposal Sites," EPA 625/6-85-006, U.S. Gov. Print Office, Washington D.C., 1985.
4. Manahan, S.E. *Hazardous Waste Chemistry, Toxicology and Treatment* Lewis Publishers, Chelsea, Michigan, 1990.
5. Thomas, J.M.; Ward, C.H. "In Situ Bioremediation of Organic Contaminants in the Subsurface," *Environ. Sci. Technol.* **23**: 760 (1989).
6. U.S. Environmental Protection Agency. *Engineering Bulletin: Soil Washing Treatment*. USEPA Report EPA 540/2-90-017. U.S. Gov. Print Office, Washington D.C., 1990.
7. Watts, R.J.; Rauch, P.A.; Leung, S.W.; Udell, M.D. "Treatment of Pentachlorophenol-Contaminated Soils Using Fenton's Reagent," *Haz. Waste Haz. Mater.* **7**: 335 (1990).
8. Tyre, B.W.; Watts, R.J.; Miller, G.C. "Treatment of Four Biorefractory Contaminates in Soils Using Catalyzed Hydrogen Peroxide," *Jour. Environ. Qual.* **20**: 832 (1991).
9. Watts, R.J.; Udell, M.D.; Monsen R.M. "Use of Iron Minerals in Optimizing the Peroxide Treatment of Contaminated Soils," *Water Environ. Res.* **65**: 839 (1993).
10. Fenton, H.J.H. "Oxidation of Tartaric Acid in Presence of Iron," *J. Chem. Soc.* **65**: 899 (1894).
11. Kolthoff, I.M.; Medalia, A.I. "The Reaction Between Ferrous Iron and Peroxides. II. Reaction with Hydrogen Peroxide in the Presence of Oxygen," *J. Am. Chem. Soc.* **71**: 3784 (1949).
12. Uri, N. "Inorganic Free Radicals in Solution," *Chem. Reviews* **50**: 376 (1951).
13. Walling, C. "Fenton's Reagent Revisited," *Acc. Chem. Research* **8**: 125 (1975).
14. Haber, F.; Weiss, J. "The Catalytic Decomposition of Hydrogen Peroxide by Iron Salts," *Proc. Royal Soc. London* **147**: 332 (1934).
15. Barb, W.G.; Baxendale, J.H.; George, P.; Hargrave, K.R. "Reactions of Ferrous and Ferric Ions with Hydrogen Peroxide. Part 1: The Ferrous Ion Reaction," *J. Chem. Soc.* **121**: 462 (1950).
16. Barbeni, M.; Minero, C.; Pelizzetti, E. "Chemical Degradation of Chlorophenols with Fenton's Reagent," *Chemosphere* **16**: 2225 (1987).

17. Murphy, A.P.; Boegli, W.J.; Price, M.K.; Moody, C.D. "A Fenton-Like Reaction to Neutralize Formaldehyde Waste Solutions," *Environ. Sci. Tech.* **23**: 166 (1989).
18. Bowers, A.R.; Eckenfelder Jr., W.W.; Gaddipati, P.; Monsen, R.M. "Treatment of Toxic or Refractory Wastewaters with Hydrogen Peroxide," *Water Sci. Technol.* **21**: 477 (1989).
19. Leung, S.W.; Watts, R.J.; Miller, G.C. "Degradation of Perchloroethylene by Fenton's Reagent: Speciation and Pathway," *J. Environ. Quality* **21**: 377 (1992).
20. Watts, R.J., "Hydrogen Peroxide for Physicochemically Degrading Petroleum-Contaminated Soils," *Remediation*, **2**:413 (1992).
21. Solomons, T.W. *Organic Chemistry*, 4th Edition, John Wiley and Sons Inc., New York, 1988.
22. Gee, B.W.; Bauder, J.W. "Particle-size Analysis," pp. 399-404 in *Method of Soil Analysis Part I*, 2nd Edition, Klute, A., Ed., ASA and SSSA, Madison, WI. 1986.
23. Nelson, D.W.; Sommers, L.E. "Total Carbon, Organic Carbon, and Organic Matter," pp. 539-579 in *Method of Soil Analysis Part III*, Page et al., Ed., ASA and SSSA, Madison, WI. 1982.
24. Jackson, M.L.; Lim, C.H.; Zelazny, L.W. "Oxides, Hydroxides, and Aluminosilicates," pp. 113-124 in *Method of Soil Analysis Part I*, 2nd Edition, Klute, A., Ed., ASA and SSSA, Madison, WI. 1986.
25. U.S. Soil Conservation Service, *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples*, Soil survey Investigation: Rep. 1. U.S. Gov. Print Office, Washington D.C., 1986.
26. Diamond, W.J. *Practical Experiment Designs For Engineers and Scientists*, 2nd Edition, Van Nostrand Reinhold, New York, 1989.
27. Masschelein, W.; Denis, M.; Ledent, R. "Specific Determination of Residual Hydrogen Peroxide," *Water Sewage Works* **32**: 69 (1977).
28. Schumb, W.C.; Satterfield, C.N.; Wentworth, R.L. *Hydrogen Peroxide*. ACS Monograph 128. American Chemical Society, Washington D.C., 1955.