On-Site Treatment of Contaminated Soils and Wastes from Transportation Maintenance Activities Using Oxidative Processes

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The treatment of contaminated timbers and soils was investigated by using catalyzed hydrogen peroxide, a procedure based on Fenton's reagent [hydrogen peroxide and iron(II)]. The process produces hydroxyl radicals, which oxidize nearly all organic contaminants. Wood posts contaminated with pentachlorophenol (PCP) and creosote were treated by the peroxide process, resulting in 84 percent degradation of the PCP and 74 percent degradation of the creosote with 6 percent hydrogen peroxide and 56 mg of Fe per L. The estimated cost was $18/kg of wood. A natural soil contaminated with 1000 mg of diesel fuel per kg was treated with a matrix of five hydrogen peroxide concentrations (1000, 5000, 10 000, 50 000, and 100 000 mg/L) and four slurry volumes (5, 10, 20, and 30 times the field capacity of the soil). The most efficient treatment was found with 1000 mg of hydrogen peroxide per L at a volume of 30 times the soil field capacity, with an estimated hydrogen peroxide cost of $15/909 kg (1 U.S. ton) of soil. Catalyzed hydrogen peroxide soil remediation may be implemented through a number of process configurations, including in situ and ex situ applications. The methodology also meets the primary policy goals of state and federal regulatory agencies, in that the waste components can be mineralized to carbon dioxide and water, which are nontoxic end products.

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 (*1*). Of the several million underground storage tanks located in the United States, it is estimated that 10 to 25 percent of them may be leaking (*2*). Therefore approximately 500,000 of the existing underground storage tanks may leak before they are replaced with new ones that have corrosion protection and leak detection systems. As a result of these releases surface soils often become contaminated with petroleum hydrocarbons that may subsequently contaminate groundwater.

The Environmental Protection Agency (EPA) is continually searching for new soil remediation technologies that provide for the destruction of contaminants with lower operational costs. Section 121(b) of the Comprehensive Environmental Response, Compensation, and Liability Act requires EPA to seek permanent solutions and alternative treatment technologies (*3*). 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 (*4*). The introduction of a strong oxidant, such as the hydroxyl radical, is one possible method for destroying hazardous contaminants. The use of Fenton's reagent, consisting of hydrogen peroxide catalyzed by iron(II), is a documented process that forms the hydroxyl radical (*5*):

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

The hydroxyl radical is a strong, nonspecific oxidant capable of degrading essentially all environmental contaminants.

Fenton's reagent was first applied to the treatment of contaminants in water. Barbeni et al. (*6*) investigated the degradation of chlorophenols, and Murphy et al. (*7*) successfully oxidized a formaldehyde waste stream. Subsequent research showed that catalyzed hydrogen peroxide can be used as a pretreatment process for wastewater that contains refractory organics or compounds that are toxic to microorganisms (*8*).

Watts et al. (*9*) first reported the use of catalyzed hydrogen peroxide for the remediation of contaminated soils, and Tyre et al. (*10*) subsequently investigated the treatment of four biorefractory contaminants in natural soils with varying organic carbon contents. They found that the stoichiometric ratios of contaminant degradation to hydrogen peroxide consumption were sensitive to both the concentration of iron addition and the soil's organic carbon content. Watts and Udell (*11*) compared the standard Fenton's reagent procedure, the sequential addition of Fe^{2+} and hydrogen peroxide, and the use of the mineral goethite as the iron source to treat silica sand contaminated with pentachlorophenol (PCP). The most efficient process for PCP degradation was the mineral-catalyzed system.

Research to date has documented optimum conditions for oxidizing contaminants in the aqueous phase by using Fenton's reagent and has provided initial data on what variables control the efficiency of treatment with contaminated soils. However minimal research has focused on real-world samples. The objective of the research described in this paper was to investigate the effectiveness and cost of treating a variety of matrices including timber samples and a natural soil system contaminated with diesel fuel.

METHODOLOGY

Timber Treatment

Contaminated posts supplied by the Washington State Department of Transportation were first analyzed by gas chromatography to

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determine the primary contaminants and their respective concentrations. Before 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 by using 0.1 g of wood at pH 3.0 along with deionized water controls. The consumption of hydrogen peroxide was monitored daily over a 2-day period.

Soil Treatment

The soil used was a Palouse loess with an organic carbon content of 0.11 percent and a field capacity of 356 ml/kg of soil. Diesel fuel was selected as the contaminant because of its widespread use. The soil was spiked at a concentration of 1000 mg/kg by adding 0.24 ml of diesel to 0.2 kg of soil.

A two-dimensional matrix was used to investigate the effects of hydrogen peroxide concentration and volume on total petroleum hydrocarbon degradation and stoichiometry. The experiment used a matrix of five hydrogen peroxide concentrations (1000, 5000, 10 000, 50 000, and 100 000 mg/L) and four volumes (5, 10, 20, and 30 times the field capacity of the soil). No iron addition was necessary because the naturally occurring iron minerals provided sufficient iron to catalyze the Fenton's reactions (*11*).

The experiments were conducted by placing 5.0 g of soil into individual vials and then adding hydrogen peroxide and adjusting the pH to 3.0. The hydrogen peroxide consumption was monitored daily; when its concentration dropped below the detection level, the samples were extracted with 6 ml of hexane and analyzed by gas chromatography.

Analyses

Hydrogen peroxide consumption was monitored by iodate titration for concentrations of >0.1 percent (*12*) and by $TiSO_4$ spectrophotometry for concentrations of ≤0.1 percent (*13*). The contaminant concentration was determined by a shake extraction and then gas chromatographic analysis (*10*). The solvent was added to the samples by using a volumetric glass pipet, and then the vials were placed on a wrist shaker for 24 hr. The extract was then analyzed by using a Hewlett-Packard 5890A gas chromatograph with a flame ionization detector and a DB-5 capillary column [10 m × 0.18 mm (i.d.)]. The wood samples were analyzed under the following conditions: initial oven temperature, 140°C; program rate, 7°C/min; final oven temperature, 220°C; injector temperature, 260°C; and detector temperature, 350°C. The samples were analyzed under the following conditions: initial oven temperature, 80°C; program rate, 5°C/min; final oven temperature, 250°C; injector temperature, 260°C; and detector temperature, 350°C.

RESULTS AND DISCUSSION OF RESULTS

Timber Treatment

Gas chromatographic analysis, using retention times, showed that the primary contaminant in the wood posts was PCP, which made up approximately 30 percent of the total contaminants. The remaining compounds were assumed to be creosote. The concentration of PCP in the outside 1 cm of the post was approximately 3000 mg/kg, and the total contaminant concentration was approximately 10 000 mg/kg. Initially 73 percent of the total contaminants were degraded by using 20 ml of 6 percent hydrogen peroxide and 56 mg of Fe per L over a 2-day period, as shown in Figure 1. A subsequent experiment with the same hydrogen peroxide and iron concentrations was conducted, but the volume was varied to determine the effect on the ratio of hydrogen peroxide consumed to wood treated. Hydrogen peroxide analysis showed that after 2 days the majority of the peroxide was gone. Figures 2 and 3 show that 20 ml of hydrogen peroxide per 0.1 g of wood remains the optimum volume, with 84 percent degradation of PCP and 77 percent degradation of total contaminants. On the basis of these conditions only limited increases in degradation occurred by increasing the dosage, which may be because of mass transfer limitations. This treatment would reduce the PCP concentration from 3000 to 480 mg/kg and the total contaminant concentration from 10 000 to 2300 mg/kg at a ratio of approximately 12 000 mg of hydrogen peroxide per g of wood. The estimated cost of hydrogen peroxide for this treatment would be $18 to treat 1 kg of wood. The treatment of contaminated wood can be achieved with catalyzed hydrogen peroxide. However the wood posts would

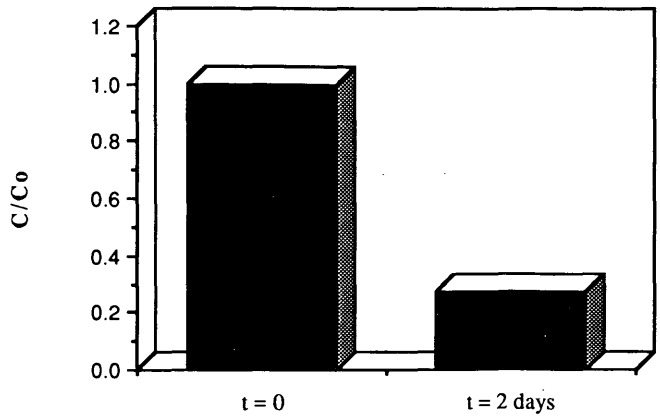

FIGURE 1 Degradation of wood contaminants using catalyzed hydrogen peroxide treatment.

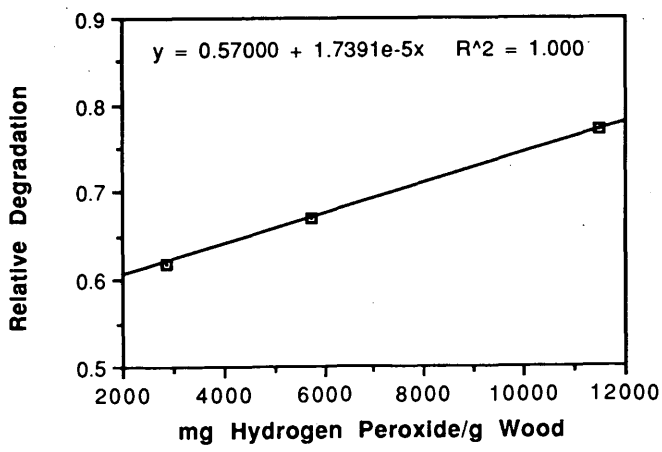

FIGURE 2 Degradation as a function of efficiency for total wood contaminants using catalyzed hydrogen peroxide.

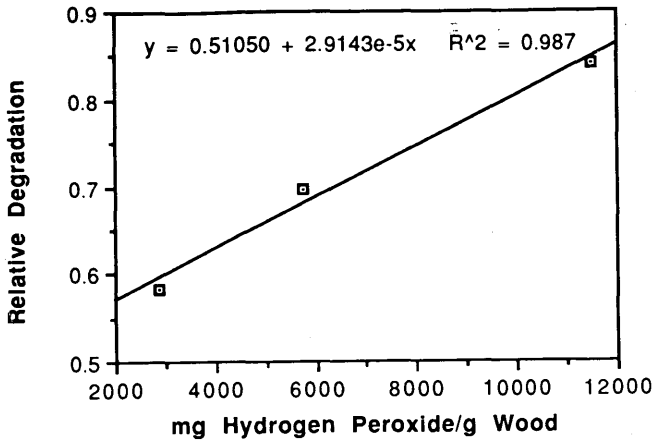

FIGURE 3 Degradation as a function of efficiency for PCP on wood samples using catalyzed hydrogen peroxide.

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 a pressure of 200 psi, 74 percent of the total contaminants and 67 percent of the PCP were degraded. Although this procedure would be more expensive and more complex, it offers promise for the treatment of contaminated timbers.

Soil Treatment

Hydrogen peroxide analysis data show that the oxidant source decomposed more rapidly in the smaller-volume soil slurries and that its concentrations dropped to below the detection level within 8 days. Table 1 shows the removal of diesel fuel from the soils for the matrix of experimental conditions. The highest degradation occurred under the conditions of 5000 mg of hydrogen peroxide per L at a volume of 30 times the field capacity of the soil. An estimated peroxide cost for this treatment is $77/909 kg (1 U.S. ton) of soil. Table 2 gives the results in efficiency (i.e., grams of hydrogen peroxide consumed per gram of diesel treated). The most efficient system was characterized by 1000 mg of hydrogen peroxide per L at a volume of 30 times field capacity. Under these conditions the estimated cost of hydrogen peroxide for this treatment would be $15/909 kg (1 U.S. ton) of soil. These results

TABLE 1 Degradation of Diesel Fuel in Palouse Loess Soil

Hydrogen Peroxide Concentration	Percent Degradation: Volume of Hydrogen Peroxide x Field Capacity			
	5	10	20	30
1000 mg/l	x	12%	20%	59%
5000 mg/l	x	19%	41%	97%
10000 mg/l	17%	28%	35%	80%
50000 mg/l	51%	47%	53%	80%
100000 mg/l	50%	62%	61%	64%

TABLE 2 Treatment Efficiency for Diesel Fuel in Palouse Loess Soil

Hydrogen Peroxide Concentration	Treatment Efficiency (g H_2O_2/g diesel): Volume of Hydrogen Peroxide x Field Capacity			
	5	10	20	30
1000 mg/l	x	36	42	32
5000 mg/l	x	112	102	59
10000 mg/l	122	148	231	145
50000 mg/l	204	428	681	624
100000 mg/l	415	636	1076	1405

provide lower costs compared with those for the conditions reported in previous work (*9,10*).

The results suggest that the low concentrations and high volumes of hydrogen peroxide provide optimum conditions for treating diesel-contaminated soils. This could be explained by the fact that the higher volume promotes desorption of the contaminant from the soil particles into the aqueous phase and then hydroxyl radical oxidation.

Engineering Applications

Watts et al. (*9*) described the advantages of adjusting soils to an acidic pH to promote Fenton-like reactions. They found that although the oxidations occur at neutral pH, hydrogen peroxide use is significantly more efficient at neutral pH. The concerns associated with the adjustment of large quantities of soils to pH 2 to 3 have been well documented (*14*). The problems associated with pH adjustment are related more to logistics than to costs. Mineral acids are relatively inexpensive, and their addition greatly improves the stoichiometry of hydroxyl radical generation. However because of the difficulty of adding acid to large volumes of soil, this may prove to be impossible. In addition interactive conditions related to slurry volume and hydrogen peroxide concentration may provide some process condition in which efficient oxidations may be maintained at acidic pH.

On-site soil remediation can be conducted under either in situ or ex situ conditions. In situ treatment involves treatment of 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 modes of applications include intermittent spraying, use of a continuous sprinkler system, or nozzle injection.

Ex situ treatment applications would involve placement of the excavated soil and the hydrogen 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. 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, in which the excavated soil is piled onto a concrete barrier with a collection system. The hydrogen peroxide solution could then be applied with a sprinkler system, allowing the solution to leach through the soil. Different soil and contaminant characteristics affect treat-

ment 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.

More risks are involved with in situ treatment because of the potential for leaching of 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 in situ application processes are developed.

Policy Considerations

The implementation of new and innovative remediation processes is based not only on its effectiveness and cost but also on its relationship to policy and the regulatory framework. A primary emphasis of remediation policy is waste destruction rather than storage or containment. As a corollary to contaminant destruction, state and federal regulatory agencies require that the process not produce by-products that are more toxic than the parent compound. Catalyzed hydrogen peroxide remediation of contaminated soils meets both of these criteria, because it has the potential to mineralize PCP and other contaminants (*9*). Because contaminants are mineralized to carbon dioxide and water, no toxic intermediates pose a threat to public health or the environment.

CONCLUSIONS

The results of the experimental investigation described here show that catalyzed hydrogen peroxide can be used to effectively treat a variety of contaminated wastes. Contaminated timbers were effectively treated to remove 84 percent PCP and 77 percent total contaminants by cutting the timbers into small pieces; this was followed by catalyzed hydrogen peroxide treatment. A possible alternative that can be used to overcome these mass transfer limitations would be the use of a pressure reactor, which may allow penetration of the hydrogen peroxide and iron solution into the wood. Diesel-contaminated soil was effectively treated by using catalyzed hydrogen peroxide. Over 90 percent diesel removal was achieved with 5000 mg of hydrogen per L and 30 times field capacity at a cost of $77/909 kg (1 U.S. ton). However the most efficient system used 1000 mg of hydrogen peroxide per L and 30 times the soil field capacity, resulting in a cost of $15/909 kg (1 U.S. ton). Continued optimization will likely lower the chemical cost for catalyzed hydrogen peroxide treatment.

A number of engineering process configurations, including in situ and ex situ applications, are available for implementation and are currently being evaluated through pilot studies in the field.

Catalyzed hydrogen peroxide soil remediation meets one of the primary policy goals of state and federal regulatory agencies in that the waste components can be mineralized, and therefore the remediation does not result in the formation of more toxic degradation products.

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