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"Catalyzed Peroxide Soil Pilot Study"

Catalyzed Peroxide Soil Pilot Study

by

Richard J. Watts          Samuel E. Dilly and Daniel Haller
Associate Professor       Graduate Students
Washington State Transportation Center (TRAC)
Washington State University
Department of Civil & Environmental Engineering
Pullman, WA 99164-2910

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EXECUTIVE SUMMARY

The remediation and treatment of petroleum-contaminated soils remains a significant problem for Washington State Department of Transportation (WSDOT) maintenance personnel. Incineration of these soils is expensive and, therefore, has limited applicability. Although bioremediation offers the most promise as a cost-effective means of decontaminating soils, some situations may occur in which bioremediation is not feasible (e.g., in cold weather; if the contaminants are toxic to microorganisms). An alternative to bioremediation is the mixing of catalyzed hydrogen peroxide into the soil, a process that generates hydroxyl radicals -- powerful oxidants that are capable of destroying nearly all regulated organic pollutants. Although catalyzed hydrogen peroxide is more expensive, it has the advantage of rapid clean up in which WSDOT maintenance personnel could simply disk in the peroxide and catalysts followed by closure within days. Based on the potential for rapid clean up the purpose of this study was to evaluate the catalyzed hydrogen peroxide process modifications that enhance the full-scale development of catalyzed hydrogen peroxide soil treatment.

Four separate substudies were conducted to evaluate the full-scale development of catalyzed hydrogen peroxide soil treatment: 1) A risk based design procedure; 2) evaluation of the most effective catalysts; 3) the depth to which the reagents penetrate Wastucna soil; and 4) evaluation of quantitative reagent needs of a soil pile to be treated.

The results of the risk-based sub-study showed that treating the more toxic aromatic constituents of gasoline was significantly more effective and economical relative to the less toxic alkanes and cycloalkanes. The associated costs for treating only the aromatics are at least five times lower than for the total gasoline fraction.

Evaluation of seven iron catalysts (iron (II) perchlorate, iron (II) sulfate, iron (III) perchlorate, iron (III) nitrate, iron (III) sulfate, an iron chelate, and iron minerals) showed that the iron (III) perchlorate was the most effective catalyst followed by iron (III) nitrate and iron (III) sulfate. However, iron (III) perchlorate is not available in commercial
quantities (i.e., > 1 pound) and iron (III) nitrate holds potential of polluting groundwater with nitrate (Safe Drinking Water Act Maximum Contaminated Level = 10 mg/L NO₃-N). Therefore, iron (III) sulfate provides the highest catalytic activity as an inexpensive and readily available catalyst.

The depth to which oxidation of the sorbed hydrocarbon hexadecane occurred in unmixed Washtucna soil was limited by the transport of the hydrogen peroxide through the soil layers. The results show that mixing the peroxide into the soil provides the most effective procedure for full-scale treatment.

Peroxide and catalyst dosages as a function of soil mass revealed no effect of soil mass on reagent requirements; i.e., the same peroxide and catalyst dosage was required regardless of the size of the soil pile that was treated.

**PROBLEM STATEMENT**

The release of petroleum products and hazardous wastes as the result of transportation maintenance activities has resulted in numerous contaminated sites throughout the state of Washington, many of which are characterized by contaminated surface soils. The most common method of soil remediation is often excavation followed by incineration or long term treatment through bioremediation or aeration. *In situ* and *ex situ* bioremediation has been effective in treating contaminated soils and groundwater; however, some contaminants are slowly biodegraded and some are toxic to microorganisms. Furthermore, the biological remediation of soils, particularly in cold temperatures, may require long periods of time. An oxidative process that can rapidly degrade biorefractory contaminants (e.g., in hours to days) may provide the potential for reaching site closure in shorter time periods than other methods of remediation.

A documented process for generating strong oxidants in aqueous solutions is the catalyzed decomposition of hydrogen peroxide by iron (II) to generate hydroxyl radicals (OH*), commonly known as Fenton's reagent:
\[ \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{OH}^- + \text{OH}^- + \text{Fe}^{3+} \] [1]

Hydroxyl radicals are strong, non-selective oxidants that react with almost all organic compounds at extremely rapid rates.

A number of factors have required investigation in the full-scale development of catalyzed hydrogen peroxide soil treatment. The form of the iron catalyst (e.g., iron (II) sulfate, Iron (III) sulfate, iron (II) perchlorate, etc.) to be used at full scale has been of concern based on its effectiveness in destroying hydrocarbons and cost for large quantities. Related to the effectiveness of the Fenton's process, some hydrocarbons (e.g., benzene, toluene, and xylenes) pose a greater risk to public health compared to alkanes and cycloalkanes. Therefore, a risk based process design focusing on the most economical treatment of the more toxic aromatic fraction would provide rapid and economical treatment. The scale up of catalyzed hydrogen peroxide systems requires investigation of the penetration of the Fenton's reagents through the soil as well as the dosage requirements as a function of the size of the pile that is treated. The optimization of these scale up considerations will provide necessary information for implementing the catalyzed hydrogen peroxide treatment of contaminated soils.

One of the primary limitations in the application of catalyzed hydrogen peroxide is effective delivery of the reagents. Iron (II) and iron (III) strongly exchange on soils, which may limit their transport during in situ application of reagents. Alternatively, hydrogen peroxide rapidly decomposes in some soils, particularly in soils of low permeability and those with high iron mineral contents. Although the kinetics of Fenton-like reactions have been thoroughly investigated in water and in soils in completely mixed reactors, no research have been completed that focuses on the rates of delivery of reacting Fenton's solutions as a function of soil porosity, organic carbon content, cation exchange capacity, etc. Quantitative relationships between the delivery rates of Fenton's reagent and soil
properties require elucidation to provide a fundamental basis for the catalyzed hydrogen peroxide treatment of contaminated soils.

**Review of Current Practice**

Physicochemical processes, such as chemical oxidations, have recently been applied to the transformation of biorefractory organic compounds (Bowers et al., 1989; Watts et al., 1990; Tyre et al., 1991; Leung et al., 1992). One mechanism for generating strong oxidants to promote waste reduction is the catalyzed decomposition of hydrogen peroxide to form hydroxyl radicals (OH\(^-\)), commonly known as Fenton's reagent (Haber and Weiss, 1934):

\[
H_2O_2 + Fe^{2+} \longrightarrow OH^- + OH^- + Fe^{3+}
\]  

(1)

Hydroxyl radicals are strong, nonspecific oxidants that react with most organic compounds at near-diffusion controlled rates (i.e., \(\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}\)). In the presence of organic compounds (R), hydroxyl radicals react by addition and hydrogen abstraction reactions:

\[
RH + OH^- \longrightarrow ROH + H^+
\]  

(2)

\[
RH + OH^- \longrightarrow R^- + H_2O
\]  

(3)

A number of competing reactions are involved in Fenton's systems including the production of perhydroxyl radical through the reaction of hydrogen peroxide and iron (III), cycling of iron (III) to iron (II) by short-lived reactants, and quenching of OH\(^-\) by iron (II) and H\(_2\)O\(_2\). These competing reactions in the Fenton's process include:

\[
OH^- + Fe^{2+} \longrightarrow OH^- + Fe^{3+}
\]  

(4)

\[
HO_2^- + Fe^{3+} \longrightarrow O_2 + H^+ + Fe^{2+}
\]  

(5)

\[
H_2O_2 + OH^- \longrightarrow H_2O + HO_2^- 
\]  

(6)

where HO\(_2\)\(^-\) = perhydroxyl radical.

Fenton's reagent has been studied extensively in the fundamental chemistry literature. The enhanced oxidation of malic acid by hydrogen peroxide in the presence of iron (II) was first reported by Fenton (1894). Haber and Weiss (1934) later proposed that OH\(^-\) is the oxidant in the Fenton's process. The oxidation of benzene, toluene,
phenylacetic acid, and phenyl-substituted alcohols by Fenton's reagent occurs primarily by hydroxyl radical addition (Walling and Johnson, 1975). However, depending on the oxidation-reduction conditions, the hydroxycyclohexadienyl radical intermediates may dimerize, be oxidized to phenols, or undergo a reversible acid-catalyzed collapse to radical cations. Hundreds of other papers have been published on the theoretical aspects of Fenton's chemistry; they have most recently been reviewed by Prousek (1995).

*Applied Fenton's Reactions in Aqueous Solutions.* The standard procedure for generating hydroxyl radicals involves the slow addition of dilute hydrogen peroxide to a degassed solution containing the substrate and excess iron (II). This procedure is well documented and has recently been applied to the oxidation of environmental contaminants in water (Barbeni et al., 1987; Bowers et al., 1989). The oxidation stoichiometry of these systems is relatively efficient with 2-10 moles H₂O₂ consumed/mole substrate degraded.

The oxidation of a number of specific organic contaminants in aqueous Fenton's systems has been studied. Early research by Merz and Waters (1949) provided evidence of the oxidation of toluene, nitrobenzene, and chlorobenzene to the products phenol, cresols, biphenyls, and benzaldehydes. Davidson and Busch (1966) used a modified Fenton's system to oxidize a waste stream of phenol and demonstrated ring opening. Barbeni et al. (1987) studied the degradation of a number of chlorophenols and documented mineralization by stoichiometric chloride recovery. Murphy et al. (1989) investigated the treatability of formaldehyde using Fe³⁺ as a catalyst, and Sedlak and Andren (1991) documented ring cleavage and partial mineralization of chlorobenzene and chlorophenol.

*Fenton's Chemistry Applied to Soil Remediation.* The use of Fenton-like reactions for soil remediation was first reported by Watts et al. (1990). They documented that pH 2-3 was optimum for the process, and that pentachlorophenol (PCP) was mineralized in silica sand systems. Leung et al. (1992) subsequently demonstrated the degradation of PCE with its accompanying mineralization. Gates and Siegrist (1995) used catalyzed hydrogen peroxide to oxidize TCE in a clay soil with emphasis on injection of the Fenton reagents for
in situ treatment. The oxidation of methyl tert-buty1 ether (MTBE) and ethyl tert-buty1 ether (ETBE) in aqueous systems and soils was investigated by Yeh and Novak (1995). They found that these gasoline additives were oxidized to tert-butyl alcohol and acetone. The authors suggested that Fenton-like reactions could provide an effective pretreatment for these compounds followed by biological degradation of the products.

By using a soil of low development sampled at different horizons, Tyre et al. (1991) were able to vary the soil organic matter with minimal differences in particle size distribution, iron oxyhydroxide content, and other physical properties in order to study the effect of organic carbon on Fenton-like soil remediation. Using varying iron (II) amendments and hydrogen peroxide concentrations, they found that, although soil organic carbon competed for hydroxyl radicals, the competition could be minimized by adjusting the reaction conditions. Tyre et al. (1991) documented that the most efficient stoichiometry (moles hydrogen peroxide consumed/moles contaminant degraded) was achieved by not adding soluble iron, suggesting that naturally-occurring iron oxyhydroxides may be promoting Fenton-like reactions. Heterogeneous catalyzed oxidation of substituted aromatics by a Fenton's system has been demonstrated using alumina-supported iron (Al-Hayek and Dore, 1990). Because soils contain various forms of iron oxyhydroxides, such as goethite (α-FeOOH), similar mineral-catalyzed oxidations may provide efficient stoichiometric use of hydrogen peroxide (Watts et al., 1993a). Ravikumar and Gurol (1994) subsequently documented that TCE and PCP were degraded in sand columns with iron oxides coating the sand as the only source of the Fenton's catalysts. Fenton-like reactions catalyzed by aquifer solids were also reported by Miller and Valentine (1995a). They proposed a mechanism for mineral-catalyzed Fenton-like reactions and hypothesized that scavenging by reactive intermediates decreased the rate of contaminant degradation at higher aquifer solids levels. Similar trends were reported by Miller and Valentine (1995b) when Fenton-like reactions were promoted in the presence of filter material.
The effect of pH on the Fenton-like remediation of contaminated soils has received widespread attention. Watts et al. (1990) documented that, although PCP was oxidized at both acidic and neutral pH regimes, the stoichiometry (i.e., moles of H$_2$O$_2$ consumed/moles PCP oxidized) was more efficient at acidic pH. However, Chen (1992) suggested that the need to adjust large volumes of soil to acidic pH regimes may limit the large scale effectiveness of Fenton's reagent for soil remediation. Pignatello and Baehr (1994) investigated iron chelates, such as Fe (III)-nitrilotriacetic acid, as Fenton's catalysts. Some of the complexes were soluble at near-neutral pH and were effective in degrading 2,4-dichlorophenoxyacetic acid (2,4-D) and metachlor at pH 6. Naturally-occurring iron minerals have been effective in promoting Fenton-like reactions at near-neutral pH (Watts et al., 1994) and the use of phosphates as a stabilizer may also enhance the effectiveness of Fenton-like reactions at near-neutral pH regimes (Kakarla and Watts, 1996).

Hydroxyl radicals react rapidly with most organic compounds by addition and hydrogen abstraction reactions to produce oxidized intermediates. Therefore, Fenton-like reactions have the potential to oxidize most hazardous organic compounds, such as chlorinated solvents as well as chlorobenzenes, chlorophenols, and other chemicals found in process waters. Although Fenton-like reactions are often complete within hours, the primary drawback to stand-alone chemical oxidation is the amount of hydrogen peroxide needed to oxidize the contaminants to carbon dioxide and water.

**PART I. EVALUATION OF FENTON'S CATALYSTS**

In contrast to water-soluble compounds, contaminants in soils are usually sorbed or present as nonaqueous phase liquids (NAPLs), which can have significant effects on Fenton's process chemistry. Fenton-like oxidations in soils have focused on the process chemistry that most effectively destroys and mineralizes biorefractory contaminants. Watts et al. (1990) first reported using Fenton-like reactions for soil remediation and showed that
pentachlorophenol (PCP) in silica sand was destroyed at a slurry pH of 2-3. Their results also confirmed that when high concentrations of peroxide are used for soil remediation, which is often necessary to oxidize contaminants in a complex matrix such as soils, soluble iron concentrations decline rapidly over the first 30 min of the reaction with subsequent formation of an amorphous iron floc over the following 3 hours. Soil-water slurries containing the iron floc were characterized by inefficient treatment stoichiometries of up to 50,000 mole H₂O₂ per mole contaminant oxidized. Tyre et al. (1991) used Fenton's reagent to oxidize PCP, trifluralin, hexadecane, and dieldrin in soils and found that iron oxyhydroxides effectively catalyze Fenton-like reactions. Watts et al. (1993) subsequently documented the most efficient oxidation of soluble PCP in silica sand was catalyzed by naturally-occurring iron oxyhydroxides; however, sorbed PCP was not oxidized with goethite as the only Fenton's catalyst. The results provided by Tyre et al. (1991) and Watts et al. (1993) suggest that naturally-occurring iron oxyhydroxides serve as an effective Fenton's catalyst. A possible mechanism for mineral-catalyzed Fenton's reactions has been proposed by Kitajima et al. [9]:

$$\text{H}_2\text{O}_2 + S \rightarrow S^+ + \text{OH}^- + \text{OH}^-$$  \[7\]

where  
S = the mineral surface  
S⁺ = an oxidized region on the mineral  
These heterogeneous mineral catalysts are effective because of their conservative nature and consistent rates of hydroxyl radical generation when high concentrations of hydrogen peroxide are used.

Iron complexes have also been studied to catalyze the Fenton-like oxidation of pesticides. Sun and Pignatello (1992) screened iron complexes for their potential to promote the oxidation of pesticides by Fenton-like reactions. Nitrilotriacetic acid (NTA), tetrahydroxy-1,4-quinone (THQ), and hexaketocyclohexane (HKCH) were most effective.
The primary advantage of the iron complexes is the potential for effective generation of hydroxyl radicals at near-neutral pH.

Diesel is commonly used as an engine fuel and refueling facilities are common throughout the world; therefore, spills and leaking storage facilities result in a need for the remediation of diesel-contaminated soils. Spencer et al. (1996) found that the most efficient Fenton’s treatment conditions for diesel-contaminated soils included 30 mM hydrogen peroxide and thirty times the field capacity of the soil with four weeks required for the reaction to reach completion. Although such large volumes of dilute peroxide were effective in oxidizing diesel in a surface soil (by a coupled desorption-mineral-catalyzed oxidation mechanism), the system will likely be impractical in the field. For example, > 9.5 l (2.5 gal) would be required to treat 1 kg (2.2 lb) of contaminated soil using the process conditions developed by Spencer et al. (1996). An alternative process condition developed by Spencer et al. (1996) is the mineral-catalyzed use of aggressive Fenton-like reactions using low slurry volumes (0.5 - 3.0 x the soil field capacity) and high hydrogen peroxide concentrations (3 to 9 M). Using these process conditions, diesel in a natural surface soil was oxidized more rapidly than it was desorbed, suggesting the potential for the Fenton-like oxidation of sorbed contaminants.

Watts et al. (1994) investigated another set of process conditions to promote the catalyzed hydrogen peroxide treatment of hexachlorobenzene-contaminated soils. They used hydrogen peroxide concentrations ranging from 3 to 300 mM catalyzed by iron (II) rather than the natural iron oxyhydroxides used by Spencer et al. (1996). Watts et al. (1994) found that oxidation of sorbed hexachlorobenzene was effective using hydrogen peroxide concentrations as low as 30 mM if catalysis is promoted by soluble iron rather than natural iron oxyhydroxides. Because of the high relative concentration of the iron mineral catalysts in a slurry with a low volume ratio of liquid to soil, the hydrogen peroxide decomposition is potentially rapid, i.e., < 8 hours. Therefore, the use of soluble iron to catalyze the Fenton-like oxidation of sorbed contaminants may provide more economical
and effective process conditions than the criteria developed by Spencer et al. (1996). The remediation of contaminated soil systems with soluble iron addition and moderate hydrogen peroxide (0.1 to 2.0 M) concentrations with low slurry volume may provide more economical process conditions.

Based on the results of previous Fenton-like soil remediation studies with multiple forms of iron catalysts, the purpose of this research was to compare iron catalysts and optimize the Fenton-like remediation of diesel-contaminated soil based on: 1) the species of the iron catalyst, 2) the hydrogen peroxide concentration, and 3) the slurry volume.

**Materials And Methods**

**Materials**

Diesel fuel was obtained from Cenex (St. Paul, MN). Diesel, which is a composite of alkanes, isoalkanes, cycloalkanes, and polycyclic aromatic hydrocarbons of carbon length C15 to C25 (Solomans, 1988), is a realistic model contaminant for remediation studies because of its widespread use and chemical variability.

Hydrogen peroxide was provided by Solvay Interox (Deer Park, TX). Iron (III) sulfate, iron (III) nitrate, and nitrilotriacetic acid were purchased from Sigma. Iron (II) perchlorate and iron (III) perchlorate were obtained from Aldrich and iron (II) sulfate, pentane, and ethyl acetate were purchased from J.T. Baker. Water was purified to greater than 17 MΩ with a Barnstead NANOpure II deionizing system.

A silty loam soil (Palouse loess) was sampled from a wheat field near Pullman, WA. Particle size distribution was determined by the pipette method (Gee and Bauder, 1986). Organic carbon was measured by combustion at 900°C with CO2 trapped in KOH and back titrated with unreacted KOH (Nelson and Sommers, 1982). Cation exchange capacity was determined by sodium acetate saturation at pH 8.2 (Soil Conservation Service, 1972). Amorphous and crystalline iron and manganese concentrations were
quantified by citrate-bicarbonate-dithionite extractions (Jackson et al., 1986). The soil characteristics are listed in Table 1.

**Sample Preparation**

Diesel, dissolved in pentane, was applied to 500 g of soil to obtain a final concentration of 1000 mg kg\(^{-1}\) diesel. The pentane was allowed to evaporate and 5 ± 0.01 g soil was placed in 40 ml borosilicate vials with Teflon-lined caps. Oxidation studies were conducted using four replicate vials and initial diesel concentrations were verified by the analysis of at least eight replicates.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Carbon (%)</td>
<td>0.33</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>18.4</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>58.8</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>22.8</td>
</tr>
<tr>
<td>CEC (cmol kg(^{-1}))</td>
<td>19.1</td>
</tr>
<tr>
<td>Crystalline Fe (mg kg(^{-1}))</td>
<td>30390</td>
</tr>
<tr>
<td>Crystalline Mn (mg kg(^{-1}))</td>
<td>690</td>
</tr>
<tr>
<td>Amorphous Fe (mg kg(^{-1}))</td>
<td>38.3</td>
</tr>
<tr>
<td>Amorphous Mn (mg kg(^{-1}))</td>
<td>30.4</td>
</tr>
<tr>
<td>pH</td>
<td>6.2</td>
</tr>
<tr>
<td>Field Capacity (ml g(^{-1}))</td>
<td>0.318</td>
</tr>
</tbody>
</table>
Experimental Procedures

The gas purge desorption procedure (Brusseall et al., 1990) was used on the spiked samples to determine the rate of diesel volatilization. To determine the duration of the Fenton-like reactions, parallel experiments were analyzed hourly for residual hydrogen peroxide. These data were used to evaluate the extent to which desorption controls the Fenton-like oxidation of diesel.

To investigate the most effective form of iron catalysts, six iron species were added to the Palouse loess to promote the Fenton-like oxidation of diesel upon the addition of hydrogen peroxide. In addition, monobasic potassium phosphate was investigated for its potential to stabilize hydrogen peroxide as a basis for enhancing the native mineral-catalyzed oxidation of diesel. Central composite rotatable experimental designs were used, which describe the combined effect of n variables on an n+1 component. The data from central composite designs were used to establish direct and interactive effects of the variables through a n-dimensional response equation. Three-dimensional response surfaces representing the effect of hydrogen peroxide and soluble iron concentrations on diesel oxidation were generated by evaluation of the regression equations.

Iron (III) perchlorate, iron (III) nitrate, iron (III) sulfate, iron (II) perchlorate, iron (II) sulfate, and iron (III)-NTA were used to catalyze slurries containing 5 g of soil and 5 ml of hydrogen peroxide. Iron concentrations ranged from 5 to 25 mM and hydrogen peroxide concentrations were varied from 0.15 to 1.5 M. Iron (III)-NTA was prepared by dissolving NTA in deionized water with concentrated NaOH prior to combining with equimolar iron (III) perchlorate in deionized water followed by pH adjustment to 6.0 with NaOH (Watts et al., 1990). The final iron complex concentrations in the slurries ranged from 2.5 mM to 25 mM. Central composite designs for the potassium phosphate addition used 5 ml hydrogen peroxide ranging from 0.15 to 1.5 M in conjunction with monobasic potassium phosphate (KH$_2$PO$_4$) concentrations from 5 to 75 mM. Upon addition of reagents, the vials were mixed using a vortex to ensure homogeneity of the iron catalyst.
and hydrogen peroxide. The reactions were allowed to proceed until the hydrogen peroxide was consumed (2 hours). The entire vial contents were then extracted and analyzed for residual total petroleum hydrocarbons (TPH).

Using the most effective catalyst and its optimum concentration, a subsequent central composite design was used to investigate the interactive effect of slurry volume and hydrogen peroxide concentration. The catalyst [iron (III) perchlorate] at a fixed concentration of 25 mM was used with hydrogen peroxide concentrations from 0.15 to 1.5 M and liquid volumes from 1.5 to 5 ml per 5 g soil. The reaction proceeded until the hydrogen peroxide decomposed to undetectable levels. The samples were then extracted and analyzed for residual TPH.

Analysis

Soil slurries were brought to a normalized volume of 20 ml with deionized water and shake extracted for 12 hours with ethyl acetate. The samples were then analyzed using a Hewlett Packard 5890A gas chromatograph with flame ionization detector and 30 m x 0.32 mm DB-1 capillary column. Chromatographic conditions included an initial oven temperature of 100 °C, final temperature of 240 °C, program rate of 15 °C minute⁻¹, injector temperature of 250 °C, and detector temperature of 280 °C. Peak integrations were summed and compared to a standard curve of diesel prepared in ethyl acetate.

Results And Discussion

Contaminant Desorption

The results of the gas-purge desorption procedure showing residual diesel as a function of time for the 1000 mg kg⁻¹ diesel-spiked soil are illustrated in Figure 1. Diesel desorption from the Palouse loess soil over 90 hours was negligible, which demonstrates that the diesel was strongly sorbed to the soil. Diesel is composed of hydrocarbons ranging from C₁₅ to C₂₅ [13], which are characterized by high octanol-water partition
coefficients. Karickhoff et al. (1981) documented that sorption of organic compounds in soils is directly proportional to the octanol-water partition coefficient; therefore, the data of Figure 1 are expected based on the hydrophobicity of the C_{15} to C_{25} hydrocarbons. The effect of sorption on soil remediation processes has been well documented. Chemicals that are sorbed are often considered to have reduced reactivity with most species used to promote remediation such as hydroxyl radicals, aqueous electrons, or microorganisms. Sheldon and Kochi (1981) stated that reactive species that are generated in the aqueous phase of two phase systems (e.g., a water-NAPL slurry or water-solids with a sorbed substrate), the NAPL or sorbed species is not usually available to react with the species present in the aqueous phase. The principles proposed by Sheldon and Kochi (1981) have been confirmed by Sedlak and Andren (1994) for chemical processes and Weber et al. (1993) and Ogram et al. (1985) for enzymatic processes. However, if Fenton-like oxidations can proceed more rapidly than desorption, at least partial oxidation may be occurring in the sorbed phase; furthermore, time requirements for soil remediation can be reduced dramatically.

The rate of Fenton-like reactions in soils is proportional to the concentration ratios of peroxide to catalyst and inversely proportional to the volume ratio of peroxide to catalyst [11]; i.e., soil systems containing a low soluble iron catalyst concentration and a large volume of hydrogen peroxide solution will be characterized by a slow rate of reaction. Using a 1:1 mass ratio of soil-to-hydrogen peroxide volume and the lowest soluble iron concentration (5 mM), the peroxide decomposed rapidly and reached undetectable concentrations within 1 hour. Because desorption was negligible, if diesel oxidation proceeded within these 1 hour reactions, then Fenton-like processes will have overcome the controlling influence of sorption.
Figure 1. Desorption of 1000 mg/kg diesel from the Palouse loess soil.
Comparison of Iron Species in Fenton-like Soil Remediation

Regression equations derived from the data of central composite experiments that evaluated the six iron species are listed in Table 2. The regression data were then plotted as three-dimensional response surfaces (Figures 2 through 6), which show the effects of H$_2$O$_2$ and iron on the percentage removal of diesel for iron amendments ranging from 5 to 25 mM and hydrogen peroxide concentrations from 0.15 to 1.5 M (with the exception of KH$_2$PO$_4$ addition which covered a range from 5 to 75 mM). The trends for each response surface were similar; the per cent loss of diesel increased as a function of catalyst concentration and hydrogen peroxide concentration. The results also show that more aggressive Fenton-like reactions were necessary to oxidize diesel over the 1 hour time period.
Table 2. Regression equations for the Fenton-like oxidation of 1000 mg kg$^{-1}$ diesel in the Palouse loess soil using six iron catalysts and KH$_2$PO$_4$ as a stabilizer.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Regression Equation</th>
<th>$R^2$</th>
<th>Equation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (III) Perchlorate</td>
<td>Diesel Degradation (%) = $33.2 + 18.6(C_{cat}) + 16.3(CH_2O_2) + 8.2(C_{cat})^2 + 3.3(CH_2O_2)^2 + 1.5(CH_2O_2)^2$</td>
<td>0.91</td>
<td>[8]</td>
</tr>
<tr>
<td>Iron (III) Nitrate</td>
<td>Diesel Degradation (%) = $32.5 + 20.4(C_{cat}) + 16.5(CH_2O_2) + 4.6(C_{cat}) + 4.6(C_{cat})^2 + 1.7(CH_2O_2)^2$</td>
<td>0.88</td>
<td>[9]</td>
</tr>
<tr>
<td>Iron (III) Sulfate</td>
<td>Diesel Degradation (%) = $43.0 + 13.0(C_{cat}) + 14.8(CH_2O_2) + 1.6(C_{cat}) + 1.9(C_{cat})^2 + 0.7(CH_2O_2)^2$</td>
<td>0.85</td>
<td>[10]</td>
</tr>
<tr>
<td>Iron (II) Perchlorate</td>
<td>Diesel Degradation (%) = $42.9 + 6.4(C_{cat}) + 10.6(CH_2O_2) + 7.9(C_{cat}) + 0.02(C_{cat})^2 + 2.2(CH_2O_2)^2$</td>
<td>0.88</td>
<td>[11]</td>
</tr>
<tr>
<td>Iron (II) Sulfate</td>
<td>Diesel Degradation (%) = $36.5 + 10.4(CH_2O_2) + 14.5(C_{cat}) + 4.5(CH_2O_2) - 2.5(CH_2O_2)^2 - 3.1(C_{cat})^2$</td>
<td>0.90</td>
<td>[12]</td>
</tr>
<tr>
<td>Iron (III)-NTA Chelate</td>
<td>Diesel Degradation (%) = $46.5 + 10.4(C_{cat}) + 9.4(CH_2O_2) + 5.3(C_{cat}) + 1.9(C_{cat})^2 - 3.9(CH_2O_2)^2$</td>
<td>0.83</td>
<td>[13]</td>
</tr>
<tr>
<td>Monobasic Potassium Phosphate</td>
<td>Diesel Degradation (%) = $38.9 + 5.9(C_{Stab}) + 7.5(CH_2O_2) + 0.5(C_{Stab}) + 3.2(C_{Stab})^2 - 4.7(CH_2O_2)^2$</td>
<td>0.86</td>
<td>[14]</td>
</tr>
</tbody>
</table>

where

$CH_2O_2 =$ Hydrogen Peroxide Concentration (M)
$C_{cat} =$ Catalyst Concentration (mM)
$C_{Stab} =$ Stabilizer Concentration (mM)
Figure 2. Response surface for diesel degradation as a function of hydrogen peroxide and iron (III) perchlorate concentration. Isoconcentration lines represent per cent diesel degraded.
Figure 3. Response surface for diesel degradation as a function of hydrogen peroxide and iron (III) nitrate concentration. Isoconcentration lines represent per cent diesel degraded.
Figure 4. Response surface for diesel degradation as a function of hydrogen peroxide and iron (III) sulfate concentration. Isoconcentration lines represent per cent diesel degraded.
Figure 5. Response surface for diesel degradation as a function of hydrogen peroxide and iron (II) perchlorate concentration. Isoconcentration lines represent per cent diesel degraded.
Figure 6. Response surface for diesel degradation as a function of hydrogen peroxide and iron (II) sulfate concentration. Isoconcentration lines represent per cent diesel degraded.
The data of Figures 2-6 show that Fenton-like reactions catalyzed by iron (III) species were more effective than reactions catalyzed by iron (II) species. Nearly 80% oxidation of the diesel was found using 25 mM iron (III) sulfate and 1.5 M hydrogen peroxide as shown in Figure 4, while the use of iron (II) sulfate additions promoted less than 70% diesel oxidation under the same conditions. Results of central composite analyses using iron (III) and iron (II) perchlorate as Fenton's catalysts showed the same trend with >99% diesel oxidation using iron (III) and 90% diesel oxidation under optimum conditions using iron (II) perchlorate. In the standard Fenton's procedure, dilute hydrogen peroxide is slowly added to a deoxygenated iron (II)-substrate solution. Such a system provides near-stoichiometric generation of hydroxyl radicals and minimizes the autooxidation of iron (II) to iron (III). However, modified Fenton-like systems are characterized by aggressive conditions promoted by the use of higher hydrogen peroxide concentrations to oxidize sorbed contaminants (Watts et al., 1993). Dilute hydrogen peroxide is normally used in Fenton's systems to minimize the oxidation of iron (II) to iron (III). With the high hydrogen peroxide concentrations necessary to desorb contaminants, iron (II) is rapidly oxidized to iron (III), resulting in an immediate demand on the hydrogen peroxide residual (equation 4). Iron (III) is a more effective catalyst because it does not place an immediate demand on the hydrogen peroxide; i.e., equation 4 becomes negligible. Murphy et al. (1989) described similar results in oxidizing formaldehyde solutions with Fenton-like reactions. Iron (II) oxidation to iron (III) was suggested as a cause of the loss of stoichiometric efficiency in formaldehyde oxidation and two iron (II) oxidation pathways were proposed. The results shown in Figures 2 through 6 are in agreement with the stoichiometry of Fenton's chemistry (equations 1-6) and the results reported by Murphy et al. (1989).
The effectiveness of different iron salts for catalyzing Fenton's reactions in aqueous solution has been well documented (Table 3). Based on these results, the most effective iron salt catalysts are:

$$\text{ClO}_4^- = \text{NO}_3^- > \text{SO}_4^{2-} > \text{PO}_4^-$$  \[15\]

Table 3. Oxidation rate constants of selected anions with hydroxyl radicals [25].

<table>
<thead>
<tr>
<th>Anion</th>
<th>$k_{\text{OH}^-}$ (M$^{-1}$ s$^{-1}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$</td>
<td>$5 \times 10^5$</td>
<td>9</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>$1.6 \times 10^6$</td>
<td>7</td>
</tr>
<tr>
<td>H$_2$PO$_4^{-1}$</td>
<td>$&lt; 1.2 \times 10^7$</td>
<td>$\sim 7$</td>
</tr>
<tr>
<td>HPO$_4^{2-}$</td>
<td>$7.9 \times 10^5$</td>
<td>9</td>
</tr>
<tr>
<td>PO$_4^{3-}$</td>
<td>$&lt; 10^7$</td>
<td>--</td>
</tr>
</tbody>
</table>

The data of Figures 2 through 6 are in agreement with the relative quenching rates listed in equation (15). Perchlorate and nitrate salts quench hydroxyl radicals at the lowest rates and, therefore, provide the highest degree of oxidation in TPH-contaminated soils. Iron sulfates provided intermediate diesel oxidation while potassium phosphate was least efficient in promoting the oxidization of diesel in the Palouse loess. Although phosphate was added as KH$_2$PO$_4$, at pH 6, both H$_2$PO$_4^-$ and HPO$_4^{2-}$ would be present in the system. Therefore, the quenching of hydroxyl radicals by phosphate species is a function of relative concentrations of H$_2$PO$_4^-$ (with $k_{\text{OH}^-} < 1.2 \times 10^7$ M$^{-1}$ s$^{-1}$) and HPO$_4^{2-}$ (with $k_{\text{OH}^-} = 7.9 \times 10^5$ M$^{-1}$ s$^{-1}$).
The higher hydrogen peroxide concentrations required to oxidize diesel-contaminated soil are comparable to the results of previous Fenton-like soil remediation studies. Watts et al. (1994) found that ≥ 0.1 M hydrogen peroxide with soluble iron oxidized sorbed hexachlorobenzene while oxidation with lower concentrations of hydrogen peroxide was controlled by the desorption rate. Spencer et al. (1996) determined that 3 to 9 M hydrogen peroxide was required to oxidize sorbed diesel using iron oxyhydroxides as the only source of iron catalysts. They also documented that, by promoting a combined desorption-oxidation mechanism using lower concentrations of peroxide, four weeks were required for diesel to desorb coupled with oxidation by mineral-catalyzed Fenton-like reactions. Because diesel did not desorb during the 1-hour time period of the Fenton-like reactions of this study (Figure 1), moderate concentrations of hydrogen peroxide (≈1.5 M) and soluble iron were capable of destroying diesel at the soil surface. Although not as efficient as the desorption-oxidation mechanism described by Spencer et al. (1996), the use of moderate concentrations of hydrogen peroxide (≈1.5 M) catalyzed by soluble iron appears to be the most effective process condition for the oxidation of sorbed hydrocarbons.

Pignatello and Baehr (1994), in studying the Fenton-like oxidation of herbicides catalyzed by iron complexes, found that some of the complexes were more effective than iron (III) perchlorate, particularly at neutral pH. To determine the potential of an iron chelate to oxidize diesel under near-neutral pH conditions, an iron (III)-NTA complex was investigated under similar conditions to the systems catalyzed by iron salts. Equation 12 listed in Table 2 describes the experimental data and the response surface showing the effects of hydrogen peroxide and iron (III)-NTA concentrations is shown in Figure 7. The maximum diesel loss under these conditions (approximately 80%) was comparable to that attained using the iron (II) perchlorate or iron (III) sulfate. However, the advantage of the iron (III)-NTA complex as a catalyst for Fenton-like reactions is the potential for conducting the reaction at near-neutral pH. The soil pH in the iron (III)-NTA system was
5.7, and the pH of the iron (III) perchlorate systems was 3.6 with an iron (III) amendment of 20 mM, which provided an equal degree (80%) diesel oxidation. Therefore, the iron complex was equally effective to iron (II) perchlorate and has the advantage of promoting Fenton-like oxidations at near-neutral pH.

Results of a central composite analysis for the addition of monobasic potassium phosphate (5 to 75 mM) and hydrogen peroxide (0.15 to 1.5 M) are shown in Figure 8 based on equation 13 of Table 2. These data show a consistent increase in diesel oxidation with KH$_2$PO$_4$ up to 40 mM and hydrogen peroxide concentrations up to 0.8 M. Higher concentrations of both reagents were ineffective in increasing diesel oxidation above 40%. This modification of the soil treatment process also required 8 hours for 90% decomposition of the hydrogen peroxide. The ability of phosphate to stabilize hydrogen peroxide is well documented (Schumb et al., 1955). Most forms of phosphate (H$_2$PO$_4^-$, HPO$_4^{2-}$, tripolyphosphate) complex multivalent cations, such as iron and other transition metals, lowering their activity as Fenton's catalysts. As a result, phosphates tend to decrease the rates at which soluble iron-catalyzed Fenton's reactions occur. However, phosphates increase the rate of mineral-catalyzed Fenton-like reactions. The rate of Fenton-like reactions is proportional to the system reducing potential and phosphate exchanged at the mineral surface may lower the surface oxidation-reduction potential to increase rates of mineral catalyzed Fenton-like reactions. Addition of phosphate as a stabilizer has potential for enhancing the mineral-catalyzed Fenton-like oxidation of contaminated soils using longer reaction times, but does not appear to provide process conditions that promote the oxidation of sorbed contaminants. Therefore, the lower diesel oxidation found with phosphate addition may be related to minimal presence of the diesel components in the soil solution and negligible desorption over the 8 hour time period of the reactions.
Figure 7. Response surface for diesel degradation as a function of hydrogen peroxide and Iron (III)-NTA chelate concentration. Isoconcentration lines represent per cent diesel degraded.
Figure 8. Response surface for diesel degradation as a function of hydrogen peroxide and monobasic potassium phosphate concentration. Isoconcentration lines represent per cent diesel degraded.
Effect of Slurry Volume

The regression equation derived from the experimental data of the central composite experiment that evaluated slurry volumes from 1.5 to 5 ml per 5 g soil and hydrogen peroxide concentrations from 0.15 to 1.5 M with 25 mM iron (III) perchlorate as the catalyst is:

\[
\text{Diesel Degradation (\%) = 51.7+7.9(V)+10.6(CH}_2\text{O}_2)\text{+1.74}(V)(CH}_2\text{O}_2)-5.8(V)-2.0(CH}_2\text{O}_2)^2 \tag{16}
\]

where

\[CH}_2\text{O}_2 = \text{Hydrogen Peroxide Concentration (M).}\]

\[V = \text{Volume [ml (5g soil)]}^{-1}.\]

The corresponding response surface for equation 16 is shown in Figure 9. The ability of Fenton-like reactions to remediate diesel-contaminated soil increased as a function of liquid volumes to a maximum at 3.5 ml (5 g soil)\(^{-1}\). An advantage of using low volumes of hydrogen peroxide with soluble iron amendments in soil systems is a reaction in which hydroxyl radicals are generated in close proximity to the sorbed contaminants. Using volumes <3.5 ml, diesel oxidation was limited by minimal contact of the soil with the liquid at volumes >3.5 ml, the excess hydrogen peroxide volume was not in contact with the soil, lowering the effectiveness of the reaction. The data of Figure 9 predict lower diesel oxidation than the investigation with iron (III) perchlorate under similar conditions (Figure 2). This anomaly may be a result of different effects of catalyst concentration and liquid volume on diesel oxidation, i.e. the catalyst may affect the oxidation in a manner unrelated to the increased volume.
Figure 9. Response surface for diesel degradation as a function of hydrogen peroxide concentration and volume. Isoconcentration lines represent per cent diesel degraded.
Environmental effects and logistics may be concerns for some forms of the iron catalyst. Iron (II) and iron (III) perchlorate, the most effective species, are currently commercially unavailable in large quantities (>1 kg), which will likely limit its use for full-scale site remediation. Iron (III) nitrate was also effective as a Fenton's catalyst. Nitrate, a primary constituent of fertilizer, is applied at rates of up to 190 kg hectare\(^{-1}\) to promote crop growth and 2-10% of the nitrate leaches into the subsoil (Brady, 1974). If nitrate migrates to drinking water, it may cause methemaglobinemia; however, primary drinking water standards allow a maximum contaminant level (MCL) of 10 mg l\(^{-1}\) NO\(_3\)-N. Although plant uptake is a removal mechanism in surface soils, threats of groundwater contamination will likely limit the use of iron (III) nitrate as a Fenton's catalyst. Iron (III) sulfate, although a less-effective Fenton's catalyst, is commonly used in fertilizer formulations and should pose no threat to public health and the environment as a catalyst for the Fenton-like remediation of contaminated soils.

The basis for an economic analysis of soil remediation systems includes capital, excavation, hauling, chemical costs, and operation and maintenance. The primary chemical cost, hydrogen peroxide, is $0.31 kg\(^{-1}\). Based on this price and the data of Figure 4, the hydrogen peroxide cost to remediate 1000 mg kg\(^{-1}\) diesel to below the most common regulatory standard of 100 mg kg\(^{-1}\) TPH is $52 (907 kg)\(^{-1}\) (ton). The primary advantages of the use of catalyzed hydrogen peroxide are the ease of operation and the cost of time and labor. A single application of catalyzed hydrogen peroxide oxidized diesel in the Palouse loess in 1-2 hours. If such reaction rates can be achieved in the field, the process would provide lower labor and monitoring costs relative to remediation processes that are controlled by desorption.

**Summary And Conclusions: Part I**

A number of iron catalysts were investigated in the remediation of a Palouse loess soil contaminated with 1000 mg kg\(^{-1}\) diesel using catalyzed hydrogen peroxide. The
catalysts included iron (III) perchlorate, iron (III) nitrate, iron (III) sulfate, iron (II) perchlorate, iron (II) sulfate, and an iron (III)-NTA complex. Of the six forms of inorganic catalysts, iron (III) perchlorate and iron (III) nitrate were most effective in oxidizing diesel in the Palouse loess soil. Central composite rotatable designs were used to investigate the effects of hydrogen peroxide and iron concentrations on the Fenton-like oxidation of diesel. The reactions were complete within 1 hour due to the low volume ratio of peroxide to catalyst. Because desorption was negligible over 90 hours, diesel oxidation occurred, at least in part, in the sorbed state. Iron (III) perchlorate was the most effective catalyst, but its use for full-scale soil remediation will be limited because it is commercially unavailable. Although not as effective as iron (III) perchlorate, iron (III)-NTA catalyzed up to 80% TPH oxidation at near-neutral soil pH. Amendments of potassium phosphate (KH$_2$PO$_4$) slowed the rate of Fenton's reaction in soil slurries, probably through the formation of a complex with soluble iron and other Fenton's catalysts; however, diesel oxidation was not significantly enhanced. These results are in agreement with previous studies which have shown that mineral-catalyzed Fenton-like reactions are most effective in oxidizing desorbed or soluble contaminants in the soil solution. Based on the results of this research, the chemical cost for the Fenton-like treatment of diesel-contaminated Palouse loess soil is $52 (907 kg)$\(^{-1}\) (ton). The cost may vary in other soils depending on soil characteristics, contaminant properties, and the contaminant concentration.

**PART II. RISK-BASED REMEDIATION OF TPH CONTAMINATED SOILS**

The common standard in the remediation of petroleum-contaminated soils has been total petroleum hydrocarbon (TPH) analyses—a practice mandated by regulatory agencies. Several different TPH analyses have been used depending on the type of petroleum contamination present at a site, including TPH-G for gasoline-contaminated soils and TPH-
D for diesel-contaminated soils; most of these analyses are based on gas chromatography/flame ionization detection. One of the most common TPH analyses, the Environmental Protection Agency (EPA) Method 418.1 (TPH-418.1), is based on infrared spectroscopy after the soil is extracted with Freon-113 (Xiang et al., 1995). The fundamental problem with such TPH analyses is that they are not based on the toxicity or environmental mobility of the hazardous fractions within petroleum; rather, all of the compounds of the petroleum fractions are given equal regulatory consideration under these analyses. However, gasoline is comprised of over 200 hydrocarbons and each exhibit widely differing toxicities and mobilities and, therefore, a range of human health risks.

Gasoline contains two very different fractions based on relative risk—monocyclic aromatic hydrocarbons (e.g., benzene, toluene, and xylenes) and C5-C12 aliphatic hydrocarbons (Watts, 1997). Aromatic compounds (BTX and other alkylbenzenes) account for 10-59% of gasoline (mass/mass), while aliphatic hydrocarbons comprise 49-62% (State of Massachusetts, 1994). Monocyclic aromatic compounds and low molecular weight aliphatics make up the majority of the hydrocarbons in gasoline, which also contains isoalkanes and a small fraction of polycyclic aromatic hydrocarbons (PAHs) and metals (Watts, 1997). Monocyclic aromatic hydrocarbons are characterized by greater toxicity and mobility than aliphatic compounds of the same carbon number (Montgomery, 1991; Sax, 1992). For example, benzene is a confirmed (Group A) human carcinogen that promotes myeloid leukemia, Hodgkin’s disease, and lymphomas. Toluene and xylenes are also toxic depending on the route of exposure; furthermore, they are experimental teratogens. In contrast, aliphatic hydrocarbons exhibit minimal chronic toxicity (Sax, 1992). Monocyclic aromatic hydrocarbons are also more mobile than aliphatic hydrocarbons in the environment with octanol-water partition coefficients two to four orders of magnitude less than corresponding aliphatic hydrocarbons (Table 4). Therefore, the monocyclic aromatic hydrocarbons not only tend to be more chronically toxic, but are also more likely to migrate to groundwater and subsurface water supplies.
Table 4. Second-Order Hydroxyl Radical Rate Constants (kOH·), Mean Solubility Values, and Octanol-Water Partition Coefficients (K_{ow}) for BTX and NDD.

<table>
<thead>
<tr>
<th>Compound</th>
<th>kOH· (L/mole-sec)</th>
<th>Water Solubility (mg/L)***</th>
<th>log K_{ow} ***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>7.8 x 10^9 *</td>
<td>1760</td>
<td>2.12</td>
</tr>
<tr>
<td>Toluene</td>
<td>3.0 x 10^9 *</td>
<td>532</td>
<td>2.73</td>
</tr>
<tr>
<td>Xylenes</td>
<td>7.1 x 10^9 *</td>
<td>163-185</td>
<td>2.95-3.26</td>
</tr>
<tr>
<td>Nonane</td>
<td>3.6 x 10^9 **</td>
<td>0.122</td>
<td>4.67</td>
</tr>
<tr>
<td>Decane</td>
<td>4.0 x 10^9 **</td>
<td>0.021</td>
<td>6.69</td>
</tr>
<tr>
<td>Dodecane</td>
<td>4.7 x 10^9 **</td>
<td>0.005</td>
<td>7.24</td>
</tr>
</tbody>
</table>

*Haag and Yao, 1992.

**Calculated using regression equation (log kOH· (water) = -1.45 + 1.12 log kOH· (air)) provided by Haag and Yao, 1992 and hydroxyl radical rate constants in air from Buxton et al., 1987.

***Watts, 1997

Current TPH methodologies do not provide a true measure of the human health and ecological risks of petroleum-contaminated sites. Furthermore, other flaws exist in TPH analyses that can limit its accuracy and cost-effectiveness in the remediation of contaminated sites. Soil organic matter and other non-petroleum organic compounds are often measured as petroleum hydrocarbons in TPH analyses resulting in false positive interferences (State of Washington, 1994). Hammon and Zahir (1995) concluded that the required addition of chlorobenzene for the preparation of standards as described in TPH-418.1 was unnecessary and resulted in a TPH value 33% higher than the actual level of contamination. These false positive results may bring relatively clean sites under regulatory scrutiny and can sometimes lead to unnecessary treatment efforts.

The limitations of current analytical methods demonstrate the need for an accurate, risk-based TPH methodology. The Massachusetts Department of Environmental Protection recently proposed a new risk-based TPH procedure that emphasizes the presence of the more toxic and mobile aromatic compounds over the aliphatic species (State of Massachusetts, 1994). In the proposed heath-based TPH method, all of the gasoline components are quantified by gas chromatography with the nonselective flame ionization
detection (FID) followed by analysis of the extract with a photoionization detector (PID), which is sensitive only to aromatic compounds. The two fractions are then normalized for relative risk and summed to obtain an adjusted TPH value. This method is based on weighted factors of 2 to 200 for aromatic compounds relative to aliphatic compounds based on established reference doses (RFIDs) and slope factors (SFS). This method may provide a more accurate measure of the human health and ecological risk at petroleum-contaminated sites relative to current methodology.

The low correlation between total TPH and human health risks combined with the analytical problems inherent in the current TPH methodology suggest that a risk-based TPH method similar to the Massachusetts model may likely be instituted nationwide. The adoption of a risk-based TPH methodology may have a significant impact on technology selection and the process design in the treatment of petroleum-contaminated sites, i.e., process dynamics that target the aromatic fractions of petroleum may be favored under the new regulations. For example, the generation of hydroxyl radicals by modified Fenton's reactions in soils may react differently with the aromatic fractions of petroleum compared to the entire spectrum of petroleum hydrocarbons. Therefore, the purpose of this research was to examine the comparative effectiveness of the Fenton-like oxidation of selected aromatic and aliphatic compounds typically found in gasoline as a basis for developing a more economical process design based on the proposed risk-based TPH standard.

**Materials And Methods**

**Materials**

Benzene, toluene, and mixed (-o, -m, and -p) xylenes (BTX) were used as representative aromatic compounds, and n-nonane, n-decane, and n-dodecane (NDD) were selected as common aliphatic components of gasoline. Benzene, toluene, xylenes, and n-decane (>99% purity) were purchased from Fisher Scientific, while n-nonane and n-
dodecane (>99% purity) were obtained from Sigma and Aldrich, respectively. Physical constants for the contaminants are shown in Table 4.

Iron (III) sulfate was purchased from Sigma and stock hydrogen peroxide (50%) was provided by Solvay Interox. All other chemicals were reagent grade. The deionized water used in the controls and stock solutions was obtained from a Barnstead NANOpure II system. The soil used was a sandy loam collected from an alluvial fan above the Carson Valley, Nevada. It was characterized for particle size distribution, cation exchange capacity, crystalline and amorphous iron and manganese oxyhydroxides, and organic carbon content (Page et al., 1982); the soil characteristics are listed in Table 5.

Table 5. Characteristics of the Carson Valley Loam.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Carbon Content (mg/kg)</td>
<td>5000</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>86.5</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>11</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>25</td>
</tr>
<tr>
<td>Crystalline Fe Oxides (mg/kg)</td>
<td>4400</td>
</tr>
<tr>
<td>Crystalline Mn Oxides (mg/kg)</td>
<td>100</td>
</tr>
<tr>
<td>Amorphous Fe Oxides (mg/kg)</td>
<td>4400</td>
</tr>
<tr>
<td>Amorphous Mn Oxides (mg/kg)</td>
<td>100</td>
</tr>
<tr>
<td>Cation Exchange Capacity (cmolc/kg)</td>
<td>4.28</td>
</tr>
<tr>
<td>pH</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Sample Preparation

Equimolar solutions of BTX and NDD were prepared and 20 ± 0.01 g of soil were weighed into 40-mL borosilicate vials with Teflon lined caps. Soil aliquots of 20 g were spiked with equimolar solutions of the hydrocarbons (15 mmol/kg BTX and/or NDD); these compounds exceeded the water solubility of all six compounds and insured that some of each was sorbed or present in a NAPL phase. The vials were hand shaken to uniformly coat the soil and were allowed to equilibrate for one hour prior to reagent addition. The procedures were conducted in triplicate and controls were performed in parallel using deionized water in place of H₂O₂.
Experimental Procedures

Gas-purge methodology (Brusseau et al., 1990) was used to determine the rate of BTX and NDD desorption from the soil slurries. In the GP procedure, an aqueous slurry of the contaminated soil is purged with nitrogen to volatilize desorbed contaminants. Of the two steps in the process—desorption and volatilization—desorption controls the rate at which the contaminant escapes from solution. Soil samples were purged with nitrogen gas at a rate of 10 mL/min and hydrocarbon residuals were quantified over 5 days. Contaminant concentrations were initially measured by extracting the aqueous slurry as well as that which was collected in gas absorbent tubes filled Carbosorb. Mass balance data showed that the residual found in the slurry inversely correlates with the mass captured in the gas sorbent tubes; therefore, subsequent analyses were based on quantifying only the hydrocarbon concentrations in the slurry.

Four variables, H$_2$O$_2$ concentration, iron (III) sulfate concentration, pH, and liquid to soil ratio (L:S), were investigated in the Fenton-like oxidation of the BTX- and NDD-spiked soils. A four-level central composite rotatable design was used, with H$_2$O$_2$ concentrations from 0 to 3% for the BTX and from 0 to 10% for the NDD. The Fenton's catalyst, iron (III) sulfate, was varied from 0 to 25 mM for both the aromatic and aliphatic compounds. The L:S ratio ranged from 0.25 mL/g to 1.0 mL/g. Two pH conditions were evaluated: an acidic pH region (pH 2-3) and a near-neutral pH region (5.5-6.5), which was governed by the natural pH of the soil combined with a ~1 unit pH drop provided by the amendment of weakly acidic iron (III) sulfate. Adjustment to pH 2-3 was accomplished through the addition of 4.5 M sulfuric acid. Following the addition of reagents, the vials were mixed to ensure homogenous contact of both hydrogen peroxide and catalyst and the reaction was allowed to proceed until the H$_2$O$_2$ was consumed (~2 hours). The systems were then shake-extracted on a wrist-action shaker for 24 hours; n-decane was used to extract the BTX samples and ethyl acetate was used to extract the NDD samples. The vials were centrifuged and analyzed for each set of hydrocarbons by gas chromatography.
Central composite rotatable experimental designs, which describe the effect of n variables on an n+1 component (Diamond, 1989), were used throughout the study. Four two-variable central composite designs were conducted in which \( \text{H}_2\text{O}_2 \) concentration and iron (III) sulfate concentration were varied at a constant L:S of 1.0 for each chemical class at both acidic and near-neutral pH regimes. Two subsequent two-variable central composites were conducted varying the \( \text{H}_2\text{O}_2 \) concentration and L:S ratio at the most effective iron amendment for each class of contaminants at the near-neutral pH regime. A final two-variable central composite analysis was performed to investigate the degradation of BTX with competition by equimolar NDD in the system. In this system containing both BTX and NDD, the soil was spiked with both the aromatic and aliphatic species and then evaluated under varying \( \text{H}_2\text{O}_2 \) concentrations and L:S ratios at near-neutral pH and with the most effective iron amendment found previously.

**Analysis**

Both BTX and NDD were analyzed on a Hewlett-Packard 5890A gas chromatograph with flame ionization detection and a 30 m x 0.32 mm Supelco 2-4044 fused silica capillary column with a film thickness of 0.25 mm. Chromatographic conditions included initial oven temperature of 40 °C, program rate of 8 °C/min, and final oven temperature of 150 °C. An injector temperature of 160 °C and a detector temperature of 200 °C were used.

**Results And Discussion**

**Desorption of BTX and NDD**

The results of the gas-purge desorption analysis for samples spiked with 15 mmol/kg BTX and NDD samples are shown in Figure 10. Approximately 20% of the NDD desorbed over 50 hrs, while desorption of BTX was nearly complete within 30 hrs. During the 2 hr reaction time of the oxidation experiments, less than 2% of the NDD desorbed, while
Figure 10. Desorption of 15 mmol/kg BTX and NDD in a sandy loam soil.
approximately 38%, 34%, and 18% of the benzene, toluene, and xylenes desorbed, respectively.

The effect of sorption on the degradation of contaminants has been well documented. Tyre et al. (1991) found that more hydrophobic contaminants were degraded more slowly than water-soluble compounds by Fenton-like reactions in soils. Weber et al. (1993) reported that sorption of pesticides to organic matter and clays limited the bioavailability of the contaminants for metabolic uptake in bioremediation systems. Therefore, the higher degree of sorption of the NDD relative to the BTX species may have an effect on its degradation by Fenton-like processes.

Relative Oxidation of BTX and NDD at Near-Neutral pH

The relative oxidation of each hydrocarbon was obtained by comparing residual concentrations to the concentrations found in deionized water controls; regression equations were then developed from the experimental data, which were then used to generate response surfaces. The regression equations for all of the systems are listed in Appendix II.

Response surfaces for the Fenton-like oxidation of benzene, toluene, and xylenes as a function of $\text{H}_2\text{O}_2$ concentration and iron (III) sulfate concentration at near-neutral pH and constant L:S of 1.0 are shown in Figures 11a-c, with isoresponse lines representing percent oxidation for the corresponding conditions. The procedure used to compare the effectiveness of Fenton-like oxidations for the six different hydrocarbons was to hold one variable constant [i.e., $\text{H}_2\text{O}_2$ concentration, iron (III) sulfate concentration, L:S, or pH] and then compare the degradation of each compound with the fixed variable. Hydrogen peroxide concentrations of 1%, 2%, 3%, and 10% were selected to provide a broad range of degradation; in a similar manner, extreme values were selected for L:S (0.25 and 1.0), pH (3 and 6), and iron (III) sulfate concentration (10 mM and 25 mM). The maximum oxidation of each compound under the given conditions was obtained by inspection and are summarized in Table 6. The data show that under the optimum condition of 2% $\text{H}_2\text{O}_2$ and
Figure 11a. Response surface for the Fenton-like oxidation of benzene at L:S = 1.0 and near-neutral pH. Isoresponse lines represent percent oxidation.
Figure 11b. Response surface for the Fenton-like oxidation of toluene at L:S = 1.0 and near-neutral pH. Isoresponse lines represent percent oxidation.
Figure 11c. Response surface for the Fenton-like oxidation of xylenes at L:S = 1.0 and near-neutral pH. Isoresponse lines represent percent oxidation.
5 mM iron (III) sulfate, >99% benzene oxidation and >90% degradation of toluene and xylenes was found.

Table 6. Relative Maximum Oxidation of BTX and NDD as a Function of H₂O₂ Concentration, Iron (III) Sulfate Concentration, and pH.

<table>
<thead>
<tr>
<th>δH₂O₂</th>
<th>δpH</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Xylenes</th>
<th>Nonane</th>
<th>Decane</th>
<th>Dodecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&lt;3</td>
<td>80%</td>
<td>70%</td>
<td>60%</td>
<td>75%</td>
<td>55%</td>
<td>20%</td>
</tr>
<tr>
<td>2</td>
<td>&lt;3</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>80%</td>
<td>60%</td>
<td>20%</td>
</tr>
<tr>
<td>3</td>
<td>&lt;3</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>90%</td>
<td>70%</td>
<td>20%</td>
</tr>
<tr>
<td>10</td>
<td>&lt;3</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;70%</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>85%</td>
<td>80%</td>
<td>70%</td>
<td>35%</td>
<td>10%</td>
<td>10%</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>&gt;99%</td>
<td>&gt;90%</td>
<td>&gt;90%</td>
<td>40%</td>
<td>15%</td>
<td>10%</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>&gt;90%</td>
<td>&gt;90%</td>
<td>&gt;90%</td>
<td>45%</td>
<td>20%</td>
<td>10%</td>
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<tr>
<td>10</td>
<td>6</td>
<td>&gt;80%</td>
<td>&gt;60%</td>
<td>&gt;30%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

L:S = 1.0

The kinetics and stoichiometry of Fenton-like reactions in soils is affected by the rate of reaction with hydroxyl radical and contaminant availability (Sedlak and Andren, 1994; Watts et al., 1994). The second-order hydroxyl radical rate constant for both BTX and NDD (Table 4) show that benzene, toluene, xylenes react with hydroxyl radicals at nearly the same rate. The desorption losses over the 2-hr time of the oxidative reactions were 38%, 34%, and 18%, respectively; however, >90% oxidation of the three aromatic compounds occurred over 2 hrs. Because BTX oxidation occurred more rapidly than desorption, the BTX components may have been degraded, at least in part, in the sorbed phase (Sedlak and Andren, 1994; Watts et al., 1994). Comparison of the oxidation of benzene, toluene, and xylenes at 2% H₂O₂ and 5 mM iron (III) sulfate with desorption rates and octanol-water partition coefficients showed that the degree of Fenton-like oxidation was inversely proportional to the K₀w. Because most of the BTX may have been oxidized in the sorbed state, the K₀w, a thermodynamic measure of hydrophobicity and sorptivity, is a logical parameter that correlates with the oxidation of sorbed BTX.
The response surfaces for the Fenton-like oxidation of nonane, decane, and dodecane as a function of $\text{H}_2\text{O}_2$ concentration and iron (III) sulfate concentration at near-neutral pH and constant L:S are shown in Figures 12a-c. The results, which are summarized in Table 6, demonstrate that >80%, >60%, and >30% degradation was achieved using 10% $\text{H}_2\text{O}_2$ and 25 mM iron (III) sulfate for nonane, decane, and dodecane, respectively. The difficulty of oxidizing hydrophobic aliphatic hydrocarbons was documented by Kakarla and Watts (1996). They found that $\text{H}_2\text{O}_2$ concentrations in the range of 15-45% were necessary to oxidize sorbed hexadecane. These results were confirmed by Stanton and Watts (1997) who found that sorbed $^{14}\text{C}$-hexadecane was nearly 87% converted to $^{14}\text{C}$-CO$_2$.

Because nonane, decane, and dodecane react with hydroxyl radical at approximately the same rate and the GP desorption profile for each compound is nearly the same, the decreasing degradation among these aliphatic compounds may have been due to their lower hydrophobicity (Table 4), which is often quantified by their octanol-water partition coefficients. Only 2% of the NDD desorbed over the 2-hr reaction time; therefore, most of the NDD oxidation occurred in the sorbed or NAPL phase or the Fenton-like reactions may have made the hydrocarbons more available for oxidative attack.

The degradation of BTX was significantly greater than NDD, even under less aggressive conditions (i.e., lower $\text{H}_2\text{O}_2$ and iron concentrations). Each of the BTX and NDD species is characterized by near-equal reactivity with hydroxyl radicals (Table 4), while the sorptivity of the NDD compounds is significantly greater than the BTX species, which probably resulted in the more effective oxidation of BTX components. One of the limitations of Fenton-like oxidation for soil remediation is the need to acidify large volumes of soil (Chen, 1992). The results of Figure 12 and Table 6 show that, if only the aromatic fractions are targeted for oxidation by Fenton-like soil remediation, the reaction proceeds effectively at near-neutral pH regimes. A process design at neutral pH would improve the
Figure 12a. Response surface for the Fenton-like oxidation of nonane at L:S = 1.0 and near-neutral pH. Isoresponse lines represent percent oxidation.
Figure 12b. Response surface for the Fenton-like oxidation of decane at L:S = 1.0 and near-neutral pH. Isoresponse lines represent percent oxidation.
Figure 12c. Response surface for the Fenton-like oxidation of dodecane at L:S = 1.0 and near-neutral pH. Isoresponse lines represent percent oxidation.
safety, costs, and logistics of *ex situ* soil treatment and enhance the potential for the *in situ* injection of reagents for deeply-contaminated soils.

**Oxidation of BTX and NDD at pH 3**

Regression equations that describe the oxidation of BTX and NDD at pH 3 in two-level [H$_2$O$_2$ and iron (III) sulfate] central composite experiments are listed in Appendix II. The response surfaces feature the same general characteristics as Figure 11a-c and 12a-c and, for brevity, only the optimal data for each surface for the Fenton-like oxidation of BTX and NDD as a function of H$_2$O$_2$ concentration and iron (III) sulfate concentration at pH 3 are listed in Table 6. As with the analyses of the near-neutral pH data, a fixed H$_2$O$_2$ concentration (2% and 10%) were used to compare the relative oxidation of the six compounds. The data show that >99% BTX degradation was achieved at 2% H$_2$O$_2$ with no iron amendment, while the highest oxidation of the alkanes, >99%, >90%, and >70%, was found at 10% H$_2$O$_2$ and 25 mM iron (III) sulfate for nonane, decane, and dodecane, respectively. As in the near-neutral pH system, the differences in water solubility and sorptive characteristics probably accounted for the changes in degradation between the two classes of compounds. The higher degradation of the contaminants, especially NDD, under the low pH regime may have been due to the increased reducing conditions (Watts *et al.*, 1990). Lou and Lee (1995) also found that low pH conditions favored BTX destruction; they hypothesized that the increase in Fe(OH)$^+$ formed at pH = 2 − 4, which has a higher activity than Fe$^{2+}$ in Fenton reactions, led to the improved contaminant destruction under the pH regime.

**Effect of Liquid:Solid Ratio on Fenton-Like Oxidations**

Regression equations for the oxidation of BTX and NDD for the two-level experiments in which H$_2$O$_2$ and L:S were varied at two fixed iron concentrations are listed in Appendix II. The optimum conditions for the Fenton-like oxidation of BTX and NDD as a function of H$_2$O$_2$ concentration and L:S ratio at near-neutral pH and two constant iron (III) sulfate concentrations (10 mM and 25 mM) are listed in Table 7. These data show that
significant degradation of BTX (> 95%) could be maintained at L:S ratios as low as 0.25, while the degradation of NDD was negligible (< 40%) at L:S < 1.0. The negligible NDD oxidation at L:S < 1.0 was not likely related to contact between the Fenton’s solution and the sorbed NDD, because the presence of free liquid is apparent at L:S ratios of ≥ 0.5. A plausible reason for negligible NDD oxidation at L:S < 1 is lower total mass of H₂O₂ present in the system available to promote the oxidation of the sorbed NDD.

Table 7. Relative Maximum Oxidation of BTX and NDD as a Function of H₂O₂ Concentration, Iron (III) Sulfate Concentration, and L:S Ratio.

<table>
<thead>
<tr>
<th>% H₂O₂</th>
<th>L:S</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Xylenes</th>
<th>Nonane</th>
<th>Decane</th>
<th>Dodecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>10%</td>
<td>10%</td>
<td>5%</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>15%</td>
<td>15%</td>
<td>5%</td>
</tr>
<tr>
<td>10</td>
<td>0.25</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>35%</td>
<td>20%</td>
<td>5%</td>
</tr>
<tr>
<td>1</td>
<td>1.0</td>
<td>&gt;99%</td>
<td>90%</td>
<td>80%</td>
<td>30%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>40%</td>
<td>10%</td>
<td>5%</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>50%</td>
<td>20%</td>
<td>5%</td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>80%</td>
<td>50%</td>
<td>10%</td>
</tr>
</tbody>
</table>

pH = 6

Competitive Oxidation of BTX and NDD

Response surfaces describing the Fenton-like oxidation of BTX and NDD when the six species were present in the soil as a function of H₂O₂ concentration and L:S ratio at near-neutral pH and constant iron (III) sulfate concentration of 5 mM are shown in Figures 13a-c and 14a-c; these data are also summarized in Table 8. The data show lower BTX oxidation relative to soils spiked with only BTX due to the presence of NDD in the system, while the NDD degradation was not significantly affected. These data suggest that the NDD species, although sorbed, either consumed or quenched hydroxyl radicals which may affect the stoichiometry and effectiveness of risk-based Fenton-like soil remediation. Nonetheless, because the water solubility and rate of desorption of BTX were greater than NDD, it was more available for hydroxyl radical oxidation.
Figure 13a. Response surface for the competitive Fenton-like oxidation of benzene at iron (III) sulfate = 5 mM and near-neutral pH. Isoresponse lines represent percent oxidation.
Figure 13b. Response surface for the competitive Fenton-like oxidation of toluene at iron (III) sulfate = 5 mM and near-neutral pH. Isoresponse lines represent percent oxidation.
Figure 13c. Response surface for the competitive Fenton-like oxidation of xylene at iron (III) sulfate = 5 mM and near-neutral pH. Isoresponse lines represent percent oxidation.
Figure 14a. Response surface for the competitive Fenton-like oxidation of nonane at iron (III) sulfate = 5 mM and near-neutral pH. Isoresponse lines represent percent oxidation.
Figure 14b. Response surface for the competitive Fenton-like oxidation of decane at iron (III) sulfate = 5 mM and near-neutral pH. Isoresponse lines represent percent oxidation.
Figure 14c. Response surface for the competitive Fenton-like oxidation of dodecane at iron (III) sulfate = 5 mM and near-neutral pH. Isoresponse lines represent percent oxidation.
Table 8. Competitive Maximum Oxidation of BTX and NDD as a Function of H₂O₂ Concentration and L:S Ratio at Constant Iron (III) Sulfate Concentration and pH.

<table>
<thead>
<tr>
<th>% H₂O₂</th>
<th>L:S</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Xylenes</th>
<th>Nonane</th>
<th>Decane</th>
<th>Dodecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25</td>
<td>30%</td>
<td>10%</td>
<td>5%</td>
<td>10%</td>
<td>10%</td>
<td>5%</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>75%</td>
<td>35%</td>
<td>15%</td>
<td>20%</td>
<td>15%</td>
<td>10%</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
<td>85%</td>
<td>50%</td>
<td>30%</td>
<td>25%</td>
<td>25%</td>
<td>&gt;10%</td>
</tr>
<tr>
<td>1</td>
<td>1.0</td>
<td>85%</td>
<td>65%</td>
<td>40%</td>
<td>25%</td>
<td>20%</td>
<td>8%</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>&gt;90%</td>
<td>85%</td>
<td>55%</td>
<td>35%</td>
<td>30%</td>
<td>10%</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>&gt;90%</td>
<td>&gt;90%</td>
<td>&gt;60%</td>
<td>&gt;40%</td>
<td>&gt;40%</td>
<td>&gt;10%</td>
</tr>
</tbody>
</table>

pH = 6 and 5 mM Iron (III) Sulfate

The results obtained in the competitive experiments are closest to what may be obtained in the field application of a Fenton-like remediation system to a gasoline-contaminated site. Even with the presence of other less-reactive compounds, the highly soluble BTX (and other substituted alkylbenzenes) will likely be degraded more rapidly than the sorbed aliphatic fractions (Watts et al., 1996).

With the scientific weakness of the current TPH methodology, a risk-based TPH standard will likely soon be implemented nationwide. Because the proposed TPH analysis method places a greater emphasis on the more toxic and mobile aromatic hydrocarbons in the determination of a risk-adjusted TPH value, the results of this research show that hydrocarbon-contaminated sites may be remediated more efficiently through the rapid destruction of the aromatic fractions (i.e., Fenton-like reactions target the compounds that are the greatest risk to public health and the environment). This change in the TPH methodology to a risk-based standard should also increase the economic advantages of Fenton's reagent through increased field application and further refinement of process design parameters.

The results of this study show that monocyclic aromatic compounds (e.g., BTX) are oxidized >90% using 2% H₂O₂, 5 mM iron (III) sulfate, and an L:S ratio of 0.3 at a
near-neutral pH regime. These conditions show that, based on a cost of $0.68/L for 50% H₂O₂ (Watts and Dilly, 1996), a BTX-contaminated site could be treated to >99% with a chemical cost of $9/metric ton. With the likely adoption of a risk-based TPH standard that emphasizes the aromatic fraction of petroleum, Fenton-like reactions have the potential to economically oxidize the same compounds that are highly regulated, under process conditions that can be easily implemented, such as near-neutral pH and low L:S ratios. Furthermore, Fenton-like reactions can effectively treat petroleum-contaminated soils on the order of days to weeks (Watts, 1992; Watts and Greenburg, 1995), while bioremediation of these sites often requires months (Mills, 1995).

Summary And Conclusions: Part II

The Fenton-like oxidation of six model compounds (three monocyclic aromatic species and three aliphatic compounds) found in gasoline was investigated as the basis for a risk-based process design of gasoline-contaminated soils. The basis for such a design is the greater health risk of aromatic species relative to the aliphatic groups. A sandy loam soil spiked with equimolar concentrations of either BTX (benzene, toluene, xylenes) or NDD (nonane, decane, dodecane) was evaluated for the most effective conditions using central composite rotatable designs with varying H₂O₂ concentrations, iron concentration, pH, and liquid-solid (L:S) ratios. The aromatic species were degraded > 90% under relatively mild conditions [2% H₂O₂ and 25 mM Fe (III) sulfate] within 2 hr. Furthermore, the Fenton-like oxidation of the monoaromatic compounds was effective at near-neutral pH regimes and an L:S ratio as low as 0.3. Alternatively, the oxidation of NDD occurred only at H₂O₂ concentrations ≥ 10% under acidic pH regimes.

Competitive studies, in which both BTX and NDD were added to the soil, showed that when NDD was introduced into soils containing BTX, the relative BTX degradation was lower, possibly due to competition with hydroxyl radicals by the NDD in the system. The results of the competitive study demonstrate that based on a chemical cost of $0.68/L
for 50% \( \text{H}_2\text{O}_2 \), >99% BTX degradation could be achieved at a cost of $9/metric ton without pH adjustment. The costs to treat a petroleum-contaminated site using modified Fenton’s reactions are competitive with bioremediation, while offering the additional benefit of more rapid clean-up times. Under new risk-based TPH regulations, the economic incentives of Fenton-like remediation systems could increase, especially in situations where rapid clean-up times are necessary.

**PART III: TRANSPORT OF HYDROGEN PEROXIDE THROUGH SOIL**

Early work on the use of Fenton-like processes for the remediation of contaminated soils focused on the addition of excess reagents (iron (II) and \( \text{H}_2\text{O}_2 \)). Watts et al. (1990) documented the mineralization of high concentrations of pentachlorophenol (PCP) using 7% \( \text{H}_2\text{O}_2 \) and 8 mM iron (II) at pH 3. Perchloroethylene (PCE) and octachlorodibenzo-p-dioxin (OCDD) were also oxidized using similar process conditions (Watts et al. 1991; Leung et al. 1992). Tyre et al. (1991) investigated the Fenton-like oxidation of four contaminants in soils and found that the more hydrophobic compounds were oxidized slowly with higher stoichiometric \( \text{H}_2\text{O}_2 \) requirements. Tyre et al. (1991) also hypothesized that the natural iron oxyhydroxides present in the soil may be capable of catalyzing the Fenton-like reactions:

\[
\text{H}_2\text{O}_2 + S \rightarrow \text{OH}^\bullet + \text{OH}^- + \text{S}^+ \quad (15)
\]

where S is the surface of the iron mineral. Watts et al. (1993) compared the catalysis of \( \text{H}_2\text{O}_2 \) by iron oxyhydroxides to the standard Fenton’s technique and the addition of excess reagents, and found that the iron oxyhydroxides provided the most efficient stoichiometry (i.e., moles contaminant degraded/mole \( \text{H}_2\text{O}_2 \) consumed).

The application of catalyzed \( \text{H}_2\text{O}_2 \) under *in situ* conditions for oxidizing sorbed contaminants may be limited by the instability of the \( \text{H}_2\text{O}_2 \) in the system and sorption of the contaminants. When added to soil, \( \text{H}_2\text{O}_2 \) is unstable due to the presence of inorganic
and organic reactants (Britton 1985). Inorganic reactants include catalysts such as iron oxyhydroxides and manganese oxyhydroxides, as well as transition elements resulting from mineral dissolution. The most common organic catalysts are enzymes, such as catalase and peroxidase, which are produced to detoxify H$_2$O$_2$ in the cellular and extracellular environment (Huling et al. 1991). Catalase is the most active of the naturally-occurring inorganic and enzymatic catalysts which decompose H$_2$O$_2$ (Nicholls and Schonbaum 1963).

Because H$_2$O$_2$ is unstable in soil systems, it may be difficult to apply to the surface of a soil for in situ remediation without decomposing close to the surface. In the only work of this nature, Ravikumar and Gurol (1994) studied the remediation of contaminated commercial sand in soil columns using catalyzed H$_2$O$_2$. However, sorption of the contaminants, pentachlorophenol (PCP) and trichloroethylene (TCE), did not limit contaminant degradation because the oxidation occurred primarily in the aqueous phase. More commonly, contaminants are strongly sorbed to soils, and the design of in situ remediation based on rates of desorption may not be feasible. Sedlak and Andren (1994) reported that sorption significantly affected the transformation rates of polychlorinated biphenyls (PCBs) in a Fenton’s system. Furthermore, Sheldon and Kochi (1981) stated that most compounds not present in the aqueous phase (i.e., those found in other phases), are not available for reactions with hydroxyl radicals because the oxidants are generated in the aqueous phase.

Recent studies have shown that aggressive Fenton-like reactions have the potential to oxidize sorbed contaminants. Watts et al. (1994) documented the oxidation of sorbed hexachlorobenzene (log K$_{OW}$ = 6.2), which was degraded more rapidly than it was desorbed with H$_2$O$_2$ concentrations greater than 30 mM using soluble iron (II) at H$_2$O$_2$:Fe molar ratios of 2:1. They hypothesized that the rapid rates of oxidation were due either to the ability of hydroxyl radicals to oxidize sorbed contaminants or to changes in the sorption properties under the redox conditions of the high H$_2$O$_2$ concentrations. Furthermore,
Stanton and Watts (1995) documented the oxidation of hexadecane in the sorbed phase in batch reactors using H₂O₂ in the high percent range (10-50%). Hexadecane oxidation was confirmed by near quantitative recovery of ¹⁴C-hexadecane as ¹⁴C-CO₂. Regardless of the mechanism, the results show that high stoichiometric quantities of H₂O₂ are capable of oxidizing sorbed contaminants.

Although Fenton-like reactions have been shown to be effective in oxidizing a wide range of contaminants in soils at the bench-scale level, few studies have been conducted with quantities of soils beyond a few grams, whether in batch ex situ reactors, or the in situ surface application of H₂O₂. Therefore, the purpose of this research was (1) to investigate the decomposition of H₂O₂ as a function of soil depth under a range of conditions in a highly reactive soil of low permeability, (2) determine the depth to which sorbed hexadecane can be oxidized in the soil, and (3) assess the effectiveness of stabilization in the promotion of Fenton-like reactions at increased soil depths.

Materials And Methods

Materials

The soil used, a disturbed silt loam, was obtained from a diesel-contaminated maintenance and equipment storage yard located near Washtucna, Washington. The soil was passed through a 5 mm sieve. Particle size distribution was determined by the pipette method (Gee and Bauder 1986). The iron and the manganese contents were determined by citrate-bicarbonate-dithionite extractions (Jackson et al. 1986). Organic carbon content was established by combustion at 900°C with the evolved CO₂ trapped in KOH and measured by back titration of unreacted KOH (Nelson and Summers 1982). The cation exchange capacity (CEC) was determined by saturation with sodium acetate at pH 8.2 (U.S. Soil Conservation Service 1972). The characteristics of the soil are listed in Table 9.

<table>
<thead>
<tr>
<th>Soil Property</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Carbon (%)</td>
<td>0.55</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>43.6</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>52</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>4.4</td>
</tr>
<tr>
<td>Fe (mg/g)</td>
<td>35.2</td>
</tr>
<tr>
<td>Mn (mg/g)</td>
<td>0.514</td>
</tr>
<tr>
<td>Cu (mg/g)</td>
<td>0.0252</td>
</tr>
<tr>
<td>P (mg/g)</td>
<td>1.07</td>
</tr>
<tr>
<td>CEC (cmol(+)/kg)</td>
<td>13.3</td>
</tr>
</tbody>
</table>

Hexadecane (99% purity) was purchased from EM Science and stock hydrogen peroxide (50%) was obtained from Solvay Interox (Deer Park, TX). Potassium phosphate (monobasic) was purchased from Fisher Scientific. All chemicals were of reagent grade. Hexadecane (0.1 mmole/kg) was spiked onto the soil in a solution of ethyl acetate, which was allowed to evaporate after thoroughly mixing the soil. Soil columns (5 cm i.d.) were made of polyvinyl chloride (PVC). They were internally lined with chemically inert Tedlar (PTFE) sheeting (Du Pont, NY), and capped at the base with standard 5 cm PVC caps (containing holes for drainage) covered with aluminum foil at the base. Soil columns were prepared by packing the soil in increments of 50 g and uniformly tapping the columns. All columns were prepared in sets of three to provide triplicate experiments.

**Screening of Hydrogen Peroxide Stabilizers**

Phosphates and silicates are recognized as effective stabilizers against the decomposition of H₂O₂ (Schumb et al. 1955). The effectiveness of monobasic potassium
phosphate (KH₂PO₄), dibasic potassium phosphate (K₂HPO₄), sodium tripolyphosphate (Na₅P₃O₁₀), and silicic acid (SiO₂·nH₂O) in increasing the depth of migration of H₂O₂ and the potential depth of Fenton-like oxidations was investigated. The columns used were packed with the Washtucna soil to a depth of 12.5 cm. Up to four spikes of 4.5 M H₂O₂, stabilized with 75 mM (as P or Si) of KH₂PO₄, K₂HPO₄, Na₅P₃O₁₀, or SiO₂·nH₂O were applied to the columns. The use of 75 mM stabilizer concentrations was based on the results of preliminary screening. The volume added to the columns was approximately 5% greater than the field capacity of the soil to ensure total saturation of the column. The experiments were repeated with higher H₂O₂ concentrations (9 M & 15 M) stabilized with 75 mM KH₂PO₄.

Hydrogen Peroxide and Phosphate Dynamics

In order to investigate the behavior of H₂O₂ in the presence of the most effective stabilizer (KH₂PO₄) in the soil columns, 15 M H₂O₂, mixed with a range of stabilizer (KH₂PO₄) concentrations from 0 to 150 mM, was applied to a series of columns ranging from 2 to 15 cm in depth. The 15 M H₂O₂ was added in increments of 10 mL over a period of 5 hours to minimize its aggressive reactions. The total volume of H₂O₂ added to the columns was equivalent to the field capacity of 25 cm of soil. The column eluent was analyzed for residual H₂O₂; in addition, PO₄-P was measured in the column eluent that received the 75 mM KH₂PO₄ amendment.

Hexadecane Oxidation

Based on the results of Stanton and Watts (1995) using ¹⁴C-hexadecane, H₂O₂ concentrations in the 6.5-15 M range are required to oxidize sorbed hexadecane in natural soils. Based on their results, a number of process parameters were evaluated to establish the conditions that enhance the oxidation of hexadecane with soil depth. The process variables included H₂O₂ concentration, number of H₂O₂ applications, and pH. Hydrogen peroxide applications, stabilized with 75 mM KH₂PO₄, were made at concentrations of 4.5 M, 9 M, and 15 M to evaluate their effect on hexadecane oxidation. Four applications of
15 M H2O2, stabilized with 75 mM KH2PO4, were made to assess the effect of multiple H2O2 applications on hexadecane oxidation. The effect of pH was investigated using an influent solution of 15 M H2O2 stabilized with 75 mM KH2PO4 adjusted to pH 2 with 1 M H2SO4, pH 7 with 1 M NaOH, and no pH adjustment (i.e., the pH of 5.9 ± 0.5 was dictated by the KH2PO4). The H2O2 solutions were applied to the Washtucna soil in 12.5 cm columns, using a volume 5% greater than the soil field capacity. Control experiments were conducted in parallel with the same volume of deionized water. Sampling was conducted by collecting triplicate soil aliquots at successive depths after withdrawing the Tedlar-packed soil from the columns.

Central Composite Optimization Experiments

To optimize hexadecane oxidation, two-level central composite rotatable design experiments (Diamond 1989) were performed and response surfaces were generated to determine the optimum stabilizer concentration and soil depth for hexadecane oxidation. The range of variables included KH2PO4 concentrations from 0 to 75 mM and column depths of 0 to 25 cm. Fixed variables included a H2O2 concentration of 15 M, and a soil pH of 5.9 ± 0.5 which was governed by the concentration of KH2PO4 added.

Analysis

Residual hexadecane was measured on a Hewlett-Packard 5890A (Palo Alto, CA) gas chromatograph after shake extracting from the soil in ethyl acetate for 8 hours. The gas chromatograph was equipped with a 0.53-mm (ID) x 15-m Supelco SPB-5 (Belleforte, PA) capillary column and flame ionization detector. The chromatographic conditions included injector port temperature, 250°C; detector temperature, 350°C; and initial oven temperature, 150°C programmed at the rate of 10°C/min to a final temperature of 220°C. Orthophosphate concentrations in the eluent were measured using the Murphy-Riley technique (Adams 1990). Hydrogen peroxide concentrations were quantified by iodometric titration with sodium thiosulfate (FMC 1989).
Results And Discussion

Screening of Hydrogen Peroxide Stabilizers

The effect of four stabilizers on H₂O₂ decomposition in 12.5 cm deep Washtucna soil columns is shown in Table 10. The data of Table 10 indicate that only monobasic potassium phosphate (KH₂PO₄) increased the depth of migration of H₂O₂, with a corresponding potential to promote Fenton-like reactions deeper in the soil column. Hydrogen peroxide stabilized with dibasic potassium phosphate (K₂HPO₄) decomposed vigorously, producing fumes and bubbles for the first few minutes after its addition to the soil column. The pH of the soil solution increased to 8.7 on K₂HPO₄ addition, which may have caused aggressive H₂O₂ decomposition, suggesting that the stabilizing activity of K₂HPO₄ did not significantly offset the pH effect. Silicic acid (SiO₂·nH₂O) and sodium tripolyphosphate (Na₅P₃O₁₀) were also ineffective in stabilizing H₂O₂ in the Washtucna soil (Table 10).

<table>
<thead>
<tr>
<th>Stabilizer</th>
<th>1 Application</th>
<th>2 Applications</th>
<th>3 Applications</th>
<th>4 Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH₂PO₄</td>
<td>&lt;0.03</td>
<td>0.040</td>
<td>0.110</td>
<td>0.123</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>Na₅P₃O₁₀</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>SiO₂·nH₂O</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
</tbody>
</table>

TABLE 10. Concentrations (M) of H₂O₂ in column eluent showing the effect of stabilizers on H₂O₂ decomposition as a function of number of applications. The experiments were conducted in 12.5 cm columns using an initial H₂O₂ concentration of 4.5 M.
The increase in \( \text{H}_2\text{O}_2 \) stability probably resulted from the inactivation of the primary catalysts (e.g., transition elements such as iron), either by precipitation reactions or by conversion to relatively inactive complexes (Schumb et al. 1955). However, a significant level of \( \text{H}_2\text{O}_2 \) decomposition was evident, which was probably by mineral-catalyzed Fenton-like reactions or non-hydroxyl radical mediated decomposition reactions (Watts et al. 1993). The use of high concentrations of \( \text{H}_2\text{O}_2 \) (in the percent range) negated the possibility of enzymatic \( \text{H}_2\text{O}_2 \) decomposition because catalase and peroxidase are destroyed by such aggressive oxidation reactions (Schumb et al. 1955).

The addition of \( \text{Na}_5\text{P}_3\text{O}_{10} \) also slowed the rate of \( \text{H}_2\text{O}_2 \) migration through the soil column compared to the other stabilizers. Soil clogging may have occurred as a result of precipitation of cations (\( \text{Fe}^{2+}, \text{Cu}^{2+}, \text{Mn}^{2+} \), etc.) by \( \text{Na}_5\text{P}_3\text{O}_{10} \) resulting in decreased hydraulic conductivity (Aggarwal et al. 1991). While the precipitation of the metal catalysts should have reduced the rate of \( \text{H}_2\text{O}_2 \) decomposition, the decreased permeability may have, in turn, increased the contact time with other catalysts (e.g., iron oxyhydroxides) resulting in relatively high rates of \( \text{H}_2\text{O}_2 \) decomposition. Nonetheless, \( \text{KH}_2\text{PO}_4 \) was the most effective of the four stabilizers, with the lowest rate of \( \text{H}_2\text{O}_2 \) decomposition and the appearance of detectable \( \text{H}_2\text{O}_2 \) concentrations in the eluent after two applications. The data of Table 10 also show that, with up to four surface applications, the \( \text{H}_2\text{O}_2 \) concentration in the eluent increased as a function of the number of applications, which was verified by similar experiments using higher \( \text{H}_2\text{O}_2 \) concentrations (stabilized with 75 mM \( \text{KH}_2\text{PO}_4 \)) (Table 11). However, the increase in the eluent \( \text{H}_2\text{O}_2 \) concentration with the number of applications was not significantly greater for higher initial \( \text{H}_2\text{O}_2 \) concentrations (9 M, 15 M); the eluent \( \text{H}_2\text{O}_2 \) concentrations after four surface applications were 0.123 M, 0.254 M, and 0.353 M corresponding to initial \( \text{H}_2\text{O}_2 \) concentrations of 4.5 M, 9 M, and 15 M, respectively.
TABLE 11. Concentrations (M) of H$_2$O$_2$ in column eluent showing the effect of initial H$_2$O$_2$ concentration (stabilized with 75 mM KH$_2$PO$_4$) on its decomposition as a function of number of applications. The experiments were conducted in 12.5 cm columns.

<table>
<thead>
<tr>
<th>Initial concentration</th>
<th>1 Application</th>
<th>2 Applications</th>
<th>3 Applications</th>
<th>4 Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5 M H$_2$O$_2$</td>
<td>&lt;0.03</td>
<td>0.040</td>
<td>0.110</td>
<td>0.123</td>
</tr>
<tr>
<td>9 M H$_2$O$_2$</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>0.150</td>
<td>0.254</td>
</tr>
<tr>
<td>15 M H$_2$O$_2$</td>
<td>&lt;0.03</td>
<td>0.039</td>
<td>0.114</td>
<td>0.353</td>
</tr>
</tbody>
</table>

Because KH$_2$PO$_4$ was the most effective stabilizer in decreasing the rate of H$_2$O$_2$ decomposition and promoting its transport through the soil column, it was used in subsequent studies for optimizing H$_2$O$_2$ stabilization and maximizing hexadecane oxidation with soil depth.

**Hydrogen Peroxide and Phosphate Dynamics**

A response surface for H$_2$O$_2$ residual in the soil columns as a function of the stabilizer (KH$_2$PO$_4$) concentration and column depth is shown in Figure 15. Concentrations of KH$_2$PO$_4$ up to 150 mM stabilized the H$_2$O$_2$, allowing it to migrate in the soil column to 14 cm. The depth of detectable H$_2$O$_2$ increased to 10 cm with KH$_2$PO$_4$ concentrations in the range of 5 mM to 30 mM; however, the relative increase in H$_2$O$_2$ migration was minimal at KH$_2$PO$_4$ concentrations > 30 mM. The maximum depth of detectable H$_2$O$_2$ residual with no stabilizer addition was approximately 4.5 cm; therefore, the addition of 150 mM KH$_2$PO$_4$ provided stability to the H$_2$O$_2$, allowing it to reach almost three times the depth of the unstabilized formulation.
Figure 15. Response surface for H2O2 decomposition in the soil columns as a function of stabilizer (KH2PO4) concentration and soil depth. Contours represent the percent H2O2 residual.
Figure 16. Relative H$_2$O$_2$ and PO$_4$-P concentrations as a function of soil depth. The initial H$_2$O$_2$ concentration was 15 M and the initial KH$_2$PO$_4$ concentration was 75 mM.
The data of Figure 16 show that more than 90% of the unstabilized 15 M H₂O₂ decomposed in the top 2 cm of the soil columns, while with the 75 mM KH₂PO₄ formulation, the H₂O₂ remained at detectable concentrations to the 11 cm depth. By multiple regression, the PO₄-P concentration correlated with the H₂O₂ residual (R² = 0.79), with a decrease in the concentration of both species as a function of depth in the soil column. Phosphorus fixation on soils is well documented; phosphorus species usually distribute onto the solid phase by ion exchange and other partitioning mechanisms (Brady 1974). As a result, it is removed from the aqueous H₂O₂ as it passes through the soil column, with corresponding reduced stability of the H₂O₂. Therefore, the behavior of the stabilized H₂O₂ as it travels through the soil approaches that of the unstabilized H₂O₂, and its rate of decomposition increases dramatically. Because of the high degree of phosphate fixation, doubling the KH₂PO₄ concentration from 75 to 150 mM increased the depth of H₂O₂ migration by only 3.0 cm [from 11.0 cm to 14 cm (Figure 15)].

**Hexadecane Oxidation**

The oxidation of hexadecane as a function of soil depth with one application of H₂O₂ stabilized with 75 mM KH₂PO₄ is shown in Figure 17. With the application of 4.5 M H₂O₂, hexadecane was oxidized to 58 μmole/kg at the surface and 78 μmole/kg at 2 cm, and hexadecane oxidation at greater depths was negligible (<5%). The effectiveness of 9 M H₂O₂ was greater for depths between 0 to 6 cm. However, the highest hexadecane oxidation at any depth using 9 M H₂O₂ was to only about 65 μmole/kg (i.e., 35% degradation). Therefore, the 4.5 M and the 9 M H₂O₂ may not provide sufficiently aggressive conditions to oxidize sorbed hexadecane. The 15 M H₂O₂, however, oxidized >80% hexadecane (to <18 μmol/kg) in the top 5 cm of the soil column. These data are in agreement with the results of Stanton and Watts (1995), who found that the oxidation and subsequent recovery of ¹⁴C-labeled hexadecane as ¹⁴C-CO₂ was proportional to the concentration of H₂O₂ used to promote Fenton-like oxidations. Their results suggest that other mechanisms (e.g., oxidation-reduction reactions at mineral surfaces) may be
occurring during mineral-catalyzed Fenton-like reactions in soils. Hexadecane residuals below 5 cm were of approximately 62 μmole/kg (38% degradation); the 74 μmole/kg concentration at 8 cm appears to be an anomaly associated with analytical error. The data of Figure 17 show minimal desorption of hexadecane (< 10%) when deionized water was applied to the soil column. Therefore, hexadecane remediation occurred in the sorbed state or the Fenton-like oxidations affected the sorption properties of the system resulting in increased rates of desorption in the presence of H₂O₂ (Watts et al. 1994). Significant oxidation of hexadecane did not occur below the 6 cm depth for any of the H₂O₂ concentrations investigated. Based on the data of Figure 16, the phosphate was likely removed from the aqueous H₂O₂ as it passed through the soil column resulting in decreased H₂O₂ stability, and corresponding decreased hexadecane oxidation with depth. Because 15 M H₂O₂ was the only concentration effective in promoting the Fenton-like oxidation of sorbed hexadecane, only 15 M H₂O₂ was used in subsequent experiments.

The effect of multiple H₂O₂ applications on hexadecane oxidation is documented in Figure 18. Additional H₂O₂ applications did not provide increased hexadecane oxidation relative to a single application. The loss of catalytic activity may be due to a change in the state of iron oxyhydroxide catalysts or the oxidation-reduction potential of the system (Barcelona et al. 1991). Therefore, only one application of H₂O₂ was made in subsequent oxidation experiments. High residual concentrations of hexadecane were observed at the top of the soil column (zero depth) compared to the portion of the soil column up to 5 cm depth. Hexadecane (specific gravity = 0.77) added to the system in excess of the sorptive capacity of the soil may have floated on the slurry surface and settled on top of the soil after the system was flooded with H₂O₂.
Figure 17. Effect of H₂O₂ concentration on hexadecane oxidation with soil depth.
Figure 18. Effect of multiple H$_2$O$_2$ applications on hexadecane oxidation with soil depth.
Figure 19. Effect of pH on hexadecane oxidation as a function of soil depth.
The effect of pH on the Fenton-like oxidation of hexadecane (Figure 19) shows that at pH 7, the H$_2$O$_2$ penetrated only the top few cm of the column. Visual inspection indicated vigorous oxygen evolution, suggesting that the H$_2$O$_2$ was consumed within the first few minutes. Watts et al. (1990) documented that H$_2$O$_2$ decomposition increases as a function of pH, with the highest decomposition rate occurring in the basic range. Oxygen evolution is the predominant route of H$_2$O$_2$ decomposition at neutral pH (Dixon and Norman 1962):

$$\text{H}_2\text{O}_2 \xrightarrow{\text{iron(III)}} \frac{1}{2}\text{O}_2 + \text{H}_2\text{O}$$

In addition, quenching of OH$^*$ by H$_2$O$_2$ may be occurring:

$$\text{OH}^* + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^* + \text{H}_2\text{O}$$

where HO$_2^*$ is perhydroxyl radical. Although 70% hexadecane loss (to 30 μmole/kg) occurred at the top of the soil column, the oxidation then decreased linearly to 10% (90 μmole/kg) loss at a depth of 6 cm. The extent of hexadecane oxidation for the pH-KH$_2$PO$_4$ (i.e., the pH of 5.9 ±0.5 dictated by the KH$_2$PO$_4$) and the pH 2 systems were not significantly different. The profiles for the pH-KH$_2$PO$_4$ and the pH 2 systems show approximately 90% oxidation to 10 μmole/kg in the top 5 cm of the soil; hexadecane loss then decreased to 30% at the 10 cm depth. The effect of pH on the effectiveness of the Fenton-like remediation of contaminated soils has received significant attention. Watts et al. (1990) documented that, although pentachlorophenol was oxidized at both acidic and neutral pH regimes, the stoichiometry (i.e., the moles of pentachlorophenol oxidized/mole of H$_2$O$_2$ consumed) was more efficient at acidic pH. However, Chen (1992) suggested that the need to adjust large volumes of soil to acid pH regimes may limit the large scale effectiveness of Fenton’s reagent for soil remediation. Iron ligands and naturally-occurring iron minerals have been effective in promoting Fenton-like reactions at near-neutral pH (Pignatello and Baehr 1994; Watts et al. 1994). The results of Figure 19 and Table 12 show that the use of phosphate as a stabilizer may also enhance the effectiveness of Fenton-like reactions at near-neutral pH regimes.
TABLE 12. Effect of KH$_2$PO$_4$ addition on pH of the soil solution in the Washtucna soil.

<table>
<thead>
<tr>
<th>KH$_2$PO$_4$ (mM)</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil solution pH</td>
<td>7.2</td>
<td>6.4</td>
<td>6</td>
<td>6</td>
<td>5.7</td>
<td>5.6</td>
<td>5.6</td>
<td>5.4</td>
</tr>
</tbody>
</table>

The results of H$_2$O$_2$ stability and hexadecane oxidation (Figures 15-20) served as the basis for subsequent studies based on central composite rotatable designs. Using a single application of 15 M H$_2$O$_2$ at the soil field capacity plus an extra 5% volume, a two-level central composite analysis was performed based on the independent variables of stabilizer (KH$_2$PO$_4$) concentration and depth. The system pH was dependent on the concentration of KH$_2$PO$_4$ added to the system (Table 12), but was in the same range (pH 5.9 ± 0.5) described by Sun and Pignatello (1992), who used iron chelates to enhance Fenton-like reactions at near-neutral pH. Using statistical procedures provided by Diamond (1989), the empirical data were fit to the following second-order polynomial:

$$\text{Hexadecane Oxidation (\%) = 89.559 - 0.481 (P) - 9.061 (Depth) + 0.010 (P)^2 + 0.245 (Depth)^2 + 0.003 (P) (Depth)}$$

$$R^2 = 0.97$$

where

$P =$ Stabilizer (KH$_2$PO$_4$) concentration (mM)

Depth = Soil depth (cm)

A response surface in which the percent hexadecane oxidation as a function of stabilizer (KH$_2$PO$_4$) concentration and soil depth calculated from equation (18) (Figure 21)
shows that hexadecane oxidation at a specific soil depth was not significantly different with the variation in KH$_2$PO$_4$ concentration from 0 to about 30 mM. With KH$_2$PO$_4$ concentrations greater than 30 mM, however, hexadecane oxidation increased as a function of the stabilizer concentration. In trends similar to Figure 18, the hexadecane oxidation decreased as a function of depth (from >90% oxidation to 10 μmole/kg for the top 2 cm of the soil column to 20-40% oxidation for the 10-15 cm depth with KH$_2$PO$_4$ concentrations ranging from 60-75 mM). Based on the desorption data shown in Figure 18, hexadecane oxidation occurred more rapidly than it was desorbed in the Washtucna soil. The data of Figure 21 show that, in the reactive, low-permeability Washtucna soil, the depth to which the oxidation of a sorbed contaminant can be achieved is a function of the H$_2$O$_2$ stability (i.e., the ability to provide a high concentration [~15 M] of H$_2$O$_2$ to sorbed contaminants at a specific depth of the soil column).

Because hexadecane oxidation is dependent on H$_2$O$_2$ residual, the data of Figures 15 and 21 have been combined (Figure 22) which shows an inverse relationship between the decomposition of H$_2$O$_2$ and the percent hexadecane oxidized. Conversely, the extent of hexadecane oxidation was directly proportional to the H$_2$O$_2$ residual at each depth, with H$_2$O$_2$ concentrations in the 5 to 15 M range required to oxidize sorbed hexadecane without soluble iron addition. These results are in agreement with the data of Figure 18, which indicates that significantly greater hexadecane oxidation was found with 15 M H$_2$O$_2$ relative to 9 M and 4.5 M H$_2$O$_2$. Similar findings were noted by Stanton and Watts (1995).
Figure 20. Response surface for hexadecane oxidation in the soil columns as a function of stabilizer (KH$_2$PO$_4$) concentration and soil depth. Contours represent the percent hexadecane oxidized.
Figure 21. Response surfaces for hexadecane oxidation and H$_2$O$_2$ decomposition in the soil columns as a function of stabilizer (KH$_2$PO$_4$) concentration and soil depth. Solid contours represent the percent hexadecane oxidized and dashed contours represent the percent H$_2$O$_2$ residual.
The results of Figure 22 also distinguish an effect of KH$_2$PO$_4$ addition. The results document that a KH$_2$PO$_4$ stabilizer concentration $> 30$ mM provided increased hexadecane oxidation while maintaining minimal H$_2$O$_2$ decomposition. Increased concentrations of KH$_2$PO$_4$ enhanced H$_2$O$_2$ stability which, in turn, provided sufficient H$_2$O$_2$ residual to promote Fenton-like oxidations of sorbed hexadecane. The data of Figures 16 and 22 suggest the following mechanism for limiting the depth of Fenton-like reactions in the highly reactive Washtucna soil:

\[
\text{PO}_4 \text{ fixation} \rightarrow \text{Increased H}_2\text{O}_2 \text{ consumption} \rightarrow \\
\text{Decreased potential of Fenton-like reactions}
\]

(19)

Based on the proposed critical pathway, an alternative approach is to first saturate with KH$_2$PO$_4$ followed by H$_2$O$_2$ addition, which may result in increased H$_2$O$_2$ stability and, consequently, increased depth of Fenton-like reactions.

**Engineering Significance**

Surface soils contain total iron concentrations ranging from 0.5 to 5% (Brady, 1974). The Washtucna soil (iron oxyhydroxide content = 3.52%) is characterized by relatively high total iron content, which provides a significant mass of catalyst for mineral-catalyzed Fenton-like reactions. The Washtucna soil is also characterized by low permeability, which may enhance the rapid decomposition of unstabilized H$_2$O$_2$ due to its prolonged contact time with the soil iron oxyhydroxides. In a field study described by Spain et al. (1989), the enzymatic decomposition of H$_2$O$_2$ was considered to be a major mechanism of H$_2$O$_2$ decomposition during its field application as an oxygen source for in situ bioremediation. However, the use of higher concentrations of H$_2$O$_2$ (in the percent range), when H$_2$O$_2$ is used as an abiotic, Fenton-like oxidant, may reduce this problem by inactivating catalase (Britton 1985; Huling et al. 1991). On the other hand, the rapid
inorganic decomposition of H₂O₂ when added to high-iron soils may negatively affect its potential for *in situ* application.

The stabilization of H₂O₂ with KH₂PO₄ enhanced the oxidation of hexadecane by Fenton-like reactions, and the data show that it is possible to oxidize sorbed hydrophobic contaminants in a highly reactive natural soil up to 15 cm using high H₂O₂ concentrations. Ravikumar and Gurol (1993) treated pentachlorophenol (PCP) and trichloroethylene (TCE) in soil columns packed with contaminated sand using catalyzed H₂O₂. However, oxidation under the conditions of their reactions was not limited by desorption. Sedlak and Andren (1994) documented that Fenton’s reactions using dilute H₂O₂ did not oxidize sorbed polychlorinated biphenyls (PCBs). However, Watts et al. (1994) showed that aggressive Fenton’s reactions have the potential to oxidize sorbed hexachlorobenzene, possibly by attacking the surface-sorbed contaminant by the hydroxyl radicals which are generated in the aqueous phase. Watts et al. (1991) documented that Fenton-like oxidations are capable of oxidizing octachlorodibenzo-p-dioxin (OCDD) in soils. Many highly hydrophobic contaminants, such as polycyclic aromatic hydrocarbons (PAHs) and dioxins, are strongly sorbed and are, therefore, trapped in the top 10 cm of soils. Even though the depth to which H₂O₂ can be delivered in a highly reactive soil of minimal permeability is low, *in situ* remediation of highly hydrophobic contaminants may be practical, because these compounds are strongly sorbed to soils, and often remain in the first few cm of soil following surface disposal or spills. Alternatively, H₂O₂ residuals may be delivered much deeper in a sandy soil column which is characterized by high permeability.

The supply of hydrogen peroxide is the primary cost of Fenton-like soil remediation. Based on a cost of $0.72/L for 50% H₂O₂ and saturation of the soil to field capacity of 0.25 mL/g, the cost to remediate a hydrophobic compound is $167/909 kg (ton) of soil. This cost represents a worst-case extreme; the oxidation of less hydrophobic contaminants would likely require lower H₂O₂ dosages. Nonetheless, such a cost may be
justified for the remediation of chlorinated dioxins, polychlorinated biphenyls, and other problem compounds.

Unlike other soil remediation studies (Ravikumar and Gurol 1994; Tyre et al. 1991), the results of this research document process conditions that promote the in situ oxidation of a sorbed, hydrophobic contaminant. Soil washing has recently been investigated to enhance the desorption of hydrophobic contaminants in contaminated soils (O’Neill et al. 1993). A limitation of soil washing is the necessary treatment of the wash water. An advantage of Fenton-like oxidations for soil remediation may be a rapid combined desorption/oxidation process in which hydrophobic contaminants are not only removed from the sorbed state, but simultaneously oxidized. Furthermore, the remediation is rapid (minutes to hours), which provides the potential to reach site closure over a short time frame.

Summary And Conclusions: Part III

The potential for applying H₂O₂ to the surface of contaminated soils to promote Fenton-like reactions was investigated using columns packed with a soil of high iron content and low permeability. Four stabilizers were screened for their ability to provide detectable H₂O₂ concentrations through 12.5 cm soil columns. Only KH₂PO₄ was effective in stabilizing H₂O₂ to produce detectable H₂O₂ concentrations. Silicic acid did not stabilize H₂O₂, and the stabilizing effect of K₂HPO₄ was negated by the high rate of decomposition at pH 8.7 provided by its dibasic characteristics. Visual inspection of lower oxygen evolution during the use of Na₅P₃O₁₀ suggested a decreased rate of H₂O₂ decomposition, but the stabilizing effect was lower than KH₂PO₄.

Hydrogen peroxide and phosphate dynamics were investigated using 15 M H₂O₂ in columns 2 to 15 cm in depth. Unstabilized H₂O₂ decomposed aggressively, and was consumed in the top 2 to 4 cm of the soil column. Addition of 150 mM KH₂PO₄ provided enough stability to allow the H₂O₂ to reach three times the depth of the unstabilized
formulation. The phosphate was removed from the formulation as it passed through the soil column, probably by ion-exchange or other fixation processes, further decreasing the H$_2$O$_2$ stability.

Hexadecane oxidation studies were performed using KH$_2$PO$_4$-stabilized H$_2$O$_2$ to investigate the process variables of optimum H$_2$O$_2$ concentration, number of applications, and effect of pH. A single application of 15 M H$_2$O$_2$ with no pH adjustment (i.e., the pH dictated by the KH$_2$PO$_4$) provided maximum hexadecane oxidation. Control experiments with deionized water showed minimal (<10%) hexadecane desorption suggesting that oxidation occurred in the sorbed phase. Subsequent investigations were conducted using a two-level central composite rotatable design. Response surfaces for hexadecane oxidation based on stabilizer (KH$_2$PO$_4$) concentration and soil depth suggested a critical value of 30 mM KH$_2$PO$_4$ concentration for the Washtucna soil beyond which an increase in the stabilizer concentration decreased the rate of H$_2$O$_2$ decomposition and increased the hexadecane oxidation. Furthermore, the central composite results showed a decrease in the percent hexadecane oxidized along the depth of the soil column with greater than 90% hexadecane oxidation in the top 2 cm of the soil column which then decreased to 20-40% oxidation in 10-15 cm depth for high stabilizer concentrations between 60 to 75 mM.

The results indicate that, in a soil of high iron content and low permeability, even stabilized H$_2$O$_2$ decomposes rapidly, negating the potential for applying H$_2$O$_2$ to oxidize contaminants beyond a few cm. Although the surface application of stabilized H$_2$O$_2$ to oxidize deep contamination in soils of high permeability and low iron content may be feasible, injection of H$_2$O$_2$ or use of ex situ slurry reactors may provide a more economical design for highly reactive, impermeable soils characterized by deep contamination.
PART IV: SCALE UP OF CATALYZED PEROXIDE TREATMENT SYSTEMS

One concern in the application of Fenton-like reactions to contaminated soils is the field-scale application. Soil matrix complexity and \( \text{H}_2\text{O}_2 \) transport throughout the soil column are primary concerns. Abundant information is available in the literature for successful lab-scale application; however, to date, not a single effective scaleup study has been reported and no quantitative relationships for the scaling up of Fenton-like reaction efficiency have been developed. Thus, the objective of this segment of research use to quantify scale-up of Fenton-like reactions for the remediation of diesel contaminated silica sand.

Materials And Methods

Materials

Diesel fuel was chosen as the experimental contaminant due to its widespread use in the transportation industry and resulting frequency as a groundwater and soil pollutant. Total petroleum hydrocarbon (TPH) concentrations of 2000 mg/kg are typical in contaminated soils. Composed of over 160 different aromatic and aliphatic hydrocarbons, diesel contains aliphatics with chain lengths between 15-25 carbon atoms. The distillation range is between 200-400°C. Diesel was obtained from Cenex Corporation (St. Paul, MN).

Silica sand was obtained from a beach area located along the Snake River, approximately 30 miles west of Pullman, WA. The soil is a naturally occurring, cohesionless sand with minimal organic content. The density was determined to be 1.42 kg/L.

Iron (III) sulfate was purchased from Boliden Intertrade, Inc. (Atlanta, GA). Stock hydrogen peroxide (50%) provided by Solvay Interlox (Deer Park, TX), and ethyl acetate
from Fisher Chemical (Santa Clara, CA) were used. Deionized water was purified to
greater than 18 MΩ with a Barnstead NANO pure II deionizing system.

Experimental Procedures

Traditional experimental methods require optimization through an iterative single-
variable analysis where all other parameters are held constant. The analysis of several
variables through this process is time-intensive, inefficient, and ignores the possibility of
variable interaction. Central composite rotatable design is a more effective procedure which
produces a response equation based on empirical data.

A four variable rotatable central composite of 31 trials was used to determine the
interactions between iron catalyst, H₂O₂ concentrations, soil mass, and liquid to solids
(L:S) ration, in relation to TPH degradation.

The Snake River sand was weighed and placed in 25 gallon plastic refuse
containers for diesel contamination. Diesel was added intermittently while sand was being
placed into the container to a level of 2000 mg/kg. The container then was vigorously
shaken and the soil mixed and agitated to attempt uniform concentration of diesel
throughout the reactor. Ferric sulfate (Fe₂SO₄) solution was added at the required
concentration, and deionized water was supplemented to obtain the desired L:S ration.
Finally, the H₂O₂ addition initiated the reactor experiment.

The pH monitored, but remained in the desired 2-3 range due to the Fe₂SO₄. In the
control trials where no Fe₂SO₄ was used, pH of 2-3 was obtained through the addition of
sulfuric acid. Other control trials were performed without the addition of H₂O₂.

After a minimum of 8 hours reaction time, three separate samples were extracted
from the reactor using a 10 cm diameter stainless steel pipe. Each of these samples was
divided into three sections of soil depth in the reactor. A final sample set of nine (9) 20
gram (± 0.01) samples, three from each defined soil depth of the reactor (top 4 cm, middle
4 cm, lower 10 cm), was used. Excess liquid was drained and the soil remained at field
capacity prior to analysis. Samples were placed into 40ml borosilicate vials with 10ml of
ethyl acetate, secured with Teflon lined caps, and placed on a wrist-action shaker for 24 hours. The vial contents were then centrifuged and the extract was analyzed for residual diesel concentration.

**Contaminant Desorption**

Desorption analysis of diesel contaminated silica sand was performed using the gas purge desorption procedure. A glass vial filled with 20 grams of sand was contaminated to 2000 mg/kg, the 20 ml of water was added. Air stones were placed in the vials to generate a desorption gradient in the liquid-soil media. Residual diesel concentrations were measured at four hour intervals up to 48 hours to determine the maximum loss of diesel due to volatilization during the study.

**Analysis**

Residual diesel concentrations were measured by gas chromatography with flame ionization detection using a Hewlett-Packard 5890A gas chromatograph (GC). Instrument conditions were set at an initial oven temperature of 100°C, program rate of 15°C/min, final oven temperature of 240°C, and injector and detector temperatures of 250°C.

Resulting sample chromatograph peaks were compared against peaks generated by prepared diesel concentration controls. Diesel concentration controls were formulated at 2000 ppm, 1000 ppm, 500 ppm, 200 ppm, and 50 ppm. From this analysis, residual diesel concentrations in each sample were determined, and simultaneously, the remediation of contaminant determined.

**Results and Discussion**

**Contaminant Desorption**

Prior to determining the effectiveness of Fenton-like reactions for the treatment of diesel, desorption experiments were performed to assess the dynamics of the contaminants during oxidation. The results of the gas-purge desorption analysis for 2000 mg/kg spiked diesel samples are shown in Figure 22. The results show that approximately 20% of the
Figure 22. Desorption of 2,000 mg/kg diesel in the Snake River sand.
diesel desorbed over 48 hours. Because contaminants are removed from the system rapidly after they are desorbed, gas-purge results represent the maximum desorption possible in the system without the use of another factor that may enhance desorption. Therefore, if >20% diesel oxidation occurred over the same time period, the Fenton-like reaction either enhanced desorption or oxidized the sorbed contaminants.

Response Equation Analysis

The experimental data were fit to a second order function using the procedures outlines by Diamond (1989). The response equations were used to compare observed values with those calculated from the equations. The calculated values were used to develop surface plots that assisted in analyzing the four variable matrix. The initial equation was:

\[
\% \text{ Degradation} = 47.9 + 4.53 (C_{H2O2}) - 8.31 (C_{Fe(III)}) + 2.55 (C_{L:S}) - 4.83 (C_{soil \ mass}) - \\
5.98 (C_{H2O2})^2 + 2.52 (C_{Fe(III)})^2 - 1.51 (C_{L:S})^2 - 5.12 (C_{soil \ mass})^2 + \\
5.47 (C_{H2O2})(C_{Fe(III)}) + 0.69 (C_{H2O2})(C_{L:S}) + 8.68 (C_{H2O2})(C_{soil \ mass}) - \\
2.34 (C_{Fe(III)})(C_{L:S}) - 3.13 (C_{Fe(III)})(C_{soil \ mass}) + 0.64 (C_{L:S})(C_{soil \ mass})
\]

\[R^2 = 0.99\]

Each term was then evaluated for significance using a t-test. The terms that did not show significance at the 90% confidence level were eliminated. Application of the t-test to equation 20 resulted in the elimination of every term containing the variable L:S, along with several other variables. The final regression equation, less the terms that did not meet the required confidence levels, is:

\[
\% \text{ Degradation} = 47.9 + 4.53 (C_{H2O2}) - 8.31 (C_{Fe(III)}) - 4.83 (C_{soil \ mass}) - 5.98 (C_{H2O2})^2 - \\
5.12 (C_{soil \ mass})^2 + 5.47 (C_{H2O2})(C_{Fe(III)}) + 8.68 (C_{H2O2})(C_{soil \ mass})
\]

\[R^2 = 0.90\]

Equation 21 was used to generate response surfaces describing the empirical data. A series of 10 surface plots was established by holding two variables constant while varying the remaining two in order to establish diesel oxidation in the original two variables.
Evaluation of L:S Ratio

Response surfaces for hydrogen peroxide concentration vs. L:S ratio are characterized by a linear relationship for all soil masses (20g to 50,000g) as shown in Figures 23 and 24. The vertical lines indicate L:S is not significant in influencing the treatment of the diesel.

Liquid to solid ratios from 0.25 to 1.0 covered in this experiment produced a standing aqueous layer above the soil matrix. The large volume of hydrogen peroxide located above the soil held most of the iron in solution. This resulted in the production of the hydroxyl radical above the saturated soil. Therefore, most of the hydrogen peroxide may have reacted in the aqueous phase before it could penetrate the soil.

Temperature also appeared to have an effect on hydroxyl radical production. The temperature of the systems increased as the reaction occurred. Millro et al. (1989) and Christensen et al. (1993) found that the temperature of the aqueous layer increases the rate of hydroxyl production. The rate may have been fast enough that excess hydroxyl radical production occurred in the overlying aqueous layer. A temperature gradient was found between the aqueous phase and the soil phase of the system. While the aqueous phase temperature was elevated, the soil phase remained cooler.

Spencer (1994) found that diesel contaminated soils showed more effective degradation when less hydrogen peroxide was added to the soil matrix and a lower L:S ratio was used. By lowering the L:S to the point where no standing layer of liquid exists, the hydrogen peroxide is forced to penetrate into the soil and react more closely to the sorbed contaminant. In addition, Haller (1996) noted anomalies in the effect L:S ratio plays in the degradation of the petroleum compounds benzene, toluene, xylene (BTX) and nonane, decane, dodecane (NDD). At near neutral pH, lower L:S ratios (0.25) increased degradation of BTX even though the absence of a predominate aqueous layer hindered hydroxyl radical transport, yet NDD oxidation was greater at L:S ratios near 1.0.
Figure 23. Response surface for the degradation of diesel as a function of liquid-to-solid (L:S) ratio and hydrogen peroxide concentration at a fixed iron (III) concentration of 50 mM. Contour lines represent percent diesel degraded.
Figure 24. Response surface for the degradation of diesel as a function of liquid-to-solid (L:S) ratio and hydrogen peroxide concentration at a fixed iron (III) concentration of 37.5 mM. Contour lines represent percent diesel degraded.
Evaluation of Soil Mass

Figures 25 and 26 show the effect of linear scale up of diesel contaminated soils over the range of 20g to 50,000g with linear surface plots demonstrating that soil mass was not a factor in the remediation of diesel. These results show that the effectiveness of diesel treatment is not influenced by soil mass.

Diesel fuel concentrations at the bottom of the soil depth were relatively larger than in the samples taken at the top layer, i.e., depth of the contamination was the most significant factor in remediation efforts. The top layer of soil was characterized by the most effective remediation because it was in direct contact with the hydroxyl radicals. The lower soil layers relied on the transport of hydrogen peroxide before transformation to the hydroxyl radicals could occur. Transport of hydrogen peroxide to lower soil depths before reacting may have been enhanced by adding the hydrogen peroxide directly to the soil and then flushing it through with the deionized water and iron mixture.

Evaluation of Iron (III) Species

Iron (III) sulfate was used to catalyze the Fenton-like reaction in oxidizing the diesel fuel with a maximum remediation of 44% at an iron (III) concentration of 32 mM. Comparing Figures 23 to 24 and Figures 25 to 26 show that increasing iron (III) concentrations beyond their optimum point resulted in less degradation. The optimum iron (III) sulfate concentration, as shown in Figure 27, was found to be 32 mM. Increasing the iron concentration beyond this point decreases the efficiency of the reaction by producing the hydroxyl radical in the aqueous layer, rather than near the contamination in the soil. The results shown in Figures 24 and 25 demonstrate the remediation potential for each iron concentration; 44% for the 37.5 mM iron (III) and 33% for the 50 mM iron (III), evaluated at 25% H₂O₂. In order to increase the potential for remediation, it is necessary to move the iron and H₂O₂ as close to the contamination as possible, possibly through the use of natural iron minerals in the soil. This would require lowering the L:S ratio to eliminate standing
Figure 25. Response surface for the degradation of diesel as a function of soil mass and hydrogen peroxide concentration at a fixed liquid to solids ratio of 0.64 ml/g and iron (III) fixed at 50 mM. Contour lines represent percent diesel degraded.
Figure 26. Response surface for the degradation of diesel as a function of soil mass and hydrogen peroxide concentration at a fixed liquid to solids ratio of 0.64 ml/g and iron (III) fixed at 37.5 mM. Contour lines represent percent diesel degraded.
Figure 27. Response surface for diesel degradation as a function of iron (III) and hydrogen peroxide concentration. Contour lines represent percent diesel degradation.
water above the soil, or eliminating the amount of iron held above the soil in the aqueous layer.

Naturally occurring mineral iron in the soil does not place an immediate load on the aqueous layer because it is located within the soil and not in the aqueous layer. The trial involving no additional iron (III) displayed the greatest remediation at 81%. The reaction time was noticeably longer for this reaction, on the order of several hours instead of within 15 minutes when iron (III) was added. The rate of hydroxyl radical production by the naturally occurring iron is limited by the rate of its desorption from the soil. The iron is located closer to the sorbed contaminants, allowing the hydroxyl radicals to be in close proximity when they are formed. The amount of iron naturally occurring in soil is generally low enough to require additional iron. Therefore, optimization of the iron species is required as shown in Figure 27.

Iron also serves the secondary function of reducing the pH to below 3, which allows the system to operate more efficiently. Iron (III) sulfate acidifies the water when added, therefore eliminating the need for addition of an acid to lower the pH. The trial possessing no iron (III) sulfate required the addition of sulfuric acid to lower the pH from 8 to less than 3. All other trials had their pH lowered to the desired range of 2 to 3 simply by the addition of iron (III) sulfate.

**Summary And Conclusions: Part IV**

The effect of soil mass was investigated in the treatment of diesel contaminated soil. Scaling up soil mass from 20g to 50,000g did not effect the ability to degrade diesel fuel. Figures 25 and 26 show the linear relationship of remediation percentage and soil mass throughout the entire range of soil masses. Over the range studied, L:S did not effect the ability to remediate the soil. Optimum iron (III) sulfate conditions were found to be 30 mM. High iron concentrations appeared to lower the degradation of diesel fuel. The results show better results at 37.5 mM iron (III) sulfate concentrations compared to the 50 mM concentrations in Figures 23 and 25, demonstrating the possibility of excess iron to
inhibit remediation. Therefore, optimum concentration of iron (III) must be determined for each system.

Implementation

The results of this research have documented the following important points that serve as a basis for implementing catalyzed hydrogen peroxide in the field:

1. The most effective catalyst for hydrogen peroxide treatment is ferric sulfate, which is inexpensive and readily available. Because ferric sulfate is a weak acid, its addition to the soil automatically lowers the pH of the soil for the catalyzed peroxide reaction. After the oxidation reaction is complete, most soils will revert to neutral pH as a result of their natural buffering capacity. An alternative catalyst is an iron chelate (e.g., iron complexed with nitrilotriacetic acid (NTA), a building block of detergents), which works effectively at neutral pH. A drawback of using the iron chelate is that it would have to be freshly prepared in the field. In summary, the results of this project show that 2500 mg/L of ferric sulfate or ferric sulfate-NTA should be mixed into the soil before adding peroxide.

2. The slow rate that hydrogen peroxide moves through soils results in the need for mixing the reagents into the soil. The Washtucna soil that was used in the hydrogen peroxide soil transport study is of low permeability and has high catalytic reactivity, and therefore represents a worst-case matrix for soil treatment. However, to provide certainty that the catalyzed hydrogen peroxide treatment will work, the reagents should be tilled into the soil.

3. The results of the scale-up study show that reagent dosages are proportional to the amount of soil treated. In other words, scale up is linear, which makes dosage requirement calculations for the treatment straightforward. For example, if one liter of 2% hydrogen peroxide is needed to treat 1 kg of soil, then 1,000 liters of 2%
hydrogen peroxide would be required to treat 1,000 kg of soil or 10,000 liters of
2% hydrogen peroxide would be required to treat 10,000 kg of soil.

4. The key to effective treatment using catalyzed hydrogen peroxide is targeting the
most toxic and cancer-causing components of gasoline and petroleum, such as
benzene, toluene, and xylenes. These chemicals, which are commonly aromatic,
are degraded very easily and cost effectively by catalyzed hydrogen peroxide, while
the relatively nontoxic alkanes do not breakdown effectively with the peroxide
treatment. The use of a Risk Based Corrective Action (RBCA) would provide
economical clean up criteria for catalyzed peroxide treatment with costs in the range
of $9 per ton of soil. The use of such risk-based clean up criteria is being embraced
by most state environmental agencies, including the Washington State Department
of Ecology. With an approval by the Washington State Department of Ecology,
economical and fast treatment of petroleum contaminated soils with catalyzed
hydrogen peroxide could be achieved.

As the results unfolded during this study, it became evident that comparing five
reactor schemes would be impractical. The mixing required, as well as the need for
hydrogen peroxide concentrations of at least 1%, negated the possible use of many of the
reactor configurations, such as the application of dilute hydrogen peroxide to the surface
with a sprinkler or drip system. Therefore, the remainder of the research focused on
studies that would advance the implementation of catalyzed hydrogen peroxide soil
treatment.

Based on the results of this project, catalyzed hydrogen peroxide treatment of
petroleum contaminated soils can be implemented as follows:

1. Using the RBCA method of TPH analysis to measure the total TPH with
subsequent classification of the total TPH into aromatic TPH and aliphatic TPH.

2. Lay out the contaminated soil to a depth that can be mixed with a rototiller or bucket
loader.
3. Disk in 2500 mg/L FeSO₄ so that all of the soil is wetted.

4. Disk in 2% hydrogen peroxide to wet all of the soil.

5. Treatment will be complete within one day. The success of the treatment should be verified based on risk-based TPH analysis.
REFERENCES


