UNIVERSITY OF CALGARY

Remediation of Diesel-Contaminated Soils

Using Fenton's Reagent:

A Laboratory Study

by

Peng Xu

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE

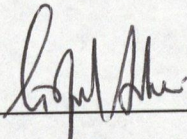DEGREE OF MASTER OF SCIENCE

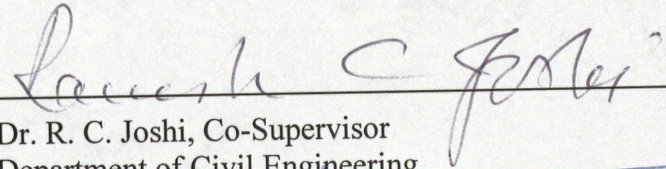DEPARTMENT OF CIVIL ENGINEERING

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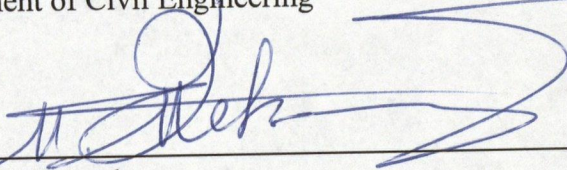# UNIVERSITY OF CALGARY

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Remediation of Diesel-Contaminated Soils Using Fenton's Reagent: A Laboratory Study" submitted by Peng Xu in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering.
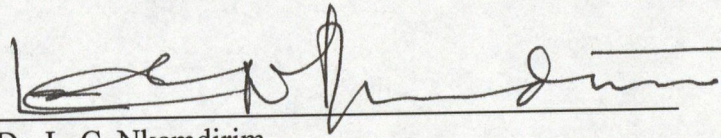
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ABSTRACT

This study evaluated the process variables affecting Fenton oxidation in soils spiked with diesel using vial tests. Infiltration and injection tests were also conducted in compacted soils.

Test results indicated that pH adjustment and iron amendment had no effect on the two field soils. Treatment stoichiometry (moles of diesel degraded/moles of H_2O_2 consumed) obtained experimentally agreed with those from literature. Diesel oxidation was confirmed by CO_2 generation during treatment. For the loose sandy and clayey soils, optimum H_2O_2 dosages were 8 mL of 5% and 4 mL of 10% H_2O_2 per gram of soil, or 2:1 (H_2O_2:soil) by volume with 20% H_2O_2. Surfactant (SDS) enhanced diesel degradation when SDS concentration was over CMC (critical micelle concentration). Sequential application of H_2O_2 produced positive results. H_2O_2 instability was obvious in infiltration tests leading to low degradation efficiency, whereas H_2O_2 injection into soil resulted in higher treatment stoichiometry as compared with infiltration tests.

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LIST OF ABBREVIATIONS

AOP	Advanced oxidation process
BTEX	Benzene, toluene, ethylbenzene and xylene
BTX	Benzene, toluene and xylene
BOD	Biochemical oxygen demand
CMC	Critical micelle concentration
COD	Chemical oxygen demand
DCB	Dichlorinated biphenyl
DCE	Dichloroethylene
DCM	Dichloromethane
DCS	Diesel component standard
DRO	Diesel range organics
Fe^{2+}	Ferrous ion
Fe^{3+}	Ferric ion
FID	Flame ionization detector
GC	Gas chromatography
H_2O_2	Hydrogen peroxide
$HO_2\cdot$	Perhydroxyl radical
LNAPL	Light non-aqueous phase liquid
MFR	Modified Fenton's reaction
NAPL	Non-aqueous phase liquid
NTA	Nitrilotriacetic acid
$OH\cdot$	Hydroxyl radical
OS	Ottawa sand
PAH	Polycyclic aromatic hydrocarbons
PC	Percent concentration
PCB	Polychlorinated biphenyls
PCE	Tetrachloroethylene
PCP	Pentachlorophenol

PTFE	Polytetrofluoroethylene
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
SDS	Sodium dodecyl sulfate
SVOC	Semi-volatile organic compounds
SH	Silty clay soil
TCD	Thermal conductivity detector
TCE	Trichloroethylene
THE	Total extractable hydrocarbons
TNT	Trinitrotulene
TPH	Total petroleum hydrocarbons
TPHCWG	Total Petroleum Hydrocarbon Criteria Working Group
UC	Sandy silt soil
UST	Underground storage tanks
VOC	Volatile organic compounds

in the context of cost, treatment time, post-treatment requirements and effectiveness in *in situ* applications (Dineen, 1991).

Stringent environment regulations and tightening fiscal budgets have necessitated the development of innovative treatment technologies. Advanced oxidation process (AOP), a chemical treatment method, is one of the technologies that show promise in destroying and degrading hazardous wastes in water and soils using various oxidants. The mostly documented application thus far has been based on the use of Fenton's reagent, a mixture of hydrogen peroxide and ferrous iron. The decomposition of hydrogen peroxide promoted by iron catalyst is generally referred to as Fenton's reaction. It takes advantage of the hydroxyl radicals generated to oxidize target compounds. The hydroxyl radicals, OH·, are powerful, non-specific oxidants and can react with most organic contaminants at a diffusion rate of about 10^7-10^{10} L/mol·s (Walling, 1975).

Fenton's reaction has been widely used in aqueous wastewater treatment for several decades (Barbeni *et al.*, 1987; Murphy *et al.*, 1989). It was first introduced to treat contaminated soils in the early 1990s (Watts *et al.*, 1990). Various work has been done to understand the mechanisms of Fenton's reagent to remediate contaminated soils. The treated organic contaminants include: chlorinated solvents such as dichloroethylene (DCE), trichloroethylene (TCE), tetrachloroethylene (PCE) (Ravikumar and Gurol, 1994; Gates and Siegrist, 1995; Leung *et al.*, 1992; Tang and Huang, 1997); munitions such as TNT and cyclonite (RDX) (Li *et al.*, 1997; Bier *et al.*, 1999); wood preservatives, pesticides/herbicides such as creosote, pentachlorophenol (PCP), and trifluralin (Kawahara *et al.*, 1995; Watts *et al.*, 1990; Tyre *et al.*, 1991); and petroleum hydrocarbons including gasoline and diesel (Watts *et al.*, 2000; Peters *et al.*, 2001; Watts and Dilly, 1996; Spencer *et al.*, 1996). Only limited field applications of this AOP technology were reported to remediate soils contaminated with petroleum products (Watts, 1992; Mahmoud *et al.*, 2000).

The oxidation process using Fenton's reagent has the advantages of easy operation, low cost of chemicals and labor, and short treatment time. Besides, it destroys source contaminants rather than displaces them. A positive outcome of Fenton's reaction is the complete or partial mineralization of the organic contaminants in the form of water and carbon dioxide. *In situ* delivery of hydrogen peroxide plus iron catalysts into subsurface using conventional injection techniques makes chemical oxidation method an attractive consideration. Moreover, injection of chemical oxidants into subsurface can decrease the treatment time significantly to days or weeks, rather than years, especially at unfavorable site conditions.

As a middle distillate and semi-volatile petroleum product, diesel induces environmental problems that require solutions different from that caused by gasoline. Some insoluble fractions in diesel are usually adsorbed on soil particles or are present as non-aqueous phase liquid (NAPL) in soil interstitial pore space. This significantly changes Fenton's process chemistry in soil that is mainly derived from Fenton's reaction in aqueous solutions. Despite the fact that Fenton's reaction offers many advantages over most established technologies, its applications in field sites are still limited due to technical uncertainty, site heterogeneity and sometimes regulatory barriers (Yin and Allen, 1999). As the usage of Fenton's reagent in treating diesel-contaminated soil has not been adequately studied and reported, there is a need to understand the major factors affecting the ultimate treatment efficiency in order to make the most use of Fenton's reagent in soil remediation.

1.2 RESEARCH OBJECTIVES

The primary goal of this research is to understand and evaluate some key process variables in Fenton's reaction that affect remediation efficiency of diesel-contaminated soils on laboratory scale. The specific objectives of this study are as follows:

- To investigate the major process variables associated with Fenton's reaction to treat diesel-contaminated soils of three different textures in vial batch tests;

- To evaluate the possibility of using other technologies to enhance remediation efficiency of diesel-contaminated soils in conjunction with Fenton's reagent; and

- To assess the validity of the vial test results in compacted soil through infiltration column tests and injection tests to more closely simulate field conditions.

1.3   THESIS ORGANIZATION

The thesis consists of five chapters. A brief summary is given below:

- Chapter 1 gives a general description of diesel contamination in soils, concept of Fenton's reagent and Fenton's reaction, as well as the objectives of the thesis;

- Chapter 2 includes detailed diesel characterization, its fate and transport in soil matrix, a brief review on Fenton's reaction and its applications, and factors affecting Fenton's reaction in soil;

- Chapter 3 describes materials and methods used in the laboratory experiments;

- Chapter 4 discusses the experimental results from laboratory investigations and presents analysis; and

- Chapter 5 gives conclusions and the recommendations for future research.

CHAPTER TWO

LITERATURE REVIEW

Energy is one of the basic necessities in modern world since it is essential to power the engine of the economy and improve our standard of living. Amongst the different sources of energy used, those derived from petroleum-based products have made the greatest contribution. In Canada, thirty-eight percent of total secondary energy demands were met by oil products in 1997 (National Energy Board, 1999). In the U.S., oil supplies represent nearly 40 percent of all the energy consumed (US DOE, 2002).

Due to the huge demand of petroleum products, inadvertent releases of petroleum hydrocarbons on land have become common occurrences during storage and transportation. In particular, gasoline and diesel discharges are commonplace considering their huge productions and ubiquitous uses in every aspect of our life. With increased awareness of adverse effect of petroleum contamination on human health and the environment, more stringent regulations have been stipulated, mandating cleanup of soils contaminated by gasoline and diesel. Forty-one out of fifty states in the U.S. have established diesel contamination action and cleanup levels for soil and water (AEHS, 2002). The complex interactions between soil particles and various contaminants further complicate the cleanup processes, necessitating the development of effective remediation technologies.

2.1   DIESEL CONTAMINATED SOIL AND THE ASSOCIATED PROBLEMS

Diesel is one of the most common petroleum products, second only to gasoline in terms of production and usage. According to API Statistics (2002), diesel fuel and heating oil production in the U.S. was more than 222.6 billion litres in the year 2001, accounting

for about 12% of the total petroleum hydrocarbons. This represented about 2.8% increase over the previous year. The trend has continued in 2002 at a steady increase of approximately 15% in middle distillate fuel production over the previous year. Canada also saw an overall increase of diesel fuel sale to about 23.5 billion litres in 2000, approximately 5.6 percent increase over 1999 (Statistic Canada, 2001). Diesel fuel is the refined middle distillate product of crude oil manufactured in fractionating tower at petroleum refineries. Once refined, it is transported through the pipelines to central distribution points known as bulk terminals. From the bulk terminals, the fuel is distributed either to retail service stations or to various smaller independent bulk distributors. The individual distributors store diesel fuel and other petroleum products mostly in USTs.

Leaks from USTs during storage and accidental surface spills during transportation are the two dominant sources of diesel contamination in subsurface. According to a report (US EPA, 2000a), there were 760,000 federally regulated storage tanks in the U.S. at the end of 1999. Over ninety five percent of these tanks stored petroleum products, including diesel fuel. It was also reported that as high as fifteen percent of all these USTs were not in compliance with relevant use regulations. Leaks were primarily due to corrosion of tanks, faulty installation and inadequate operating and maintenance procedures (Lyman et al., 1990). Over 418,000 USTs releases had been confirmed as of September 2001. Scaling these figures by 2.5, the ratio of gasoline to diesel plus heating oil used, gives a rough estimate of the widespread soil contamination impacted by diesel fuel leaked from USTs (API Statistics, 2002).

Surface spill due to pipeline ruptures and transportation tank accidents is another source of petroleum contamination in soil. It is estimated that on average there are about 70 spills per day reported in the U.S. alone, either in water or on land (US EPA, 2000d). Although exact numbers of spills/leaks are not known, the magnitude has been significant in terms of both frequency and volume of diesel discharges involved. For instance, a release of 223,300 litres of diesel fuel occurred from the puncture of an

underground transfer line in 1975. Only a small amount of diesel fuel was recovered whereas most of the released diesel traveled laterally and downward, leaving a oil plume mostly at depths from 3.3 to 33 meters, within a 10 to 33 meters radius of the spill point (Rosenblatt *et al.*, 1994). Likewise, up to 874,340 litres of diesel fuel were released when a pipeline ruptured near Atchison, Kansas in 1999 (US EPA 1999). Another example of significant diesel releases was a tank train derailment near Marion County, Iowa in 2001 that involved damage of six tank cars causing release of estimated 189,250 litres of diesel fuel (US EPA, 2001).

Surface spills/discharges of diesel fuel that result in diesel impoundment on land are easily discovered. Their impacts therefore can be minimized via emergency response. Some on-land diesel spills/discharges may come in contact with surface aquifers or percolate deep into subsurface depending on geological conditions. Leaks from USTs, however, are more difficult to detect. It is common that UST leaks are not detected until significant amount of discharge occurs. Some released diesel is retained in unsaturated soil during its downward migration. The diesel retained in soil serves as a potential source of groundwater contamination if the impacted soil is not cleaned up.

The problems associated with diesel surface spills/releases and diesel-contaminated soils can be one or any combination of the followings:

- Soil impacted with significant amount of diesel can act as a source of contamination for groundwater supplies;

- Vapors from lighter part of diesel constituents can migrate and accumulate in underground utility vaults, sewer lines and basement, creating serious fire or explosion hazards;

- Large volume of diesel release on land can present a potential source of contamination for surface waters and certain food crops grown in the immediate proximity of impact soil; and

- Soil contaminated with diesel may become sterile for vegetation growth.

2.2 FATE AND TRANSPORT OF DIESEL IN SUBSURFACE SOIL

The fate and transport of diesel in soil are closely related to its physical and chemical properties. To effectively remediate diesel-contaminated soils, comprehensive knowledge of these properties is therefore crucial for selection of appropriate remedial strategy and proper design of remedial technology.

2.2.1 Physiochemical Properties of Diesel Fuel

In general, the term "diesel" refers to hydrocarbon fuels that are intended for compression ignition engines, or the diesel engines. Diesel is a complex mixture of petroleum hydrocarbons produced by the distillation of crude oil. More specifically, No.2 diesel consists of hydrocarbons with carbon numbers predominantly in the range from about C_9 to C_{20} (Millner *et al.*, 1992). Its boiling temperatures are between about 160 °C and 360 °C. Different types and grades of diesel fuel are·manufactured to obtain the desired operating characteristics. For example, large and low speed engines use special No. 4 diesel, also termed as marine diesel, for ship propulsion, whereas commercial trucks and railroad locomotives use mainly No. 2 diesel fuel due to its high performance and good ignition characteristics. Arctic diesel meets the specific requirements for engine to work under extremely low temperatures (Block *et al.*, 1991).

The formulation of different types of diesel fuel is determined by the desired physical characteristics. As a result, diesel fuels are loosely defined by specifications such as sulfur content, permitted levels of water, sediment and acidity, ash and carbon residuals from combustion, safety standard, etc. These specifications are to ensure that the engine works with maximum efficiency and the diesel engine exhaust meets the relevant air pollution regulations (US EPA, 2002). Not thoroughly defined in diesel fuel

specifications, however, are its chemical compositions that are of environmental concerns. Diesel fuel compositions differ widely because of the differences in usage, refinery configurations and processes, as well as the sources of crude oil. The properties of No. 2 diesel fuel of interest to environmental engineers are presented in Table 2.1.

2.2.1.1 Physical Properties

The physical properties of diesel such as volatility, density, solubility and viscosity determine its fate and mobility in soils. Diesel fuel is generally regarded as semi-volatile organic compound (SVOC). Less volatile than gasoline, diesel is more likely to vaporize than heavy oil such as jet oil and lubricant. It was reported that one-day and five-day diesel volatilization tests at 20°C result in about 25% and 57% weight loss, respectively (Environment Canada, 2002a). As gaseous phase is always more diffusive, volatilized compounds in diesel can migrate more easily in soil matrix, causing further contamination in soil and pore water. Moreover, diesel vapor can pose potential fire and explosion hazards when it accumulates to reach high vapor concentration in underground utility liners, sewer pipes and basements through soil cracks.

Diesel fuel is such a complex mixture of hundreds of individual components that its density is usually represented loosely by a range rather than by a single value. Density of diesel manufactured in Canada ranges from 0.82 to 0.87 g/cm^3 (Environment Canada, 2002a). Obviously diesel fuel will float on top of water if bulk volume of diesel happens to reach groundwater. Like most liquids, the density of diesel fuel decreases when ambient temperature increases.

Table 2.1: Properties of No. 2 diesel of interest to environmental engineers

Index	Specifications
API Gravity	39
Specific Gravity	0.82 – 0.87
Flash Point, C°	> 40
Pour Point, C°	- 30
Viscosity, cSt	
@ 40 C°	1.3 – 4.1
Sulfur, weight %	0.1
Surface Tension, dynes/cm	
@ 0 C°	27.7
@ 15 C°	26.5
@ 25 C°	23.8
@ 40 C°	22.7
Initial Boiling Point, C°	
10 % Point	155
50 % Point	225
90 % Point	295
Final Boiling Point	388
Flammability Limits in Air (volume %)	1 - 6
Aqueous Solubility (mg/L)	
@ 22 C°, in fresh water	2.8 – 39.1
@ 22 C°, in distilled water	2.3 – 8.3
Carbon on 10 % Bottoms	0.03 – 0.06
Cetane Number	45 - 46

Adapted from *Environment Canada, 2002a*

The rate of dissolution of individual diesel components varies, and its solubility is approximately inversely proportional to its molecular weight. The lighter hydrocarbons tend to dissolve more easily than the heavier fractions. More volatile compounds such as benzene, toluene, ethylbezene and xylene (BTEX) exhibit higher water solubility, as indicated in Table 2.2. Other compounds, including methylnaphthalene, naphthalene, phenanthrene, phenol, cresol and quinoline, are also more soluble and extremely soluble as compared to heavier polycyclic aromatic hydrocarbons (PAHs). The overall water solubility of diesel at 22°C lies between 2.3 mg/L and 8.3 mg/L in distilled water, and between 2.8 mg/L and 39.1 mg/L in fresh water, respectively.

The viscosity, an indicator of the potential for diesel to flow, determines the transport behavior of diesel in subsurface soil system. Generally, the viscosity of diesel fuel ranges between 1.3 and 4.1 centistokes (Environment Canada, 2002a; Stone, 1991). Diesel is 2 to 7 times more viscous than gasoline. Hence, diesel fuel as a free product percolates through a uniform unsaturated soil at least two to seven times slower than gasoline. Pure water has a viscosity of about one centistoke, indicating that diesel fuel will travel through soil at a rate about one and a half to four times slower than that of water.

2.2.1.2 Chemical Composition

Diesel contains many individual components, and it is almost impossible to identify and quantify all its chemical constituents. The refineries make every effort to improve the yield of usable product by blending certain cracked products as well as some additives. Depending on the source of crude oil and refinery process, the amount of the major components and trace constituents may vary. Of compositional interests are the alkanes and aromatics that are the dominant constitutes in diesel fuel. Table 2.2 and 2.3 provide specific physiochemical properties for typical constituents of No. 2 diesel with environmental and public health significance.

Table 2.2: Physiochemical properties for compounds of interest in No. 2 diesel

Compound	Carbon No.	Log K_{ow}	Solubility (mg/L)	Vapor Pressure (atm)
Volatile Organics				
Benzene	6	2.13	1780	0.125
Ethylbenzene	8	3.13	152	0.0125
Toluene	7	2.69	515	0.0375
Xylene	8	3.18	180	5.76
Polycyclic Aromatic Hydrocarbon				
Pyrene	16	5.18	0.132	1.17×10^{-7}
Benzo(a)anthracene	18	5.91	0.011	6.0×10^{-9}
Chrysene	18	5.79	0.0015	1.06×10^{-9}
Benzo(a)pyrene	20	6.04	0.0038	2.1×10^{-10}
Benzo(e)pyrene	20	6.44	0.004	2.38×10^{-10}
Benzo(b)fluoranthene	20	5.80	0.0015	6.67×10^{-8}
Benzo(j)fluoranthene	20	NA	0.002	NA
Benzo(k)fluoranthene	20	6.00	0.001	4.07×10^{-11}
Dibenzo(a,h)anthracene	22	6.75	0.0005	1.33×10^{-8}
Indeno(1,2,3-cd)pyrene	22	7.00	0.062	1.0×10^{-9}
Benzo(ghi)perylene	22	6.50	0.0003	2.22×10^{-10}
2-Methylnaphthalene	11	3.86	24.6	1.11×10^{-4}
Naphthalene	10	3.37	31	3.63×10^{-4}
Phenanthrene	14	4.57	1.1	1.62×10^{-6}
Phenol	6	NA	82800	0.35
Cresol	21	NA	19320	0.1
Quinoline	9	NA	100	NA

Adapted from *Rosenblatt et al., 1994; Potter and Simmons, 1998*

NA: Not applicable

Table 2.3: Molecular weight, formula and concentration for compounds of environmental concern in No. 2 diesel

Compound	Molecular Weight	Concentration (mg/L)	Molecular Formula
Volatile Organics			
Benzene	78	82	C_6H_6
Ethylbenzene	106	800	C_8H_{10}
Toluene	92	800	C_7H_8
Xylene	106	800	C_8H_{10}
Polycyclic Aromatic Hydrocarbon			
Pyrene	202	41	$C_{16}H_{10}$
Benzo(a)anthracene	228	1.3	$C_{18}H_{12}$
Chrysene	228	1.4	$C_{18}H_{12}$
Benzo(a)pyrene	252	0.6	$C_{20}H_{12}$
Benzo(e)pyrene	252	0.11	$C_{20}H_{12}$
Benzo(b)fluoranthene	252	0.26	$C_{20}H_{12}$
Benzo(j)fluoranthene	252	0.26	$C_{20}H_{12}$
Benzo(k)fluoranthene	252	0.03	$C_{20}H_{12}$
Dibenzo(a,h)anthracene	278	0.02	$C_{22}H_{14}$
Indeno(1,2,3-cd)pyrene	276	0.02	$C_{22}H_{12}$
Benzo(ghi)perylene	276	0.03	$C_{22}H_{12}$
2-Methylnaphthalene	142	6700	$C_{11}H_{10}$
Naphthalene	128	2730	$C_{10}H_8$
Phenanthrene	178	1500	$C_{14}H_{10}$
Phenol	94	6.8	C_6H_6O
Cresol	324	54.3	$C_{21}H_{24}O_3$
Quinoline	129	9.2	C_9H_7N

Adapted from *Rosenblatt et al., 1994; Stone, 1991*

There may be appreciable variation in the hydrocarbon composition of middle distillate fuels. For No. 2 diesel, alkanes (normal, branched chain alkanes and cycloalkanes) and aromatics are the most abundant components found in diesel, constituting about 70% to 80% and 20% to 30% of total diesel mass, respectively (Rosenblatt *et al.*, 1994). The branched chain alkanes are predominantly monomethyl, dimethyl, and trimethyl-substituted paraffins. Alkyl benzenes, particularly C_6 and C_8 alkyl benzenes, are common light end components of diesel fuel. Naphthalene, phenanthrene, acenapthene, acenapthylene, fluorene, fluoranthene, and pyrene have also been identified in diesel fuel. As shown in Table 2.3, the most predominant compounds in aromatics are naphthalene, phenanthrene and methyl substituted napthalenes. It is worth mentioning that diesel fuel is somewhat toxic, primarily due to the presence of PAHs, such as BETX and benzo(a)pyrene. They are known carcinogens (Stone, 1991). Even though found in trace levels, the carcinogenic effect of these compounds makes them the often target analytes during environmental evaluation. Millner *et al.* (1992) documented a detailed discussion on the assessment of carcinogenic risks caused by diesel fuel based on large amounts of available data.

2.2.2 Fate and Transport of Diesel in Subsurface Soil

Petroleum hydrocarbon released in the form of light non-aqueous phase liquid (LNAPL) is the most common occurrence related to soil contamination. As discussed previously, diesel fuel is a typically multi-component mixture with varying degrees of water solubility, viscosity, vapor pressure, and density. These diversities in physiochemical properties control the states of diesel fuel existence as a whole and its transport in the subsurface soil. The transport of diesel in the subsurface environment also depends upon the geological and hydrogeological conditions of the sites at which diesel leaks/spills occur. For example, soil permeability affects the percolation rate of diesel and its spill geometry.

If sufficient diesel is released in favorable conditions either on land surface or in subsurface, they will travel predominantly downward via the most permeable paths under the influence of gravity. The released diesel ceases vertical movement as it encounters a physical barrier such as low permeability layer. In the case when diesel released reaches groundwater, the free diesel spreads laterally on top of the groundwater table. The soluble fractions dissolve and move with the flowing groundwater, rendering potential to contaminate water supplies nearby, as conceptually demonstrated in Figure 2.1. If a small volume of diesel fuel is released and/or impounded, gradual vertical/lateral movement of the released diesel will begin. During the course of transportation, diesel is retained in the soil micropores by capillary force as liquid residuals, adsorbed on soil particles by sorption, and partitioned into gaseous phase. The downward/lateral movement of contiguous diesel will cease so long as soil pores can hold the total diesel mass, a case when the residual saturation capacity of the vadose zone is larger than that of the released volume. Figure 2.2 presents the conceptual model under this condition. Certain amount of diesel retained in the soil may be leached out by subsequent precipitations and ultimately migrate to groundwater. As a result, the retained diesel may serve as a source of further contamination. This type of contamination, if close to underground water sources, needs to be monitored or treated to prevent further groundwater contamination.

During this complex transport process, diesel free product may partition into one or more of the four phases in the unsaturated zone, i.e., vapor (in soil gas), aqueous (dissolved in water), residual (adsorbed onto soil particles), and free (LNAPL). The partitioning between phases is dominantly controlled by physiochemical properties of diesel components such as solubility, vapor pressure, octanol/water partition coefficient, and polar/ionic characteristics. It also depends on properties of the soil matrix, including
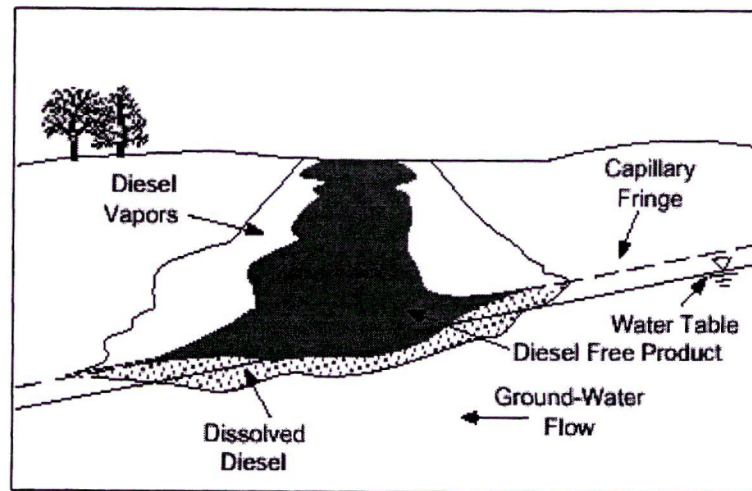
Figure 2.1: Conceptual model for the migration of large amount diesel in subsoil

(Modified after *Newell et al., 1995*)
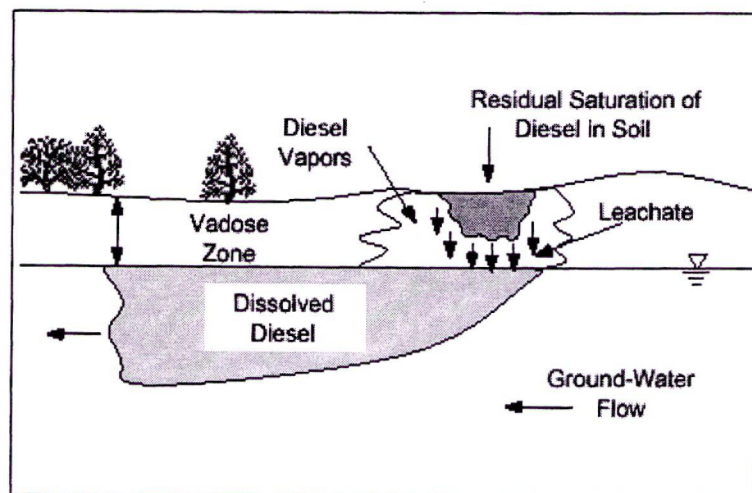
Figure 2.2: Conceptual model for the migration of small amount diesel in subsoil

(Modified after *Newell et al., 1995*)

soil mineralogy, soil texture, organic matter content, surface charge and area, permeability/porosity, and soil homogeneity (Newell et al., 1995).

Certain amount of diesel in both the residual and free phases vaporizes (volatilizes) and dissolves (solubilizes) to become components of the soil vapor and/or pore water/groundwater until equilibrium is achieved. Diesel in the vapor phase is much more mobile and can migrate relatively great distances along preferential flow paths such as fractures, joints, utility line conduits, and sand layers. The dissolved diesel fractions can migrate along with underground water or even with continuous pore water. The interaction between soil particles and diesel results in adsorption of diesel on to solid surface. The adsorption is primarily associated with properties such as octanol/water partition coefficients of diesel components and organic matter content of the soil matrix. Needless to say, adsorption slows the movement of diesel compounds in unsaturated soil. The four-phase distribution of petroleum hydrocarbons in soils is site-specific and varies within spatial and temporal frames (Newell et al., 1995).

Most released petroleum products in soil environment are subject to continuous chemical and biological transformations, leading to "weathering" of the released products. These two major processes can alter diesel mixture compositions after years of exposure to the environment. Chemical reactions such as oxidation and reduction are the most significant abiotic processes (Dragun et al., 1991). Free radical oxidations are the preferable pathway because it requires much less activation energy. Oxidants of small quantities present in the subsurface environment, such as hydroxyl radicals (OH·), ozone (O_3) and oxygen (O_2), can initiate or enhance this process. Many aromatics and substituted aromatics like benzene, naphthalene, ethylbenzene, and phenol can undergo free radical oxidation. Extremely reduced soil may register a redox potential of − 0.3 V, and chemical reduction should be expected if the potential of the soil system is less than that of the organic chemicals of concern (Dragun et al., 1991).

Soil serves as the home for numerous microorganisms capable of performing biological transformation. As unsaturated soil typically contains 10^5 to 10^8 viable bacterial cells per gram of soil, many organic chemicals in soil can be degraded to certain degree by biological process (Mihelcic, 1998). Bioremediation is the most important biological process that biodegrades petroleum products in soil environment (Dragun et al., 1991). It is the microbially mediated chemical transformation of organic compounds to form new product compounds. Since biodegradation is largely attributed to the activities of some specific bacteria, the rate of transformation can be artificially augmented by manipulation of various factors. Bioremediation occurs primarily in upper vadose zone because this zone is usually well aerated and can support abundant microbial life.

Because of the transformations by chemical reactions and biological processes, both the nature and concentration of the released diesel change and the diesel tends to become heavier, more viscous, and more immobile. The rate and degree of weathering are related to the characteristics of the contaminants mediated by environmental factors, which include: volatility and solubility of the compounds in the petroleum products; particle size distribution and porosity of the soil matrix; moisture retention characteristics of the soil; redox potential in soil system; bacteria species and concentration; concentration of contaminants; nutrient concentrations; and soil temperature and pH (Dragun et al., 1991; Newell et al., 1995).

2.3 SOIL REMEDIATION TECHNOLOGIES

Contamination remediation technologies are divided broadly into two categories: *Ex situ* and *in situ* technologies. *Ex situ* technologies involve the excavation prior to on-site or off-site treatment/disposal of contaminated materials. These methods are relatively fast, well controlled, more efficient in treating contaminants of high concentrations, and have been used for most remediation projects in North America (US EPA, 2000c). *In situ* technologies, on the other hand, extract and/or treat the contaminants within their geological environment. These remediation techniques clean up contamination on site

without necessarily excavating the soils, thus proving less intrusive to the environment. *In situ* treatment of contaminated soils is often more cost-effective and preferred for moderate contaminant concentrations at large and deep sites. Brief descriptions of the technologies that are commonly used to treat soils contaminated by diesel are presented below.

2.3.1 Disposal

Disposal is one of the most common remediation technologies to treat diesel-contaminated soils. The approach is to first excavate the contaminated soil followed by disposal at regulated landfills. In general, landfills for hazardous materials can accept diesel-contaminated soil at any concentration as diesel fuel contains less hazardous compounds. Special permits, however, are required prior to disposal. Ordinary landfills can accept diesel-contaminated soils whose concentrations are limited within a certain range. The acceptance range varies from place to place. For instance, landfills in Calgary processed 45,000 tons of soils containing hydrocarbons in 2002, including diesel-contaminated soils from decommissioned USTs within the city limit (Morse, 2003). The acceptance criteria for total petroleum hydrocarbons (TPH) and BTEX are less than 30,000 ppm, and 0.5 mg/L, respectively. Other criteria such as flash point and concentration of certain metals also apply. Disposal is the preferred option when volumes are relatively small and when additional testing, documentation, and permit for alternative technologies are to be sought.

Landfill disposal of contaminated soil has two main disadvantages, cost and long-term liability. Cost of this treatment option increases as the availability of landfill sites become scarce. As this technology basically transfers the problem for one site to the others, possible leaching through the liner and potential subsequent groundwater contamination is a great concern. When dealing with small volume of contaminated soil, however, none of the two drawbacks is a major disadvantage and disposal is a widely practiced option.

2.3.2 Bioremediation

Bioremediation is the most common practice to treat hydrocarbon contaminations due to its low cost and simplicity. It is widely accepted by almost all regulatory agencies, and about 28 percent of all demonstration projects in the U.S. employed bioremediation (US EPA, 2000c). The biological process usually degrades hazardous materials to innocuous ones such as carbon dioxide, methane, water, inorganic salts, and biomass. The process requires the appropriate conditions of temperature, pH, moisture content, inorganic nutrients, and an electronic acceptor. Different from the natural attenuation, enhanced bioremediation can increase degradation rates by supplying rate-limiting nutrients, electron acceptors, and/or adjusting site environment (Dineen, 1991; Nyer *et al.*, 1996).

Bioremediation processes have been successfully used in municipal and industrial waste treatment systems for many years. *In situ* bioremediation has been a common practice in soil remediation. Huesemann (1994) outlined the necessary steps in treating hydrocarbon-contaminated soils using land treatment procedure, an *in situ* managed treatment that involves contaminated soil in the tillage zone and saturated subsurface zone. He conducted three case studies and demonstrated the successful application of bioventing, which used induced low-flow-rate air injection through unsaturated soil matrices, without nutrient addition, to stimulate indigenous microorganisms to degrade diesel-contaminated soils *in situ*. Bioventing was shown to be particularly useful for *in situ* reduction of TPH content.

Typical *ex situ* applications include treatment of excavated contaminated soils in (1) land farming, an on-site land-based unit that is operated under similar conditions as an *in situ* land treatment with leachate collection system and liner to prevent migration and loss of contaminants; (2) soil-pile treatment, an aerated soil-pile system in which nutrients are mixed with the soil and oxygen is delivered through air pipes placed in the

pile; and (3) composting, a biological process used to treat soils with high concentration of biodegradable organic compounds (Ward *et al.*, 1995).

Downey *et al.* (1992) studied the remediation of diesel-contaminated soils using combined physical and biological treatment. They reported that *in situ* respiration increased the rate of bacteria consumption of fuel residual whereas soil vapor extraction system at the same time effectively removed the volatile fraction of diesel from the soil. According to Huesemann (1994), diesel fuel in soils is usually biodegraded into alcohols, aldehydes, ketones, organic acids, and ultimately to carbon dioxide and water.

The disadvantages of bioremediation are its uncertain results, relatively long treatment time and dependence in most case on ambient temperature and site conditions, especially for *in situ* treatment. Consequently, treatability studies conducted in the laboratory are often inaccurate predictors of rate and extent for field remediation. High molecular weight hydrocarbons are normally hard to biodegrade under most natural conditions.

2.3.3 Thermal Treatment

Thermal treatment technologies use high temperature to either physically separate or chemically oxidize contaminants in soils and sediments (Lighty *et al.*, 1993; Magee *et al.*, 1993). Thermal desorption and incineration are two established treatment technologies commonly used, accounting for approximately 18 percent of all the demonstrative remediation projects in North America (US EPA, 2000c). The basic idea of thermal desorption is to physically separate the organic contaminants from soil matrices by enhancing volatilization at temperature generally below 800°C. The treatment is generally applied in a unit called thermal desorber, which can be stationary or mobile. Some critical parameters affecting treatment efficiency include concentration and type of contaminants, residence time, pretreatment and post-treatment strategies.

Incineration, also referred to thermal destruction, is a thermal process that destroys rather than separates contaminants at very high temperatures (800°C-1200°C). It is a high temperature oxidation reaction between combustible substances and oxygen under controlled conditions. Direct-fired rotary kilns and fluidized bed system are the two main techniques used in incineration. Thermal treatment has been widely used in treating petroleum-contaminated soils. It is also applicable to chemical contaminants such as volatile organic compounds (VOCs), SVOCs, polychlorinated aromatics, and pesticides. A full-scale demonstration using direct-fired desorber was conducted to treat a synthetic diesel contaminated soil spiked to concentration of 5,000 ppm. Test results of the treated soil showed little or no hydrocarbon and aromatic volatiles detected (Lighty *et al.*, 1993).

The main disadvantage of this method is the cost and the offgas release permit required. The cost of thermal desorption is said to be moderate to treat diesel-contaminated soil, depending on many factors such as contamination level, soil particle size distribution, soil moisture content, etc. Incineration, however, is expensive and far more intensive for diesel-contaminated soils than is generally required in most cases (Dineen, 1991). Though combustion products of diesel are relatively harmless, regulatory agencies and local communities have been particularly sensitive to the gas release produced during thermal treatment.

2.3.4 Fixation/*In Situ* Encapsulation

Fixation is a process that immobilizes contaminants in place to prevent the migration of contaminants into surrounding environment. The most common fixation technology is stabilization/solidification, or S/S (Colombo *et al.*, 1994). S/S is defined as the processes that encapsulate the waste in a monolithic solid of high-structural integrity that reduces the risk posed by wastes by converting the contaminants into a less soluble, less mobile, or less toxic form without changing necessarily their physical nature. These processes may involve a chemical interaction between the waste and the solidifying

reagents, and/or mechanically bind the waste in the monolithic structure. As a result, the contaminants get encapsulated and their migration is restricted.

S/S is a sophisticated technology based on extensive field experience, and has been practiced extensively (US EPA, 2000c). Typical option for fixing of diesel-contaminated soil is a process by which strong base is used to convert hydrocarbons to organic acid, followed by treatment with a dissolved silica polymer. The silica solution then reacts with the organic acid, effectively encapsulating the waste in amorphous silica. The use of soluble silicate processes can be limited because its effectiveness is particularly sensitive to operational parameters such as order of silicate addition, type and duration of mixing, and the amount of silicate added (Colombo et al., 1994).

Fixation processes are relatively expensive and not well documented. The concept is promising, but soil heterogeneity and wide variations in soil permeability make thorough mixing of the added chemical throughout the soil matrix difficult. In addition, long-term stability of the immobilized chemicals has not been well understood.

2.3.5   Soil Washing/Soil Flushing

Soil washing is an *ex situ* water-based process that employs chemical and physical extraction and separation processes to remove various types of contaminants from soil matrix, whereas soil flushing is the enhanced *in situ* mobilization of contaminants in the impacted soil for recovery and treatment (Mann et al., 1993). In soil washing, the contaminated soil is excavated and pretreated to remove oversized particles, and washed with water along with surfactants or augmenting agents. Depending on the site characteristics and contaminant nature, removal rates of semi-volatile organics can be between 40% and 90%. Soil washing performance is closely related to two key soil characteristics: particle size distribution and cation exchange capacity. Many contaminants tend to bind to the finer silt and clay particle fractions of the soil. They become difficult to separate from the soil. As a result, this treatment process is often

employed as a pretreatment in contaminant reduction of feedstock for further remediation processes such as thermal treatment, and bioremediation.

In situ soil flushing uses water mixed with surfactants to accelerate the geochemical reactions that alter contaminant concentrations in groundwater systems and contaminant transport mechanisms (Mann *et al.*, 1993). The overall process includes site charaterization, fluid injection and contaminant recovery. As soil flushing depends on fluid movement in the subsurface, it is highly effective when the soil is as homogeneous and permeable as in sand and sandy silt. The contaminant is recovered through nearby pumping well; therefore, favorable site conditions are crucial to successful applications. When contaminants are insoluble or strongly adsorbed to soil particles, the effectiveness of soil flushing is likely to be very limited. Diesel, as a typical SVOC, is a target contaminant suitable for soil flushing process.

The disadvantages of soil washing/soil flushing, besides those already discussed, are the need to collect water/surfactant/contaminant mixture after washing/flushing and the need to dispose of or treat the liquids.

2.3.6 Phytoremediation

Phytoremediation is the use of plants to partially or substantially remediate selected contaminants in soil, sludge, sediment, and waste water. It utilizes a variety of plant biological processes and the physical characteristics of plants to aid remediation (Pivetz, 2001). These processes primarily include rhizodegradation, rhizofiltration, phytodegradation, phytoextraction, and phytostabilization. The processes can lead to contaminant degradation, removal, or immobilization. Phytoremediation can be applied *in situ* or *ex situ* and can address organic compounds such as petroleum hydrocarbons, gas condensates, crude oil, chlorinated compounds, pesticides and explosive compounds plus inorganics including heavy metals and radioactive materials. It was reported that

the cost of phytoremediation could be as low as $60,000 US to remediate one acre of 20 inch-thick hydrocarbon contaminated sandy loam (Salt *et al.*, 1995).

Banks *et al.* (2000) evaluated the effect of phytoremediation on the fate of petroleum contaminants using three plant species in a pilot project. In a laboratory study, Hou *et al.* (2001) used ryegrass to stimulate diesel degradation in cup and column. TPH loss was found linked to the root intensity. Based on their test results, they indicated that care should be taken when scaling up laboratory tests to the field.

Phytoremediation is a low cost, aesthetically pleasing, environmentally acceptable option as compared to other conventional technologies. Its effectiveness may be limited by the long treatment time and by high contaminant concentrations that are likely to be toxic or could cause an unacceptable decrease in plant growth. This method has not been well documented and further work is needed to enable the selection, breeding, or genetic modification of plants specifically for phytoremediation of hydrocarbon contamination in soil.

2.4   SOIL REMEDIATION USING MODIFIED FENTON'S REACTION

Chemical oxidation uses oxidants to destroy or degrade a variety of wastewater, contaminated sediment and soil. The oxidants are generally inexpensive, commercially available, easily delivered to subsurface with conventional injection equipment, and provide shorter treatment time. The oxidation process is advantageous over conventional technologies because of the ease of operation and cost of time and labor. For instance, pump-and-treat technology was reported to require considerable prime investment (between $14-17 million US) over a long time (30 years or longer), and may not actually clean up the source of the contamination (US EPA, 1998). In a laboratory study, Watts and Dilly (1996) reported the cost of $52 US to degrade 907 kg sandy loam soil from 1,000 mg/kg TPH to below 100 mg/kg. The oxidants generally used in oxidation process are hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$),

and ozone (O_3). The use of hydrogen peroxide has been the most common thus far, primarily in the form of Fenton's reagent.

2.4.1 Modified Fenton's Reaction (MFR)

Hydrogen peroxide solution is clear, colorless, water-like in appearance, and can mixed with water in any proportion. It has been widely used as a powerful oxidizer in odor control, enhanced physical separation of biochemical oxygen demand (BOD) and/or chemical oxygen demand (COD) and a source to supplement oxygen for municipal, industrial wastewater and drinking water systems (OxyPure, 2002). When catalyzed by ferrous ion, H_2O_2 decomposes rapidly to produce hydroxyl radical, $OH\cdot$. The decomposition is generally referred to as Fenton's reaction. Haber and Weiss (1934) found that the hydroxyl radical, $OH\cdot$, is one of the intermediate products in Fenton's reaction. They proposed the following equation to describe this reaction:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH\cdot \qquad (2.1)$$
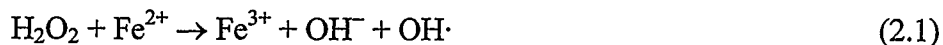
The standard Fenton's reaction involves slow addition of a dilute H_2O_2 solution to a rapidly stirring substrate-iron (Fe^{2+}) solution and proceeds according to Equation 2.1. The production of hydroxyl radicals in Equation 2.1 has rate constants varying between 53 L/mol·s and 76 L/mol·s (Walling, 1975; Huling et al., 2000). Though the oxidizing capability of hydrogen peroxide is higher than potassium permanganate but lower than ozone, the hydroxyl radicals produced in Fenton's reaction are strong, non-specific oxidant with reactivity only second to fluorine, as clearly shown in Table 2.4.

Hydroxyl radicals are capable of oxidizing most organic compounds at a diffusion rate of about 10^7-10^{10} L/mol·s. Reaction pathway is usually reactant-specific and associated with reaction mechanisms. Several mechanisms are possible between hydroxyl radicals and organic contaminants. The following two are more effective in the destruction of petroleum hydrocarbons (Bishop et al., 1968; Sedlak and Andren, 1991; Watts and Dil-

Table 2.4: Oxidation power of common oxidants

Relative Species	Relative Oxidation Power ($Cl_2 = 1.0$)
Fluorine	2.23
Hydroxyl radical	*2.06*
Atomic oxygen (singlet)	1.78
Ozone	1.55
Hydrogen peroxide	1.31
Perhydroxyl radical	1.25
Permanganate ion	1.24
Hypobromous acid	1.17
Chlorine oxide	1.15
Hypochlorous acid	1.10
Hypiodous acid	1.07
Chlorine	1.00
Bromine	0.80
Iodine	0.54

Adapted from *Nesheiwat and Swanson, 2000; US Peroxide, 2002*

ly, 1996; Nesheiwat and Swanson, 2000):

- Oxygen addition: hydroxyl radical adds to an unsaturated organic compound (alkenes or aromatic rings) to first form a free-radical that is eventually transform to organic product, as demonstrated in Equation 2.2:

$$RH + OH\cdot \rightarrow ROH + H^+ \tag{2.2}$$

- Hydrogen abstraction: free radical and water are initially formed when hydroxyl radical reacts with saturated compounds (Equation 2.3), followed by further reactions depending on oxidant concentration and pH.

$$RH + OH\cdot \rightarrow R\cdot + H_2O \tag{2.3}$$

Reaction products of an organic compound during Fenton's reaction are environment sensitive. Sedlak and Andren (1991) proposed several end products for chlorobenzene treated with Fenton's reagent. The end products can be dichlorobiphenyl (DCB) in the absence of oxygen, and chlorobenzoquinone in the presence of oxygen.

The rate constants for the above two reactions are apparently contaminant-specific. For instance, Haag and Yao (1992) reported the reaction rate constants of hydroxyl radicals with dichloromethane and phthalates in aqueous phase were $2.2\text{-}5.8 \times 10^7$ M $^{-1}\cdot$s $^{-1}$ and 4.0×10^9 M $^{-1}\cdot$s $^{-1}$, respectively. Tyre $et\ al.$ (1991) also observed the first-order rate constant for the degradation of pentachlorophenol was much higher, but somewhat lower for hexadecane and dieldrin. Tang and Huang (1996) found the consumption of OH$\cdot$ by 2,4-dichlorophenol in aqueous phase extremely fast and the rate constant for the oxidation was in the range from 10^7 to 10^{10} M $^{-1}\cdot$s $^{-1}$.

Fenton's reaction has been used extensively to oxidize a wide range of industrial organic compounds in aqueous solutions. Bishop *et al.* (1968) found that oxidation of organic residuals by catalyzed hydrogen peroxide in municipal waste was effective in removing 98% of alkyl benzene sulfonate. The treatment process was favorable when pH was between 3 and 5. Barbeni *et al.* (1987) investigated the Fenton's oxidation of di- and trichlorophenols in aqueous solution. Using mass balance analysis, they measured the residual chlorophenol, chloride, and total organic carbon. The results suggested mineralization of chlorophenol after the treatment. Murphy *et al.* (1989) also reported successful oxidation of a waste stream of formaldehyde under bench-scale conditions.

Innovative in concept, using Fenton's reagent to treat contaminated soil is far short of a established technology. Less than 5% of over 600 field demonstration projects sponsored by governments in North America were treated with chemical oxidation methods since the mid-1980s (US EPA, 2000c). Few field applications have been reported using this remedial technology to treat petroleum hydrocarbon impacted soils (Watts, 1992; Mahmoud *et al.*, 2000).

This technology is promising due to the uniqueness shown below:

- Hydrogen peroxide is relatively cheap, commercially available and easily operable;

- Catalyzed hydrogen peroxide is readily delivered to deep subsurface and/or areas at locations with restricted access;

- The technology can destroy contaminants in a short time frame and with reasonable cost; and

- Generation of nontoxic end products (carbon dioxide and water) in the Fenton's oxidation eliminates and/or minimizes the need to further deal with secondary contaminants.

Carbon dioxide is one of the greenhouse gases and considered a major contributor of global warming. As AOPs, including Fenton's reaction, are new technologies, their large-scale applications have been fairly limited. Therefore, the amount of CO_2 generated from these oxidation processes is trivial as compared with the amount of carbon dioxide produced from the combustion of fossil fuels.

Several shortcomings limiting more widespread use of Fenton's reagent have been identified. They are:

- Potential spreading of free phase contaminants, as Fenton's reaction is extremely exothermic and the heat generated can vaporize and mobilize the contaminants;

- Adverse impact on indigenous microorganisms by the inherent toxicity of high concentration of H_2O_2, thus diminishing the potential of natural attenuation; and

- Uncertainty of effectiveness in field applications due to lack of in-depth understanding of the technology that is highly site-specific.

Watts *et al.* (1990) first documented the use of Fenton-like reactions for the remediation of pentachlorophenol-contaminated soils. Since then, experimental work on the use of Fenton's reaction to treat contaminated soils has been conducted using various contaminants as model compounds under varying conditions (Tyre *et al.*, 1991; Watts *et al.*, 1993; Ravikumar and Gurol, 1994; Watts and Dilly, 1996; Kakarla, 1997). It was later found that modified Fenton's reaction (MFR), the use of mineral irons present in soils as catalysts and application of high concentration H_2O_2 to enhance treatment efficiency, is often needed to destruct biorefractory/recalcitrant organic compounds and promote contaminant desorption from soil matrices (Watts *et al.*, 1991; Spencer *et al.*, 1996). Many process variables affect the outcome of modified Fenton's reaction. The key variables include volume and concentration of hydrogen peroxide, mineral and soluble iron catalyst, soil pH, and soil matrix.

2.4.2 Process Variables Affecting MFR to Remediate Contaminated Soils

2.4.2.1 Irons and Iron Oxides

Iron is a vital component for decomposition of hydrogen peroxide in Fenton's reagent. In standard Fenton's reaction, excess iron is added into aqueous solution to guarantee complete oxidation of organic substrate. The maximum amount of iron required to catalyze the decomposition of hydrogen peroxide is case specific. Study by Ravikumar and Gurol (1994) showed that treatment efficiency was increased by increasing soluble iron concentration. Similar trend was observed when treating hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) using hydrogen peroxide (Bier et al., 1999). The ratios between the amounts of H_2O_2 used and iron catalyst added were shown to affect the optimum treatment efficiencies. Various H_2O_2 : Fe^{2+} molar ratios, such as 11:1, 100: 1, and 1440:1, were proposed by different investigators under various conditions (Tang and Huang, 1996; Barbeni et al., 1987; Bier et al., 1999).

Other than ferrous ion, ferric ion was also capable of catalyzing the decomposition of hydrogen peroxide, therefore effectively degrading contaminants in Fenton-like reaction (Watts and Dilly, 1996; Pignatello, 1992). More significantly, Watts et al. (2000) observed similar amount of degradation of benzene, toluene and xylene (BTX) using hydrogen peroxide catalyzed by Fe^{3+} iron solution at both pH 3 and near-neutral pH regimes. They stressed that $Fe_2(SO_4)_3$ is commercially available in large quantities and poses no threat to public health when external iron amendment is needed in field application.

In many cases, Fenton's reaction occurs when hydrogen peroxide is solely introduced into soils. The mineral iron oxides present in soil serve as catalysts to promote Fenton's reaction. Tyre et al. (1991) studied the oxidation of pentachlorophenol (PCP), hexadecane, trifluralin, and dieldrin in soils using Fenton's reagent. They found that the most efficient treatment stoichiometry during treatment occurred without the addition of

soluble iron but using goethite (α-FeOOH), a naturally-occurring iron oxide. Miller and Valentine (1995) and Kakarla (1997) hypothesized the following mechanism as heterogeneous catalytic reaction on the soil surface:

$$H_2O_2 + S \rightarrow HO\cdot + OH^- + S^- \tag{2.4}$$

where S refers to iron minerals on soil particle surface. Watts *et al.* (1993) found that iron oxyhydroxides (hematite (α-Fe$_2$O$_3$)) effectively catalyzed H$_2$O$_2$ decomposition to treat soils contaminated with PCP. Ravikumar and Gurol (1994) used Fenton's reagent to treat surface sand in both column and vial test, and concluded that 80% to 90% PCP and trichloroethylene (TCE) were degraded with and without external soluble iron amendment. Pignatello and Baehr (1994) used certain soluble Fe^{3+} complexes (Fe-L) as catalysts to degrade herbicides 2,4-dichlorophenxyacetic acid and metolachlor. They concluded that Fe-L plus H$_2$O$_2$ was superior to the Fenton's reagent itself (H$_2$O$_2$ + Fe^{2+}) in terms of contaminant degradation.

2.4.2.2 pH of Soils

The efficiency of Fenton's or Fenton-like reaction is related to soil pH not only for degradation of contaminants, but also for conserving H$_2$O$_2$. Watts *et al.* (1990) in their pioneer work observed that silica sand and a natural soil contaminated with PCP could be effectively oxidized by iron-catalyzed hydrogen peroxide when pH is between 2 and 3. They observed H$_2$O$_2$ decomposition rate was pH dependent, and increased substantially from lower pH to higher pH. However, the corresponding rate constants for PCP degradation decreased significantly from pH 4 to pH 8, resulting in low treatment efficiencies at high pH regime. Likewise, Bier *et al.* (1999) observed the fastest rate for RDX transformation and mineralization treated with Fenton's reagent at pH 3. Low pH (< 3) is favorable to keeping iron salts in ionic state, or they would precipitate in colloidal form at high pH (Nesheiwat and Swanson, 2000). Lou and Lee

(1995) argued that more $Fe(OH)^+$ forms at low pH and the activity of $Fe(OH)^+$ is higher than Fe^{2+} in Fenton's oxidation.

pH adjustment is more feasible in aqueous systems than in soil systems soil because of buffering effect by some soil constituents. In practice, it is not viable to acidify the impacted site to accomplish higher treatment efficiency. Some investigators documented cases when effective degradation took place in Fenton's reaction at near neutral pH. In their laboratory-scale experiment with soils contaminated with 2-methylnaphthalene, n-hexadecane and diesel fuel, Chen *et al.* (1998) observed that the percentage of destruction of the three model contaminants by hydrogen peroxide was higher at pH 7 than at pH 2. Pignatello and Baehr (1994) also reported that some of the complex in soil matrices were soluble at near-neutral pH and were effective in degrading 2,4-dichloro-phenoxyacetic acid and metolachlor.

2.4.2.3 Hydrogen Peroxide

Hydrogen peroxide is the source of OH·. Sustainable supply of hydroxyl radicals from decomposition of hydrogen peroxide is crucial to effective contaminant oxidation in Fenton's reaction. Some competing reactions during Fenton's oxidation, especially those taking place in soil matrix, can be "sinks" for hydroxyl radicals and hydrogen peroxide. These non-productive reactions affect the ultimate treatment stoichiometry, the moles (grams) of contaminant degraded to mole (grams) of H_2O_2 consumed.

Excess of H_2O_2 reacts with OH·, increasing the rate of H_2O_2 consumption while decreasing hydroxyl radicals available to oxidize the contaminants (Huling *et al.*, 2000). Kakarla (1997) observed that some H_2O_2 was wasted when reacted with soil organic and inorganic substances. H_2O_2 decomposed very rapidly at shallow depth and could hardly generate OH· below the surface soil. They experimented four stabilizers in a series of soil column tests and found out that the addition of one stabilizer, monobasic potassium phosphate (KH_2PO_4), increased the depth to which H_2O_2 was detected in the

soil by three times of soil columns without stabilization. As implied by Pignatello and Baehr (1994), hydroxyl radicals are highly reactive and nonselective, and therefore the consumption/decomposition of the oxidant by soil components, including soil organic matter, can make complete oxidation of contaminants uneconomical.

The amount and concentration of hydrogen peroxide used in Fenton-like reaction is crucial - for economic viability of any remedial activity. Aggressive oxidation using high concentration and large amount of hydrogen peroxide can promote contaminant degradation, but balance has to be maintained between remediation efficiency and cost of operation. Spencer *et al.* (1996) experimented soil samples in two scenarios using Fenton's reagent as the oxidant, high volume/low concentration and low volume/high concentration. They concluded that the high volume/low concentration system was more efficient stoichiometrically. Watts *et al.* (1990) suggested that treatment stoichiometry of 1:600 to 1:3,000 was required to undergo aggressive soil treatment. Watts and his colleagues (1999) also observed oxidation stoichiometries ranging from 1:140 to 1:370 (by weight) in a study involving one sand and one clayey soil.

2.4.2.4 Soil Matrices

Hydroxyl radicals react favorably with contaminants in aqueous solution, and any adsorbed contaminant in soil matrix needs to desorb first before it can be effectively oxidized (Leung *et al.*, 1992; Watts and Dilly, 1996; Kakarla, 1997). Sorption, a soil texture related property, is usually associated with soil organic matter content and influences the degradation efficiency of Fenton's reaction in soil media. Generally, soil with more fine clay particles is usually prone to adsorb organic compounds, and needs more effort to remove the contaminants tightly bound to soil particles.

Watts *et al.* (1999) reported distinct oxidation stoichiometry in two soils of different texture and attributed the difference to varying organic matter content. Soils with high organic matter content usually are more difficult to remediate. In other documentations,

greater removal of pendamethalin and faster degradation of two contaminants in soils with lower organic carbon content in soil slurries were reported (Miller and Valentine, 1995; Tyre *et al.*, 1991). In field applications, effect of soil texture on remedial activities has to be fully addressed before any operation begins.

2.4.3 Potential Use of Fenton's Reagent with Other Remedial Technologies

Contaminant oxidation using Fenton's reagent is very appealing because of its relatively low cost, easy implementation and innocuous end products. Fenton's reagent in conjunction with other remedial technologies has been also used to treat contaminated soils.

Surfactant enhanced washing of hydrophobic organics is suitable for removing adsorbed contaminants in soil matrices to residual levels (Pennell *et al.*, 1994). Sexe *et al.* (2000) investigated the feasibility of using soil washing to first remove PAH contaminants from soil and destroy them in the resulting wastewater solution through Fenton oxidation. They found that over 99% of PAH parent contaminant was destroyed in a nonionic surfactant solution for a low organic sandy soil. Their results also indicated that surfactant and soil organic matter in soil washing solution were significant sinks for hydrogen peroxide.

Fenton's reagent was also used as a pretreatment to enhance biodegradation of some recalcitrant PAHs. In one study by Carberry and Yang (1994), biodegradation rate constants for two polychlorinated biphenyls (PCBs) congeners in soil increased 3 and 5 times over untreated soil samples. Their results suggest that higher molar ratio of H_2O_2/PCBs leads to higher percentage removal of PCBs. Martens and Frankenberger (1995) found that the use of Fenton's reagent as a pretreatment promoted the mineralization of spiked PAHs in soil by an average of 87%. Pretreatment of the soil with a surfactant followed by Fenton oxidation increased the PAH degradation rate to 84% and 83% for phenanthrene and fluoranthene, respectively, compared with no

addition of Fenton's reagent. They concluded that PAHs become more readily degradable after treatment with Fenton's reagent, particularly when surfactants are used.

2.4.4 Pilot-Scale and Field Applications of Modified Fenton's Reaction

Fenton's reaction is a relatively new technology and few field remediation projects using this advanced oxidation method has been documented in literature. Though *in situ* oxidation using Fenton's reagent is commercially available and a Geo-Cleanse Process® is patented under U.S. Patent No. 5525008, only limited field cases using Fenton's reagent were reported to treat chlorinated solvent in groundwater by US EPA (US DOE, 1999; GCI, 2002; Wilson, 1995; US EPA, 1998). The followings are some documented larger scale applications that involved remediation of hydrocarbon-contaminated soil using Fenton's reagent.

Watts (1992) documented a pilot-scale *ex situ* remediation of petroleum-contaminated soil from an equipment storage yard near Reno, Nevada. Treatability test was carried out to optimize the process variables prior to the pilot study. Guided by the treatability study, pilot study was conducted at pH 3 with no soluble iron addition, hydrogen peroxide volume of four times field capacity, and hydrogen peroxide concentrations of either 2 percent or 7 percent. The soil was first excavated from field site and then slowly added to the fifty-five-gallon poly drum reactors. The reaction proceeded for one to three days. The results showed that total petroleum hydrocarbons of more than 2,000 mg/kg were successfully oxidized to below the 100 mg/kg action level.

Field application using Fenton's reagent was implemented to remediate residual hydrocarbons in subsurface soil adjacent to structures with restricted access in Alberta, Canada (Mahmoud *et al.*, 2000). Bench test of two soil samples with 24-hour treatment showed 85 to 95 percent reduction in total extractable hydrocarbons (THE) for clay and sand, respectively. Two applications of hydrogen peroxide, 2,000 L of 16% and 1600 L

of 20%, were injected in two-day period. The chemical analysis demonstrated that almost all the TPHs from soil samples after treatment were below the provincial regulatory criteria. In this case, remediation was completed in a short time frame, and was relatively inexpensive when compared to the traditional excavation and removal approach.

CHAPTER THREE

MATERIALS AND METHODS

3.1 MATERIALS AND EQUIPMENT

3.1.1 Chemicals

Commercial hydrogen peroxide containing 30% by weight of H_2O_2, dichloromethane (CH_2Cl_2), or DCM, and sulfuric acid (H_2SO_4) were purchased from EM Science. Ferrous sulfate heptahydrate ($FeSO_4$) $\cdot 7H_2O$) and ferric sulfate hydrate ($Fe_2(SO_4)_3$ $\cdot nH_2O$) were obtained from Fisher Scientific Company. The chemicals for iodometric titration were: potassium iodide solution (KI) from BDH Company, sodium thiosulfate solution (NaS_2O_3) from VWR Scientific Products, starch indicator, and ammonium molybdate tetrahydrate (($NH_4)_6Mo_7O_{24}$ $\cdot 4H_2O$) from EM Science. Sodium Dodecyl Sulfate ($NaCH_3(CH_2)_{11}SO_4$), or SDS, was purchased from BDH Company for use in surfactant enhancement tests. All the chemicals were reagent grade. Other standard mixtures essential in calibration for chromatographic analysis included diesel component standard (DCS) and No. 2 diesel fuel, which were purchased from SupelCo and Chromatographic Specialties Inc., respectively. Tap water was purified to greater than 18.3 $M\Omega$·cm with a Barnstead Ultrapure Water System. The purified water was used to prepare diluted stock solutions and for control experiments. Diesel used as target contaminant throughout the entire experimental study was obtained from a local gas station.

3.1.2 Soils

Soils were collected from two field sites of distinct geological conditions. One was from a construction site on campus at University of Calgary. Another sample, from a site at Springbank Hill, was provided by Golder Associates Ltd., Calgary, Alberta. The two soils were hereafter designated UC soil and SH soil in this study. Sieve and hydrometer analyses were performed to determine soil particle size distribution in accordance with the procedures outlined in ASTM 422-63 (ASTM, 2001). Based on United States Department of Agriculture Classification System, UC soil and SH soil were characterized as sandy silt and silty clay, respectively (Roberts, 1996). Figure 3.1 illustrates the particle size distributions for the two soils. Ottawa sand used in the study was a mixture of sands with particle sizes of 0.72 mm, 0.25 mm and 0.15 mm in proportions of 25%:55%:20% by weight, and designated as OS. Being basically iron-free and with negligible organic matter content, Ottawa sand was used to elucidate some process variables in Fenton's reaction that otherwise may not be effectively evaluated in UC and SH soils.

Soil organic matter content and total iron content for UC and SH soils were determined by AGAT Soil Laboratory, Calgary, Alberta. Relevant physiochemical properties of Ottawa sand were obtained from other sources (ITC, 2001). The soil pH was measured using a pH meter in accordance with ASTM D 4972-01 (ASTM, 2001). Some soil characteristics are given in Table 3.1.

3.1.3 Test Equipment

Borosilicate vials fitted with PTFE-lined screw caps were purchased from VWR and used as batch reactors in Phase I study. Soil samples were first allowed to react with reagents in vials for a period of time. Then the soil-slurries were centrifuged at 2800 rpm using a centrifuge manufactured by Fusion Company to attain liquid-solid phase separation.

Shake extractions with solvent DCM were carried out in vials on a Multi-Wrist-Shaker, which was manufactured by Lab Line Instruments Inc. The Luer tip Yale 10 mL glass syringe from B-D Company and 0.45 µm PTFE syringe microfilter from Nalge Nunc International were used to filter the particulates in the extract. Volume of gas generated during Fenton's reaction was measured using a system shown schematically in Figure 3.2. The concentrations of oxygen and carbon dioxide were determined using a Hewlett Packard P200 portable gas chromatograph (GC) equipped with Thermal Conductivity Detector (TCD).
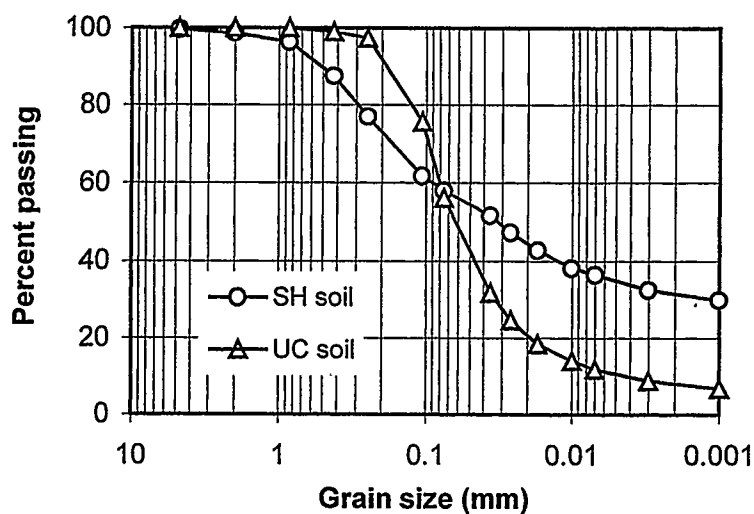
Figure 3.1: Particle size distribution of UC and SH parent soils

Hydrogen peroxide concentration was measured using standard iodometric titration setup (Kolthoff *et al.*, 1969). A 9025 Microcomputer pH meter manufactured by Hanna Instruments was used to determine soil pH after appropriate calibration. Diesel range organics (DRO) was analyzed on a Hewlett-Packard 6350 gas chromatograph (GC) fitted with flame ionization detector (FID) and an HP autosampler using a 2 mL HP GC vials. Capillary column used is of Agilent 19091J-433 (30 m × 0.25 mm) fused with Phenyl Methyl Siloxane of 0.25 μm in thickness. The chromatographs were analyzed using a HP ChemStation software.

Table 3.1: Characteristics of the soils used in this study

Characteristic	Sandy Silt (UC)	Silty Clay (SH)	Ottawa Sand (OS)
Gravel (%)	0	1.4	0
Sand (%)	63.9	44.0	100
Silt (%)	36.1	23.2	0
Clay (%)	7.9	31.4	0
Organic matter (%)	0.40^1	1.87^1	$< 0.1^2$
Total iron content (mg/kg)	$10,900^1$	$15,500^1$	$< 260^2$
pH	8.4	8.1	7.8

[1]Data obtained from *AGAT Soil Laboratory, Calgary, Alberta, 2001*

[2]Data adapted from *Material and Chemical Data Sheet, ITC Inc., 2001*
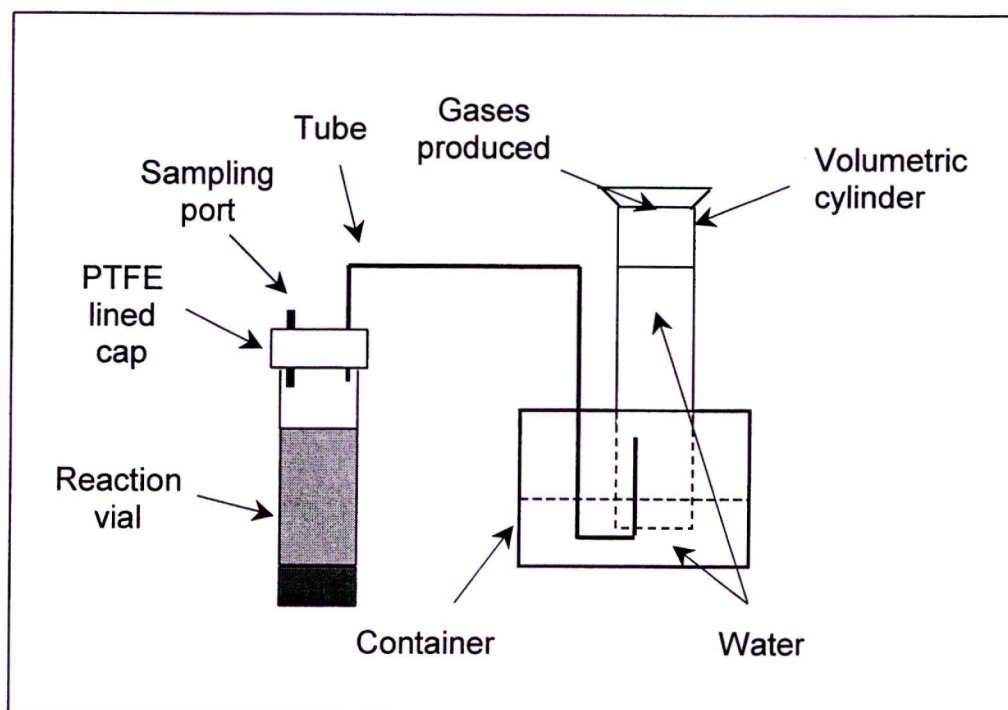
Note: No to scale

Figure 3.2: Schematic setup for gas collection and measuring system

In Phase II study, two experimental setups were used to conduct the following tests:

- Infiltration column test:

  The tests were conducted using H_2O_2 as the infiltrating liquid in a cylindrical column packed with soil sample. The test device was a permeameter-like assembly, with a column of 7.6 cm in inner diameter and 12 cm in length. Its setup is shown schematically in Figure 3.3. A piece of filter paper was placed on the bottom plate above which soil was packed. This prevented the effluent outlets, one located at central bottom and another along one side of the base, from soil blockage during H_2O_2 infiltration. Volumetric cylinders and a timer were used to collect the volume of effluent and to record sampling time.

- Injection test:

  The tests were conducted in a plexiglass cylinder tube (inner diameter 14 cm) with one end glued onto a plate, as schematically shown in Figure 3.4. The injector was a stainless steel tube (inner diameter 4 mm) with perforations around the periphery of the tube. One end of the injector had a tapered head to minimize soil disturbance during insertion. Hydrogen peroxide solution was injected using a 60 mL PlastiPak syringe purchased from B-D Company. Clear PVC tubing from Nalgene was used for connections between injector and syringe. To minimize H_2O_2 solution evaporation, aluminum foil was used to cover the opening end.

3.2   EXPERIMENTAL DESIGN

Limited studies using Fenton's reaction to treat diesel-contaminated soils are available in literature (Spencer *et al.*, 1996; Watts and Dilly, 1996; Chen *et al.*, 1998). Spiked diesel concentrations ranging from 500 mg/kg to 2,000 mg/kg were reported, whereas
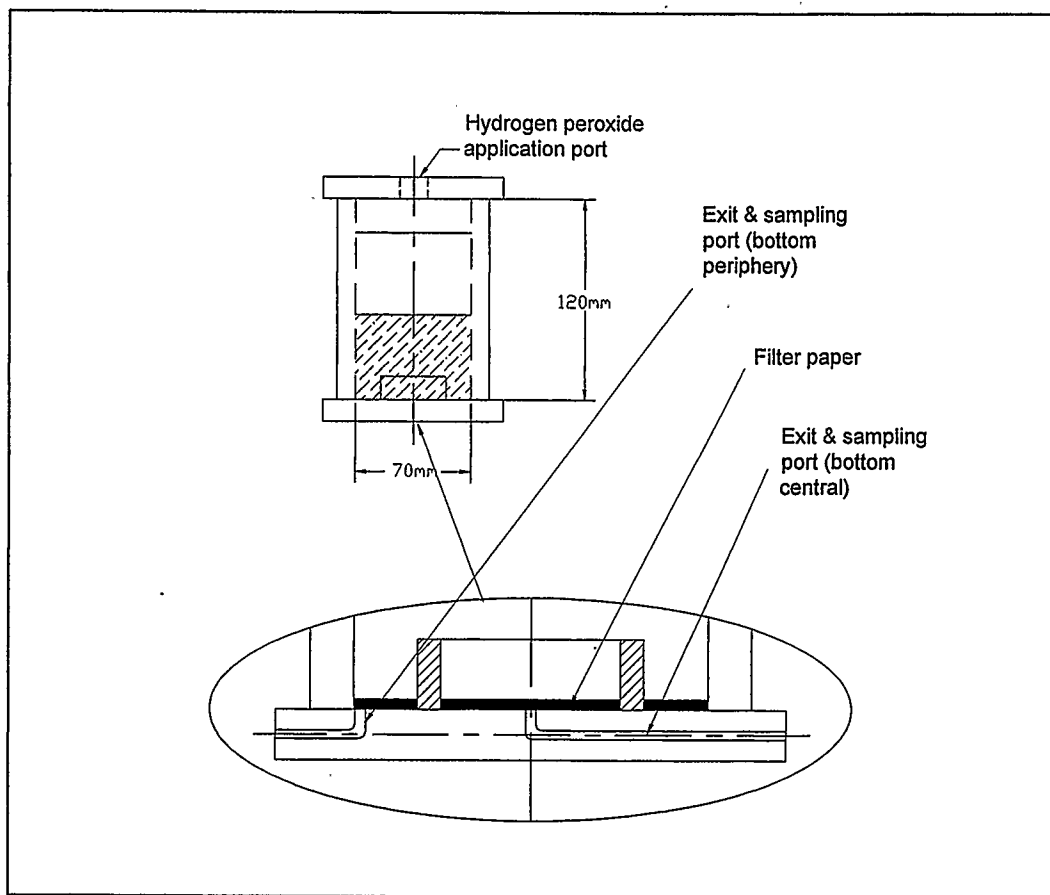
Figure 3.3: Schematic setup for column infiltration test
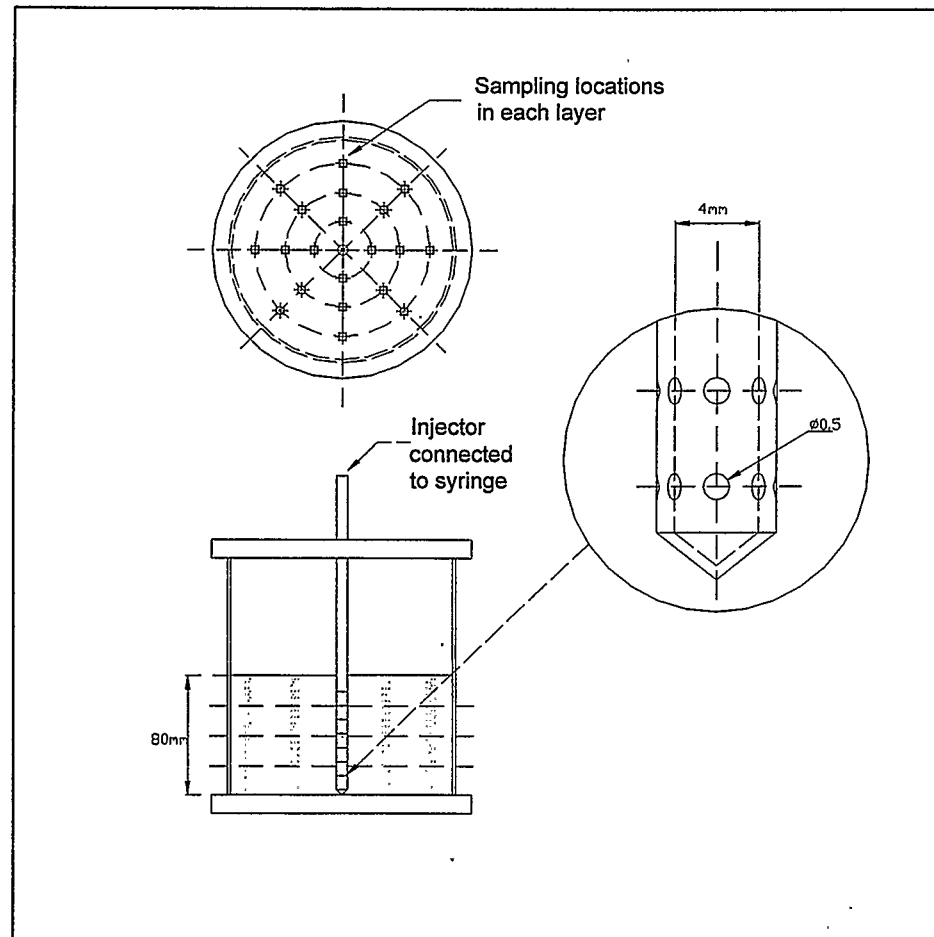
Note: No to scale

Figure 3.4: Schematic setup for injection test

the moles of H_2O_2 used were well below 10 mM per gram of soil. The moderate use of H_2O_2 and relatively low contamination levels leave much to be researched with respect to soils of high diesel concentration and use of large volume and high concentration H_2O_2 per gram of soil.

In the present study, diesel concentrations varied between 500 mg/kg and 10,000 mg/kg. In some tests, hydrogen peroxide used was as much as 70 mM per gram of soil treated. As most of the regulatory guidance associated with soil diesel contamination designates mandatory action level around 100 mg/kg, soils tested in this study covered the range of diesel contamination likely encountered in field sites (AEHS, 2002). High concentration of H_2O_2 (5% to 20%) used in this study was justifiable, considering the use of large amount of high concentration hydrogen peroxide per unit volume of soil treated in one field application (Mahmoud et al., 2000; Mahmoud, 2001). The selection of two different soils was intended to reflect the impact of soil texture. SDS surfactant was used as an enhancement to the Fenton's reaction in soil remediation.

Batch test has been effective in conducting feasibility study on laboratory scale, and served as screening procedures prior to field treatment using Fenton's or Fenton-like reactions (Mahmoud et al., 2000; Watts et al., 1992). Therefore, vial batch tests were conducted to evaluate the major process variables affecting the reactions. Samples with larger quantities of compacted soil were studied in infiltration and injection tests in order to closely simulate the field conditions.

The process variables and their values used in the tests conducted in the study are listed in Table 3.2. A range of varying H_2O_2 concentrations, 5%, 10% and 20% by weight, coupled with application volume, was used to optimize the process conditions. The optimized values were later used in tests conducted in Phase II study. The combinations of high concentration and high volume render the application of up to 70 mM per gram of soil treated in the tests. An anionic surfactant, SDS, was tested in the range between 0.1% and 2% as a pretreatment. Sequential applications of hydrogen peroxide were

tested to enhance the remediation efficiency. Other process variables such as Fe^{2+}, Fe^{3+}, soil pH, and soil texture were also evaluated.

Table 3.2: Process variables design for Fenton's reaction in this study

Process Variables	Numerical Values and Soil Types				
Phase I tests					
H_2O_2 concentration (%)	5	10	20		
H_2O_2 volume (mL)	5	10	20	40	60
Diesel concentration (mg/kg)	500	1,000	5,000	10,000	
Iron added (mg/L)	180	360	720	1800	3600
SDS concentration (%)	0.1	0.5	1	2	
Soil type	UC	SH	OS		
Phase II tests	(UC soil, 5,000 mg/kg; 10% H_2O_2)				
Infiltration test					
Soil bulk density (g/cm^3)	1.63				
H_2O_2 volume (mL)	950	1350	1750		
Injection test					
Soil bulk density (g/cm^3)	1.21	1.35			
H_2O_2 volume (mL)	200	400			

3.3   PROCEDURES

3.3.1   Preparation of Diesel Contaminated Soils

Both UC and SH soils were crushed using a ceramic pestle and mortar, sieved with a 2 mm sieve (US standard sieve No. 10), and air-dried under the fume hood. The dried soils were placed in a big glass bottle and spiked with specific amount of diesel dissolved in DCM solvent. The bottle was then tightly sealed with a fitted cover and mixed on a tumbler for 30 minutes to ensure homogeneous distribution of diesel in soil matrix. DCM in the soil was then allowed to evaporate under the fume hood. The glass bottle was then stored in refrigerator at 4 °C and the spiked soils were ready for tests (Wisconsin DNR, 1995). Ottawa sand was also spiked with diesel using a similar procedure and stored in a dark, cool place.

3.3.2   Phase I Tests

In this study, batch test was initiated by adding 5 grams of soil sample into a vial of suitable volume, followed by addition of hydrogen peroxide and/or other reactants, e.g., aqueous iron catalyst and surfactant. Preliminary test results shown in Figure 3.5 suggested that the 30-minute reaction period was sufficient. Therefore, reaction time for vial batch tests in this study was designated as 30 minutes unless otherwise noted.

In experiments where residual H_2O_2 concentration had to be determined, the liquid phase was volumetrically measured and transferred to 250 mL Erlenmeyer flasks followed by standard iodometric titration process described by Kolthoff *et al.* (1969). The residual supernatant in the vial was decanted. The settled soil sediment was then centrifuged at high speed and later transferred to aluminum pans. The pans were placed under fume hood and the soil sediments were air-dried for four hours. Then the dried soil sample was ground and ready for soil extraction. All tests in the study were

duplicated for statistical significance. The ambient temperature in the laboratory was around 21 °C.
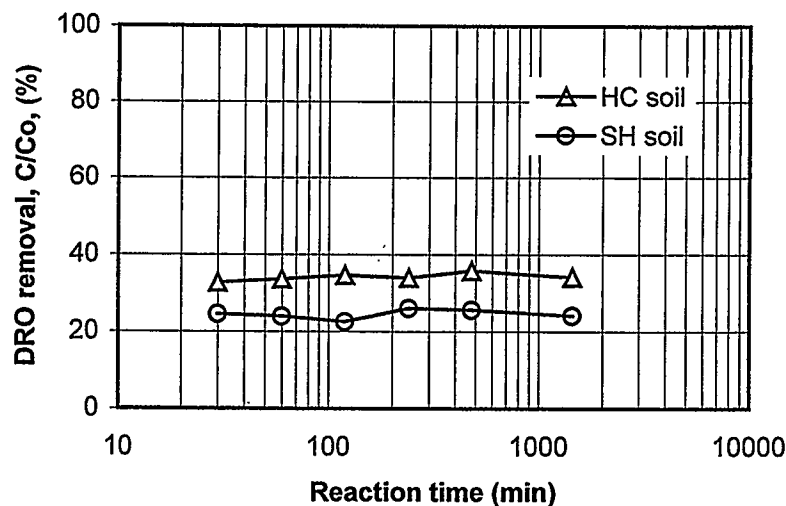
Figure 3.5: Effect of reaction time on DRO removal for both HC and SH soils

(10 mL, 10% H_2O_2, 5 g of soils, 5,000 mg/kg diesel)

Detailed description of experimental procedures in vial batch tests is given below:

3.3.2.1 Hydrogen Peroxide Consumption

Ottawa sand spiked with 5,000 mg/kg diesel was used in the tests. Effect of iron catalyst on hydrogen peroxide decomposition was tested by adding 10 mL of 5%, 10% and 20% H_2O_2 coupled with or without external iron amendments. Residual H_2O_2 concentrations were measured against contact time. Hydrogen peroxide consumption promoted by both ferrous and ferric ions were tested using Ottawa sand treated by 10 mL of 5% and 20% H_2O_2. Both soluble irons were amended at concentration of 720 mg/L.

To further demonstrate the effect of ferric and ferrous ions on the degradation of diesel. A total of 5 mL of reagent solution was used. Five concentrations of Fe^{2+}, Fe^{3+} and two concentrations of hydrogen peroxide were added in such a way that the final concentrations of the reactants were 10%, 20% for H_2O_2, and 0, 180 mg/L, 360 mg/L, 720 mg/L, 1,800 mg/kg and 3,600 mg/L for both ferrous and ferric ions.

3.3.2.2 Soil Buffering Capacity and pH Effect on Diesel Degradation

Soil pH was first measured as outlined in relevant ASTM method in vials containing UC, SH and OS soils. The soil slurries were then added with sulfuric acid to decrease soil pH, followed by pH measurement. For UC and SH soils, as much as 1.8 mL sulfuric acid was used, the amount sufficient to block the Fenton's reaction as practiced by many investigators (Watts *et al.*, 1991; Li *et al.*, 1997).

Effect of soil pH on remediation efficiency was conducted using OS soil spiked with 5,000 mg/kg diesel. The use of OS soil minimized the buffering effect clearly evidenced in UC and SH soils. pH of Ottawa sand was first adjusted by addition of sulfuric acid and alkali hydroxide. Then 5 mL of reagents, including 10% hydrogen peroxide plus 3,600 mg/kg ferrous ion, were applied to 5 g of soil. After reaction, the residual diesel concentration was determined.

3.3.2.3 Mineral Iron Catalysis and Optimum Ferrous Ion Addition

As UC and SH soils contained well over 1% of total iron content, tests were conducted to elucidate mineral irons catalysis in UC and SH soils containing 5,000 mg/kg diesel. Soluble iron addition in 5 mL of reagents were 0 (without external iron addition), 720 mg/L, 1,800 mg/L and 3,600 mg/L, whereas H_2O_2 concentrations were 0 (distilled water), 10% and 20%.

Similar tests were also conducted to determine the optimum usage of ferrous ion needed to achieve high diesel degradation using Ottawa sand spiked with 5,000 mg/kg diesel. In 5 mL of reagents, with varying concentrations of ferrous ion (0, 180 mg/L, 360 mg/L, 720 mg/L, 1,800 mg/L and 3,600 mg/L) and hydrogen peroxide (5%, 10% and 20%), were used.

3.3.2.4 Measurements of Gases

To determine the volume of oxygen and carbon dioxide generated in Fenton's reaction, tests were conducted using 5 grams of UC and SH soils treated with 10 mL of 10% hydrogen peroxide. Gas volume was measured in a setup shown in Figure 3.2 and recorded every five minutes until no further bubbles of gas could be observed. Gas samples were collected using gastight syringe and the percent fraction of oxygen and carbon dioxide were determined using a portable Hewlett Packard gas chromatograph (GC) equipped with Thermal Conductivity Detector (TCD).

3.3.2.5 Enhancement by Surfactant and H_2O_2 Multiple Applications

Five mililitres of 10% hydrogen peroxide were added sequentially up to a total volume of 20 mL to determine the remediation effectiveness of H_2O_2 multiple applications for UC and SH soils. Control samples were treated with one-time application of 10 mL and 20 mL of 10% hydrogen peroxide for comparison purpose. In tests of UC and SH soils pretreated by surfactant SDS, liquid to solid (volume/mass) ratio of two was selected. Therefore, 5 g of soils was first placed in the vials followed by treatment of 10 mL of SDS. The liquid-soil slurries were then kept still for one hour or agitated on wrist-shaker for certain period of time. The slurries were then centrifuged and the supernatant decanted. The remaining soil samples were treated with 5 mL of 5% and 10% hydrogen peroxide in the same procedures as in other vial tests. Concentration of SDS in soil slurries covered a range from 0.1% to 2.0%.

3.3.3 Phase II Tests

For both infiltration and injection tests, UC soil spiked with 5,000 mg/kg diesel was used. The soil, premixed with about 10% of distilled water to help easy compaction, was placed into corresponding apparatus in three separate layers. Care was taken not to segregate the material during placement. Each successive layer was compacted with 15 blows of either standard manual drop hammer (injection test) or a smaller aluminum rod. The compactness of soil was controlled through adjusting the compaction energy applied, or the height of drop. After compaction, the mass of compacted soil specimen was weighed and the height measured. The recorded data was later used to calculate the bulk density of each soil specimen.

Infiltration column test was intended to verify the process variables obtained from vial batch tests, specifically the optimized amount of H_2O_2 per gram of soil. Each column contained about 335 g of UC soil. The soil column, with bulk densities of around 1.63 g/cm^3, was initially ponded with 1350 mL of 10% hydrogen peroxide, representing 4 mL H_2O_2 per gram of soil. Additional tests using 950 mL (30% lower) and 1750 mL (30% higher) of H_2O_2 were also conducted. The effluent was collected intermittently and analyzed for its residual hydrogen peroxide and diesel concentration. When the infiltration ended, soil along the central axis as well as outer boundary was sampled and the average diesel residual concentrations in four soil layers were determined as described in Phase I test. Control test was conducted to measure the rate of water infiltration to assess the influence of reactive infiltrate on soil hydraulic properties.

Four injection tests (I, II, III and IV) were conducted with 200 mL and 400 mL of 10% hydrogen peroxide in soils of two densities, i.e., about 1.21 g/cm^3 and 1.35 g/cm^3. Plexiglass cylinders were used for easy visual observations during the course of testing. A hole of about 4 mm in diameter was drilled in the soil column. This minimized soil column disturbance when inserting the injector. The 200 mL and 400 mL hydrogen peroxide were equivalent to about 0.6 and 1.2 times of soil field capacity. A total of 80

soil samples in four layers of the 80 cm long soil column were collected using thin-walled steel tube (inner diameter 10 cm) at 20 locations four hours after the treatment. The soil sample was then removed from the tube, sliced and ready for solvent extraction.

3.3.4 Quantification of Diesel in Soil Matrix

Chemical analysis of soil samples consisted of a series of procedures, including extraction and diesel quantification. Soil shaking extraction procedure in this study was employed to replace the otherwise tedious conventional Soxhlet extraction method. Soil sample preparation and quantification were also discussed in detail here.

3.3.4.1 Soil Extraction Method

Some state regulatory guidances were used as basis for the analyses in this study (Wisconsin DNR, 1995; Massachusetts DEP, 1998). The standard protocol for soil extraction has been Soxhlet extraction, an accepted solvent-based protocol by US EPA Method 3540C and other state environmental regulatory agencies mentioned above, for extraction of semivolatile and non-volatile organic compounds from soil matrices. However, Soxhlet extraction has some disadvantages. They are:

- The soil sample is static during the extraction process, which may limit contact between solvent and soil micropores; and
- Soxhlet extraction requires up to 24 hours of extraction, specialized apparatus, and usually large volume of solvent, which becomes prohibitive for the analysis of large numbers of samples.

Shaking extraction, on the other hand, can readily offset the above shortcomings. Its advantages include the use of simple and common equipment, reduction in volume of organic solvents, extraction of many samples simultaneously, and cumulative extraction

periods of less than three hours. It was also found to be equivalent or competitive in the removal of PAHs and surrogate spikes (Lindhardt *et al.*, 1994; Chen *et al.*, 1996). By comparing the recovery efficiencies between shake extraction and Soxhlet extraction for four biorefractory organics, Tyre *et al.* (1991) concluded that both methods showed the same relative loss of contaminants. Shaking extraction has been used to quantify soil contaminants by other researchers (Watts *et al.*, 1993; Widrig and Manning, 1995).

Because diesel was the target contaminant in this study, it was appropriate to endorse the more direct concept of diesel range organics (DRO), instead of commonly used TPHs, to evaluate the diesel contamination in soils. DRO is part of TPH, but is defined more specifically to cover organic components in diesel. DRO correspond to hydrocarbon range from C_{10} to C_{28} and boiling point range between approximately 170 °C and 430 °C (Wisconsin DNR, 1995). The hydrocarbon range and boiling point of typical diesel fuel are within the specified scope. Other organic compounds, including chlorinated hydrocarbons, phenols, phthalate esters, polynuclear aromatic hydrocarbons, kerosene, fuel oils and heavier oils are also included in DRO.

3.3.4.2 GC/FID Sample Preparation

The basic procedures for preparing samples to be analyzed using GC/FID are as follows:

- About 5 g of air-dried soil sample was put in a borosilicate vial with PTFE cap and the mass of the soil sample weighed and recorded;
- 10 mL DCM solvent was added to the sample vial and tightly capped. Then the vial was vigorously shaken for 30 min on a wrist-shaker; and
- The solvent was filtered through a 0.45 μm membrane filter after going through a sodium sulfate moisture-absorbing cartridge to remove particulates and

moisture. Then about 1 mL of the infiltrate was collected in a GC vial ready for GC/FID analysis.

To determine diesel concentration in aqueous solution, a known amount of aqueous solution was collected and extracted two times using DCM as solvent with the help of separation funnel. The combined extract was analyzed by GC/FID and the residual diesel concentration calculated. This procedure was in accordance with the extraction method outlined by Watts *et al.* (1993).

3.3.4.3 GC/FID Conditions, Retention Time Windows and Calibration

When quantifying diesel fuel using GC/FID, different components of diesel are separated as the sample travels through a column within the gas chromatograph. The eluted compounds can then be detected using a flame ionization detector (FID). The following GC/FID operation conditions were designed, and chromatographs obtained. The conditions were compromise between output resolution and running time. Initial oven temperature was set to 40 °C for 5 minutes, then ramp of 8 °C/min to final oven temperature of 290 °C and held for 10 minutes. Each GC/FID operation ran for about 47 minutes. GC was operated in splitless mode at front inlet. The injection port temperature was 290 °C, and maximum oven temperature was 350 °C. The carrier gas was helium flowing at a rate of 19.7 mL/min. Airflow was 400 mL/min, and hydrogen gas flowed at 30 mL/min.

According to the Wisconsin method, the retention time window for DRO is defined as beginning approximately 0.1 minutes before the onset of the n-decane ($C_{10}H_{22}$) peak and ending 0.1 minutes after the conclusion of the n-octacosane ($C_{28}H_{58}$) peak in the calibration run. Based on chromatographs of diesel component standard, the retention time window was determined to be from 10.0 minute to 37.0 minute. Figure 3.6 gives a

gas chromatograph for a typical diesel sample, which shows complete coverage of major diesel components by the designated retention time window.
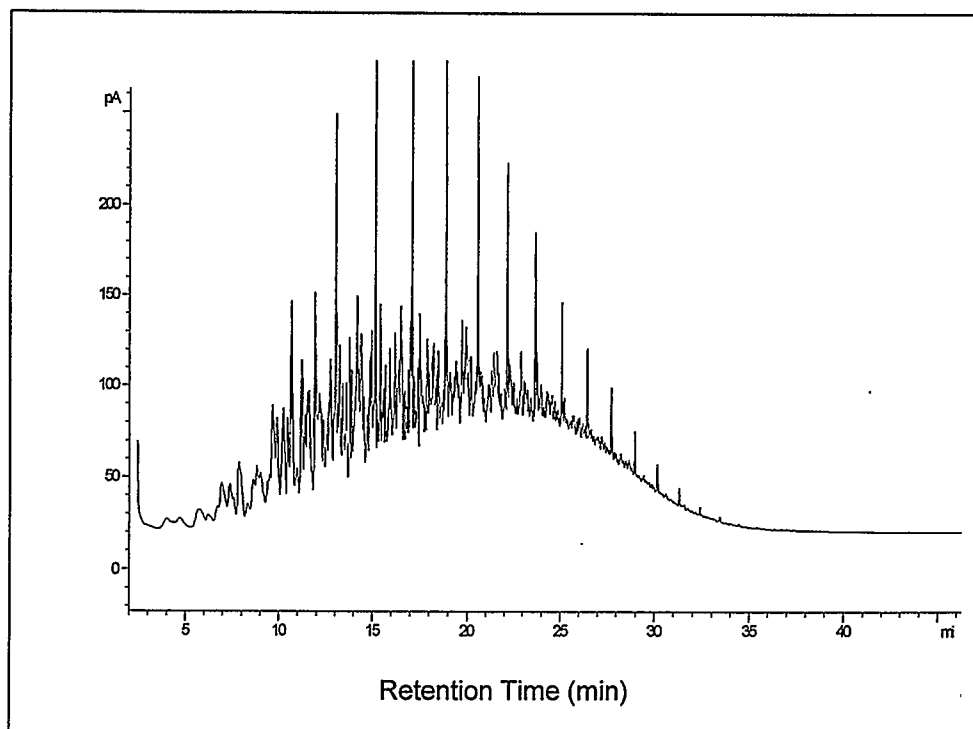
Figure 3.6: A typical GC/FID chromatogram of diesel fuel

Calibration of GC/FID system was performed to determine GC calibration curve and to check for linearity of a calibration data using the external standard procedure. DRO standards were prepared at six concentration levels. The concentrations between 200 mg/L and 10,000 mg/L corresponded to the expected range of concentrations found in samples. The calibration standards were run in GC using the exact method that would be used in the actual samples.

The stock solution of DCS and diesel was prepared in a 40 mL borosilicate vial at concentration of 10,000 mg/L and kept refrigerated at 4 C°. Standard solutions of various concentrations were made from this stock solution by adding the stock standard diesel solution to volumetric flasks and diluting to concentrations needed with solvent. On a regular basis, at least three standards were included for GC calibration purposes when soil samples were to be measured. Blanks were also included in the first run and occasionally thereafter every 10 runs to ensure that no diesel residual on laboratory equipment during GC operations existed. Figure 3.7 presents the calibration curve obtained experimentally. Linear regression of calibration standard GC response (R) against the known concentrations (mg/L) was assured considering the R^2 being 0.9999.

3.3.4.4 Quantification

Quantification was based on a direct comparison of the total GC/FID area of a sample to the total area of the DCS or self-prepared diesel standard within the retention time window. Integration of the total area was "baseline to baseline", defined as a flat baseline drawn parallel to the x-axis of chromatographic graph that includes all responses within the retention time window. In this study, placement of baseline was determined from the very onset of GC graph 0.1 minute after the running of GC. The integration showed satisfactory results because the baseline selected represented the lowest point in all GC graphs obtained.

The following equation was used to calculate the diesel concentration in soil samples based on the response of individual sample and the slope of the calibration curve:

$$C_s = (C_c \times R_s \times V_t \times D)/(R_c \times W_s) \tag{3.1}$$

where C_s = Concentration of sample, mg/kg

C_c = Concentration of standard injected, mg/L

R_s = Response for soil sample, area count

V_t = Volume of total extract, mL, which was 10 mL in the study

D = Dilution factor, value being 1 in the study, dimensionless

R_c = Response for the external standard

W_s = Total dry weigh of soil sample, gram

Note that C_c/R_c is the inverse of the slope of the calibration plot, and was determined from the regression equation.
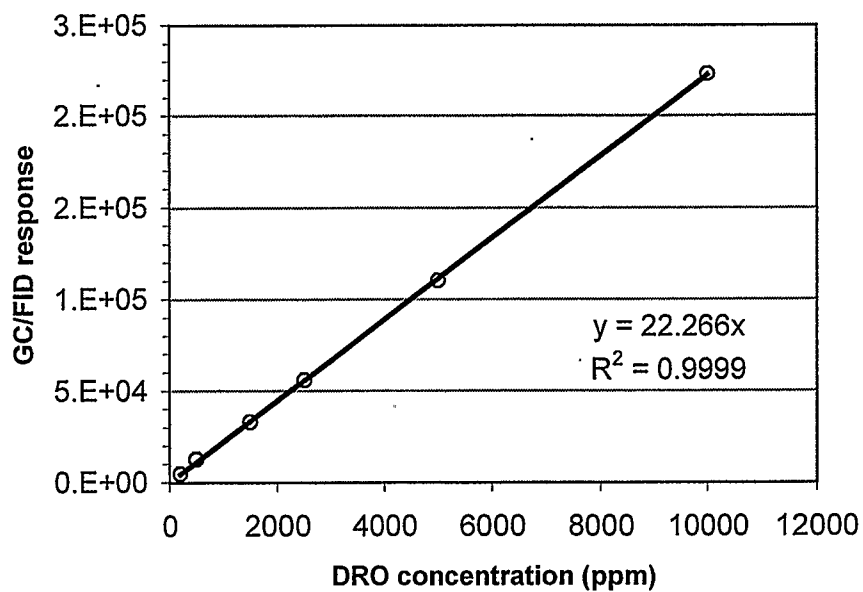

Figure 3.7: External calibration curve for GC/FID analysis

The actual concentration in the prepared contaminated soils was always lower than the nominal value due to losses caused by volatilization during solvent evaporation process and even in storage. In order to eliminate the effect of diesel loss prior to treatment, and especially to account for variability of extraction recovery efficiency, diesel residual in soil samples after treatment was represented in a normalized value, percent DRO removal/degradation, i.e., the ratio of diesel residual concentration to the concentration determined from a corresponding untreated contaminated soil samples. The normalized percent diesel removal/degradation in each sample was calculated according to the following formula, and the average value from the duplicate samples was reported:

$$\text{DRO removal/degradation (\%)} = [1-(C_i/C_0)] \times 100 \qquad (3.2)$$

in which C_i is the residual concentration of soil sample treated, and C_0 represents the concentration determined from respective untreated contaminated soil.

3.3.4.5 Fraction Approach for Analyzing TPH/DRO

TPH is a lump parameter that greatly simplifies the analysis required at contaminated sites, and thus has been adopted by most regulatory agencies as the single most important criteria as the remedial practice guidelines (AEHS, 2002). From risk assessment point of view, however, TPH approach does not address the complexity of hydrocarbon contamination in the subsurface. A fraction approach analysis was proposed and developed to estimate health risks based on the composition of a hydrocarbon source (Gustafson et al., 1997). The basic idea of the approach is to divide the hydrocarbon into measurable fractions (aliphatic and aromatic). In fact, one Alberta guideline incorporates fraction approach into its calculation of soil quality guideline for protection of potable groundwater (Albert Environment, 2001). Its two sub-fractions, F2 ($>C_{10}$-C_{16}) and F3 ($>C_{16}$-C_{34}), largely cover the range of diesel components, which is directly related to fraction division recommended by Total Petroleum Hydrocarbon

Criteria Working Group (Gustafson *et al.*, 1997). Table 3.3 gives the relevant defined fractions and some of their associated properties.

In this study, some chromatographs were analyzed using the fraction approach based on F2 and F3 sub-fraction in an attempt to show more clearly the destruction of certain diesel fractions rather than DRO. Integration events were designed according to the following retention time: from 10 minute to 22.2 minute for F2 sub-fraction, and from 22.2 minute to 37 minute for F3 sub-fraction, respectively. All quantifications of residual diesel in terms of F2 and F3 components were done within relevant retention time windows. The fraction approach can provide some more information about the treatment efficiency in terms of hydrocarbon composition and toxicity over TPH approach, and the extra information is expected to be helpful in site risk assessment (Brown *et al.*, 1999).

Table 3.3: TPHCWG hydrocarbon fractions and their associated properties

Equivalent Carbon No. Range	Solubility (mg/L)	Vapor Pressure (atm)	Log (Koc) (mg/L)
Aliphatic			
C5-C6	36.0	0.35	2.9
> C6-C8	5.4	0.063	3.6
> C8-C10	0.43	0.0063	4.5
> C10-C12	0.034	0.00063	5.4
> C12-C16	0.0076	0.0000048	6.7
> C16-C21	0.0000025	0.0000011	8.8
Aromatics			
C5-C7	1800	0.13	1.9
> C7-C8	520	0.038	2.4
> C8-C10	65	0.0063	3.2
> C10-C12	25	0.00063	3.4
> C12-C16	5.8	0.000048	3.7
> C16-C21	0.65	0.0000011	4.2
> C21-C35	0.0066	4.4×10^{-9}	5.1
> C21-C28	0.036	7.9×10^{-9}	4.8
> C28-C35	0.0012	2.4×10^{-11}	5.5

Adapted from *Brown et al., 1999*

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1   INFLUENCE OF IRON CATALYSTS

4.1.1 Fe^{2+} and Fe^{3+}

Figure 4.1 shows the H_2O_2 consumption when 10 mL of various concentrations of H_2O_2 was in contact with Ottawa sand without external iron amendment. The total iron of soil comprises of various type of iron oxides, including crystal and amorphous iron oxides. But the soluble portion was presumably the available iron that is active enough to promote Fenton's reaction. According to Table 3.1, 5 grams of Ottawa sand contain about 1.3 mg total iron (130 mg/L in 10 mL reagent solution). This amount of iron present in Ottawa sand was apparently not sufficient to substantially catalyze the decomposition of hydrogen peroxide, as demonstrated by less than 5% consumption of the original H_2O_2, regardless of hydrogen peroxide concentration. On the contrary, hydrogen peroxide of both concentrations of 5% and 20% was completely consumed in 20 minutes when 720 mg/L Fe^{2+} and Fe^{3+} were added, as shown in Figure 4.2. Within the first five minutes, minimum 94% and 86% of hydrogen peroxide were catalytically consumed by ferrous and ferric ions, respectively.

Iron in the form of soluble ferrous ion (Fe^{2+}) is commonly used as catalyst to promote decomposition of hydrogen peroxide that leads to the direct production of hydroxyl radicals in Fenton's reaction, as indicated in Equation 2.1. Hydroxyl radicals are the intermediate products that can possibly oxidize contaminants when in contact with organic contaminants. Ferric ion has also been used to catalyze the Fenton's reaction (Pignatello, 1992; Watts et al., 2000).
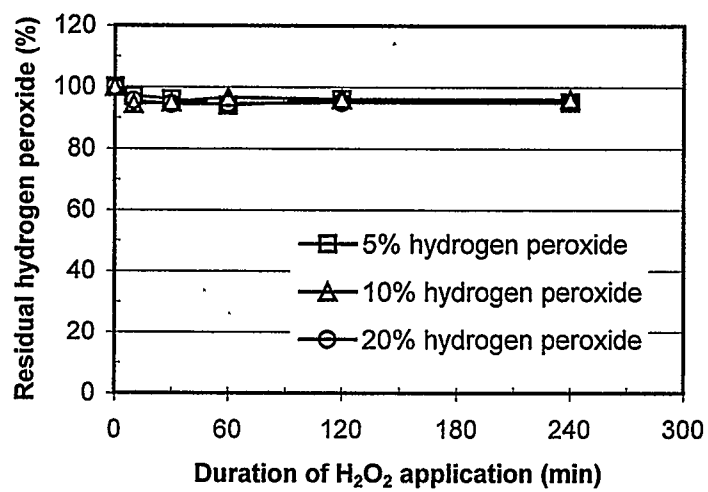
Figure 4.1: H₂O₂ consumption as a function of contact time in Ottawa sand without external iron amendment (5 g of Ottawa sand, 5,000 mg/kg diesel; 10 mL H₂O₂)
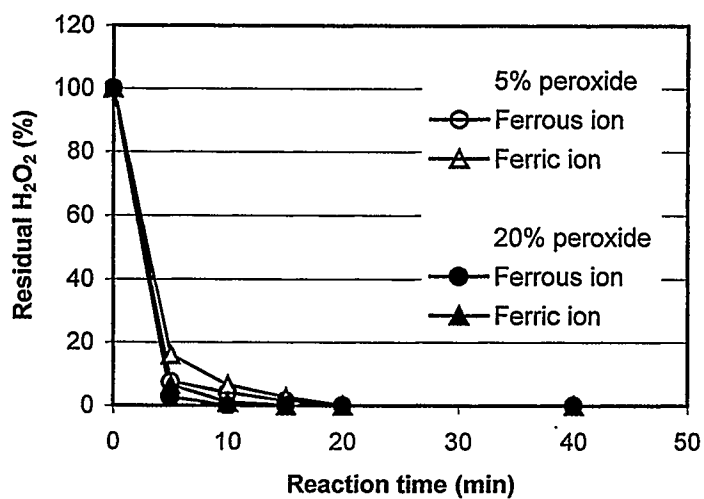
Figure 4.2: H_2O_2 consumption as a function of time with varying H_2O_2
concentrations (5 g of Ottawa sand, 5,000 mg/kg diesel;
10 mL H_2O_2; Fe^{2+} and Fe^{3+} concentration, 720 mg/L)

With the addition of ferric ion, hydroxyl radicals are produced in a two-stage process: ferric ion is first reduced back to ferrous ion by hydrogen peroxide and some short-lived reactants such as perhydroxyl radicals, $HO_2\cdot$ (Equation 4.1 and 4.2), followed by reaction between ferrous ion and hydrogen peroxide to produce hydroxyl radicals (Equation 2.1) (Huling *et al.*, 2000; Watts and Dilly, 1996):

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H^+ + HO_2\cdot \qquad (4.1)$$

$$HO_2\cdot + Fe^{3+} \rightarrow Fe^{2+} + O_2 + H^+ \qquad (2 \times 10^4 \text{ to } 1 \times 10^6 \text{ L/mol·s}) \quad (4.2)$$

The rate constant for reaction (4.1) is rarely reported, probably due to ambiguity with respect to ferric ion speciation (Huling *et al.*, 1998). But the results in Figure 4.2 indicate that H_2O_2 exhibited slower reaction rate with ferric ion than with ferrous ion. Higher H_2O_2 concentration promoted faster H_2O_2 disappearance regardless of ferrous and ferric ions, as evidenced by about 5% and 10% net increase using 20% H_2O_2 over 5% H_2O_2. This implies that application of higher concentration of hydrogen peroxide can initiate quicker generation of hydroxyl radicals, only at the expense of quick consumption or depletion of hydrogen peroxide. Complete consumption of H_2O_2 indicated that either the added soluble ions were sufficient to carry out the complete decomposition of H_2O_2, or the cycling back and forth between Fe^{3+} and Fe^{2+} in the intermediate reactions sustained the need of catalysts in Fenton's reaction.

Figure 4.3 further demonstrates the effect of ferric and ferrous ions on diesel degradation. The rate of diesel degradation showed similar trends regardless of different catalysts and varying hydrogen peroxide concentrations. Degradation efficiencies initially increased with the increase of iron concentrations, but remained flat after iron concentration reached 720 mg/L. Further increase in iron concentration up to 1,800 mg/L and 3,600 mg/L produced no significant increase in the treatment efficiencies. Lou and Lee (1995) also observed similar trend and suggested that the phenomenon was due to lack of available hydrogen peroxide that was depleted rapidly.
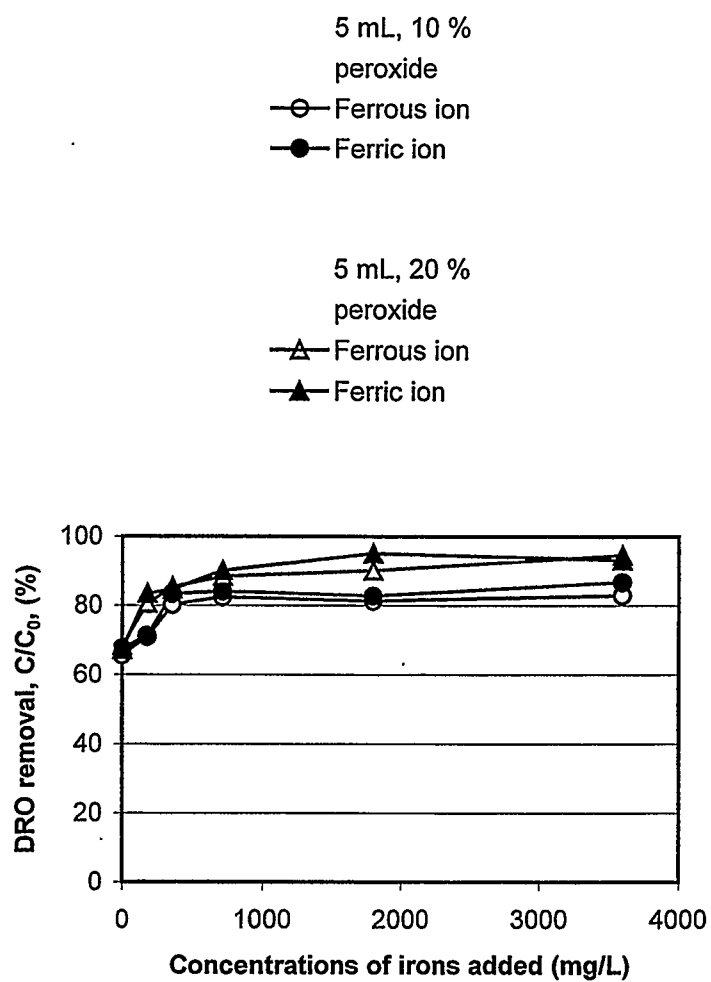
5 mL, 10 %
peroxide
—o— Ferrous ion
—●— Ferric ion

5 mL, 20 %
peroxide
—△— Ferrous ion
—▲— Ferric ion

Figure 4.3: DRO degradation as a function of ferrous and ferric ion concentrations (5 g of Ottawa sand, 5,000 mg/kg diesel)

Ferric ion catalyzed Fenton's reaction produced marginally higher values in terms of DRO removal than ferrous ion. More vigorous demand of hydrogen peroxide via ferrous ion is unfavorable to sustainable H_2O_2 presence, thus rendering hydroxyl radicals generated less opportunities to attack the target contaminants. In contrast, the slower consumption of hydrogen peroxide catalyzed by Fe^{3+} reduces the rate of H_2O_2 disappearance and allows for more close contact of oxidant with the target compounds. The difference caused by usage of Fe^{2+} and Fe^{3+}, however, was insignificant. In most field applications the valences of the iron salts do not make significant difference and ferrous iron salts are commonly used (Yin and Allen, 1999).

4.1.2 Mineral Iron Oxides as Catalysts

Regardless of the amount of soluble ferrous ion added and the concentrations of H_2O_2 applied, test results shown in Figure 4.4 indicate insignificant difference in DRO degradation between samples amended with soluble iron and those without external amendment. For example, 5 mL of 10% hydrogen peroxide degraded 34% and 13.7% of diesel for UC and SH soils without external amendment, whereas the corresponding average values of DRO degradation were 35.3% and 12.5% when the soils were amended with iron of varying concentrations. Increasing H_2O_2 concentration to 20% only increased the percentage diesel degradation, but made no significant difference between soils with and without iron amendment. The results demonstrated that external amendment of soluble iron would not affect the diesel degradation, and that naturally-occurring irons present in both UC and SH soils was able to provide sufficient catalytic activity for undergoing Fenton's reaction.

Mechanism of mineral iron as an effective catalyst is not well known, but the catalyses may occur in two ways (Tyre et al., 1991):
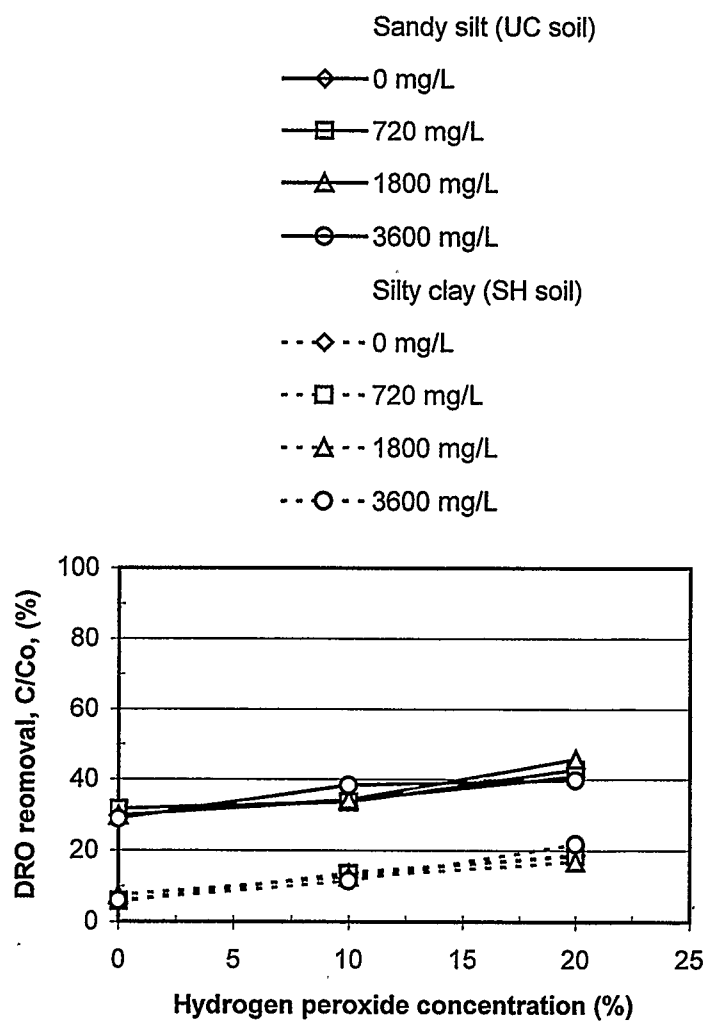
Sandy silt (UC soil)

—◇—0 mg/L

—▣—720 mg/L

—△—1800 mg/L

—⊖—3600 mg/L

Silty clay (SH soil)

- - ◇ - - 0 mg/L

- - ☐ - - 720 mg/L

- - △ - - 1800 mg/L

- - ○ - - 3600 mg/L

Figure 4.4: Effect of externally added Fe^{2+} on DRO degradation for UC and SH soils at varying H_2O_2 concentrations (5 g of soils, 5,000 mg/kg diesel; 5 mL H_2O_2 application)

- Mineral dissolution with release of soluble irons which then promote hydrogen peroxide decomposition; and

- Heterogeneous catalysis on mineral surfaces.

For mineral dissolution, the soil pH influences the state of iron salts. When iron salts dissolve at low pH, they are more active. But at high pH the dissolved irons may precipitate and become less active. For heterogeneous catalysis, hydrogen peroxide generates hydroxyl radicals and other reactive species in close proximity to adsorbed contaminants by reacting with irons on soil particle surface. In this way, hydroxyl radicals promote more effective desorption of contaminants adsorbed to soil particles and degrade them while minimizing the "scavenging" reactions that are associated with non-productive pathways.

In cases when iron amendment is needed in soil media, external soluble iron addition may not be as effective to attain homogenous distribution as in wastewater solutions. Using naturally-occurring iron as catalyst is especially beneficial in complex site conditions where homogeneous external iron addition is difficult. In field applications, the initial iron content of soil should be factored to estimate the dosing requirements of soluble iron. If the presence of mineral iron content is ignored, overdosing with iron amendment may reduce soil permeability due to iron complex formation and precipitation within pore space. Also, the presence of high levels of iron (specifically in ferrous form) has been reported to "scavenge" H_2O_2 due to undesirable reactions. Because the type and amount of local iron oxides vary from site to site, the effectiveness of the mineral irons has to be addressed prior to any potential usage. Nevertheless, most of the field practices are still using soluble iron as catalyst in Fenton oxidation (Yin and Allen, 1999; Wilson, 1995).

Figure 4.5 presents results of diesel degradation efficiencies as a function of ferrous ion concentration obtained in Ottawa sand spiked with 5,000 mg/kg diesel. For soils treated

with 5 mL of 5% and 10% hydrogen peroxide, the optimum amount of ferrous ion needed in Fenton's reaction was about 360 mg/L (360 mg/kg), whereas iron concentration of 720 mg/L (720 mg/kg) appeared to be sufficient to catalyze 5 mL of 20% H_2O_2. Iron amendment below these "critical" values decreased remediation efficiencies due to insufficient catalyst. Iron concentration above the optimum values generated no significant increase in diesel degradation as a result of complete consumption of hydrogen peroxide in the presence of excess amount of ferrous ions.

4.2   SOIL pH

Figure 4.6 shows how the two field soils, US and SH soils, resisted to the change in pH. The soil pH was around 6 after adding 0.4 mL of acid, and remained unchanged regardless of further attempt to acidify the soils. Ottawa sand, on the contrary, was readily adjusted to fairly low pH. The strong buffering capacities exhibited in UC and SH soils excluded the possibility of investigating pH effect on Fenton's reagent in the two field soils. Therefore, Ottawa sand was used to evaluate the effect of soil pH on the contaminant degradation. Results in Figure 4.7 show a general trend that diesel degradation was higher at low pH and decreased when pH of soil increased, an observation consistent with other researchers (Watts *et al.*, 1990; Bier *et al.*, 1999).

Soils buffer the acids by carbonates, silicate materials, organic matters and metal oxides in soil matrix. These processes are closely related to some soil properties such as texture, clay content and mineralogical nature of the soil. Generally, the higher the clay content in the soil, the greater its buffering capacity. SH and UC soils contain relatively high percentage of fine clay particles. Therefore, the strong buffering capacities exhibited in the two soils are reasonable.
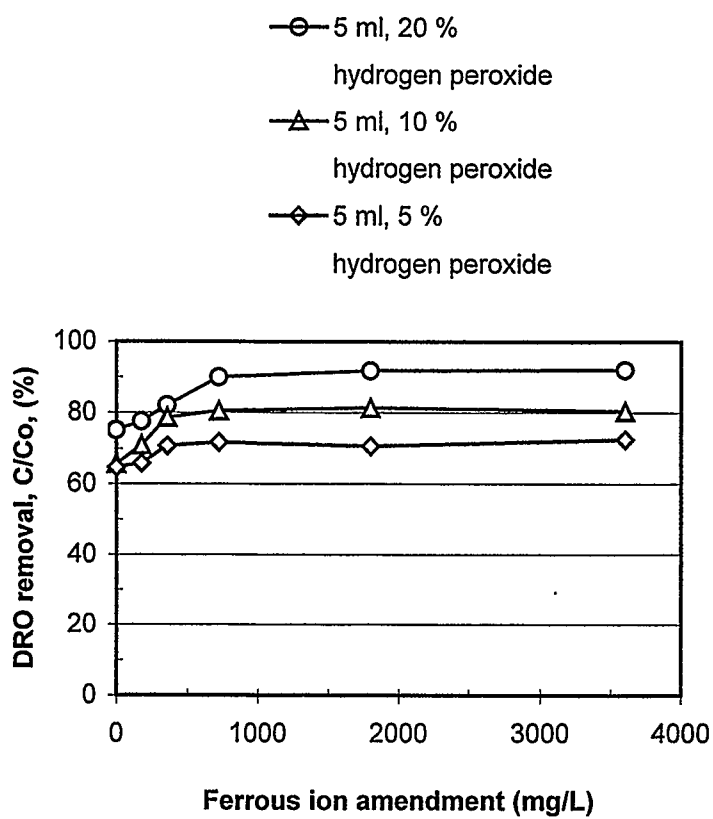
Figure 4.5: DRO degradation efficiency as a function of ferrous ion concentrations with varying H_2O_2 concentrations (5 g of Ottawa sand, 5,000 mg/kg diesel)
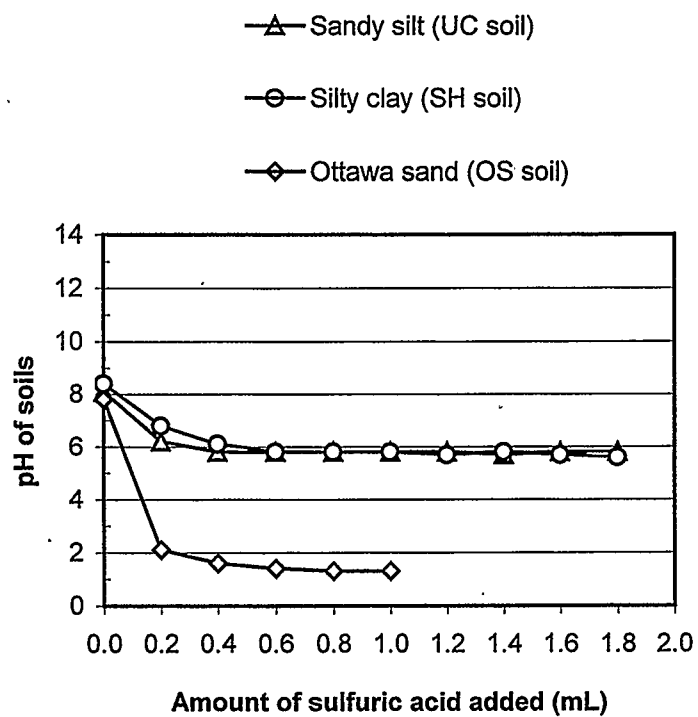
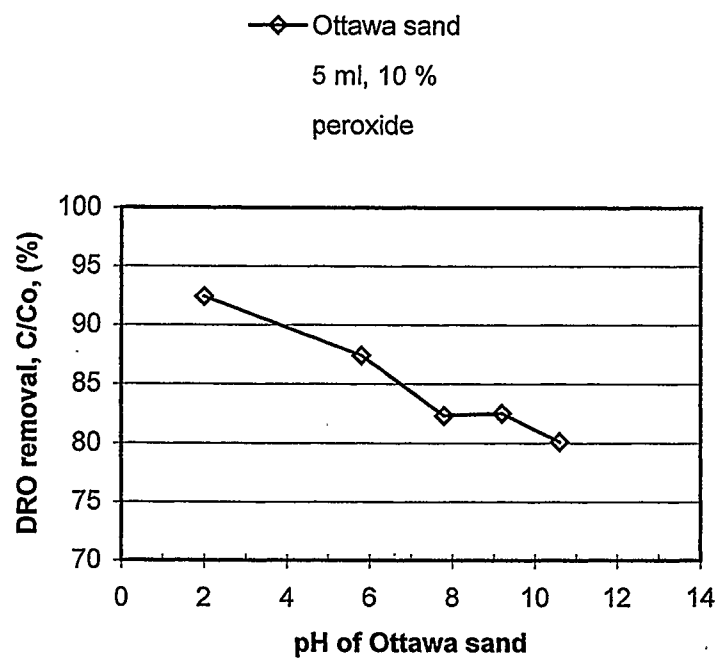Figure 4.6: Buffering capacities for SH, UC and OS soils

Figure 4.7: Effect of soil pH on DRO degradation efficiency
(5 g of Ottawa sand, 5,000 mg/kg diesel; Fe^{2+},
3,600 mg/L)

It is impractical in most cases to adjust the pH of soil to increase the treatment efficiency. Moreover, acidification could be polluting to the soils. Using chelating agent, an organic compound in which atoms form more than one coordinate bond with metals in solution, to catalyze hydrogen peroxide at neutral pH is promising (Nesheiwat and Swanson, 2000).

4.3   DIESEL DEGRADATION IN MODIFIED FENTON'S REACTION

4.3.1   Diesel Removal by Water Phase

Figure 4.8 shows the amount of water removal as a function of volume of water applied for the two field soils. About 30% and 20% of diesel was removed by water for UC and SH soils when 60 mL of water was used. Even with application of 5 mL of water, water dissolution/desorption led to about 20% and 5% DRO reduction for UC and SH soils, respectively. The DRO removal by water was obviously soil texture dependent. Sandy silt showed higher diesel removal by water than silty clay.

Diesel is a mixture of multiple compounds and certain lighter components are less hydrophobic and more soluble in water. Calculation based on diesel aqueous solubility (8.2 mg/L in distilled water) gives around 2% diesel dissolution in 60 mL distilled water, which is about an order of magnitude less than the result from the tests. Niven and Khalili (1998) once reported measured diesel solubility of 135 mg/L from a long-duration mixing experiment, a value much higher than the diesel solubility given above. Though distilled water was used, the distilled water was no longer as pure as it used to be after in contact with soil. Some organics and inorganics would dissolve in the water. As a result, the apparent aqueous solubility of the water in the soil-slurry would increase. In addition, diesel discretely and homogeneously distributed in dry soil, as in the case of this study, has more intimate contact with water. Some loosely adsorbed diesel droplets or ganglia in soil matrices may be dislocated by water. The displaced
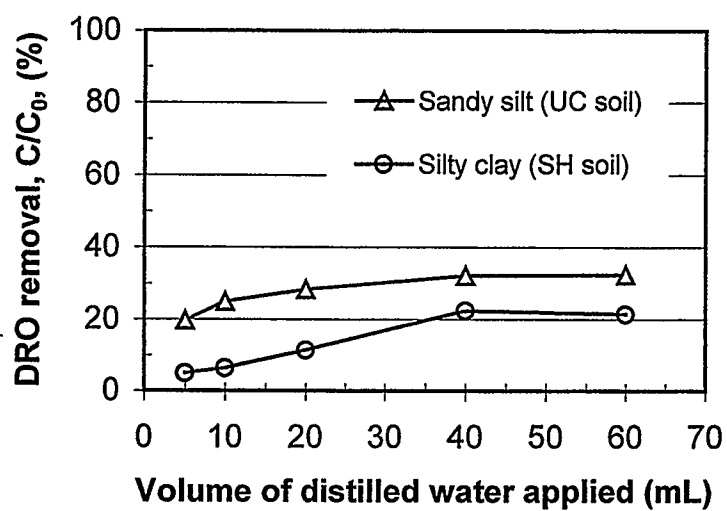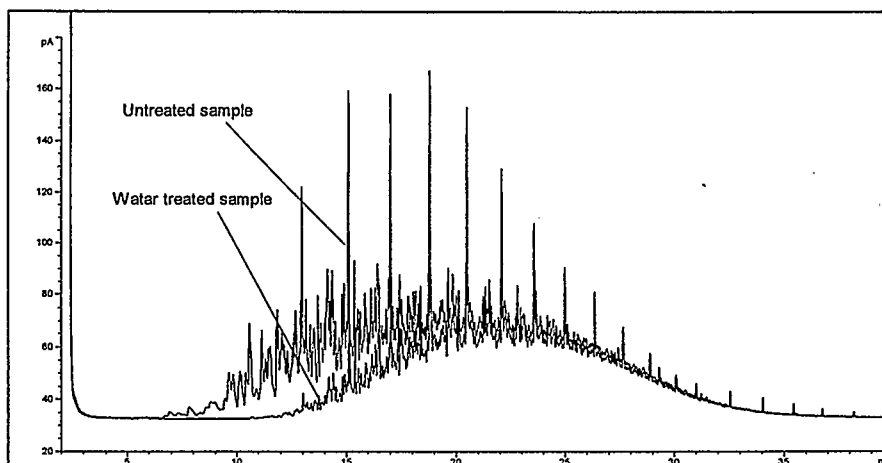
Figure 4.8: Amount of water removal as a function of water volume applied (5 g of soils, 5,000 mg/kg diesel)

diesel becomes more likely to dissolve in water, or present in NAPL state in water phase that may be flushed out of soil matrix later during experiment. These processes may also increase the apparent diesel solubility. The results of significant diesel removal by water phase are in agreement with observation by Kakarla (1997). They found 10% hexadecane (log K_{ow} = 9.07, 0.00005 mg/L in aqueous solubility) was desorbed merely by deionized water.

Qualitative demonstrations in GC/FID chromatograms are shown in Figure 4.9 (a) and (b). These humps in the figures represent the mass of residual diesel in treated and untreated soil samples. The differences between the two humps indicate the portion of diesel removed by water phase. Both UC and SH soils exhibited loss of diesel when in contact with water, though the degrees of reduction varied. Note that SH soil showed less diesel reduction than UC soil because of different soil textures. In SH soil, diesel is more likely adsorbed on soil particles or trapped in the micropores, and this makes displacement of diesel by water molecule from the sorption sites and the micropores much more difficult.

Initial diesel concentration in soils also influences the percent removal of diesel by water phase. Soils with low initial diesel concentration are susceptible to high percent removal, as shown in Figure 4.10. Because diesel dissolution is a major process for phase separation, the amount of diesel dissolved is associated with the volume of water used. The approximate amount of diesel removed in the test results in higher values for soils with less total mass of diesel (low initial diesel concentration) in terms of percent removal. Results in Figure 4.10 again revealed that percent diesel removal was noticeably influenced by soil texture. SH soil, with higher organic matter content and higher clay content, exhibited less diesel removal than UC soil, an indication that diesel was more tightly adsorbed on soil particle and/or trapped in soil micropores

(a)
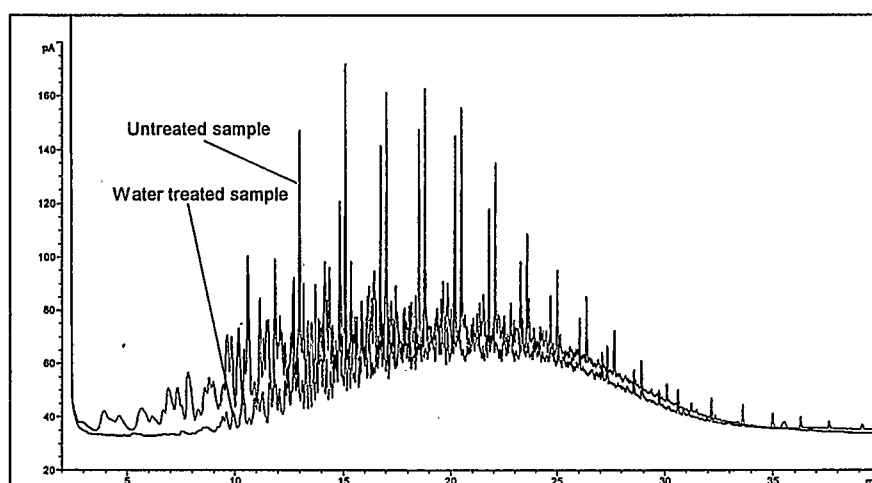
(b)

Figure 4.9: Typical chromatographs showing diesel loss due to water removal (a) sandy silt, or UC soil (b) silty clay, or SH soil
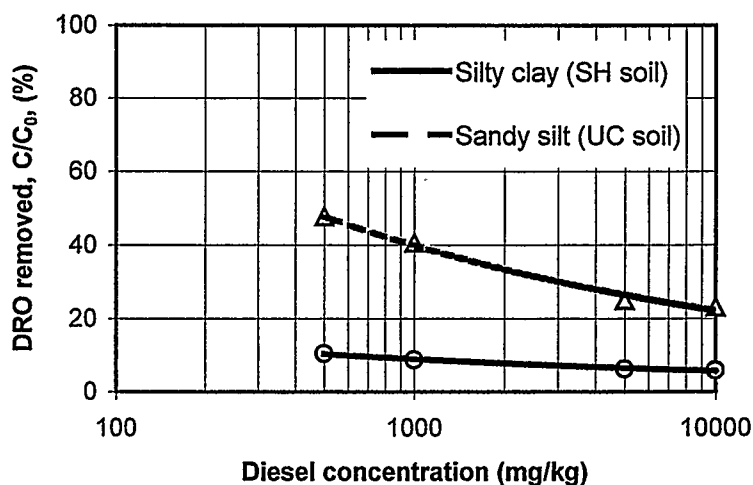
Figure 4.10: Percent DRO removal by water as a function of initial
diesel concentrations in soils (5 g soil, 10 mL water)

4.3.2 Diesel Degradation in Modified Fenton's Reaction

Contaminant degradation in modified Fenton's reaction depends on several major process variables, including H_2O_2 concentration and volume, initial diesel concentration, soil pH, iron catalyst and soil texture. Since soil pH adjustment and external iron amendment were insignificant to remediation efficiencies of SH and UC soils, only H_2O_2 concentration, volume applied and soil initial diesel concentrations were assessed experimentally in this study.

4.3.2.1 Diesel Degradation Efficiency

Figure 4.11 and 4.12 present the percent DRO removals of 5 grams of UC and SH soils treated with varying concentrations and volume of hydrogen peroxide. When using 10% and 20% hydrogen peroxide, the percentage diesel removals for both UC and SH soils increased with the increase of H_2O_2 volume up until 20 mL. Further increase in H_2O_2 volume to 40 mL and 60 mL resulted in insignificant increase in diesel degradation. With 5% H_2O_2 concentration, the percentage diesel removals showed continuous increase up to 40 mL application of H_2O_2. Likewise, H_2O_2 volume increases beyond 40 mL made not much difference in terms of percentage diesel removal. The highest diesel degradation efficiencies in all cases, about 70% and 40% for UC and SH soils, were attained when 60 mL of 20% H_2O_2 was used. However, applications of 20 mL of 10% and 40 mL of 5% H_2O_2 achieved diesel degradation efficiencies of similar magnitude, about 57.4%, 61.2% for UC soil, and 32.8% and 35.7% for SH soil. As 5 g of soil was used in the tests, it is worth noting that use of 20 mL of 10% H_2O_2 and 40 mL of 5% H_2O_2 per 5 grams of soil (or 4 mL of 10% and 8 mL of 5% H_2O_2 per gram of soil) is equivalent to about 2:1 (H_2O_2 : soil) by volume with 20% hydrogen peroxide. The 2:1 ratio is less than 7:1 ratio found in field application by Mahmoud (2001), indicating more efficient use of H_2O_2 in laboratory tests than in field application. The difference may lie in the fact that loose soils were used in the laboratory study whereas more compact, undisturbed soils were treated in complex field conditions.

The degree of diesel degradation differed with respect to concentration/volume of hydrogen peroxide and soil texture. The UC soil is generally more prone to be more effectively treated with hydrogen peroxide than SH soil. The low diesel degradation efficiencies for UC soil reflected to some extent the tight adsorption of diesel onto dry soil particles and relatively low organic matter content. Some competing and non-productive reactions during H_2O_2 decomposition process also reduce the ultimate treatment efficiency of the oxidation process.
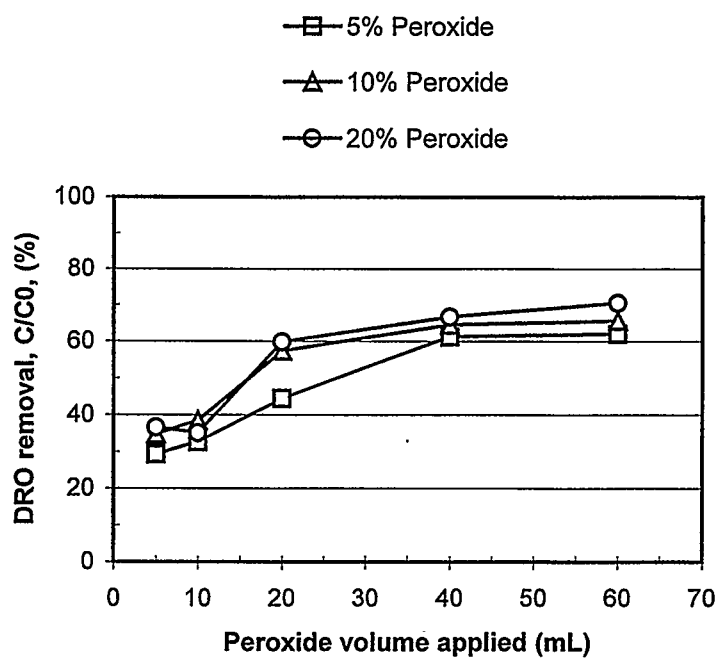
Figure 4.11: Percent DRO removal as a function of volume of

H_2O_2 of varying concentrations for UC soil
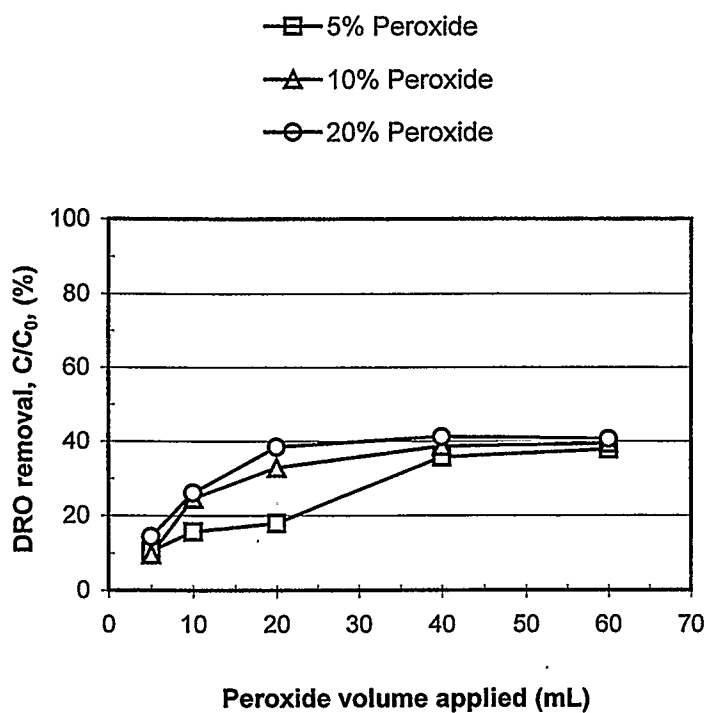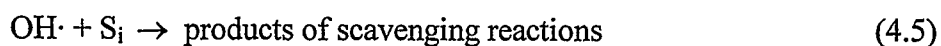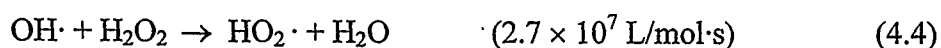
(5 g of soil, 5,000 mg/kg diesel)

Figure 4.12: DRO percent removal as a function of volume of
H$_2$O$_2$ of varying concentrations for SH soil
(5 g of soil, 5,000 mg/kg diesel)

The production of hydroxyl radicals in Equation 2.1 is a relatively slow process with a rate constant varying between 53 and 76 L/mol·s. But during catalyzed decomposition of high concentration hydrogen peroxide, numerous competitive reactions take place to consume hydrogen peroxide and "scavenge" hydroxyl radicals. These reactions include Equation 4.1, 4.2 and the followings (Huling *et al.*, 2000; Watts and Dilly, 1996):

$$OH\cdot + Fe^{2+} \rightarrow Fe^{3+} + OH^- \qquad (2.3 - 5 \times 10^8 \text{ L/mol·s}) \qquad (4.3)$$

$$OH\cdot + H_2O_2 \rightarrow HO_2\cdot + H_2O \qquad (2.7 \times 10^7 \text{ L/mol·s}) \qquad (4.4)$$

$$OH\cdot + S_i \rightarrow \text{products of scavenging reactions} \qquad (4.5)$$

where S_i is scavenger species that compete with target compounds. These reactions involve the production of perhydroxyl radical ($HO_2\cdot$) and quenching of OH· by H_2O_2 (Equation 4.1 and 4.4), cycling of ferrous ion (Fe^{2+}) and ferric ion (Fe^{3+}) by H_2O_2 and some short-lived reactants (Equation 1.1, 4.1, 4.2 and 4.3), and other OH· scavenging reaction (Equation 4.5).

Hydrogen peroxide at high concentrations can be a significant sink for OH·. According to Equation 4.4, OH· is also kinetically favorable in participating in the reaction process to generate $HO_2\cdot$. Equations 4.4 and 4.2 are chain reactions. Hydroxyl radicals generated from Equation 2.1 serve as chain initiator, whereas the perhydroxyl radicals produced in Equation 4.4 serve as chain carrier. Figure 4.13 shows the measured amount of oxygen generated in experiments of both UC and SH soils treated with 10 mL of 10% hydrogen peroxide. The relatively large amount of oxygen produced in some tests indicated the validity of the chain reactions that are scavenger of hydroxyl radials and significant sink for H_2O_2 depletion. Fenton's reaction is highly exothermic. Soil-slurry temperature of more than 90°C was observed in soil treated by 10 mL of 20% H_2O_2. The high tempera-
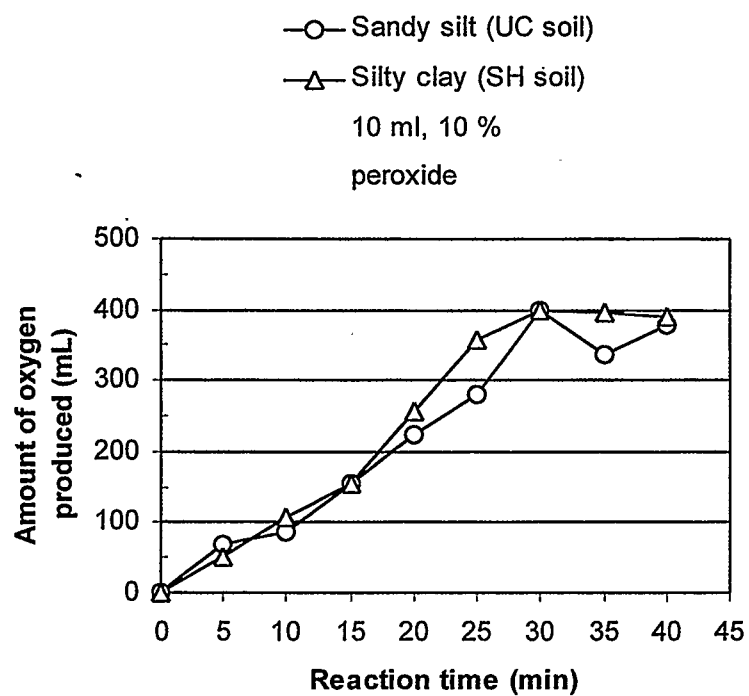
Figure 4.13: Amount of oxygen generated during Fenton's reaction
for UC and SH soils (5 g of soil, 5,000 mg/kg diesel)

ture accelerates decomposition of hydrogen peroxide, and therefore decreases the efficiency of H_2O_2 utilization (Nesheiwat and Swanson, 2000). In addition, inorganic reactants other than iron oxyhydroxides can also consume H_2O_2. Fenton-like cycling between the Mn^{2+} and Mn^{4+} oxidation states occurs via reaction with H_2O_2, but does not yield OH· (Huling *et al.*, 2000). Tang and Huang (1996) recommended moderate application of hydrogen peroxide (volume and concentration) in Fenton's reaction to achieve cost-effective remediation.

Figure 4.14 shows the relationship between soil diesel concentration and percent diesel degradation for UC and SH soils treated by 5 mL of 5% hydrogen peroxide. Soils with lower initial diesel concentration were amenable to higher DRO degradation than soils of higher diesel concentration. But the higher degradation efficiencies do not necessarily correspond to more mass of diesel destroyed. At higher initial diesel concentration, say over 5,000 mg/kg, only marginal difference in DRO degradation was observed. Similar trend was also observed in Figure 4.15 when 10 mL of 10% hydrogen peroxide was applied. The difference lies in the degree of degradation.

4.3.2.2 Diesel Mineralization

As shown in Figure 4.16, approximately 2.3 mL and 5.1 mL of carbon dioxide were generated for 5 grams of UC and SH soils treated with 10 mL of 10% hydrogen peroxide, respectively. Meaningful evaluation of contaminant oxidation in Fenton's reaction requires understanding of reaction pathways, which is not feasible for a mixture of hundreds of individual components such as diesel. As a result, assessment of diesel mineralization was attempted in this study using the amount of carbon dioxide generated in Fenton's reaction based on an arbitary reaction pathway given by Chen *et al.* (1998).
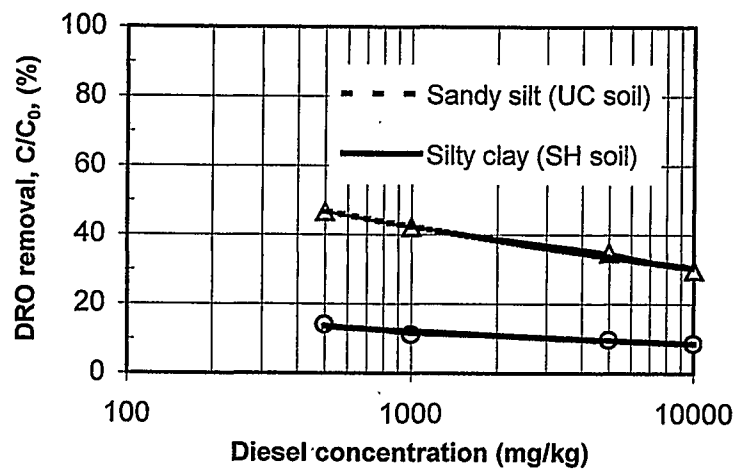
Figure 4.14: DRO degradation as a function of soil initial diesel concentrations for UC and SH soils (5 g of soil, 5 mL 5% H_2O_2)
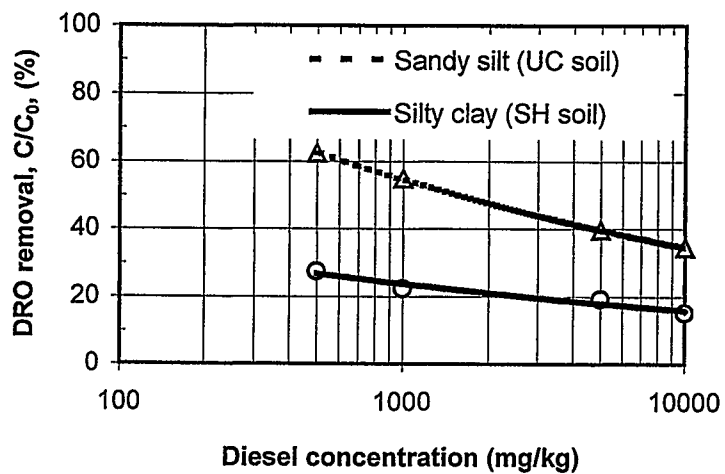

Figure 4.15: DRO degradation as a function of soil initial diesel concentrations for UC and SH soils (5 g of soil, 10 mL 10% H_2O_2)

According to Chen *et al.* (1998), heptadecane ($C_{17}H_{36}$), a normal alkane, was chosen to represent diesel simply because the molecule weight of $C_{17}H_{36}$ is approximately the average molecular weight of diesel fuel (California DHS, 1991). They also gave a reaction pathway for diesel in contact with hydrogen peroxide as shown in the following equation:

$$C_{17}H_{36} + 52\ H_2O_2 \rightarrow 17\ CO_2 + 70\ H_2O \qquad (4.6)$$
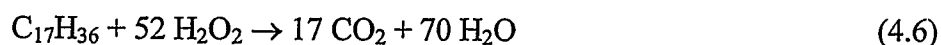
Based on Equation 4.6, the amount of $C_{17}H_{36}$ (diesel) in soils oxidized was back-calculated from the measured mass of carbon dioxide, which turned out to be 1.39 mg and 3.05 mg diesel in UC and SH soils, respectively. As 5 grams of soils (5,000 mg/kg) contain nominally about 25 mg of diesel, the respective percent diesel mineralized was 5.6% and 12.3% of the total diesel present in UC and SH soil matrices. These values are not in agreement with the experimental results, which corresponded to 33.8% and 24.5% degradation for UC and SH soils under the premise that all removed diesel was completely mineralized into gaseous carbon dioxide. Also according to Equation 4.6, about three moles of hydrogen peroxide are needed to óxidize one mole of $C_{17}H_{36}$ (diesel). Hence, production of 2.3 mL (1.36 mg) and 5.1 mL (3.05 mg) of carbon dioxide required about 100 mg and 220 mg of H_2O_2. These were much less than 10 mL of 10% hydrogen peroxide used in tests, which was equivalent to 1,000 mg hydrogen peroxide.

The disparities between the measured amounts of CO_2 generated, H_2O_2 used in tests and the relevant calculated values in line with Equation 4.6 may be attributed to various reasons. The arbitrary oxidation pathway, on which calculations was based, does not reflect the role of hydroxyl radical that is of essence in Fenton's reaction. Rather, it hypothesizes direct oxidation of $C_{17}H_{36}$ by hydrogen peroxide, which is a less powerful oxidant than hydroxyl radicals. Other factors, such as competing reactions accompany-
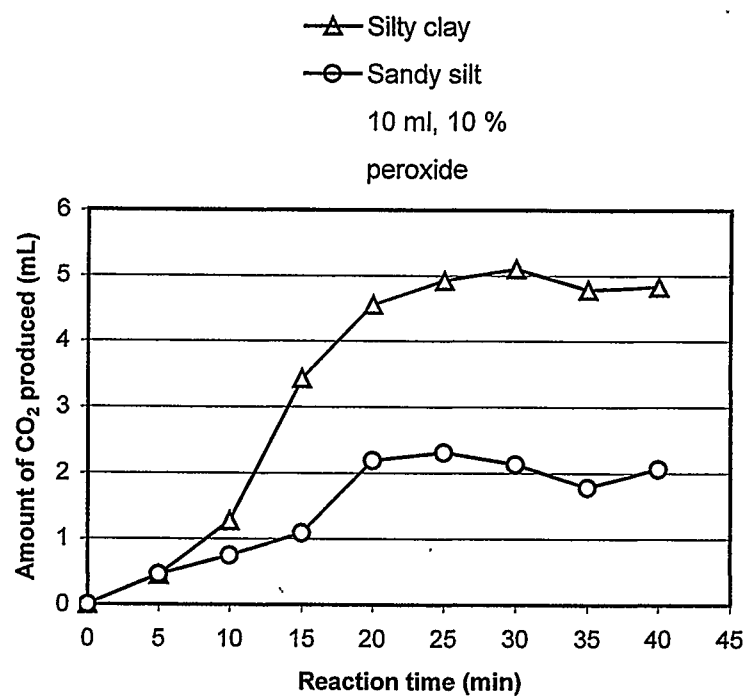
Figure 4.16: Amount of carbon dioxide generated during Fenton's reaction for UC and SH soils (5 g of soil, 5,000 mg/kg diesel)

ing Fenton's reaction and complexity associated with soil media, are also accountable. The generation of carbon dioxide during treatment with catalyzed hydrogen peroxide, nevertheless, indicated that diesel in soil matrices were oxidized by hydroxyl radicals.

4.3.2.3 Treatment Stoichiometry

Figure 4.17 and 4.18 present the reverse of diesel treatment stoichiometry, ratio of moles (mass) of diesel degraded to moles (mass) of H_2O_2 consumed, as a function of H_2O_2 volume applied based on experimental results. Applications of 20 mL of 20% H_2O_2, 20 mL of 10% and 40 mL of 5% H_2O_2 promoted more effective oxidation regardless of soil type. The average percent diesel removals were about 35% reduction for SH soil, and 60% reduction for UC soil. Correspondingly, the inverse of treatment stoichiometries were about 400:1 (20 mL of 20% H_2O_2), 245:1 (20 mL of 10% H_2O_2) and 232:1 (40 mL of 5% H_2O_2) for SH soil, whereas for UC soil the values were 255:1 (20 mL of 20% H_2O_2), 135:1 (20 mL of 10% H_2O_2) and 124:1 (40 mL of 5% H_2O_2) by mass, respectively. These values of stoichiometry, ranging from 1:124 to 1:400, are in good agreement with the stoichiometries calculated as 1:140 and 1:370 by weight observed by Watt *et al.* (1999) using sand and a clayed soil.

As expected, the maximum treatment efficiencies corresponded to the soil samples treated with 60 mL of 20% H_2O_2, accomplishing about 70% and 40% degradation in UC and SH soils, respectively. But the maximum treatment efficiencies did not correspond to optimum treatment efficiencies in terms of treatment stoichiometry. The optimum stoichiometry was related to soil samples treated with small volume of less concentrated hydrogen peroxide, as shown in Figure 4.17 and 4.18. However, these treatment stoichiometries often led to low percentage diesel degradation. Tradeoff exists between high treatment stoichiometry and low diesel percentage degradation. Combination of 40 mL of 5% hydrogen peroxide is preferred stoichiometrically, followed by 20 mL of 10% H_2O_2 with marginal difference. These were equivalent to 8 mL of 5% H_2O_2 per gram of soil or 4 mL of 10% H_2O_2 per gram of soil.
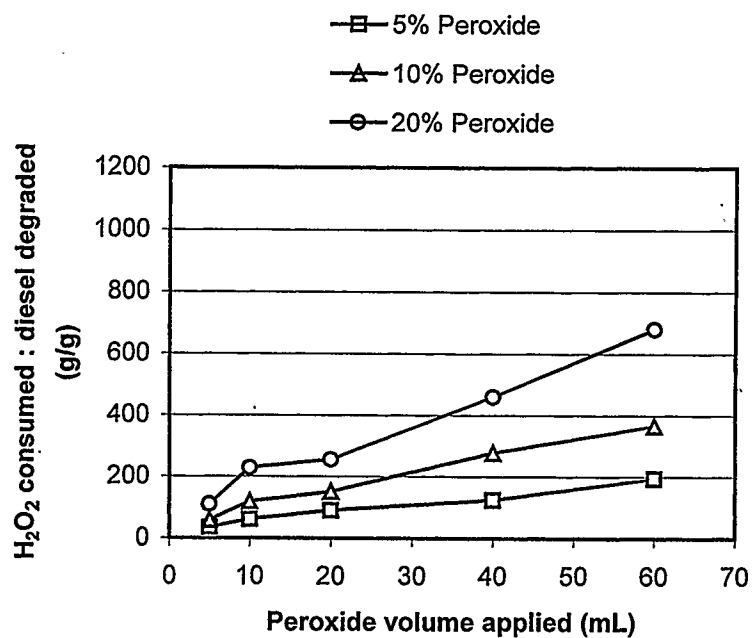
Figure 4.17: Hydrogen peroxide consumed / diesel degraded as s function of H_2O_2 volume applied for UC soil (5 g of soil, 5,000 mg/kg diesel)

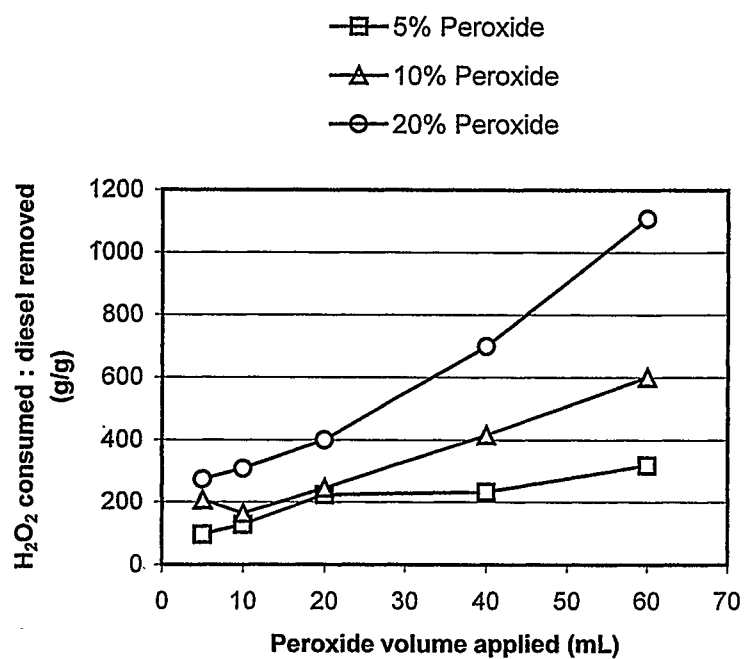—☐—5% Peroxide
—△—10% Peroxide
—⊖—20% Peroxide

Figure 4.18: Hydrogen peroxide consumed / diesel degraded as s function of H₂O₂ volume applied for SH soil (5 g of soil, 5,000 mg/kg diesel)

4.4 ENHANCEMENT OF DISEL DEGRADTION IN FENTON'S REACTION

4.4.1 Surfactant

Surfactants are compounds containing a hydrophilic and a hydrophobic (or lipophilic) group. They are popular enhancer to crude oil recovery and also used in soil remediation, such as in soil washing. They mobilize contaminants in soil matrix primarily by increasing the apparent solubility of the contaminant in water. An important index for surfactant is critical micelle concentration (CMC), the concentration at which micelles start to form and the effective solubility of contaminant begins to increase. SDS has well-known properties and is available as a sodium salt. CMC for SDS varies from 8.0 mM/L to 8.2 mM/L, equivalent to about 0.24% (w/w) (Paya-Perez *et al.*, 1996; Gabr *et al.*, 1998). Figure 4.19 presents the molecular as well as schematic structure of SDS micelle in spherical form often observed in SDS solution.
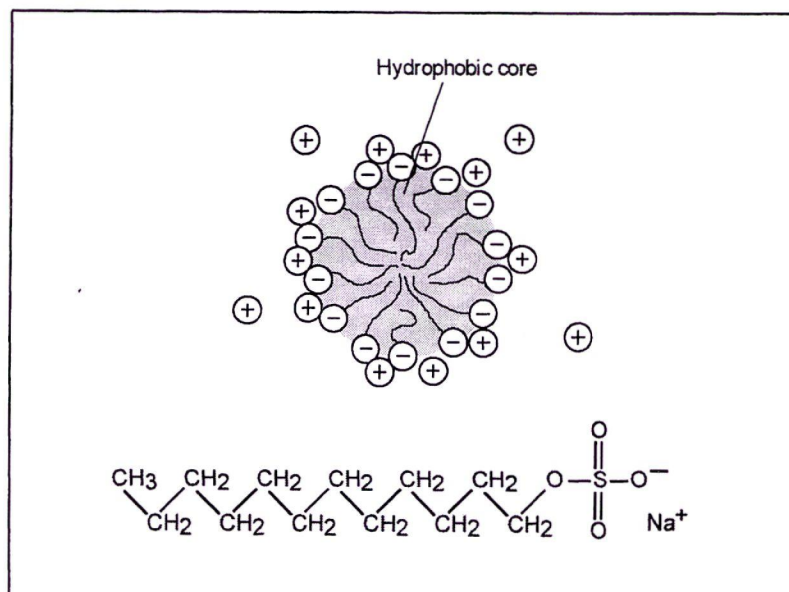

Figure 4.19: Molecular structure and schematic structure of a spherical SDS micelle as a slice through the core

(Modified after *Kline et al., 2001*)

Test results shown in Figure 4.20 and 4.21 indicate that DRO removal efficiencies in soils pretreated with SDS followed by treatment of Fenton's reagent were related to SDS concentrations. The observations are generally in accordance with surfactant mechanism. In samples with 0.1% SDS, little change in DRO degradation was observed as compared with that in the control samples. As SDS concentration was increased to 0.5%, a level higher than CMC, DRO removal efficiencies increased significantly. The net enhancements over control samples were about 13% and 6% for UC and SH soils treated with 5% H_2O_2, and about 17% and 9% for UC and SH soils treated with 10% hydrogen peroxide. When soil samples were treated with higher SDS concentration (1% and 2%), maximum net increases in DRO removal efficiencies were achieved, i.e., 28% for US soil and 15% for SH soil, respectively. These values, nevertheless, did not show proportional increases with respect to SDS concentrations.

Results of possibly further enhancement by shaking during SDS treatment are given in Figure 4.22. SH and UC soil samples with 30 minute shaking treatment exhibit about 2.2% to 5.2% net percent increase in diesel degradation over those without shaking. Prolonged shaking did not lead to more diesel degradation, as indicated by the flattened curves in Figure 4.22. The less-than expected changes in diesel degradation when surfactant was subjected to prolonged shaking may be due to the increase of SDS viscosity. When micellar solutions are converted into micro-emulsions in the aqueous system, the viscosities of these products are generally much greater than that of water (Gabr *et al.*, 1998). The viscous SDS solution in soil diminished the agitation effect by the shaker, thus decreasing the movement of SDS in soil pores. Less intimate interactions between SDS micelles and diesel adsorbed on soil particles reduce SDS efficiency. Also, possible diesel evaporation enhanced due to prolonged shaking was probably hampered by limited mass transfer of diesel vapor from soil to headspace air in the vials, as a result of the aqueous media (SDS) in between.
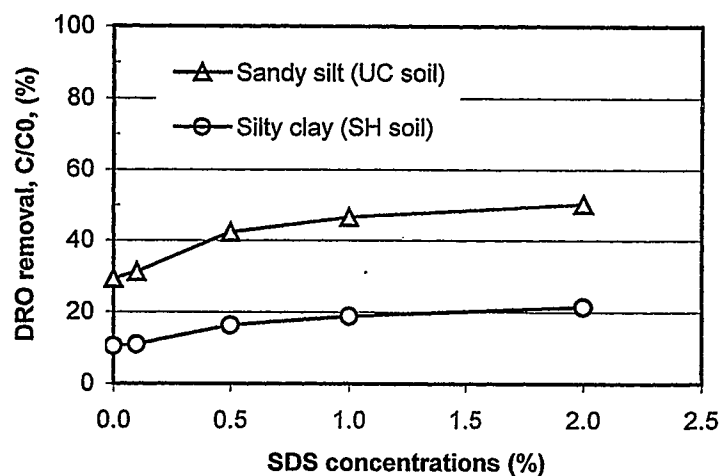
Figure 4.20: DRO removal as a function of SDS concentration (10 mL, 5% H_2O_2)
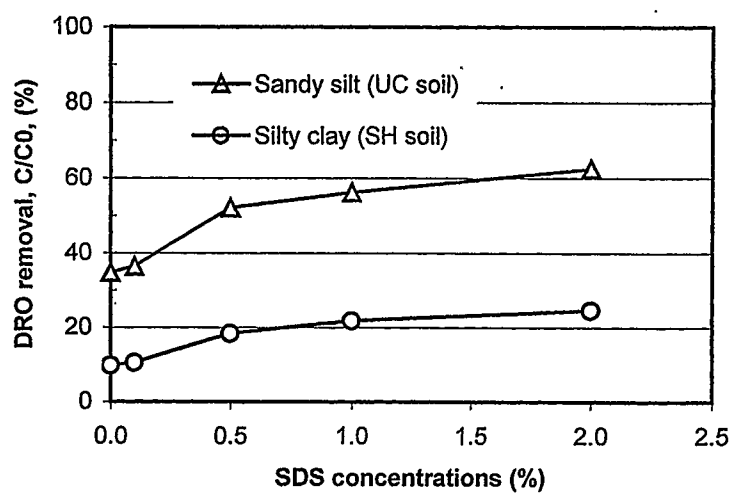
Figure 4.21: DRO removal as a function of SDS concentration (10 mL, 10% H_2O_2)

—△— UC shaked

—▲— UC control
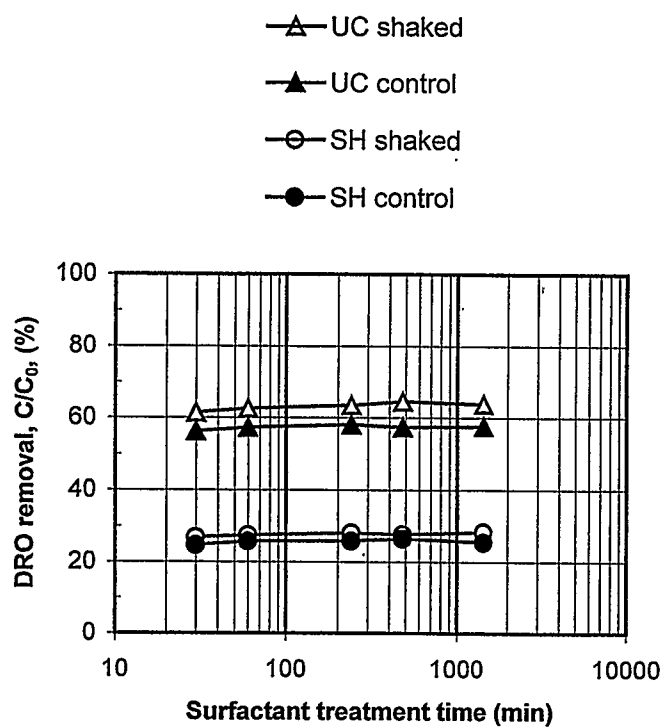
—⊖— SH shaked

—●— SH control

Figure 4.22: Effect of shaking of soil-surfactant system on the percent
diesel degradation for the UC and SH soils (5 g of soils,
5,000 mg/kg diesel; 10 mL 10% H_2O_2; 1.0% SDS)

The enhancement in diesel degradation was due to increase of water solubility of the heavier, more hydrophobic components in diesel by SDS pretreatment. GC/FID analyses using F2 and F3 fraction approach showed more fraction of heavier diesel components were removed from soil matrices as a result of effective SDS treatment, as indicated in Figure 4.23 and 4.24. For UC soil, the ratio of lighter components (F2) removed to the total components (F2+F3) removed decreased from about 85% to 63% at low (0.1%) or no SDS addition to an average of 63% at 0.5%, 1% and 2% SDS concentrations, whereas more heavier portions of diesel degraded were found to increase from around 15% (no SDS treatment or 0.1% SDS concentration) to an average of 36% (0.5%, 1% and 2% SDS concentrations). Similar trends were observed for SH soil in terms of SDS enhancement. When SDS concentrations were higher than the CMC, about 20% of the total diesel removed was from fraction of heavier components (F3/(F2+F3)). This translated into nearly double percentage increase in degrading heavier diesel components over untreated (no SDS treatment) or ineffectively treated soils (0.1% SDS concentration). Pretreatment with surfactant such as SDS can enhance the desorption of more heavier and hydrophobic portions of diesel that are otherwise less desorbed and degraded by Fenton's reagent.

4.4.2 Multiple Application of Hydrogen Peroxide

For both UC and SH soils, multiple applications of H_2O_2 showed noticeable increase in percent diesel degradation over one-time treatment, as demonstrated in Figure 4.25 and 4.26. The second sequential application of H_2O_2, up to 10 mL in total, brought about 30% and 44% overall diesel oxidation for SH and UC soils. These translated into net increases of about 30% over that of the one-time addition for the two soils. Additional sequential applications of H_2O_2 (total volume up to 20 mL), though increased overall degradation efficiencies, resulted in less net increases as compared with the two-time treatment. For example, 20 mL multiple applications merely increased the diesel removed by about 20% in both UC and SH soils.

5% peroxide

SDS level

⊡ 0.0

▧ 0.1%

▤ 0.5%

▨ 1.0%

▦ 2.0%

Figure 4.23: Percentage of F2 fraction degraded with respect to total degradation for both UC and SH soils (5 g of soils, 5,000 mg/kg diesel; 10 mL H_2O_2)

5% peroxide

SDS level

0.0

0.1%
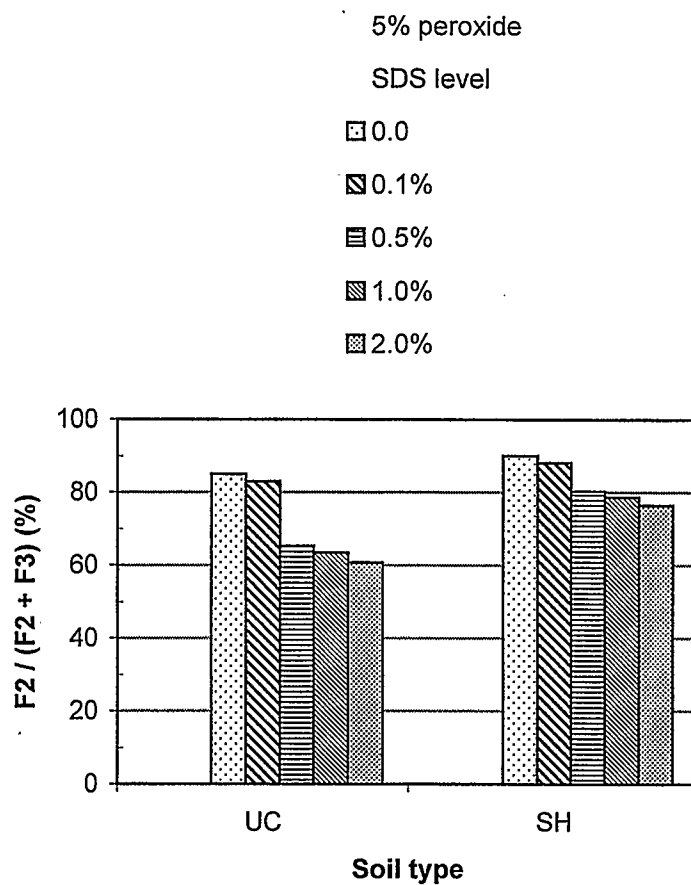
0.5%

1.0%
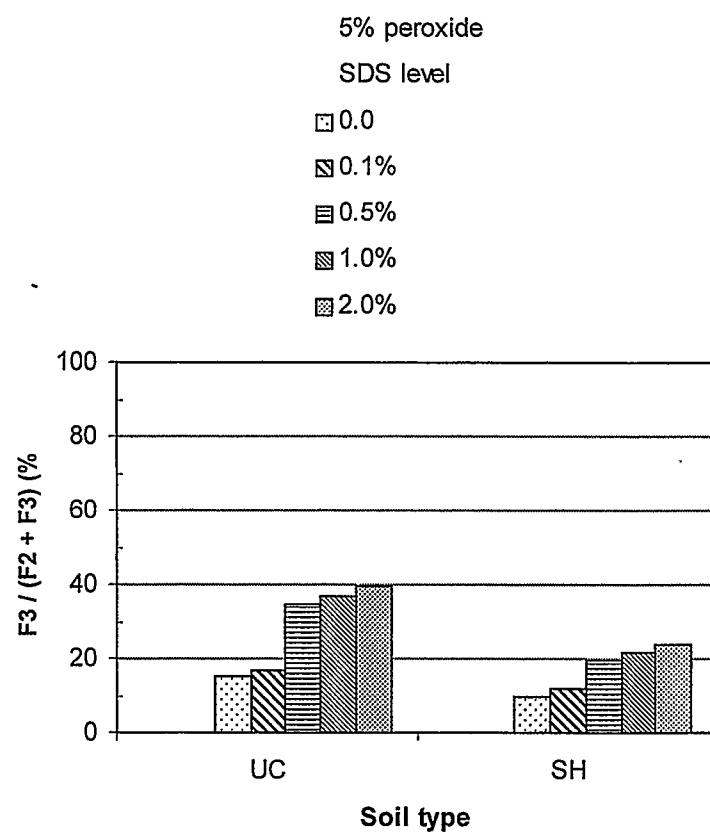
2.0%

Figure 4.24: Percentage of F3 fraction degraded with respect to total degradation for both UC and SH soils

(5 g of soils, 5,000 mg/kg diesel; 10 mL H$_2$O$_2$)

10% hydrogen peroxide

5,000 mg/kg diesel

△   One application

○   Multiple application

Figure 4.25: DRO degradation as a function of H_2O_2 volume applied

for UC soil in multiple application test (5 g of soil)

10% hydrogen peroxide

5,000 mg/kg diesel

△ One application

○ Multiple application

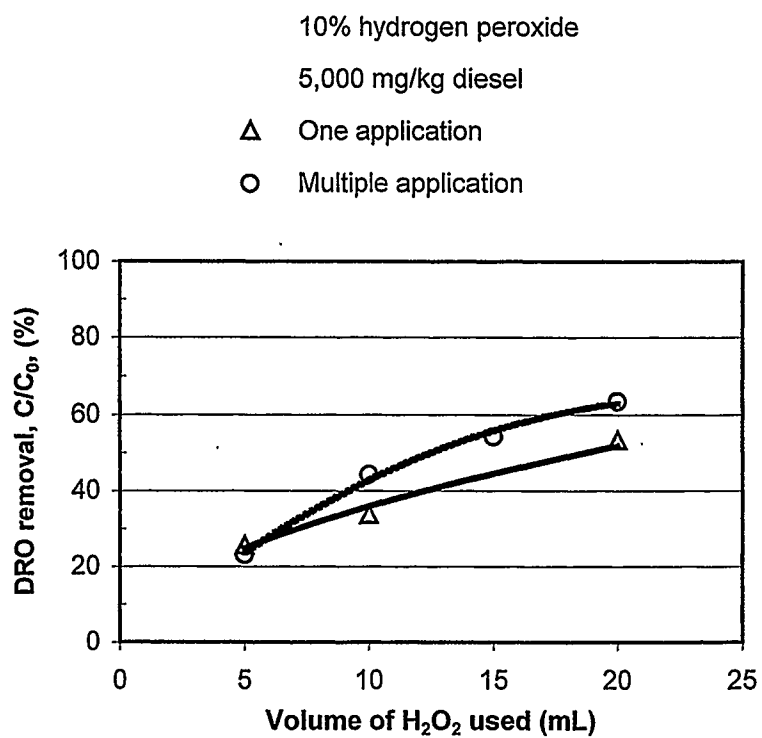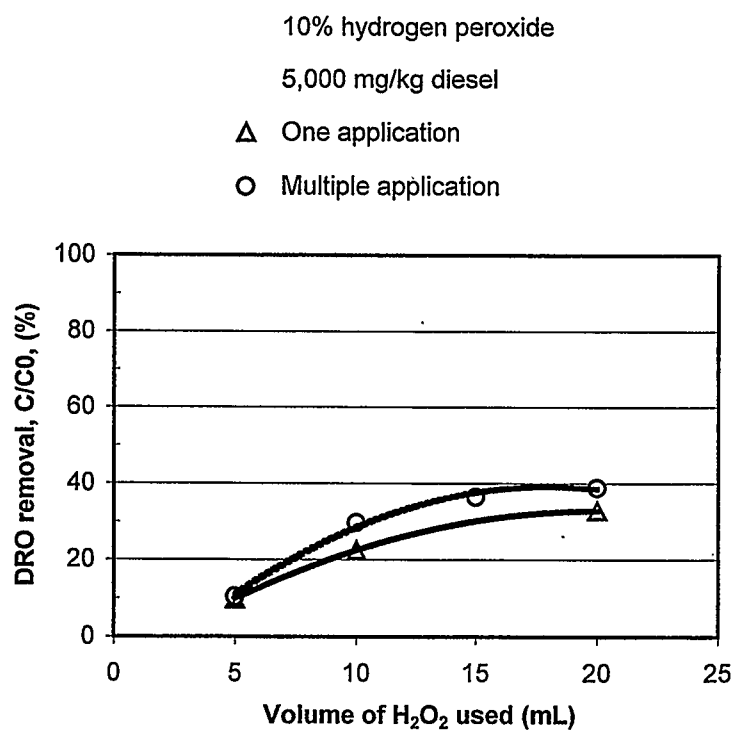**Figure 4.26: DRO degradation as a function of H_2O_2 volume applied for SH soil in multiple application test (5 g of soil)**

Desorption is generally regarded as the rate-limiting step in diesel degradation (Spencer *et al.*, 1996). Watts *et al.* (2000) suggested that high concentration of hydrogen peroxide could enhance PCP desorption from soil particles. In soil slurry, mass transfer between diesel on soil particles and hydroxyl radicals in solution was limited so long as volume of Fenton's reagent surpassed soil field capacity. In test of one-time, large volume application, H_2O_2 in the bulk solution reacted more favorably with and consumed by non-productive reactants. As a result, concentration of bulk volume of H_2O_2 in soil-slurries as well as H_2O_2 concentration gradient around soil particle surface decreased. The decrease in turn affected adversely desorption of tightly sorbed diesel. Small volume of multiple application of H_2O_2, on the contrary, may allow adsorbed diesel on the soil surface to be repeatedly exposed to hydrogen peroxide at relatively high concentration gradient, thus enhance diesel desorption and eventually increasing diesel oxidation.

As expected, sandy soil (UC) was more readily degraded by hydrogen peroxide than clay soils (SH). The two soils exhibited similar trend when treated with multiple applications of hydrogen peroxide, and differed only in percent diesel degradation.

4.5   INFILTRATION AND INJECTION TESTS

4.5.1   Infiltration Test

When infiltrated with distilled water, it took only about 15 minutes for water to saturate the soil column and generated effluent. Based on the permeability test results, hydraulic conductivity for water was calculated to be about 0.0015 cm/s. But when hydrogen peroxide was used instead of water, regardless the volume applied, it could be seen through the side of the plexiglass cell that the downward movement of H_2O_2 was greatly hindered by vigorous gas generation. It took about three hours for the effluent to exit out of the sampling ports. The Fenton's reaction occurred in the soil column generated large amount of gas and the exiting gas filled the pores, thus reducing the effective pore

space. This in turn dramatically decreased the effective hydraulic conductivity of the column soil. Based on the calculated value, the hydraulic conductivity for H_2O_2 solution was about 30 times lower than that of distilled water, which indicated that any attempt to deliver H_2O_2 into subsoil should consider the decreased hydraulic conductivity associated with H_2O_2 reactions within soil.

For all the three H_2O_2 infiltration tests, diesel in the effluent was undetectable. The results were reasonable considering that the amount of H_2O_2 used was apparently sufficient to destroy the diesel dissolved and/or present as NAPL in aqueous solutions. This was confirmed by the incomplete consumption of hydrogen peroxide found in the effluent. Residual H_2O_2 were observed about 4.5 hours after the tests began. Its concentrations were found to increase marginally with reaction time, as demonstrated in Figure 4.27. The presence of hydrogen peroxide in the effluent may be due to faster infiltration as gas generation decreased with time. Application of higher volume of H_2O_2 showed higher residual H_2O_2.

The diesel degradation showed no distinct difference regardless of sampling locations, e.g., along central axis or near the side of the column. When hydrogen peroxide was added from the top, it became unstable due to the presence of inorganic and organic reactants. Vigorous reaction occurred on the top surface of the soil samples. As shown in Figure 4.28, the top layers in each of the three tests consistently show higher diesel degradation than others as they were being constantly subjected to relatively higher H_2O_2 concentration gradient.
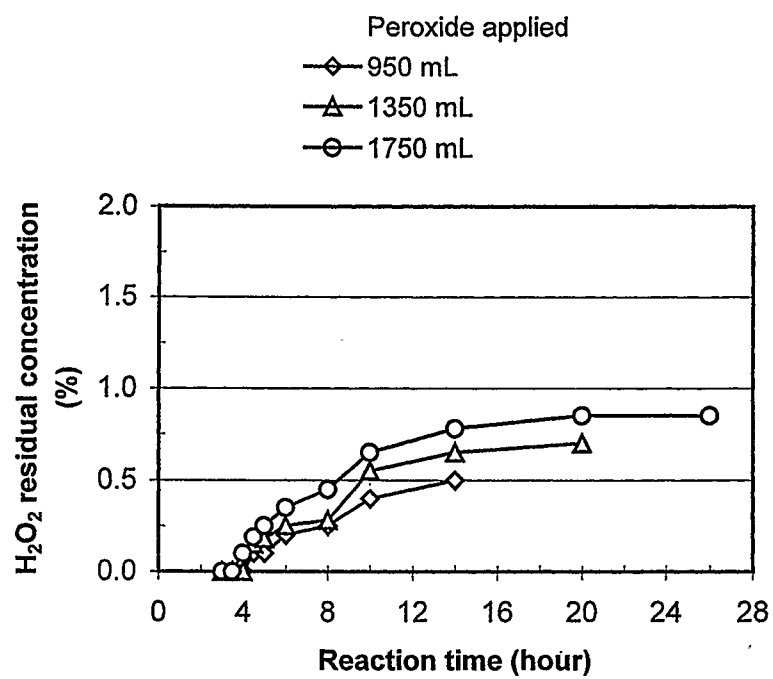
Figure 4.27: H$_2$O$_2$ residual concentrations of the effluent as a function of reaction time during infiltration tests
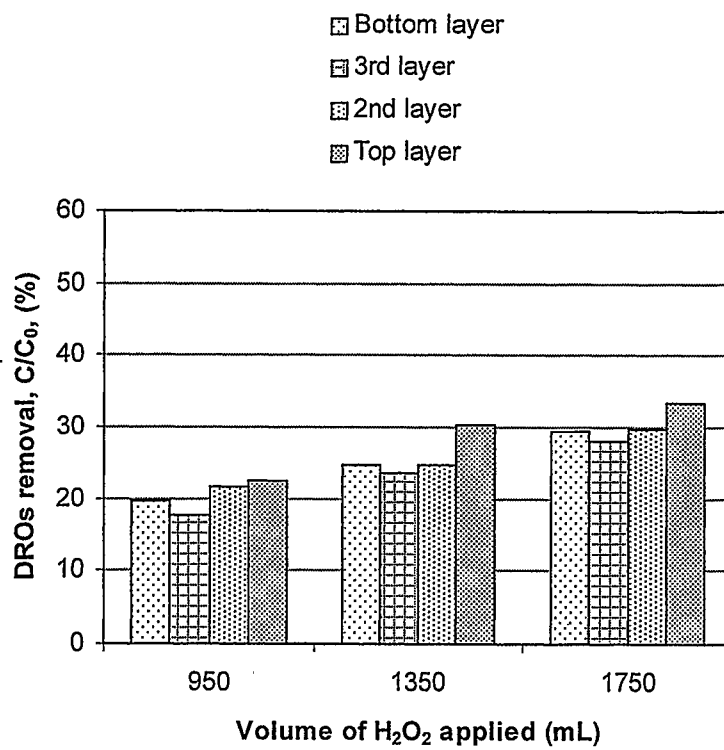
Figure 4.28: Percent DRO degradation in each layer in soil column using varying volumes of hydrogen peroxide

DRO degradation also increased with increasing volumes of H_2O_2 applied. The increase in the volume of H_2O_2 from 950 mL to 1350 mL led to an average of 51% surge of diesel degradation, whereas only about 22% rise in degradation efficiency on the average was induced by further increase of hydrogen peroxide from 1350 mL to 1750 mL. In the test infiltrated by a total of 1350 mL H_2O_2, however, only about 26% diesel were degraded, and this was lower than the 57% achieved in vial batch tests using identical concentration and volume of H_2O_2 per gram of soil. The low permeability of soil column led to most H_2O_2 ponding on the soil surface for a long period of time. The H_2O_2 decomposition close to the top surface decreased the actual concentration of the H_2O_2. It is also likely that some inorganics and/or organics desolve/diffuse back into the aqueous solution and react with the ponded hydrogen peroxide. In fact, roughly 28% reduction in concentration of bulk H_2O_2 on top of the soil sample (ponding) was observed 2 hours after the tests started.

4.5.2 Injection Test

Table 4.1 presents the mass of diesel degraded in soil samples in various layers under different conditions. The top two layers and bottom layer generally showed more mass of diesel degraded than the third layer (see Table 4.1). Percent concentrations of diesel degraded in test I decreased along column depth up to layer #3, i.e., from 10.6% in layer #1 to 8.4% in layer #2, to 5.4% in layer #3. In layer #4 the percent value increased to 9.9%. All the other three tests, though conducted with different volume of hydrogen peroxide applied in soils of varying densities, exhibited similar trend in layers in terms of percent concentration of diesel degraded.

When the soil density was lower (tests II and IV), the percent DRO removal as well as mass of diesel degraded was higher than that from more compacted soils in test I and III. Significant percentage increases in the amount of diesel degraded, ranging from 10% to 40%, were achieved when doubling the volume of H_2O_2. The only exception in

Table 4.1: Results from injection tests

		Injection I	Injection II	Injection III	Injection IV
Process variables					
Bulk density (g/cm^3)		1.35	1.21	1.34	1.23
Volume of H$_2$O$_2$ (mL)		200	200	400	400
PC (%)^1 & mass (mg) of diesel degraded					
Layer #1	PC	10.6	13.5	13.1	15.1
	Mass	134.4	171.0	166.7	192.2
Layer #2	PC	8.4	8.9	11.4	11.5
	Mass	106.5	113.1	144.8	146.5
Layer #3	PC	5.4	5.3	7.8	6.8
	Mass	68.1	67.4	99.4	86.6
Layer #4	PC	9.9	10.5	9.7	11.6
	Mass	125.2	133.6	123.7	147.7

^{1}PC stands for percent concentration

layers #4 in tests I and III, where the level of degradation was marginally different. The reason behind the inconsistency was not understood.

Though H_2O_2 was injected in the soil under pressure, some of the H_2O_2 moved upward along the injector leading to ponding. This phenomenon, also known as "refusal", is quite often occurred when injections of other liquids such as lime fly ash are made at field sites. The resulted ponding of H_2O_2 covered most of the soil surface around the injector. It was possible that significant amount of diesel was degraded in the first two layers through surface impoundment. The increase of diesel degraded in layer #4 as compared to layer #3 may be attributed to increased amount of H_2O_2 available for the lower layer possibly through side and bottom preferential flow. The consistent low diesel degradation in layer #3 seemed to confirm this explanation.

Figures 4.29 to 4.44 show 3-D plots and contour maps of the spatial distribution of diesel degraded for each layer of the four injection tests. Soils around the central axis were more effectively degraded, resulting in a cone-shaped distribution of diesel degradation efficiency. As high as 30% diesel degradation was achieved around the central axis, where injection of hydrogen peroxide started. Apparently, radius of influence was limited as a result of low soil permeability as well as fairly low injection pressure that was intended to reduce H_2O_2 ponding on soil surface. This finding agreed with the fact that no or very low percent diesel degradation was observed at certain sampling points, mostly along the outer periphery of the soil column.
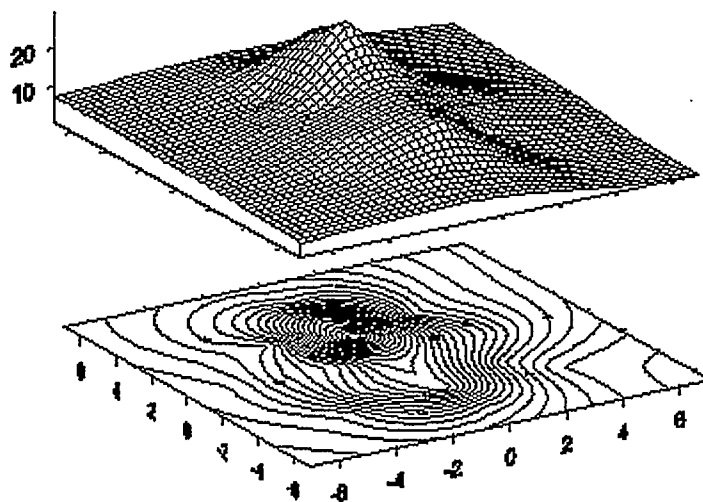
Figure 4.29: 3-D wireframe plot and contour map for diesel concentration degraded in layer #1 in injection test No. I
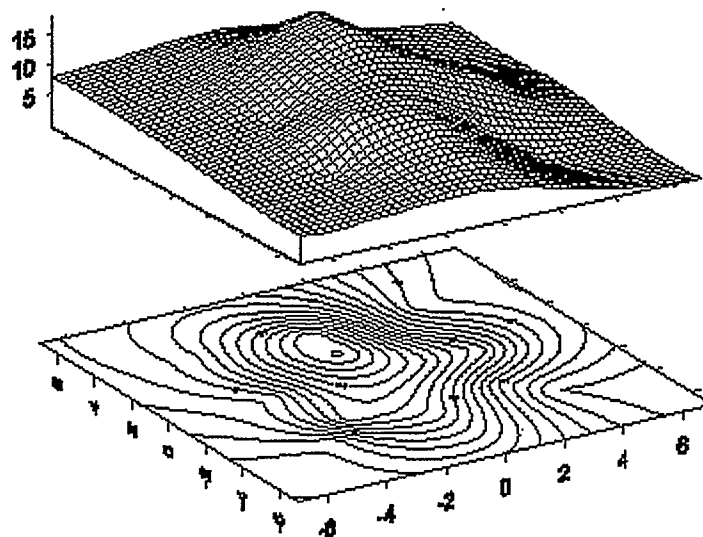

Figure 4.30: 3-D wireframe plot and contour map for diesel concentration degraded in layer #2 in injection test No. I
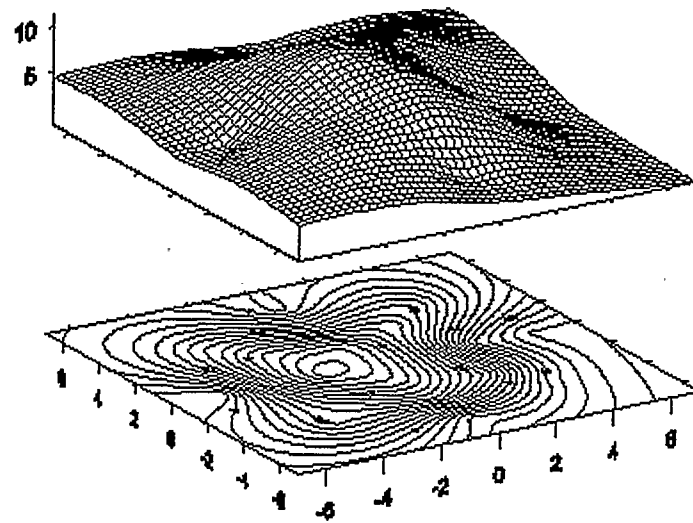
Figure 4.31: 3-D wireframe plot and contour map for diesel concentration degraded in layer #3 in injection test No. I

Figure 4.32: 3-D wireframe plot and contour map for diesel concentration degraded in layer #4 in injection test No. I

Figure 4.33: 3-D wireframe plot and contour map for diesel concentration degraded in layer #1 in injection test No. II

Figure 4.34: 3-D wireframe plot and contour map for diesel concentration degraded in layer #2 in injection test No. II

Figure 4.35: 3-D wireframe plot and contour map for diesel concentration degraded in layer #3 in injection test No. II
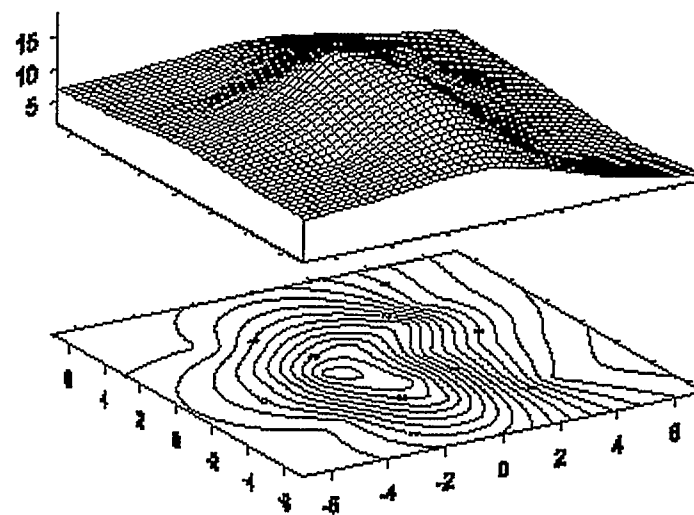

Figure 4.36: 3-D wireframe plot and contour map for diesel concentration degraded in layer #4 in injection test No. II
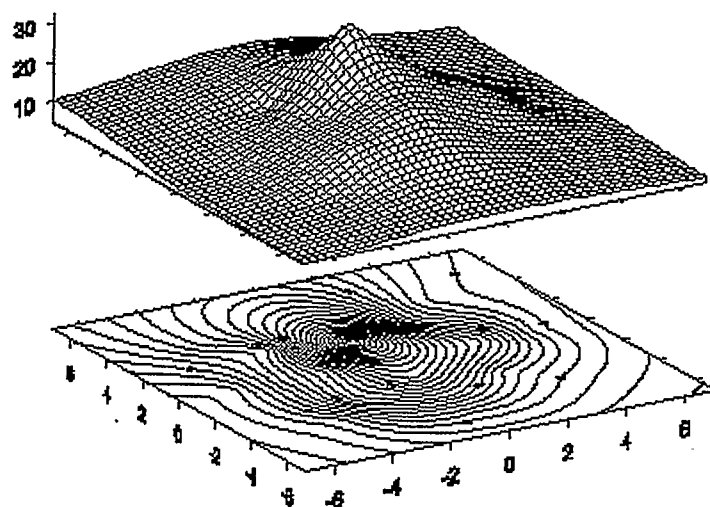
Figure 4.37: 3-D wireframe plot and contour map for diesel concentration
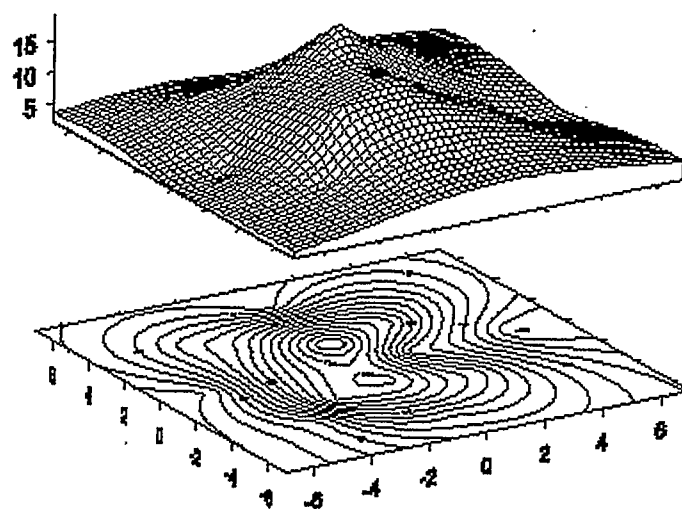degraded in layer #1 in injection test No. III

Figure 4.38: 3-D wireframe plot and contour map for diesel concentration
degraded in layer #2 in injection test No. III

Figure 4.39: 3-D wireframe plot and contour map for diesel concentration degraded in layer #3 in injection test No. III

Figure 4.40: 3-D wireframe plot and contour map for diesel concentration degraded in layer #4 in injection test No. III

Figure 4.41: 3-D wireframe plot and contour map for diesel concentration
degraded in layer #1 in injection test No. IV

Figure 4.42: 3-D wireframe plot and contour map for diesel concentration
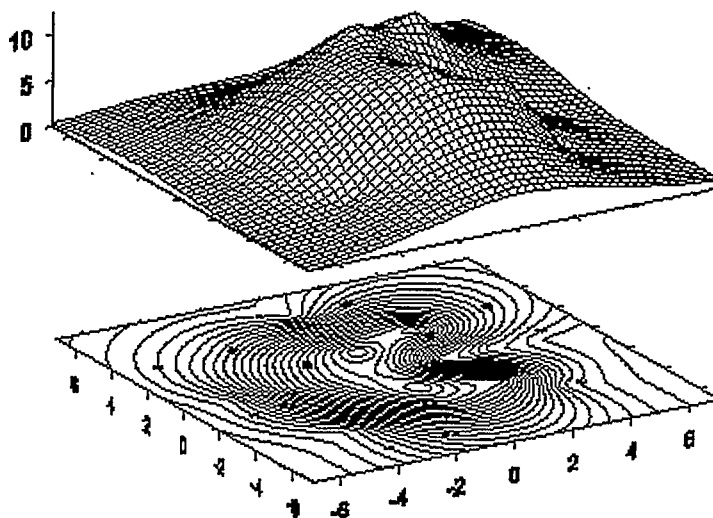degraded in layer #2 in injection test No. IV
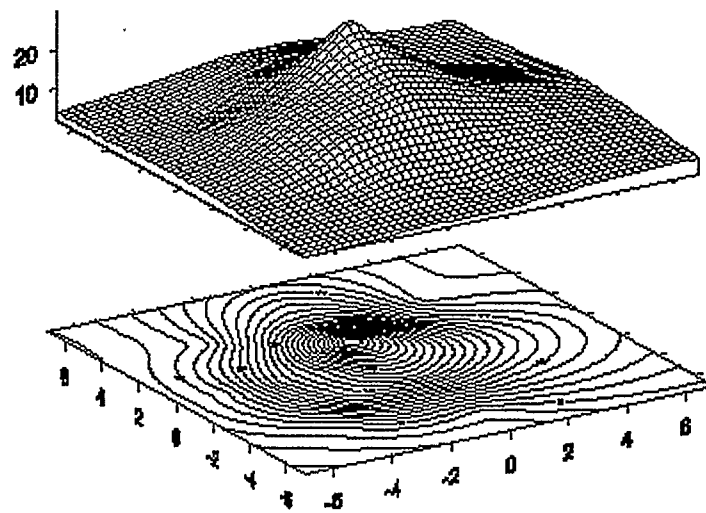
Figure 4.43: 3-D wireframe plot and contour map for diesel concentration degraded in layer #3 in injection test No. IV
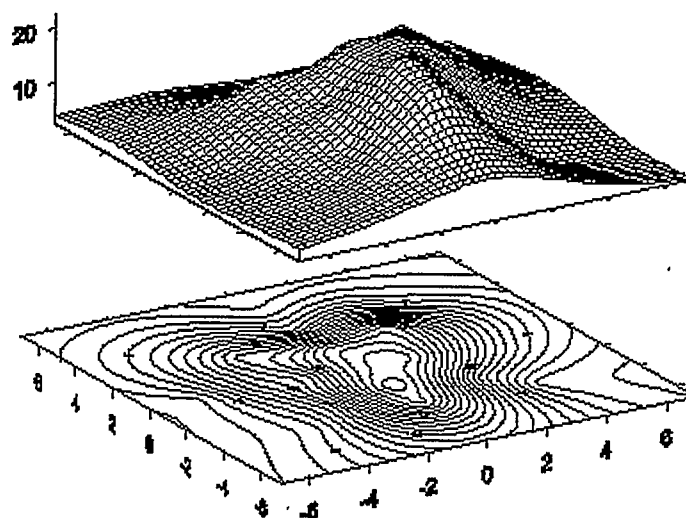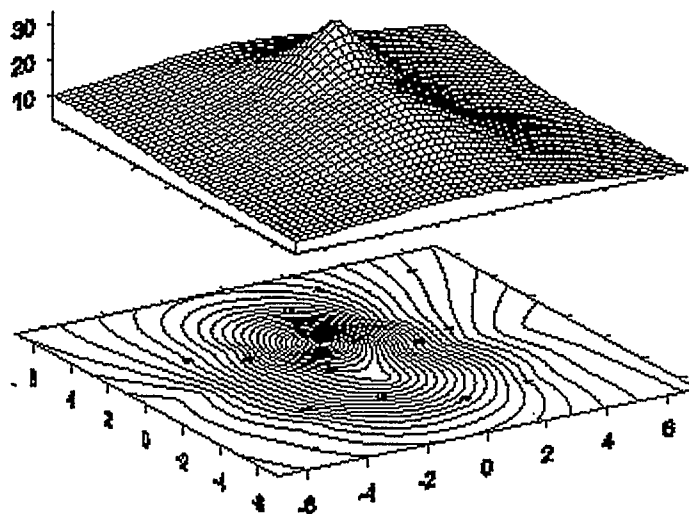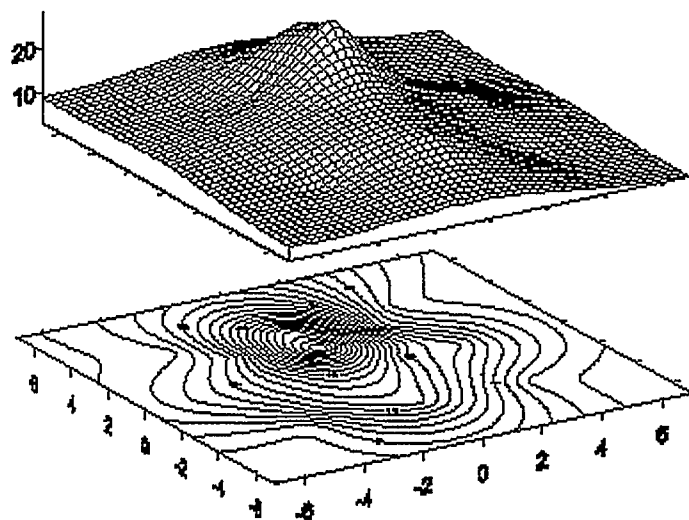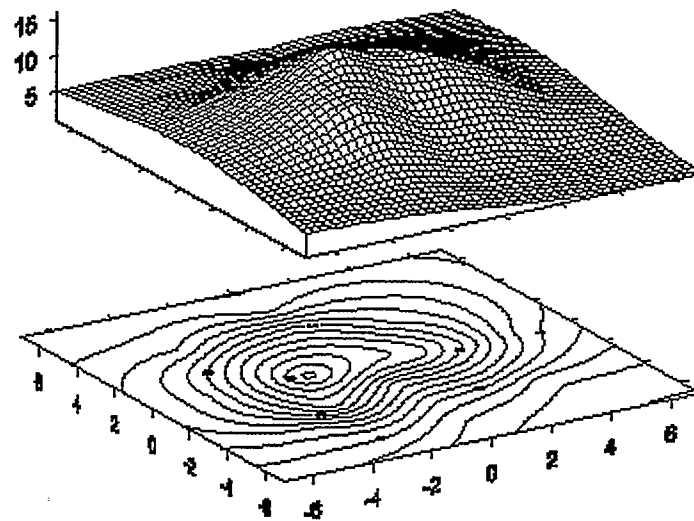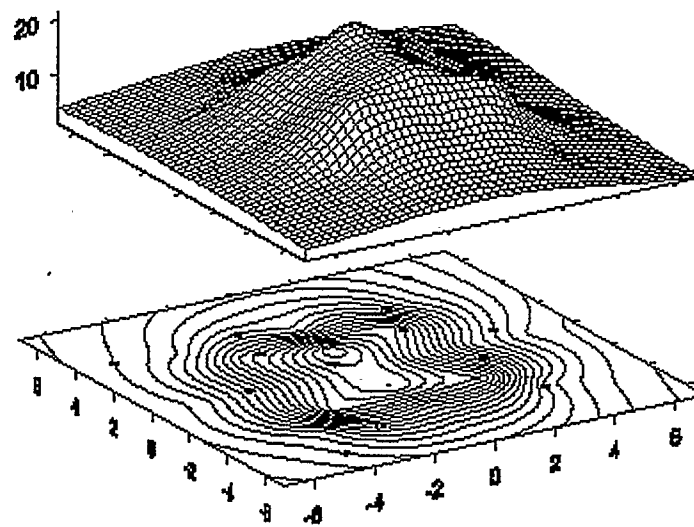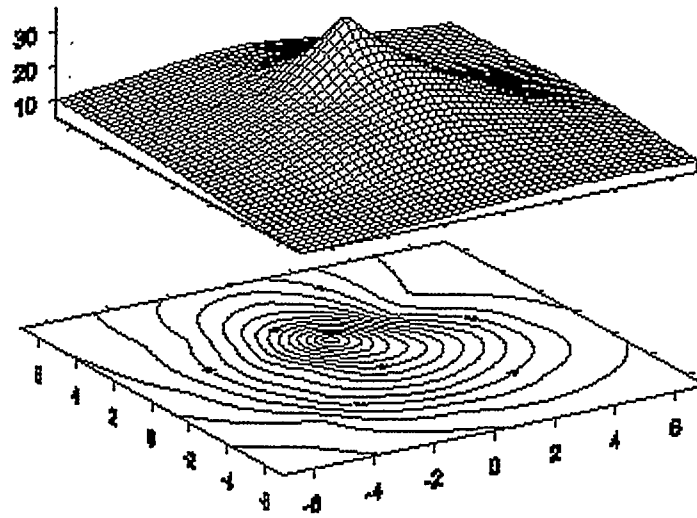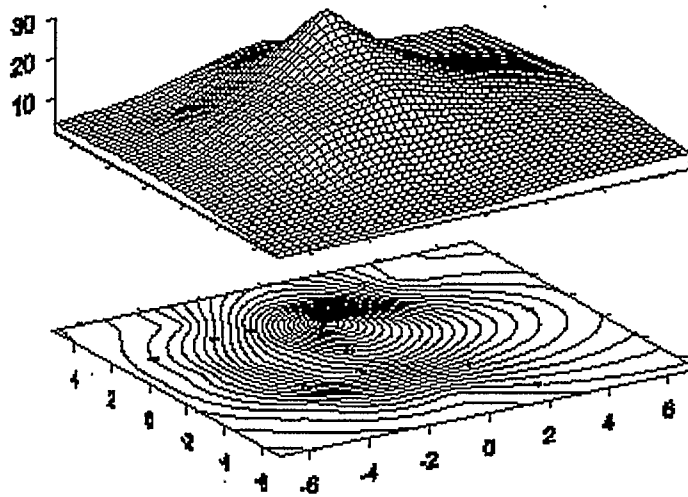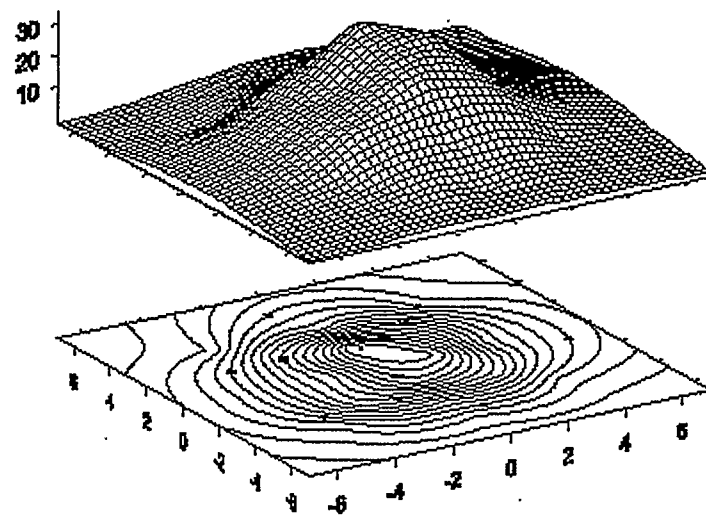

Figure 4.44: 3-D wireframe plot and contour map for diesel concentration degraded in layer #4 in injection test No. IV

CHAPTER FIVE

CONCLUSIONS AND RECOMMANDATIONS

5.1 CONCLUSIONS

Based on the laboratory experiments, the following conclusions are drawn:

- The two field soils used in this study were not amenable to pH adjustment, whereas tests with Ottawa sand showed that low pH environment favored resulted in higher diesel degradation;

- External iron amendments to the field soils showed no effect on the results of modified Fenton's reaction. Tests with Ottawa sand demonstrated that the optimum iron amendment were 360 mg/L for 5 mL of 5% and 10% H_2O_2, and 720 mg/L for 5 mL of 20% H_2O_2;

- The test data suggest that concentration and volume of H_2O_2 were the most significant process variables in modified Fenton's reaction, and that high concentration of H_2O_2 increased percentage diesel degradation at the expense of low treatment stoichiometry;

- Diesel mineralization occurred in the two field soils treated in modified Fenton's reaction as evidenced by CO_2 generation;

- The optimum dosages for remediation of the loose, disturbed sandy silt soil and silty clay soil were 8 mL of 5% H_2O_2 and 4 mL of 10% H_2O_2 per gram soil, or about 2:1 (H_2O_2 : soil) with 20% hydrogen peroxide by volume;

- Treatment of contaminated soils with sodium dodecyl sulfate (SDS) improved treatment efficiency of Fenton's reaction when SDS concentration is higher than its critical micelle concentration (CMC), whereas prolonged shaking of soil-surfactant system gave no significant enhancement;

- Sequential addition of hydrogen peroxide to the two field soils increased degradation efficiency of about 20% with four sequential 5 mL applications of 10% H_2O_2 over one-time addition of 20 mL of 10% H_2O_2;

- Infiltration tests showed that the instability of H_2O_2 on top of the samples may be the dominant sink for hydrogen peroxide consumption. Only an average of 20% to 30% of diesel degradation was achieved soil columns, indicating that surface application of Fenton's reagent was not very effective in treating compacted soil; and

- Delivery of hydrogen peroxide into soil matrix through injection proved a more effective and efficient way of degrading low permeability soil as compared to the results from infiltration tests.

5.2 RECOMMENDATIONS FOR FUTURE WORK

From this laboratory study, the followings are recommended for future research work:

- The test results from vial batch tests show that significant consumption of H_2O_2 appears to be associated with competing and non-productive reactions in soil matrices. It is recommended that future work should emphasize on the stability of hydrogen peroxide when in contact with soil in order to provide sustainable source for generation of hydroxyl radicals;

- More studies should be conducted to examine the use of chelating agents as catalysts in modified Fenton's reaction in order to achieve effective remediation at neutral pH;

- Comprehensive study is necessary to understand the degradation pathways of major diesel individual components during the treatment by Fenton's reagent;

- In-depth study on using fraction approach to characterize residual diesel is recommended to make the approach more amenable for use in risk assessment analysis;

- Further studies on hybrid techniques employing Fenton's reagent and other treatment technologies should be conducted. Examples include pretreatment of biorefractory compounds by Fenton's reagent followed by bioremediation; and
- Large-scale tests using Fenton's reagent in undisturbed soil need to be conducted to take account of the complexity encountered in field conditions.

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