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MODIFIED FENTON OXIDATION OF HYDROCARBON CONTAMINATED SOILS WITH CaO_2: MICROBIAL SURVIVAL AND SURFACTANT PRODUCTION

by

Abraham Matthew Northup

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Abraham Matthew Northup

MODIFIED FENTON OXIDATION OF HYDROCARBON CONTAMINATED SOILS WITH CaO_2: MICROBIAL SURVIVAL AND SURFACTANT PRODUCTION

Abraham Matthew Northup, Ph.D.

Western Michigan University, 2007

The efficacy of CaO_2 for use in modified Fenton's (MF) reactions was investigated in this study, with the goal of developing a CaO_2–based MF oxidation technology for use in *in situ* chemical oxidation. Traditionally, liquid H_2O_2 (HP) is used, and is injected into the subsurface in excess to ensure a sufficient radius of influence. CaO_2 was investigated as an alternative source of H_2O_2 for MF reactions.

First, the rate of dissolution of powdered CaO_2 and the yield of HP was investigated. Our results showed that the rate of dissolution of CaO_2 and the corresponding yield of HP increases with decreasing pH. At a pH of 6 CaO_2 is dissolved within 4 hours and the yield of HP is 82% of theoretical. The use of CaO_2 as a source of H_2O_2 for the MF oxidation of tetrachloroethene (PCE), and 2-propanol, a hydroxyl radical scavenger, was used to demonstrate that the removal of PCE was due to oxidation by hydroxyl radicals. A comparison was made between HP and CaO_2 based MF reactions with respect to PCE oxidation. The data indicate that CaO_2 is able to sustain MF reactions longer and more efficiently than HP (i.e., less moles HP per mol PCE consumed).

A comparison was made between biological and modified Fenton (MF) chemistry with respect to the effectiveness of treating hydrocarbon-contaminated soil. The MF treatment was performed using both HP with Fe^{3+} and a CaO_2-based oxidant to allow for

comparisons between different MF oxidants. The MF treated systems had temporarily elevated surfactant concentrations with respect to both the control and biologically treated soils, indicating surfactant production during chemical hydrocarbon oxidation. Enhanced total petroleum hydrocarbon (TPH) removal was observed as a result of MF treatment with hydrocarbon removal being greater with the CaO_2 treatment relative to HP treatment. At the end of the treatment period there was no significant decrease in viable bacterial numbers between MF and biological treatments.

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CHAPTER I

INTRODUCTION

Background

ISCO Technologies

In situ chemical oxidation (ISCO) is a process in which chemical oxidants are used to degrade organic contaminants into ions or dissolved constituents that are generally found in the environment, such as chloride and carbon dioxide. There are four primary types of ISCO that will be discussed in this brief overview, which include: permanganates, persulfates, ozone, and modified Fenton's (MF) reagent. The oxidation potential of these respective oxidants and their related derivatives are shown in Table 1, along with oxygen and chlorine as a comparison.

Chemical Oxidant	**Oxidation Potential (V)**
Hydroxyl Radical	2.8
Sulfate Radical	2.5
Ozone	2.1
Sodium Persulfate	2.0
Hydrogen Peroxide	1.8
Permanganates	1.7
Chlorine	1.4
Oxygen	1.2

Table 1: Oxidation potential for common oxidants. (ITRC, 2005)

As with all remediation processes certain site conditions may exist that render the process to be ineffective or cause unwanted reactions with co-contaminants. Two of the primary conditions that tend to plague ISCO techniques are the possibility for oxidation of metals and oxidant scavenging by native organic material (NOM) as well as dissolved species (Huling and Pivetz, 2006; ITRC, 2005; Rock et al., 2001; Watts and Teel, 2006). Oxidant scavenging is discussed further in the section on MF reagent. The ability of ISCO to oxidize metals is a concern due to an increase in solubility of some of these co-contaminants. Rock et al. demonstrated that during MF reactions Cr(III), which is relatively immobile in the subsurface, was oxidized to Cr(VI), which is a carcinogen and highly mobile in the subsurface (2001). Thus the potential for oxidation of metals and scavenging by NOM should be evaluated before using ISCO at a given site.

ISCO processes have, in many cases, reduced the treatment time of contaminated sites from years, using conventional treatment methods, to months (U.S. Environmental Protection Agency, 1998). The application of ISCO has been proven effective in situations where bioremediation has failed, primarily as a result of the range of contaminants or climate conditions, or both (Ferguson et al., 2004; U.S. Environmental Protection Agency, 1998). The oxidants used in ISCO are readily available and application is generally less invasive and disruptive compared to most other methods of remediation.

Permanganates

There are two common forms of permanganate that can be applied with respect to ISCO, potassium permanganate ($KMnO_4$) and sodium permanganate ($NaMnO_4$). Potassium permanganate is a crystalline solid and can be mixed with water to form a solution for injection into the subsurface, but this solution is limited to 4% based on the solubility of the $KMnO_4$ (ITRC, 2005). Sodium permanganate is commonly supplied as a 40% concentrated liquid, which is diluted on site before injection (ITRC, 2005). The use of $NaMnO_4$ provides greater flexibility in remediation systems because a wide range of concentrations is possible, as opposed to $KMnO_4$, which is limited by solubility.

As with all ISCO technologies there are advantages and drawbacks, specific to the technology that need to be considered before application. Permanganates are stable and persistent in the subsurface and are effective over a wide range of pH values (3-12). The stability and persistence of permanganates allows for a large radius of influence (ROI) when injecting into the subsurface (Huling and Pivetz, 2006; ITRC, 2005; Watts and Teel, 2006). Unsaturated hydrocarbons, particularly with a carbon-carbon double bond, are highly oxidizable by permanganates (ITRC, 2005). However, permanganates are not able to effectively oxidize saturated aliphatic compounds and most aromatics (ITRC, 2005). One of the by-products of oxidation using permanganate is $MnO_2(s)$ which precipitates in the soil and can reduce subsurface porosity and permeability, possibly limiting future injections. Also, aggressive, exothermic, reactions can occur when sodium permanganate is applied at greater than a 10% solution (ITRC, 2005).

Persulfates

There are several types of persulfates that are commercially available, which consist of ammonium persulfate ($(NH_4)_2S_2O_8$), sodium persulfate ($Na_2S_2O_8$), and potassium persulfate ($K_2S_2O_8$) (ITRC, 2005). Potassium persulfate is generally not used due to limited solubility (6% at 25°C), whereas sodium persulfate (40% at 25°C) and ammonium persulfate (46% at 25°C) have significantly higher solubilities (ITRC, 2005).

Ammonium persulfate is not used due to the release of ammonium during dissolution, which is regulated in groundwater (ITRC, 2005). Reactions 1 and 2 indicate how the sulfate radical ($\bullet SO_4^-$) is formed using different methods of activation.

$$S_2O_8^{2-} \rightarrow 2SO_4^{-\bullet}$$

Reaction 1: Formation of sulfate radical by heat activation

$$Fe^{2+} + S_2O_8^{2-} \rightarrow 2SO_4^{-\bullet} + Fe^{3+}$$

Reaction 2: Formation of sulfate radical by ferrous iron activation

One of the advantages of using sodium persulfate for ISCO is that oxidation can occur by both persulfate anions and sulfate radicals, both of which are powerful oxidants (Table 1). However, the oxidation of organic contaminants by persulfate anions tends to be kinetically sluggish, whereas oxidation by sulfate radicals is favored (Huling and Pivetz, 2006; ITRC, 2005). The primary drawback when using persulfate for ISCO is that in order to produce sulfate radicals an activator needs to be present, such as ferrous iron or heat (Reactions 1 and 2). There is no Fe cycling mechanism present for persulfate activation such as that in MF (Reactions 4-8) therefore when the ferrous iron is depleted no further production of sulfate radicals can occur. The amount of iron injected is also limited due to the possibility of clogging wells with amorphous iron oxides. However, any naturally available ferrous iron in the subsurface will also be utilized, but again when the available iron is oxidized the formation of sulfate radicals will cease. The lack of an iron cycling mechanism and resultant rapid use of iron limits the ROI for persulfate remediation efforts.

Ozone

Ozone (O_3) is a very powerful oxidant (Table 1) but ozone can also form hydroxyl radicals via Reaction 3, which is also a powerful oxidant (Table 1). There are two methods for ozone application; it can be sparged into the subsurface as a gas or it can be dissolved in water and then injected (ITRC, 2005).

$$O_3 + OH^- \rightarrow O_2 + \bullet OH$$

Reaction 3: Formation of hydroxyl radical from ozone

The injection of ozone is advantageous to indigenous microorganisms due to the release of oxygen during hydroxyl radical formation (Reaction 3). However, ozone can kill microorganisms if applied in high enough concentrations or with long injection times, but this is generally temporary and limited to near the sparge point (ITRC, 2005). Another advantage of ozone injection is that ozone gas sparging can be effective in managing vadose zone contamination. Off gassing during ozone sparging may require that a soil vapor extraction system be used in conjuction with the sparging operation to account for volatilization of contaminants (Huling and Pivetz, 2006; ITRC, 2005; Watts and Teel, 2006).

Modified Fenton's Reagent

As with persulfate, hydrogen peroxide is a powerful oxidant (Table 1) but only at high concentrations (>0.1%) and typically 2-20% HP is injected during MF ISCO (ITRC, 2005; Watts and Teel, 2005). Initial research by Fenton showed that small amounts of ferrous iron (Fe^{2+}) in the presence of H_2O_2 results in a solution capable of oxidizing tartaric acid (1894). Subsequent work by Haber and Weiss (1934) indicated that the hydroxyl radical (•OH) was the oxidant produced in the Fenton's reagent (Reaction 4). The hydroxyl radical is also a powerful oxidant (Table 1). In a series of articles, Merz and Waters demonstrated that reaction stoichiometry could be used in order to determine the ability of the hydroxyl radical to oxidize various organic compounds (1947; 1949). Later work by Walling introduced catalyzed H_2O_2 propagations (CHP) or commonly referred to as modified Fenton's (MF) reagent (1975). In MF chemistry •OH are produced by slowly combining dilute H_2O_2 with a solution of excess Fe^{2+} (Walling, 1975). If $Fe^{2+}$is not present or present in low concentrations but ferric iron (Fe^{3+}) is present, then Fe^{2+} can be generated (Reactions 5-8) (Kwan and Voelker, 2003; Walling, 1975).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + \bullet OH + OH^-$$

Reaction 4: Formation of hydroxyl radical from hydrogen peroxide

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$$

Reaction 5: Reduction of iron and formation of perhydroxyl radical

$$HO_2^{\bullet} \leftrightarrow O_2^{-\bullet} + H^+ \text{ (pKa=4.8)}$$

Reaction 6: Deprotonation of perhydroxyl radical to form superoxide radical anion

$$O_2^- + Fe^{3+} \rightarrow Fe^{2+} + O_2$$

Reaction 7: Reduction of iron by superoxide radical anion

$$\bullet OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$$

Reaction 8: Formation of perhydroxyl radical

In 1990 it was suggested that MF reagent could be used to treat contaminated soils, but optimal performance was achieved under acidic conditions (Watts et al.). The acidic conditions were required in order to maintain sufficient iron solubility (Pignatello and Baehr, 1994). However, the buffering capacity of soils and groundwater generally inhibits the application of a remedial technology where acidic conditions are required. Iron-chelates were used to further modify Fenton's reagent in order to effectively treat organic contaminants under near neutral pH conditions (Luzzatto et al., 1995; Pignatello and Baehr, 1994; Sun and Pignatello, 1992; Zepp et al., 1992). Chelated iron can be applied directly to MF systems or chelators can be applied in order to increase the solubility of native iron-bearing minerals in the system (Watts et al., 1999b; Watts et al., 1993). In practice very little chelated iron, if any, is injected during MF treatment and the system is effectively iron limited relying primarily upon native iron, which is done to prevent clogging of the injection wells by amorphous iron oxide deposits (Huling and Pivetz, 2006; ITRC, 2005).

The •OH is a non-discriminate oxidant that reacts with most organic compounds, including highly chlorinated alkenes and aromatics (Haag and Yao, 1992). However, the •OH does not react with perchlorinated alkanes such as tetrachloromethane (i.e. carbon tetrachloride, CT) and hexachloroethane, although these contaminants are degraded in MF systems (Smith et al., 2004; Teel and Watts, 2002). Watts et al. (1999a) suggested that efficiency of MF systems is the result of a combination of reactive species produced from MF related reactions. The reactive species proposed by Watts et al. (1999a) include the •OH, $O_2^{-\bullet}$ (superoxide radical anion) , and HO_2^- (hydroperoxide anion). The production of •OH and $O_2^{-\bullet}$ are illustrated above in Reactions 4-8, the formation of HO_2^-

is illustrated below in Reaction 9. Teel and Watts (2002) used chloroform to scavenge reductants from solution during MF treatment of CT. When just •OH were present (during chloroform scavenging) no degradation of CT occurred, but when other reductants were present (no chloroform scavenging) the CT was degraded, suggesting that either the $\bullet O_2^-$ or HO_2^- was responsible for the CT degradation (Teel and Watts, 2002). Similar work by Smith et al. (2004) found evidence suggesting that CT degradation during MF treatment is caused by $\bullet O_2^-$.

$$HO_2^{\bullet} + O_2^{-\bullet} \rightarrow HO_2^- + O_2$$

Reaction 9: Formation of hydroperoxide anion

The non-discriminate reactivity of the •OH can cause unwanted reactions to occur resulting in either •OH sinks or •OH scavenging in natural systems. Sinks for •OH generally occur by degradation of native organic material (NOM) during MF treatment (Bissey et al., 2006; Bogan and Trbovic, 2003; Brezonik and Fulkerson-Brekken, 1998; Huling et al., 2001). There have also been reports of •OH scavenging in natural systems by carbonate, bicarbonate, nitrate, sulfate, chloride, and phosphate (Bower and Miller, 2002; Brezonik and Fulkerson-Brekken, 1998; Buxton et al., 1988; Lipczynska-Kochany et al., 1995; Pignatello, 1992). However, MF dose is generally much greater than the capability of a natural system to suppress •OH attack of contaminants.

CaO_2-Based MF Chemistry

The instability of HP results in a disproportionation reaction, which accounts for the primary loss of HP during MF treatment (see Reaction 10) (Buda et al., 2003; Neyens and Baeyens, 2003; Watts et al., 1999b). In order to prevent the decomposition of HP a stabilizer, such as phosphate, is used (Watts et al., 1999b). Phosphate may help to inhibit HP decomposition in the presence of metal oxyhydroxides, transition elements, and soil surfaces but does not prevent decomposition by biological processes (Pardieck et al., 1993; Spain et al., 1989; Watts et al., 1999b). There is evidence to suggest that calcium peroxide (CaO_2) may be a more effective source of H_2O_2 than liquid HP with respect to enhanced contaminant removal (Arienzo, 2000; Nuttall et al., 2000). During this process H_2O_2 release is regulated by the dissolution of CaO_2, which limits the availability of H_2O_2 and possibly decreases the decomposition of H_2O_2 (refer to Reaction 11). The dissolution of CaO_2 in unbuffered, water saturated soils has been documented to proceed for over one month (Cassidy and Irvine, 1999). Calcium peroxide will be used in this study as a comparison to liquid HP as well as to determine the effectiveness of H_2O_2 production from CaO_2 in MF reactions.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Reaction 10: Decomposition of hydrogen peroxide

$$CaO_{2(s)} + 2H_2O \rightarrow H_2O_2 + Ca(OH)_{2(s)}$$

Reaction 11: Formation of hydrogen peroxide from calcium peroxide dissolution

MFC Toxicity

Another popular alternative to chemical treatment of organic contaminants has been intrinsic bioremediation where the indigenous bacterial communities mineralize the contaminant (Bradley et al., 1997; Oh et al., 2003). The effect of modified Fenton's (MF) reactions on bacteria is debated in the scientific literature. There does not seem to be a consensus upon whether or not simultaneous chemical and biological oxidation of contaminants can occur. Some evidence suggests that a combination of bioremediation and MF reactions may increase contaminant removal (Aunola et al., 2006; Bittkau et al., 2004; Büyüksönmez et al., 1999; Howsawkeng et al., 2001; Nadarajah et al., 2002; Nam et al., 2001). Other evidence suggests that there may be a toxic effect of MF reactions towards indigenous bacteria (Büyüksönmez et al., 1998; Palmroth et al., 2006a; Palmroth et al., 2006b). A study by Miller et al. reported a decrease in soil toxicity towards microorganisms due to pesticide oxidation via MF treatment (1995). Microbial survival will be investigated in this study.

Purpose

The yield of H_2O_2 from CaO_2 in water over a range of pH values was tested in the first half of this study. The ability of calcium peroxide to induce the MF reactions to produce hydroxyl radicals, and then determine if the hydroxyl radical were responsible for contaminant oxidation was also tested. A comparison of the effectiveness of PCE oxidation by MF oxidation using both liquid HP and powdered CaO_2 was also investigated in this portion of the study.

During the second half of this study a hydrocarbon contaminated soil was treated using two different types of MF reagents, liquid HP and calcium peroxide powder. Previous reports have identified increased solubilization and desorption of contaminants during MF treatment, which may be attributed to the production of surfactants during treatment, but this explanation has not been proposed by these authors (Kakarla and

Watts, 1997; Watts and Stanton, 1999; Yeh et al., 2003). Laboratory and field applications of MF reactions generally results in foaming and the source of foaming has yet to be ascertained but is a strong indicator of surfactants being produced. The primary goal of this portion of this study was to quantify surfactant production during MF treatment and then determine what effect the surfactant production would have on hydrocarbon concentration in the aqueous phase. During this portion of the study a comparison was also made between liquid HP and calcium peroxide MF reagents with respect to microorganism survivability as well as total petroleum hydrocarbon (TPH) removal.

CHAPTER II

CALCIUM PEROXIDE (CaO_2) FOR USE IN MODIFIED FENTON CHEMISTRY

Abstract

The use of calcium peroxide (CaO_2) powder as a source of H_2O_2 to promote modified Fenton (MF) chemistry was studied. First, the rate of production and yield of H_2O_2 from CaO_2 dissolving in water at pH 6, 7, 8, 9, and 12-13 (i.e., unbuffered CaO_2) was measured. The rate of CaO_2 dissolution increased as pH decreased, from 62 hr for complete dissolution at pH 12-13 to only 4 hr at pH 6. The yield of H_2O_2 also increased with decreasing pH, from zero at pH 12-13 to 82% at pH 6. The ability of CaO_2 to promote MF oxidation of PCE was demonstrated with a hydroxyl radical (•OH) scavenger (2-propanol) at pH 8. The scavenger inhibited PCE oxidation, but 97% of the PCE was oxidized without it. Release of Cl^- showed that PCE was mineralized. Finally, PCE oxidation was compared with liquid H_2O_2 (pH 7) and with CaO_2 (pH 6, 7, 8, 9). Liquid H_2O_2 showed the lowest efficiency (mol H_2O_2 consumed/mol PCE oxidized) and the greatest temperature increase, disproportionation to O_2, and PCE volatilization. CaO_2 was a more efficient oxidant than liquid H_2O_2 at all pH values because it only releases H_2O_2 upon dissolution, reducing the loss to O_2 and volatilization. CaO_2 performed optimally at pH 8.

Introduction

Fenton chemistry involves the catalyzed decomposition of H_2O_2 by Fe^{2+} to form the hydroxyl radical (•OH) (Reaction 4), a strong and relatively indiscriminate oxidant that reacts with most contaminants at near diffusion-limited rates (Walling, 1975). Conventional Fenton chemistry, used primarily to treat waters and wastewaters, uses excess Fe^{2+} and meters in limiting amounts of H_2O_2, which results in nearly stoichiometric (1:1) conversion of H_2O_2 to •OH. Conventional Fenton chemistry also maintains a pH below 3, which is impractical in the subsurface because of the buffering capacity of geologic materials. As a result, *in situ* chemical oxidation (ISCO) applications typically use modified Fenton (MF), or Fenton-like chemistry, which operates at circum-neutral pH (Watts and Teel, 2005). In MF-ISCO, iron can be added as salts of Fe^{2+} or Fe^{3+} (Watts and Dilly, 1996), or native iron-containing minerals (e.g., goethite, ferrihydrite) can be used (Kong et al., 1998; Yeh et al., 2003). If insufficient Fe^{2+} is added, or if only Fe^{3+} is originally present, the Fe^{2+} in Reaction 4 is regenerated by various reactions (Kwan and Voelker, 2003). The low solubility of Fe^{3+} at neutral pH requires chelants (e.g., EDTA) to increase Fe^{3+} in the aqueous phase (Nam et al., 2001; Sun and Pignatello, 1992). High concentrations of H_2O_2 are injected during MF-ISCO to ensure a sufficient radius of influence (Watts and Teel, 2005). As such, MF-ISCO is conducted under conditions of limiting Fe and excess H_2O_2, the opposite of conventional Fenton chemistry.

The instability of H_2O_2 in the subsurface is the most serious limitation of MF-ISCO. Liquid H_2O_2 (2 to 12%) is typically injected in ISCO (Watts and Teel, 2005), but its half-life is only minutes to hours ((ESTCP), 1999). Disproportionation (Reaction 10) constitutes the major loss of H_2O_2 at neutral pH (Buda et al., 2003; Watts et al., 1999b). It consumes H_2O_2 without producing •OH, and releases O_2 gas which clogs pores around injection wells and promotes contaminant volatilization (Chen et al., 2001; Xu et al., 2006). Reaction 10 is catalyzed by metals, catalase and peroxidase enzymes, and native organic matter (Watts and Teel, 2005). Reaction 10 is quite exothermic (ΔG^{o}=-119.2 kJ/mol) (Hess, 1995), and as temperature rises it is favored over Reaction 4 (Schumb et al., 1955). This positive feedback cycle can rapidly degrade all available H_2O_2 to O_2. Phosphate is often used as a stabilizer (Baciocchi et al., 2004), and supposedly works by precipitating metals and forming stable complexes with H_2O_2 (Hinchee et al., 1990). However, even high phosphate concentrations do little to reduce the loss of H_2O_2 to O_2 in the presence of Fe (III) at pH 7 (Hinchee et al., 1990; Watts et al., 1999b).

Recent studies suggest that calcium peroxide (CaO_2) is a more effective source of H_2O_2 for ISCO than liquid H_2O_2 (Bogan et al., 2003; Northup and Cassidy, 2007). CaO_2 dissolves to form H_2O_2 and $Ca(OH)_2$ via Reaction 11, liberating a maximum of 0.47 g H_2O_2/g CaO_2 (Vol'nov, 1966) and heat (ΔG^{o}=-20.7 kJ/mol) (Königstein et al., 1998). The advantage is that H_2O_2 release is auto-regulated by the rate of CaO_2 dissolution, reducing disproportionation since not all the H_2O_2 is available at once as with liquid H_2O_2. Technical grade CaO_2 powder (50% CaO_2/50% $Ca(OH)_2$) is the least expensive form, and is injected as a slurry in water. Aquifers are less permeable to solids than liquids, but this may not be a disadvantage relative to liquid H_2O_2 because disproportionation also clogs pores (Xu et al., 2006).

Evaluating the utility of CaO_2 in MF chemistry is difficult because the literature is lacking in controlled studies on the rate of dissolution of CaO_2 in water and the yield of H_2O_2. Because CaO_2 has been used mostly to release O_2 for bioremediation there is confusion in the literature about its behavior with regard to H_2O_2 production, and it has even been postulated that O_2 is formed directly from CaO_2 instead of H_2O_2 (Schmidtke et al., 1999). Varying pH is the main reason for the conflicting information. Unless a buffer is added the pH increases to 12-13. However, the rate of CaO_2 dissolution and the stability of H_2O_2 increase with decreasing pH. Arienzo (2000) reported that the concentration of H_2O_2 in a 0.2% slurry of CaO_2 increased from 380 mg/L to 1200 mg/L as the pH was decreased from 11 to 3. Rates of dissolution were not reported. White et al. (1998) and Cassidy and Irvine (1999) measured O_2 release for 2 months in soils with unbuffered CaO_2, but Northup and Cassidy (2007) showed that CaO_2 was exhausted within 2 days at pH 8. The instability of H_2O_2 at high pH makes it impossible to identify as an intermediate. It is also difficult to distinguish biological from chemical oxidation of contaminants since both are oxidative processes with the same products. This difficulty is exacerbated by recent findings that aerobic biodegradation co-exists with MF oxidation of contaminants in soils, even at high doses of liquid H_2O_2 (Ndjou'ou et al., 2006).

The ability of CaO_2 to produce •OH has not yet been demonstrated. Northup and Cassidy (2007) compared the treatment of a soil contaminated with petroleum hydrocarbons using a commercially available CaO_2-based oxidant and liquid H_2O_2 at pH of 8. CaO_2 removed 96% of total petroleum hydrocarbons (TPH), compared with 74% using liquid H_2O_2. Since a biological control showed only 30% reduction, they concluded that the TPH removal in the test reactors was due to MF oxidation. This study indicated that CaO_2 was a more efficient source of H_2O_2 for MF chemistry than liquid H_2O_2. Bogan et al. (2003) also reported that CaO_2 performed better than liquid H_2O_2 in removing polycyclic aromatic hydrocarbons (PAH) from soil. However, these two studies did not demonstrate •OH-mediated MF oxidation.

This research is the first to demonstrate that CaO_2 can promote MF oxidation of contaminants. First, the yield of H_2O_2 from CaO_2 and the time required for dissolution was determined at various pH values. Second, a •OH scavenger (2-propanol) was used to show that the observed oxidation of tetrachloroethene (PCE) by CaO_2 at pH 8 was due to the production of•OH. Finally, the performance of MF oxidation of PCE using liquid H_2O_2 (pH=7) and CaO_2 (pH=6, 7, 8, and 9) was compared in closed reactors. Temperature was monitored, and PCE volatilization and disproportionation of H_2O_2 to O_2 were quantified. Oxidant efficiency (mmol H_2O_2 consumed/mmol PCE oxidized) was calculated directly for H_2O_2, and estimated for CaO_2 using the yield of H_2O_2 measured at each pH value in the first set of experiments.

Materials and Methods

Materials

Technical grade CaO_2 (50% CaO_2/50% $Ca(OH)_2$) and liquid H_2O_2 (50%) were provided by Solvay (Houston, TX). Tetrachloroethene (PCE) (99.9%), 2-propanol (99.9%), and hexane (99.9%) were purchased from Acros Organics (Pittsburgh, PA). Anhydrous disodium ethylenediaminetetraacetate (EDTA) (99%) ($C_{10}H_{14}O_8N_2Na_2$), anhydrous ferric sulfate ($Fe_2(SO_4)_3$), monosodium phosphate monohydrate ($NaH_2PO_4•H_2O$) and disodium phosphate heptahydrate ($Na_2HPO_4•7H_2O$) were purchased from Aldrich (Milwaukee, WI).

Reactor Set-Up

The 4 L Pyrex reaction vessels used in these studies had a maximum liquid volume of 2 L. The contents were mixed with a magnetic stirrer at maximum speed. The reactors were kept in a temperature controlled room at 10°C to simulate groundwater temperatures. Each reactor had a custom-fitted lid with 4 ports. Three of the ports housed dedicated probes to measure pH, temperature, and dissolved O_2 (DO). The use of the fourth port was different for each study. During the studies on H_2O_2 yield from CaO_2, the fourth port was open. In the •OH scavenging study of PCE oxidation, the fourth port vented to the atmosphere and was fitted Supleco ORBO® (activated carbon) tubes to trap and quantify PCE volatilized. Three tubes were placed in series to ensure that PCE did not breakthrough. For the studies comparing MF oxidation of PCE with H_2O_2 and CaO_2 the ORBO® tubes were again used to capture PCE, but the were connected to a 1 L Tedlar® gas sampling bag to collect and quantify the O_2 released. Each gas sampling bag had a polypropylene valve and septum fitting to measure air pressure and draw samples. The gas bags were vacuum-emptied before being fitted on the reactors. The reactor set-up was pressure tested by injecting air into the bags, and was capable of maintaining a pressure of 2 atm for 3 months. Since the highest pressure measured in the studies was 1.24 atm, the reactor set-up was deemed suitable for capturing and quantifying O_2 released.

Buffer Solutions and Doses of Modified Fenton Reagents

Buffer solutions used in the reactors were made in de-ionized water using $NaH_2PO_4•H_2O$ and $Na_2HPO_4•7H_2O$. Table 2 shows the pH values tested, the doses of

$NaH_2PO_4{\bullet}H_2O$ and $Na_2HPO_4{\bullet}7H_2O$ used (in g/L), and the buffer strength (in mM). Each reactor had a 2 L of the appropriate buffer. Preliminary testing verified that each buffer solution was able to maintain the desired pH with the dose of CaO_2 and other reagents used. The dose of CaO_2 for all reactors was 4 g technical grade powder, resulting in a 0.2% slurry (w/v). With a purity of 50%, the actual mass of CaO_2 added to each reactor was 2 g, or 1 g CaO_2/L. According to equations 10 and 11, the 2 g of CaO_2 added per reactor contain a maximum theoretical mass of O_2 of 444.0 mg (13.88 mmol O_2), and a maximum theoretical mass of H_2O_2 of 943.4 mg (27.76 mmol H_2O_2), or 472 mg H_2O_2/L (13.88 mM H_2O_2). In the experiments on H_2O_2 yield only CaO_2 was added to the buffers. In the studies with PCE, each reactor also received 80 mg of Fe(III) to promote MF chemistry via reaction 4 and 40 mg EDTA to serve as a chelant. The reactor testing liquid H_2O_2 in the comparative studies received a dose of 27.76 mmol H_2O_2 (13.88 mM), the maximum theoretical amount contained in the 2 g dose of CaO_2.

pH	**$NaH_2PO_4{\bullet}H_2O$ (g/L)**	**$Na_2HPO_4{\bullet}7H_2O$ (g/L)**	**Buffer strength (mM)**
6	12.1432	3.2176	100
7	2.9181	7.733	50
8	0.1884	4.994	20
9	0.01	2.6605	10
12-13[a]	None	None	None

[a] the pH of a 0.2% (w/v) slurry of unbuffered technical grade CaO_2 in water.

Table 2: Concentrations of buffers used to maintain the desired pH values during testing with CaO_2 and H_2O_2.

Sample Handling and Preparation for PCE Analyses

PCE was extracted from duplicate 10 mL unfiltered samples of reactor liquid with 2 mL of hexane by mixing in 25 mL screw-cap test tubes on a wrist action shaker for 6 hours. After centrifuging, the hexane was extracted with a syringe and placed in 2 μL vials for PCE analyses. PCE trapped in the ORBO® tubes was extracted in the same fashion by sacrificing each tube in 2 mL of hexane and 10 mL of added de-ionized water.

Analyses

All analyses were done in duplicate. H_2O_2 was only measured in the aqueous phase, which is justified by its complete miscibility in water and low volatility (Hess, 1995). H_2O_2 was measured in the filtrate from 10 mL samples from the reactors passed through a 0.45 μm filter. The H_2O_2 was quantified using a Hach DR 5000 spectrophotometer after color was developed with titanium sulfate (Schumb et al., 1955). The pH was monitored continuously with an Orion probe and meter. Temperature was also measured continuously with a Vernier stainless steel probe. The DO was measured before oxidant addition and after oxidation was complete using a YSI Instruments probe. A water manometer was used to measure air pressure in the gas bags after chemical oxidation was complete. Duplicate 25 mL gas samples were then taken from the sampling bags and injected into an Illinois Instruments-3600 O_2 Analyzer to measure O_2. The O_2 analyzer was calibrated between 20% and 30% O_2 concentrations. Cl^- was measured in samples of reactor filtrate with a Thermo Orion specific probe.

PCE was analyzed in duplicate hexane extracts using a Hewlett-Packard 6890 gas chromatograph (GC) with electron capture detection and a DB-1 fused-silica capillary column (15m x 0.317 mm id, 0.25 μm film thickness). The oven was at 40°C for 5 min, and increased 5°C/min to a final temperature of 130°C. The injector and detector were at 240°C and 350°C, respectively. PCE concentrations are reported as mg/L.

Measuring O_2 Released from CaO_2 and H_2O_2

The total amount of O_2 released was determined by adding the amount of O_2 released from CaO_2 or H_2O_2 to the aqueous phase and the gas phase, and subtracting from this the amount of O_2 originally present in the reactor. The initial amount of aqueous-phase O_2 was calculated by multiplying the DO concentration by 2 L. The initial amount of gas-phase O_2 was calculated using the atmospheric O_2 concentration (20.9%) and the volume of headspace without the gas bag (2125 mL). After the reactions with added CaO_2 or H_2O_2 were complete, the amount of aqueous-phase O_2 was again determined by multiplying the post-reaction DO concentration by 2 L. The gas-phase release of O_2 was calculated from the O_2 in the gas sampling bag, using a headspace volume of 3125 mL (i.e., 2125 mL + 1 L from the gas bag).

Results and Discussion

Yield of H_2O_2 from CaO_2 Dissolution at Different pH Values

Figure 1 shows the release of H_2O_2 with time in the reactors from dissolution of CaO_2 for the different pH values tested. Table 3 lists the % yield of H_2O_2, the associated increase in temperature and the time required for complete CaO_2 dissolution. Complete dissolution of the CaO_2 in the reactors was verified by adding concentrated HCl to a sample to reduce the pH to 2 and then measuring H_2O_2 concentration. No increase in

H_2O_2 concentration after acidification indicated that all the CaO_2 had been dissolved. Although O_2 was not measured in these studies, it can be assumed that any CaO_2 not converted to H_2O_2 was released directly as O_2 (Vol'nov, 1966). The O_2 yield listed in Table 2 was calculated using this assumption. The continuously monitored pH data are not shown in Figure 1 because the buffer solutions maintained the target pH throughout CaO_2 dissolution. The pH of the unbuffered CaO_2 remained between 12 and 13.

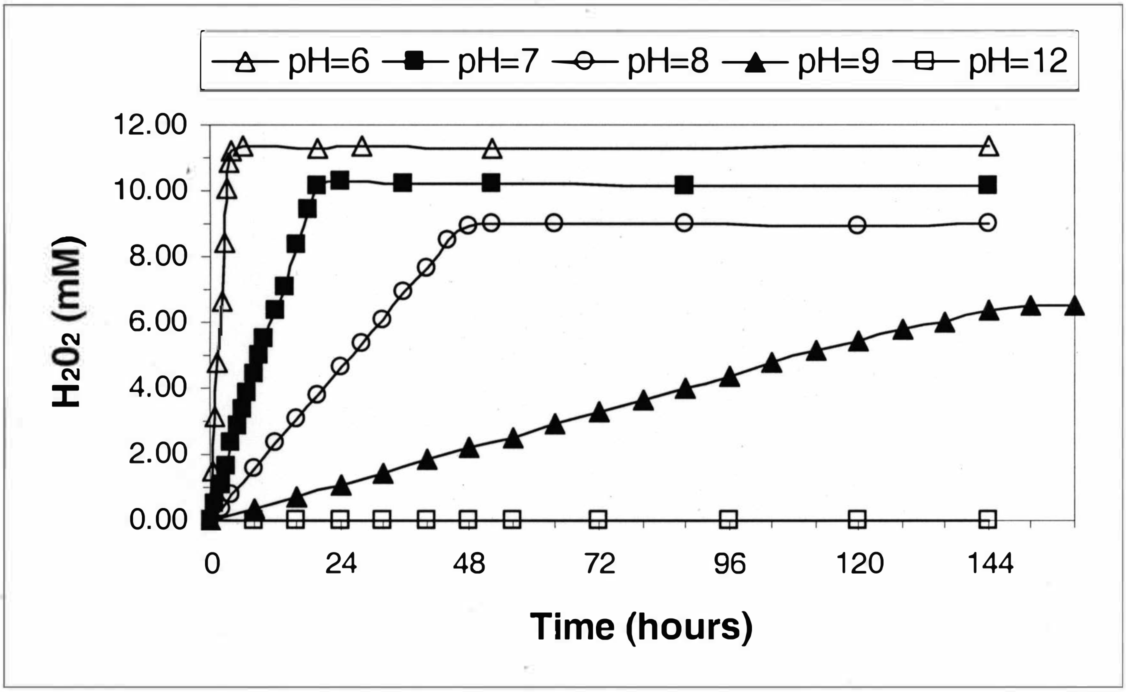

Figure 1: Release of H_2O_2 from CaO_2 dissolving in water during the first 160 hours at the various pH values tested. For pH 12-13, CaO_2 dissolution had not reached completion after 160 hours.

pH	H_2O_2 Yield[a] (mmol)	% H_2O_2 Yield[b]	% O_2 Yield[c]	Increase in temp. (°C)	Time required for dissolution
6	22.75	82	18	8.2	4 hr
7	20.53	74	26	3.7	20 hr
8	18.04	65	35	1.8	52 hr
9	13.06	47	53	0.7	6 d
12-13	0	0	100	0	62 d

[a] from the final aqueous H_2O_2 concentration measured (i.e., mM x 2L).

[b] based on a 100% theoretical yield of 27.76 mmol H_2O_2 from the 2 g CaO_2 added.

[c] calculated assuming that the CaO_2 not released as H_2O_2 was released as O_2.

Table 3: The H_2O_2 yield from CaO_2, the associated increase in temperature, and the time required for complete CaO_2 dissolution at the pH values tested.

It is clear from Figure 1 and Table 3 that the yield of H_2O_2 and the dissolution rate of CaO_2 increased with decreasing pH. Unbuffered CaO_2 (pH=12-13) had no measurable H_2O_2 production. Although only the first 160 hours of data were shown in Figure 1, unbuffered CaO_2 required more than 2 months to dissolve completely. This is consistent with rates of O_2 release in soils with unbuffered CaO_2 reported in the bioremediation literature (Cassidy and Irvine, 1999; White et al., 1998). In contrast, CaO_2 was dissolved within 4 hours at pH 6, and within 52 days at pH 8. This is consistent with the findings of Northup and Cassidy (2007), who showed that a CaO_2-based oxidant buffered at pH 8 was exhausted within 2 days in soil. Higher rates of CaO_2 dissolution also resulted in a greater temperature increase, because the dissolution of CaO_2 is exothermic. Temperature increased over 8°C at pH 6. The H_2O_2 released in these studies was stable because there was nothing added to the reactors to catalyze its decomposition (e.g., Fe and organic compounds). The % yield of H_2O_2 decreased from 83% of the theoretical maximum (27.76 mmol) at pH 6 to 47% at pH 9, and was zero with unbuffered CaO_2. Values of pH lower than 6 were not tested in these studies, because the purpose was to investigate the use of CaO_2 for MF (i.e., quasi-neutral pH) reactions. Moreover, the cost of MF-ISCO increases with decreasing pH because of increased buffer requirements (Table 2).

Scavenger Studies with 2-Propanol to Verify •OH-Mediated PCE Oxidation

Figure 2 shows the results of the study using CaO_2 at pH 8 to oxidize PCE with and without a •OH scavenger (2-propanol). A control reactor that received only PCE was also maintained for comparison. The other two reactors received PCE along with CaO_2, Fe(III), and EDTA, and one of these also received 2-propanol. The dose of CaO_2 was the same as in the previous studies (4 g). The dose of PCE in all three reactors was 6 mmol (3 mM, or 500 mg/L), and the dose of 2-propanol was 10 mM. Using 2-propanol was based on its effectiveness as a scavenger of •OH (Buxton et al., 1988; Howsawkeng et al., 2001; Ndjou'ou et al., 2006). Analyses done at the end of the experiments (60 hours) verified that no CaO_2 and no measurable amount of unreacted H_2O_2 remained in the MF reactors.

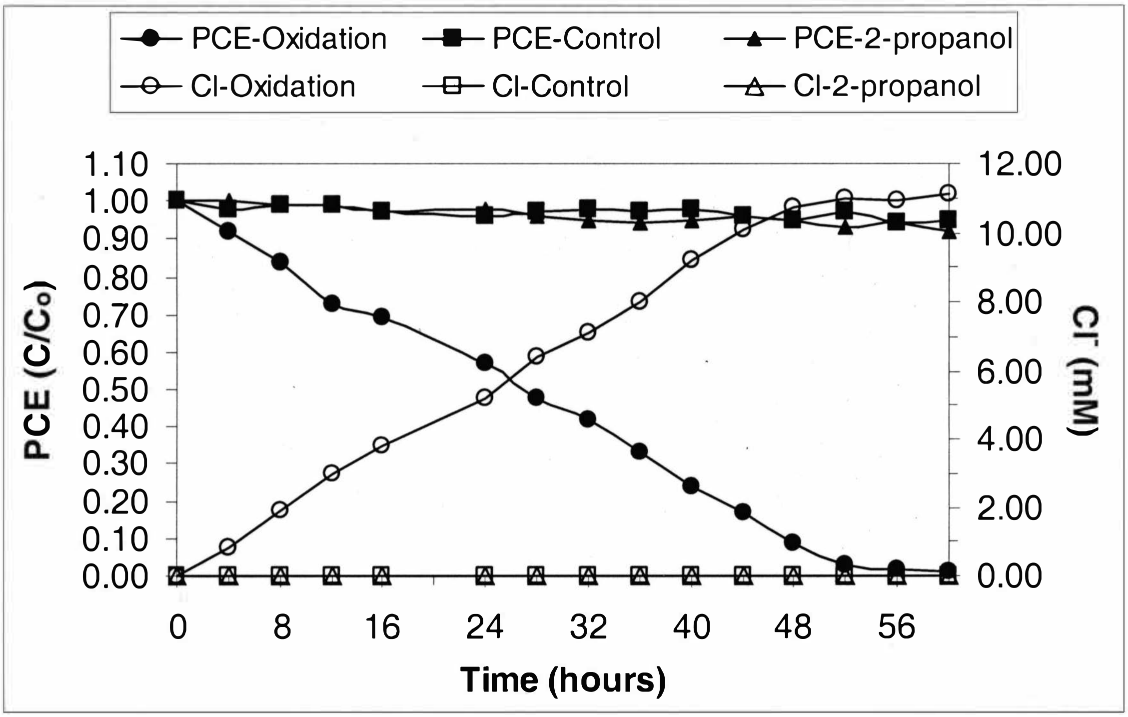

Figure 2: PCE removal and Cl^- release with time in a control with no oxidants, and in reactors with CaO_2-based MF chemistry with and without an •OH scavenger (2-propanol).

Figure 2 shows that in the MF reactor without 2-propanol PCE was nearly completely removed (99%) within 52 to 60 hours. This is consistent with the time required for CaO_2 dissolution at pH 8 in the previous studies (Figure 1, Table 3). Extraction and analysis of the ORBO® tubes showed that only 2% (0.12 mmol) of the PCE removed was due to volatilization. Concentrations of Cl^- in this reactor increased simultaneously with PCE removal, indicating that PCE was mineralized. The final Cl^- concentration was approximately 11 mM, resulting in a ratio of 3.7 mmol Cl^- released/mmol PCE oxidized. This is similar to molar ratios observed by Ndjou'ou et al. (2006) for MF oxidation of PCE in soils using liquid H_2O_2. The amount of PCE oxidized (5.83 mmol, or 97%) was obtained by subtracting the mmol volatilized from the total mmol removed. In contrast, the reactor with 2-propanol behaved like the control, showing no PCE removal except via volatilization (3%). This reactor also showed no measurable release of Cl^-. These results indicate that the PCE oxidation in the reactor without 2-propanol was caused by •OH produced via Reaction 4. These results, along with those of the previous study, also demonstrate that CaO_2 at quasi-neutral pH releases H_2O_2 which participates in MF oxidation.

Comparing MF Oxidation of PCE with H_2O_2 (pH=8) and CaO_2 (pH=6, 7, 8, 9)

The performance of liquid H_2O_2 (pH=7) and CaO_2 (pH=6, 7, 8, 9) for MF oxidation of PCE was investigated. In the tables and figures, each reactor is denoted by the oxidant used followed by the pH in parentheses (e.g., CaO_2 (8) is used for the reactor with CaO_2 buffered at pH 8). Figure 3 is a plot of temperature in the reactors during the first 24 hours. Figure 4 shows the total percentage of PCE removed in the reactors, and the percent volatilized vs. oxidized. Table 4 lists the increase in temperature, O_2 released, PCE removed via volatilization and oxidation, and calculated values of oxidant efficiency. The molar ratio of Cl- released to PCE oxidized is not listed, but ranged from 3.6-3.8 for all reactors, indicating PCE mineralization. The pH data are not shown because readings did not vary from the target pH. The reactors were closed and samples of the contents were taken only after reactions were complete. The reactor with H_2O_2 was considered finished reacting after 40 minutes, and the reactors with CaO_2 were considered finished according to the time for CaO_2 dissolution in Table 2. Gas samples were first taken to measure O_2 and the post reaction DO reading was taken, after which the reactors were opened for sampling. Analyses verified that no solid CaO_2 or H_2O_2 remained.

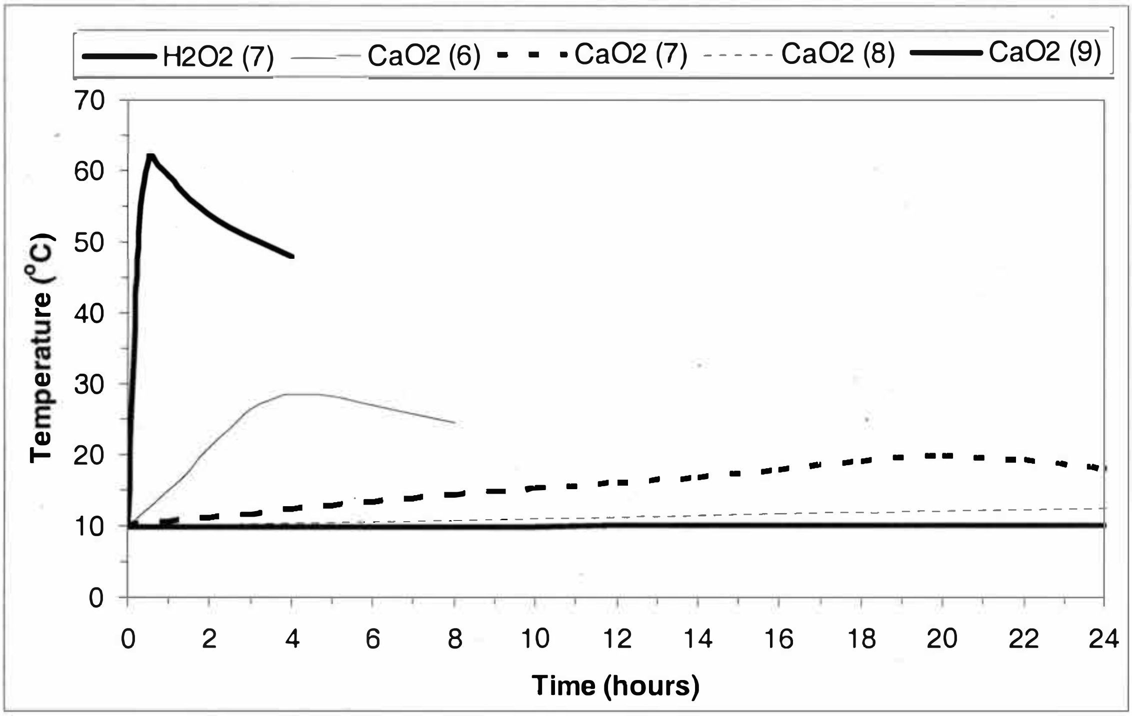

Figure 3: Temperature variations with time in the reactors promoting MF oxidation of PCE with liquid H_2O_2 at pH 7 and with CaO_2 at pH 6, 7, 8, and 9.

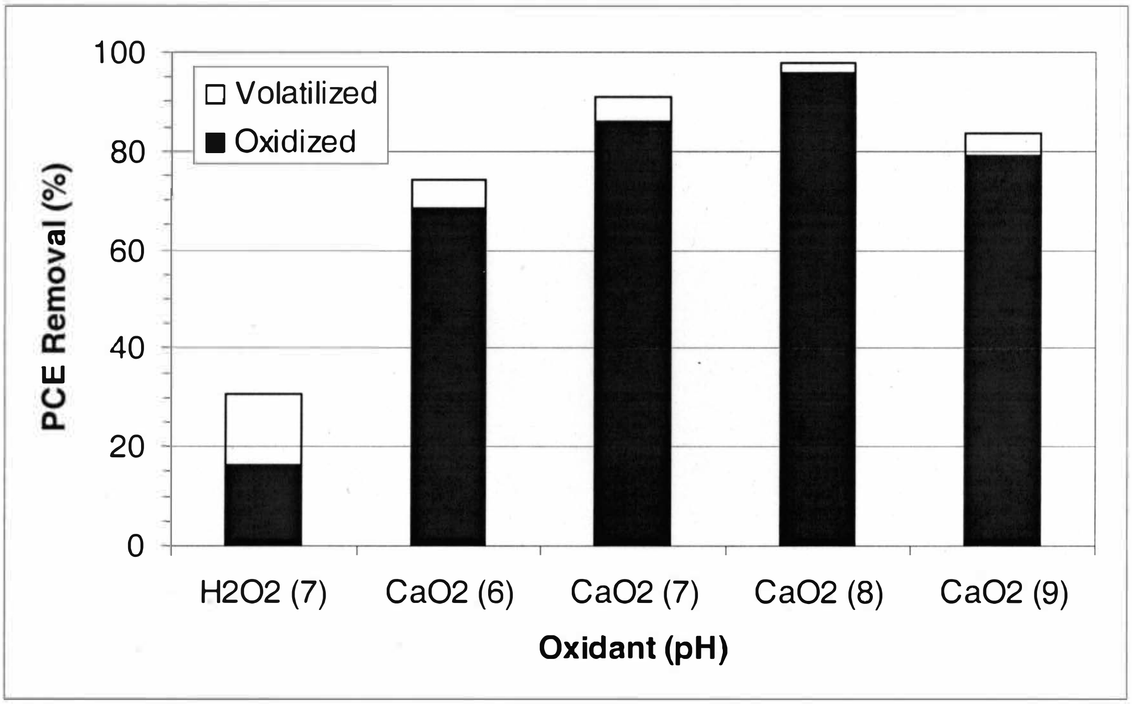

Figure 4: Total PCE removal and percent volatilized vs. oxidized in the reactors promoting MF oxidation of PCE with liquid H_2O_2 at pH 7 and with CaO_2 at pH 6, 7, 8, and 9.

Oxidant (pH)	**Increase in temp. (°C)**	**O_2 released (mmol)**	**PCE removed (mmol)**	**PCE volatilized (mmol)**	**PCE oxidized[a] (mmol)**	**Efficiency[b] (mol H_2O_2[c] /mol PCE)**
H_2O_2 (7)	52.3	12.82	1.84	0.86	0.98	28.3
CaO_2 (6)	18.5	7.90	4.46	0.36	4.10	5.5
CaO_2 (7)	9.7	7.22	5.46	0.29	5.17	4.0
CaO_2 (8)	4.8	5.64	5.88	0.12	5.76	3.1
CaO_2 (9)	1.6	5.15	5.02	0.28	4.74	2.8

[a] PCE oxidized = total mmol PCE removed-mmol PCE volatilized.

[b] mmol H_2O_2 consumed/mmol PCE oxidized.

[c] mmol H_2O_2=27.76 for H_2O_2 (7), and for CaO_2 the H_2O_2 yields from Table 2 were used.

Table 4: Results from the comparative studies of MF oxidation of PCE using H_2O_2 and CaO_2 at the various pH values tested.

Temperature readings (Figure 3) are an indication of the rate and time of completion of reactions promoted by CaO_2 and H_2O_2. Because CaO_2 dissolution, H_2O_2 disproportionation, and •OH-mediated PCE oxidation are all exothermic, an increase in temperature indicates that one or more of these reactions is still occurring, and a decrease in temperature indicates that these reactions have ceased. The greater the rate of these reactions, the greater is the rate and extent of temperature increase. The temperature in the reactor with liquid H_2O_2 increased to 62.3°C within 35 minutes and then began to decrease because H_2O_2 was depleted. In contrast, the temperature maxima in the reactors with CaO_2 were all less, and occurred later than with liquid H_2O_2. This indicates that CaO_2 was able to maintain oxidation reactions over a longer period of time than liquid H_2O_2. The temperature maxima in the reactors with CaO_2, and the time at which they occurred, decreased with increasing pH, which can be explained by decreasing rates of CaO_2 dissolution with increasing pH (Figure 1). In fact, the temperature maxima in the reactors with CaO_2 coincided with the time required for CaO_2 dissolution at each pH value (Table 3). This illustrates how the rate of CaO_2 dissolution auto-regulates the rate of release of H_2O_2 and its participation in chemical reactions, and shows that the rate of MF oxidation using CaO_2 can be controlled simply by changing the pH.

Table 4 lists the maximum temperature increase in the reactors during MF oxidation of PCE. The exothermic reactions in the system (i.e., CaO_2 dissolution, disproportionation of H_2O_2, and MF oxidation) cannot be distinguished from temperature increase alone. However, temperature increase in the CaO_2-based MF reactors was over twice that for the corresponding pH in the CaO_2 dissolution experiments without MF chemistry (cf. Tables 3 and 4). This shows that the energy released by MF oxidation and/or disproportionation was slightly more than twice that from dissolution of CaO_2. Dissolution of CaO_2 is exothermic (ΔG^o=-20.7 kJ/mol) and Fenton oxidation of organics releases a similar amount of energy (Königstein et al., 1998; Wadley and Waite, 2004). However, by far the most exothermic reaction in MF systems is H_2O_2 disproportionation (ΔG^o=-119.2 kJ/mol) (Hess, 1995). A direct relationship was observed between temperature increase and O_2 release (Table 4), a measure of disproportionation. The O_2 released can be assumed to have come from decomposition of H_2O_2, or from O_2 released directly by CaO_2 that was never available as H_2O_2. It was assumed that there was no other source of O_2 except CaO_2 or H_2O_2 and that no O_2 was consumed by biodegradation. The first assumption is supported by the common use of O_2 to measure H_2O_2 disproportionation (Chen et al., 2001; Watts et al., 1999b). The second assumption is supported by the fact that; (1) PCE and EDTA are essentially non-biodegradable aerobically (Nortemann, 1999; Vogel et al., 1987), (2) the reactors were not amended with microorganisms, and (3) the high H_2O_2 concentrations would likely inhibit any microbial activity (Hess, 1995).

The greatest release of O_2 (12.82 mmol) was observed in the reactor with liquid H_2O_2 (Table 4). Vigorous bubbling was also observed with liquid H_2O_2, another sign of rapid O_2 release. High losses of H_2O_2 to O_2 are characteristic of MF systems using liquid H_2O_2, even with large amounts of phosphate buffer (Baciocchi et al., 2004; Chen et al., 2001; Watts et al., 1999b). This scavenging of H_2O_2 is the major drawback of using liquid H_2O_2 in MF-ISCO. The O_2 released from CaO_2 at pH 7 was 7.22 mmol, markedly less than with liquid H_2O_2, even though the pH and the phosphate buffer concentration were the same for both. All the CaO_2 reactors showed much less O_2 release than liquid

H_2O_2, despite the fact that CaO_2 releases considerable O_2 without MF reagents (Table 3). In fact, the O_2 release from the CaO_2-based MF systems decreased with increasing pH, even though the amount of O_2 released from CaO_2 without MF reagents increases with increasing pH (Table 3), and despite the fact that the stability of H_2O_2 decreases with increasing pH (Hess, 1995). This apparently paradoxical behavior can be explained by the decreasing rate of CaO_2 dissolution and H_2O_2 release with increasing pH. These results show that CaO_2, by maintaining lower levels of H_2O_2, can reduce disproportionation losses and that these losses can be controlled by varying the pH.

CaO_2 also achieved a much greater extent of PCE oxidation than liquid H_2O_2, at all the pH values tested (Table 4, Figure 4). Figure 4 illustrates the % removal of PCE, and the relative contribution of volatilization vs. chemical oxidation. Only 31% of the PCE was removed in the reactor with liquid H_2O_2, and nearly half of this was due to volatilization. This is not surprising, since liquid H_2O_2 also resulted in the greatest release of O_2 and the highest temperature, both of which encourage volatilization. For CaO_2, a pH of 8 provided the greatest total removal of PCE (98%), and only 2% of this was due to volatilization, whereas 96% was attributed to chemical oxidation. These results confirm those obtained with CaO_2 at pH 8 in the•OH scavenging studies (Figure 2), and show that CaO_2 performed optimally at pH 8.

The oxidant efficiency (mmol H_2O_2 consumed/mmol PCE oxidized) was calculated directly for H_2O_2 using the dose applied (27.76 mmol), and was estimated for CaO_2 using the yield of H_2O_2 measured at each pH value in the experiments on CaO_2 dissolution (Table 3). It is not certain that the H_2O_2 yield from CaO_2 was the same in the MF system as in the system without Fe, EDTA and PCE. However, attempts in previous experiments to directly measure H_2O_2 released from CaO_2 (data not shown) showed that the H_2O_2 was too short-lived to be measured. CaO_2 and H_2O_2 were completely consumed in all the reactors. The values of oxidant efficiency in Table 4 are comparable to those reported by Crimi and Siegrist (2005). There was an inverse relationship between oxidant efficiency and loss of oxidant to O_2 released, because H_2O_2 lost to disproportionation cannot form•OH and chemically oxidize PCE. Liquid H_2O_2 showed an oxidant efficiency of 28.3 mmol H_2O_2 consumed/mmol PCE oxidized. This is far greater than values obtained for CaO_2, even though CaO_2 released considerably less than the theoretical maximum of 27.76 mmol H_2O_2 (Figure 1, Table 3), which was the dose of liquid H_2O_2 used. This clearly shows that liquid H_2O_2 was an inefficient MF oxidant compared with CaO_2 at any pH. The efficiency of CaO_2 as a MF oxidant increased with increasing pH, from 5.5 at pH 6 to 2.8 at pH 9, even though the yield of H_2O_2 decreases with increasing pH (Figure 1, Table 3). As with O_2 release, this trend can be explained by the lower rate of H_2O_2 release from CaO_2 with increasing pH.

The results from these studies suggest that regulating the rate of availability of H_2O_2 using CaO_2 increases the efficiency of MF oxidation relative to using liquid H_2O_2 by reducing losses of H_2O_2 to disproportionation. Liquid H_2O_2 proved quite unstable and inefficient, even with a strong phosphate buffer. Furthermore, the results of these studies indicate that the optimal pH for CaO_2 in MF chemistry is 8. Below this pH the rate of release of H_2O_2 from CaO_2 is too fast, causing excessive disproportionation (Figure 3, Table 4). The resulting temperature increase and O_2 release encourage contaminant volatilization. Furthermore, maintaining a CaO_2-based MF system at a pH below 8 requires considerably more phosphate buffer to be used (Table 2), which increases cost.

As pH rises above pH 8, the amount of H_2O_2 released from CaO_2 decreases rapidly (Figure 1, Table 3), and CaO_2 becomes less effective for MF treatment, and more suitable for releasing O_2 for bioremediation. Northup and Cassidy (2007) showed that a commercially available CaO_2-based MF oxidant at pH 8 was able to promote chemical oxidation and biodegradation of petroleum hydrocarbons.

Conclusions

Rapid decomposition of liquid H_2O_2 in soils limits the applicability of modified Fenton (MF) chemistry for *in situ* chemical oxidation (ISCO). We conclude from these laboratory studies that CaO_2 can be a more efficient source of H_2O_2 for MF oxidation of PCE than liquid H_2O_2. The rate of release of H_2O_2 from CaO_2 is auto-regulated by the rate of CaO_2 dissolution, which can be controlled by adjusting the pH. The rate of CaO_2 dissolution increases markedly with decreasing pH. In this study, 62 days were required for complete dissolution of unbuffered CaO_2 (pH=12-13), whereas only 4 hours were required when CaO_2 was buffered at pH 6. The yield of H_2O_2 from CaO_2 also increases considerably with decreasing pH. The yield of H_2O_2 from a 0.2 % (w/v) slurry of technical grade CaO_2 (50% purity) increased from 47% (13.06 mmol) at pH 9 to 82% (22.75 mmol) at pH 6. Studies of MF treatment of PCE showed that CaO_2 at all pH ranging from 6 to 9 was a more efficient source of H_2O_2 for MF oxidation of PCE than liquid H_2O_2 at pH 7. Liquid H_2O_2 showed excessive disproportionation to O_2, increasing temperature dramatically and volatilizing nearly as much PCE it oxidized. By releasing H_2O_2 only upon dissolution, CaO_2 (at pH 6, 7, 8, 9) achieved a much greater oxidant efficiency (mmol H_2O_2 consumed/mmol PCE oxidized), and resulted in much less PCE volatilization and greater PCE oxidation than liquid H_2O_2. The optimal performance of CaO_2 was observed at pH 8, which is recommended for MF-ISCO applications. The ability of CaO_2 at pH 8 to promote MF oxidation of PCE via the production of hydroxyl radicals was demonstrated in these studies.

CHAPTER III

EVIDENCE FOR THE PRODUCTION OF SURFACTANTS ACCOMPANYING THE CHEMICAL OXIDATION OF HYDROCARBONS IN SOILS

Abstract

A hydrocarbon-contaminated soil was treated in laboratory slurry reactors using modified Fenton (MF) chemistry and biodegradation. Treatment with liquid hydrogen peroxide (HP) plus Fe^{3+} was compared with a calcium peroxide (CaO_2)-based MF oxidant (Cool-Ox^{TM}). During oxidation, samples of slurry filtrate were tested to quantify hydrocarbon concentrations and bulk surfactant concentrations, using the critical micelle dilution method. The results showed that both oxidants resulted in the temporary accumulation of surfactants to maximum levels of over 4 times the critical micelle concentration, but that surfactants were completely removed by the end of treatment. Removal of surfactants was complete within 2 hours with liquid HP vs. 2 days for the CaO_2-based oxidant. For both chemical oxidants, hydrocarbon concentrations in filtrate were 3 to 4 orders of magnitude greater than in the biological control. Both oxidants showed enhanced removal of the high molecular weight fractions of the petroleum hydrocarbons relative to biological treatment, though this effect was greater with the CaO_2-based oxidant than with liquid HP. The chemical treatments did not considerably reduce numbers of culturable hydrocarbon-degrading microorganisms suggesting that chemical and biological oxidation can occur simultaneously in soils.

Introduction

Chemical oxidation with Fenton reactions is a powerful tool for the destruction of many contaminants (Wadley and Waite, 2004), and involves the catalyzed decomposition of H_2O_2 by Fe^{2+} to form the hydroxyl radical (•OH) (Reaction 4). If only Fe^{3+} is originally present, or the dose of $Fe^{2+}$is insufficient, the Fe^{2+} required in reaction 4 can be generated via Reactions 5 through 8 (Kwan and Voelker, 2003; Walling, 1975). The •OH radical is a strong oxidant, reacting with most contaminants at near diffusion-limited rates ($>10^9$ M^{-1} s^{-1}).

Conventional Fenton's chemistry maintains a pH at or below 3, which is impractical in soils because of their buffering capacity. As a result, many soil remediation applications use a Fenton-like or modified Fenton's (MF) treatment which produces hydroxyl radicals at a pH near neutral. There are variations in how H_2O_2 and Fe are provided to soils in MF systems. Iron can be added as salts of Fe^{2+} or Fe^{3+} (Watts and Dilly, 1996), or native iron-containing minerals (e.g., goethite, ferrihydrite, magnetite) can be used (Kong et al., 1998; Yeh et al., 2003). Organic chelating agents can be added to MF systems to increase rates of hydroxyl radical production by enhancing the presence of Fe^{3+} in the aqueous phase (Nam et al., 2001; Sun and Pignatello, 1992), though this increases costs. An alternative to liquid H_2O_2 is adding metal (Ca, Mg) peroxides, which release H_2O_2 when they dissolved in water (Arienzo, 2000; Bogan et al., 2003; Schumb et al., 1955).

MF oxidation in laboratory and field studies usually produces foam, a strong indication of surfactant production. Many reports of MF treatment of organic contaminants in soil have made observations that could be attributed to surfactant production, though none have suggested this as a possible cause. Yeh et al. (2003) reported the "solubilization" (i.e., increase in aqueous phase concentration) of non-aqueous phase trichloroethylene (TCE) during MF treatment. Bogan et al. (2003) investigated MF treatment of polycyclic aromatic hydrocarbons (PAH), and found that adding vegetable oil enhanced the removal of high molecular weight (i.e., 5- and 6-ring) PAH. Although they attributed this to the preferential partitioning of the high molecular weight PAH into the vegetable oil, which was then oxidized, an alternative explanation is that surfactants produced during oxidation of vegetable oil and/or PAH preferentially increased the presence of the 5- and 6-ring PAH in the aqueous phase, thereby enhancing their extent of oxidation. Nam et al. (2001) reported that MF oxidation of PAH followed by biodegradation resulted in 20-60% greater removal of 5-and 6-ring PAH compared with biodegradation alone. This could be explained by the production of surfactants during MF oxidation, which would render high molecular weight PAHs more available to microorganisms in the aqueous phase. Finally, Kakarla and Watts (1997) and Watts and Stanton (1999) observed that desorption and oxidation of hydrophobic petroleum hydrocarbons increased with increasing doses of MF reagents. These findings also could be attributed to surfactant production caused by the MF reactions.

In this study a soil contaminated with petroleum hydrocarbons was treated with two MF reagents, liquid HP and calcium peroxide-based powder. The main goal of this work was to quantify the production of surfactants during MF treatment and their effect on the presence of hydrocarbons in the aqueous phase. The effect of the two treatments on the number of culturable hydrocarbon-degrading microorganisms was also investigated.

Materials and Methods

Contaminated Soil

The hydrocarbon-contaminated soil used in these studies was collected from the Sydney Tar Ponds site, in Sydney, Nova Scotia, Canada. The soil was first sieved to remove particles larger than 2 mm. The sieved soil was homogenized in a portable cement mixer for 2 hours. Characterization of the homogenized soil was done according to Methods of Soil Analysis (1986), and the results of the analyses are listed in Table 5.

Reactors

The 3 slurry reactors were setup as described by Cassidy et al. (2002). Volatile contaminant losses were quantified with powdered activated carbon traps. The 10-L glass vessels had a slurry volume of only 5 L in order to leave room for foam. Slurry batches were made by adding tap water to 2 kg dry soil to a volume of 5 L, for a solids concentration of 40% (w/v). A mechanical mixer set at 300 rpm provided mixing.

Modified Fenton and Biological Treatments

The liquid HP treatment consisted of adding the following to the reactor in sequence, 50 mL of a phosphate solution buffered at a pH of 8 (the same pH as the slurry) containing 200 mg Fe^{3+} (as ferric sulfate), 30 mg of EDTA (4 g as tetrasodium-EDTA, and 6 g as disodium-EDTA), and finally 100 mL of 50% HP. Initial tests were conducted to ensure that the buffer maintained the slurry at a pH of 8. The CaO_2-based treatment consisted of adding 50 g of Cool-Ox™ powder, obtained from DeepEarth Technologies, Inc. (Alsip, IL, USA).

Analyte	Result	Units
sand-sized particles	45	% (w/w)
silt-sized particles	32	% (w/w)
clay-sized particles	23	% (w/w)
total Fe	3	% (w/w)
total carbonates	4	% (w/w)
pH	8.0 ± 0.3 (7)[a]	
TPH concentration	10,604 ± 850 (10)	mg/kg
Hydrocarbon-Degrading Microorganisms	7.3 ± 0.3 (5)	log CFU/g soil

[a] mean ± standard deviation (number of measurements).

Table 5: Properties of the homogenized contaminated soil before treatment.

Cool-Ox™ is buffered at a pH of 8, so no additional buffer was necessary. The biological control was aerated with a diffuser stone and received ammonia and phosphate to provide a ratio of C:N:P of 100:10:1, which is sufficient to achieve complete biodegradation of hydrocarbons (Eweis et al., 1998). No buffer was added to the biological control. The pH remained at 8 during the study period in all reactors.

Analyses

All analyses were in triplicate, unless otherwise reported. Surfactant and microbial measurements were done as described by Hudak and Cassidy (2004). Surfactant analyses were made on filtrate from slurry passed through a 0.45 μm filter. Surface tension (ST) was measured with a Tantec CBVP-Z Tensiometer. Bulk surfactant concentrations were quantified with the critical micelle dilution (CMD) method. ST remains constant at some minimum value (30-36 dynes/cm) when surfactant concentrations are above the critical micelle concentration (CMC). Serial dilution of the sample reduces surfactant levels below the CMC, which causes the to ST increase. The CMD is the inverse of the dilution factor. Hence, a CMD of 4 represents a surfactant concentration of 4 times the CMC. Triplicate 5 g samples of soil were taken for microbial enumeration using plating techniques that used petroleum hydrocarbons as the only carbon source. Total Petroleum Hydrocarbons (TPH) and concentrations of the 4 individual fractions (F1, F2, F3, and F4) were quantified according to method described by the Canadian Council of Ministers of the Environment, or CCME (2001). The pH of the slurry was monitored with a pH probe.

Results

Surfactant Production

Figures 5 and 6 show time profiles of surface tension (ST), surfactant concentrations (CMD) and total petroleum hydrocarbons (TPH) measured in the filtrate of the slurry treated with liquid HP, and the CaO_2-based oxidant, respectively. No evidence of surfactant production was observed in biological control.

Figures 5 and 6 both show similar patterns of surfactant accumulation and removal, though the time scale is hours for liquid HP treatment compared with days for the CaO_2-based oxidant. With both MF treatments, ST values decreased from the background value of approximately 72 dynes/cm (the ST of water) to values between 30 and 35 dynes/cm soon after addition of the oxidants. This is a clear indication of surfactant production and accumulation in the slurry. Foaming, another sign of the presence of surfactants, was also observed with both MF treatments, and was particularly vigorous with liquid HP.

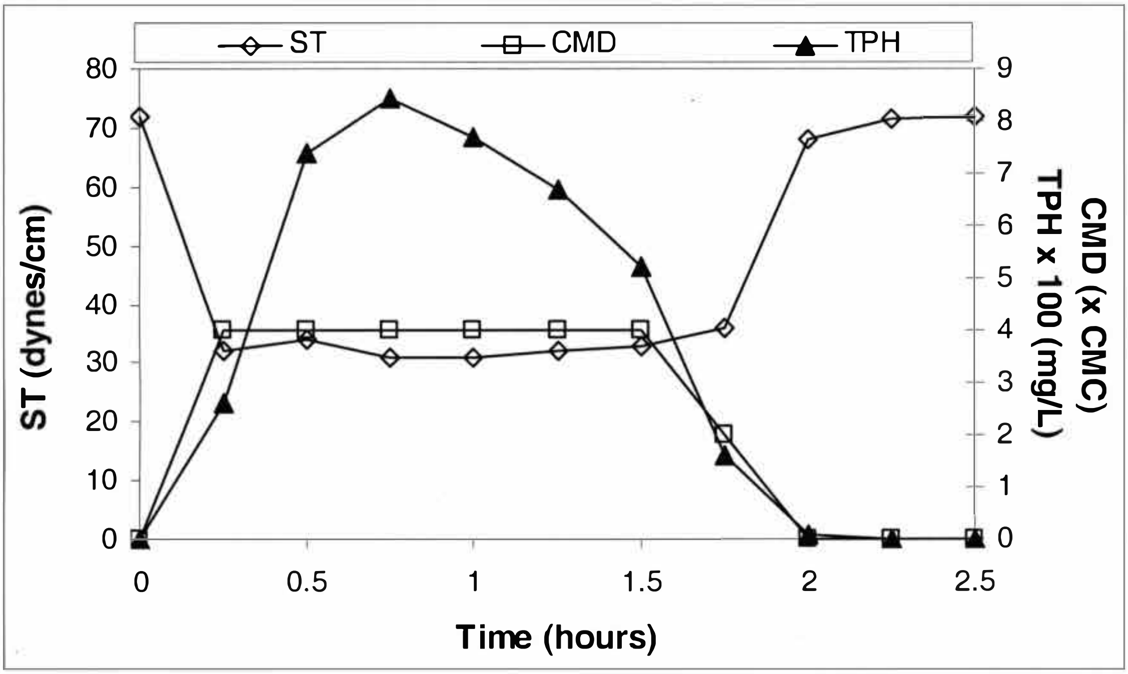

Figure 5: Time profiles of surface tension, surfactant concentrations and total petroleum hydrocarbons measured in the filtrate of the slurry treated with liquid HP.

As ST values dropped, CMD and filtrate TPH concentrations increased from essentially zero to maximum levels, which are also clear indications that surfactants were produced and accumulated as a result of chemical oxidation. Surfactants partition hydrophobic compounds such as petroleum hydrocarbons, thereby increasing their presence in the aqueous phase. Filtering removes non-aqueous phase hydrocarbons, so that only emulsified and/or surfactant-partitioned TPH is measured (Hudak and Cassidy, 2004; Tadros, 2005). However, as time progressed with both treatments, surfactants were clearly removed, evidence for which is an increase in ST and decreases in CMD and filtrate TPH to background levels.

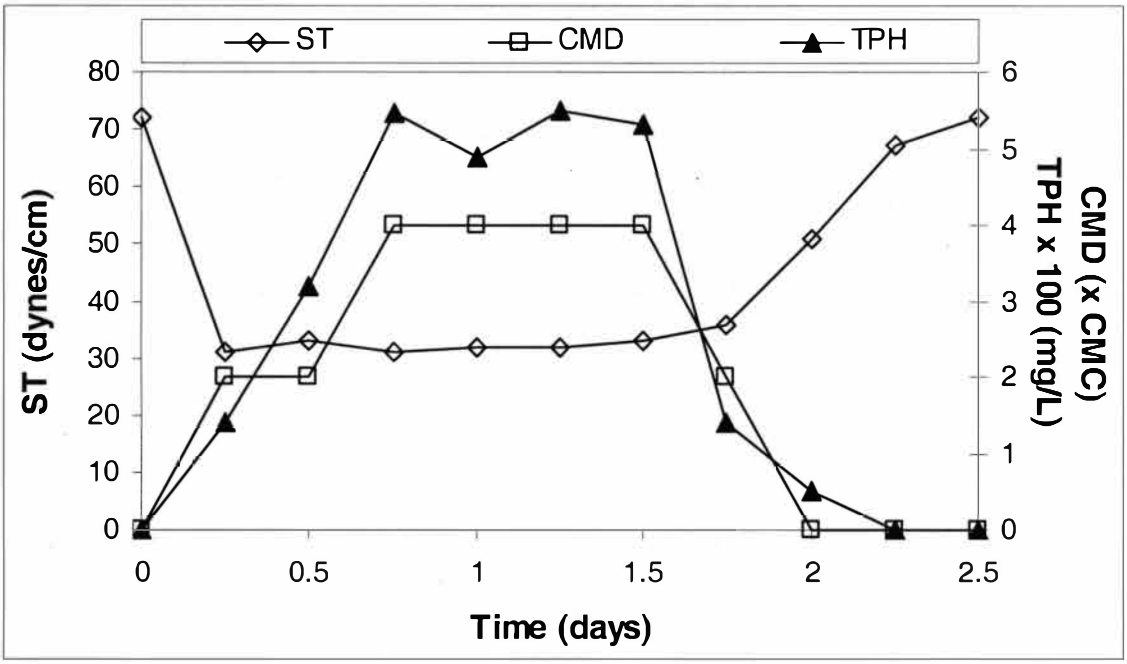

Figure 6: Time profiles of surface tension, surfactant concentrations and total petroleum hydrocarbons measured in the filtrate of the slurry treated with the CaO_2-based oxidant.

The exact mechanisms of the production of the surfactants and their chemical composition were not determined in these studies. The CMD method only measures bulk surfactant concentrations. However, the data in Figures 5 and 6, combined with the absence of any evidence of surfactant production in the biological reactor clearly demonstrate that surfactants were produced and temporarily accumulated during chemical oxidation, and that these surfactants increased the aqueous-phase presence of the hydrocarbon contaminants. The most probably mechanism for producing the surfactants is that chemical oxidation of the hydrocarbons, and/or the native organic material (i.e., humic substances) produced intermediate compounds that have surfactant properties. Oxidation by •OH takes place primarily via electrophilic addition to alkenes and aromatics, and via hydrogen abstraction from saturated hydrocarbons (Aschmann et al., 2004; Walling and Johnson, 1975). The intermediates formed by partial oxidation include various alcohols, aldehydes and ketones, and carboxylic acids. Biological oxidation of alkanes also forms alcohols and fatty acids as intermediates (Eweis et al., 1998). These oxygen-containing functional groups on a hydrophobic hydrocarbon skeleton result in surfactant-like behavior (Tadros, 2005). Ohlenbusch et al. (1998) showed that partial •OH oxidation of humic substances breaks them down into their polyphenolic building blocks, which have surfactant-like properties. The humic content of this soil was not able to be determined, but its dark color suggests that it may have significant quantities of native organics. Partial oxidation of the chelator EDTA may also have produced surfactants in the liquid HP reactor. It is not known whether the CaO_2-based oxidant contained similar organic compounds, as its composition is proprietary.

The mechanisms of removal of the surfactants produced are also not clear from the results of this study. Probably further chemical oxidation of the partial oxidation products that served as surfactants took place. In addition, biological degradation of the surfactants may have taken place simultaneously with chemical oxidation (see discussion on microbial counts below). It is unlikely that volatile removal of the surfactants was significant, since they tend to be water soluble and have high molecular weights (Tadros, 2005). The time profiles in Figures 5 and 6 suggest that at the beginning of the treatment cycle, the rate of surfactant production exceeded the rate of removal, until a steady state was observed in the middle of the cycle where rates of production and removal were equal. Towards the end of the cycle, the rate of removal exceeded the rate of production, until no measurable quantity of surfactants remained.

Though the time profiles of surfactant production showed a similar pattern with both MF treatments, there were important differences (cf. Figures 5 and 6). The most important difference was the time during which surfactants were present in the slurry, two days for the CaO_2-based oxidant vs. only 2 hours for the liquid HP. This means that surfactants were available at rates above the CMC for a longer period of time in the slurry treated with the CaO_2-based oxidant than the slurry receiving the liquid HP treatment. This finding is important to the discussion of removal of individual hydrocarbon fractions (see below). It is not known exactly why these two MF oxidants reacted so differently with the same contaminated soil, but these results clearly show that the CaO_2-based oxidant sustained chemical reactions over a significantly longer period of time than the liquid HP treatment. The most likely reason for this is that the H_2O_2 required for the Fenton reactions described in Equations 4-8 is released slowly from CaO_2 as it dissolves in water, whereas in the liquid HP system all the H_2O_2 is available at once. Consistent with this is the observation that foaming was much more intense and short-lived in the reactor with liquid HP than the one with the CaO_2-based oxidant. Another difference is that maximum filtrate TPH concentrations were somewhat higher with liquid HP treatment (8.5 mg/L) than with CaO_2-based oxidation (5.5 mg/L), even though the maximum CMD values were identical (4 x the CMC). This can be explained by the insensitivity of the CMD method of measuring surfactant concentrations. The filtrate TPH measurements strongly suggest that the true maximum surfactant concentrations were somewhat higher in the liquid HP reactor.

Hydrocarbon Removal and Microbial Counts

Tables 6 and 7 list the data collected on TPH concentrations and removals, and on counts of culturable hydrocarbon-degrading microorganisms at the end of treatment. The two MF treatments were maintained for 1 week, but the bioreactor was maintained for 1 month because rates of biodegradation are slower than chemical oxidation. As seen in Table 6, total TPH removal was only 29.6% for biological treatment, compared with removals of 73.7% and 95.6% for liquid HP and CaO_2-based treatments, respectively. Volatile TPH removal was quite small in all reactors. Plate counts using petroleum hydrocarbons as the sole carbon source indicate that chemical oxidation did not reduce hydrocarbon degraders significantly (Table 6). Microbial counts with CaO_2-based treatment were statistically equivalent (i.e., within standard deviations) to those observed with biological treatment, and those for liquid HP were only an order of magnitude lower than biological treatment.

The microbial counts in Table 6 suggest that chemical oxidation of contaminants in soil can take place simultaneously with biological oxidation, which is possibly the most important finding of this work. Biological processes have traditionally been considered incompatible with chemical oxidation because of excessive death and/or inactivation of the native microorganisms. However, results from several recent studies suggest that MF reactions can co-exist with chemical oxidation. Büyüksönmez et al. (1998) showed that pre-acclimation of *Xanthobacter flavus* FB71 to MF reactions sharply reduced the toxicity of the hydroxyl radicals to that species. Büyüksönmez et al. (1999) showed that addition of *X. flavus* to a MF system oxidizing tetrachloroethene (PCE) resulted in 10% greater mineralization of PCE than stand-alone MF reactions.

Howsawkeng et al. (2001) also found evidence for simultaneous chemical oxidation of PCE and aerobic assimilation of oxalate (OA) by *X. flavus* in the presence of MF reactions. These three studies were done in aqueous systems with a microbial pure culture. However, in a soil with trinitrotoluene contamination, levels of phospholipids (a surrogate measure of viable biomass) were unaffected or showed an increase after MF treatment compared with controls. Even with conventional Fenton's treatment (pH of 2, 1 day residence time) of a soil contaminated with polycyclic aromatic hydrocarbons in a slurry reactor, total heterotrophic plate counts were only reduced from 10^8 to 10^4 per mL slurry (EPA, 1997). MF reactions are more compatible with microbial reactions than conventional Fenton's chemistry because the pH is near neutral. In this study, it is possible that the enhanced hydrocarbon concentrations in the aqueous phase (i.e., filtrate) caused by the presence of surfactants increased the growth rates of hydrocarbon-degrading microorganisms by increasing the bioavailability of the hydrocarbons. Ongoing research with other contaminated soils also indicates that MF oxidation and biological of contaminants takes place simultaneously.

Treatment	**Final TPH Conc. (mg/L)**	**Total TPH removal (%)**	**Volatile TPH removal (%)**	**Microbial Counts (log CFU/g)**
Biological	7,465 ± 466 [a]	29.6%	0.2%	7.5 ± 0.7
Liquid HP	2,785 ± 428	73.7%	0.6%	6.2 ± 0.3
CaO_2-based	465 ± 133	95.6%	0.5%	7.4 ± 0.4

[a] mean ± standard deviation (all based on triplicate measurements).

Table 6: Results from measurement of TPH and hydrocarbon-degrading microorganisms at the end of treatment in all three reactors.

Table 7 lists the concentrations and the removals of the individual hydrocarbon fractions for each treatment. For all three treatments the removal of the smallest molecular weight fraction (F1) was greatest and that for the highest molecular weight fraction (F4) was the lowest. This is typical for all remediation applications, and results from the lower availability of the F3 and F4 fraction in the aqueous phase, where all chemical and biological reactions take place. As a result, the most difficult criteria to meet in Canada are those for the F3 and F4 fractions. Biological treatment resulted in very little of F3 and no removal of F4. In contrast, the MF chemical oxidants showed significant removal of F3 (71.6% to 96.9%) and F4 (48% to 88.7%), even though the MF reactors were only maintained for 1 week, whereas the biological reactor was maintained for 1 month. This explains the increasing use of chemical oxidation vs. biodegradation, despite higher costs.

Treatment	**F1 (C_6-C_{10})**	**F2 (C_{11}-C_{16})**	**F3 (C_{17}-C_{34})**	**F4 (>C_{34})**
Concentrations (mg/kg)				
Untreated[a]	861 ± 104	3,944 ± 339	3,120 ± 302	2,679 ± 271
Biological[b]	124 ± 61	1675 ± 309	2954 ± 420	2712 ± 571
Liquid HP[b]	52 ± 17	455 ± 79	885 ± 243	1393 ± 222
CaO_2-based[b]	14 ± 9	49 ± 21	98 ± 36	304 ± 88
Percent Removal				
Biological	85.6%	57.5%	5.3%	-1.2%
Liquid HP	94.0%	88.5%	71.6%	48.0%
CaO_2-based	98.4%	98.8%	96.9%	88.7%

[a] mean ± standard deviation (based on 10 measurements).
[b] mean ± standard deviation (based on 3 measurements).

Table 7: Concentrations and removals of the individual hydrocarbon fractions for each treatment in the study.

The CaO_2-based oxidant considerably outperformed the liquid HP treatment, particularly for removal of F3 and F4. One possible reason for this is the much longer period of time during which surfactants were present in the slurry with the CaO_2-based oxidant compared with liquid HP (Figures 5 and 6). This provided a longer contact time between the surfactants and the contaminated soil, which allowed more F3 and F4 hydrocarbons to be partitioned into the aqueous phase and chemically oxidized and/or biodegraded.

Summary and Conclusions

Biological treatment of a petroleum-contaminated soil was compared with two modified Fenton treatments at a pH of 8. One used liquid HP, and the other used a CaO_2-based oxidant. The results from this study clearly demonstrated that modified Fenton chemistry was superior to biological treatment in terms of reducing total petroleum hydrocarbon concentrations, and particularly in removing the high molecular weight fractions of petroleum ($>C_{17}$). One reason for this may have been the production and accumulation of surfactants to levels greater than 4 times the critical micelle concentration in reactors treated with the chemical oxidants, whereas none was observed with biological treatment. The results from this study also showed that chemical oxidation did not considerably affect microbial numbers, suggesting that chemical and biological oxidation of contaminants in soils can proceed simultaneously.

CHAPTER IV

SUMMARY OF CONCLUSIONS

The purpose of the first portion of this study was to demonstrate that the dissolution of CaO_2 produces H_2O_2, which can be used for MF ISCO. The results of this study indicate that the dissolution of CaO_2 does release H_2O_2, which is a function of pH. The chemical oxidation of PCE was also tested and MF treatment using CaO_2 was more efficient (mol H_2O_2 consumed/mmol PCE oxidized) than MF treatment using liquid HP. PCE oxidation using liquid HP MF treatment resulted in excessive production of O_2, which resulted in excessive volatilization of PCE as opposed to oxidation. The increased PCE volatilization during treatment using liquid HP is the result of increased temperature and stripping from O_2 due to the disproportionation reaction. The greater efficiency of CaO_2 is due to the auto-regulation of H_2O_2 production through dissolution, which allows for a more controlled reaction. Optimal PCE oxidation efficiency for CaO_2 was determined to be at a pH of 8, which is now recommended for remediation applications.

During the second part of this study a comparison was made between biodegradation, liquid HP MF, and CaO_2 MF for treatment of a hydrocarbon-contaminated soil. The best performance (i.e. % percent removal of hydrocarbons) was achieved with CaO_2 MF while biological treatment performed the worst, especially with the high molecular weight fractions. During the treatment period surfactants were produced and temporarily accumulated in the MF reactors, where as none was observed in the biological reactor, which may account for the superior performance of chemical oxidation during this study. Also, microbial populations were not found to decrease significantly during chemical oxidation in this study, which suggests that simultaneous biodegradation and chemical oxidation processes can occur.

The implications of these studies are significant in that a better understanding of the modified Fenton's process was achieved with respect to chemical oxidation of hydrocarbons. It was determined that CaO_2 is a more efficient source of H_2O_2 for MF treatment than liquid H_2O_2, which was previously not recognized. During the MF oxidation of hydrocarbons, intermediate organic compounds are formed that have surfactant like properties, which enhance desorption and emulsification of hydrocarbons allowing for more complete treatment by oxidation. These studies will contribute to the scientific literature on MF oxidation and will help to improve future mitigation efforts at hydrocarbon contaminated sites. By understanding the process more efficient application of remedial systems will be gained, which is the ultimate goal for this type of research.

There are several aspects of the MF process that need to be investigated in order to fully recognize how the process works. First, the mechanisms by which surfactants are produced and destroyed need to be determined. The surfactants that are produced also need to be characterized for each contaminant, because they are likely to be different depending on the contaminants being oxidized. Also, the tendency of the surfactants to be biodegraded should be investigated. An autoclaved control showed that the surfactants were not removed, compared with a biologically active reactor (refer to appendix C). This indicates that the surfactants are biodegradable. It was determined in these studies that simultaneous biodegradation and chemical oxidation processes can exist, but the relative contribution of each to overall hydrocarbon removal should be investigated. There is also a need for cheaper, less toxic chelants, possibly lignosulfonates, which should be investigated. Finally, the radius of influence during injection of CaO_2 slurry needs to be investigated, which needs to be estimated for proper application of this type of treatment.

Appendix A

Data Relevant to Chapter II: Calcium Peroxide (CaO_2) for use in Modified Fenton Chemistry

time (hours)	pH=6	pH=7	pH=8	pH=9	pH=12
0	0.00	0.00	0.00	0.00	0.00
0.5	1.50				
1	3.12	0.50			
1.5	4.76				
2	6.68	1.06	0.35		
2.5	8.41				
3	10.09	1.62			
3.5	10.88				
4	11.24	2.35	0.76		
5		2.85			
6	11.32	3.38			
7		3.88			
8		4.41	1.56	0.32	0.00
9		4.97			
10		5.50			
12		6.38	2.32		
14		7.06			
16		8.32	3.06	0.74	0.00
18		9.41			
20	11.29	10.15	3.79		
22					
24		10.26	4.65	1.09	0.00
28	11.32		5.35		
32			6.09	1.44	0.00
36		10.24	6.91		
40			7.65	1.85	0.00
44			8.53		
48			8.94	2.24	0.00
52	11.29	10.21	9.00		
56				2.53	0.00
64			8.97	2.94	
72				3.29	0.00
80				3.65	
88		10.15	9.00	4.03	
96				4.35	0.00
104				4.76	
112				5.12	
120			8.94	5.44	0.00
128				5.76	
136				6.00	
144	11.32	10.18	8.97	6.35	0.00
152				6.50	
160				6.53	

Table A-1: H_2O_2 (mM) generation data for Figure 1.

Time (hours)	PCE-Oxidation	PCE-Control	PCE-2-propanol	Cl^- Oxidation	Cl^- Control	Cl^-2-propanol
0	1.00	1.00	1.00	0.00	0.00	0
4	0.92	0.98	1.00	0.80	0.00	0
8	0.84	0.99	0.99	1.90	0.00	0
12	0.73	0.99	0.99	3.00	0.00	0
16	0.69	0.97	0.97	3.80	0.00	0
24	0.57	0.96	0.98	5.20	0.00	0
28	0.48	0.97	0.96	6.40	0.00	0
32	0.42	0.98	0.95	7.10	0.00	0
36	0.33	0.97	0.94	8.00	0.00	0
40	0.24	0.98	0.95	9.20	0.00	0
44	0.17	0.96	0.96	10.10	0.00	0
48	0.09	0.95	0.95	10.70	0.00	0
52	0.03	0.97	0.93	11.00	0.00	0
56	0.02	0.94	0.94	10.90	0.00	0
60	0.01	0.95	0.92	11.10	0.00	0

PCE values C/C_0
Cl- values in mM

Table A-2: Data for Figure 2.

Time (hours)	H_2O_2 (7)	CaO_2 (6)	CaO_2 (7)	CaO_2 (8)	CaO_2 (9)
0.00	10.00	10.00	10.00	10.00	10.00
0.25	50.90				
0.50	62.30	12.45			
0.60	61.90				
0.75	60.70				
1.00	59.20	15.09	10.47		
1.05	58.90				10.07
1.50	56.00	17.79			
2.00		20.91	11.00		
2.50	52.00	23.74			
3.00		26.48	11.53		
3.50		27.78			
4.00	48.00	28.50	12.22		
5.00		28.26	12.69		
6.00			13.19		
7.00			13.66		
8.00		24.50	14.16	10.83	10.08
9.00			14.69		
10.00			15.19		
12.00			16.02		
14.00			16.66		
16.00			17.85	11.63	10.18
18.00			18.88		
20.00			19.68		

22.00			19.13		
24.00			18.10	12.48	10.27
28.00			16.50		
32.00				13.25	10.35
36.00					
40.00				14.08	10.46
44.00					
48.00				14.80	10.55
52.00					
56.00				14.20	10.62
64.00					10.72
72.00					10.81
80.00					10.90
88.00					10.99
96.00					11.07
104.00					11.17
112.00					11.26
120.00					11.34
128.00					11.42
136.00					11.48
144.00					11.60
152.00					11.55
160.00					11.23

Table A-3: Temperature (°C) data for Figure 3.

MF Oxidant (pH)	**% PCE Oxidized**	**% PCE Volatilized**
H_2O_2 (7)	16.33	14.33
CaO_2 (6)	68.33	6.00
CaO_2 (7)	86.17	4.83
CaO_2 (8)	96.00	2.00
CaO_2 (9)	79.00	4.67

Table A-4: Data for Figure 4.

Appendix B

Data Relevant to Chapter III: Evidence for the Production of Surfactants Accompanying the Chemical Oxidation of Hydrocarbons in Soils

Liquid Hydrogen Peroxide			
Time (hours)	**Surface Tension (dynes/cm)**	**Critical Micelle Dilution (x CMC)**	**Total Petroleum Hydrocarbons x100 (mg/L)**
0	72	0	ND
0.25	32	4	2.6
0.5	34	4	7.4
0.75	31	4	8.45
1	31	4	7.7
1.25	32	4	6.71
1.5	33	4	5.2
1.75	36	2	1.61
2	68	0	0.09
2.25	71.4	0	ND
2.5	72	0	ND

Table B-1: Data for Figure 5.

Cool-Ox™			
Time (days)	**Surface Tension (dynes/cm)**	**Critical Micelle Dilution (x CMC)**	**Total Petroleum Hydrocarbons x100 (mg/L)**
0	72	0	ND
0.25	31	2	1.4
0.5	33	2	3.2
0.75	31	4	5.45
1	32	4	4.9
1.25	32	4	5.5
1.5	33	4	5.3
1.75	36	2	1.4
2	51	0	0.5
2.25	67.4	0	ND
2.5	72	0	ND

Table B-2: Data for Figure 6.

Appendix C

Autoclaved Soil Treated With Cool-Ox™

The soil treated in this experiment was the same as the soil used in Northup and Cassidy (2007) in the *Journal of Advance Oxidation Technologies*. The soil was autoclaved three times to ensure that all microorganisms were killed so that biodegradation of hydrocarbons would not occur. The experimental set-up and treatment with a CaO_2 based MF reagent is exactly the same as that described in Northup and Cassidy (2007). The time profile in figure 7 shows a decrease in surface tension (ST) as total petroleum hydrocarbons (TPH) and critical micelle dilution (CMD) increase shortly after application of the oxidant. This indicates that there is production and accumulation of surfactants during the treatment of this contaminated soil. The production of surfactants in a sterile soil is important in proving that the surfactants are not of biological origin, but rather the result of partial oxidation of other hydrocarbons. However, there was no indication for the removal of surfactants in the sterile reactor, which indicates that surfactants are biodegradable.

Autoclaved* Soil Treated With Cool-Ox™			
Time (days)	Surface Tension (dynes/cm)	Critical Micelle Dilution (x CMC)	Total Petroleum Hydrocarbons x100 (mg/L)
0	71.9	0	0
0.25	32.3	2	1.4
0.5	31.4	2	3.2
0.75	31.7	4	5.45
1	32	4	5.3
1.25	31.8	4	5.5
1.5	31.9	4	5.3
1.75	31.7	4	5.5
2	31.4	4	5.7
2.25	31.9	4	5.5
2.5	31.6	4	5.6

*Autoclaved three times

Table C-1: Data for Figure 7.

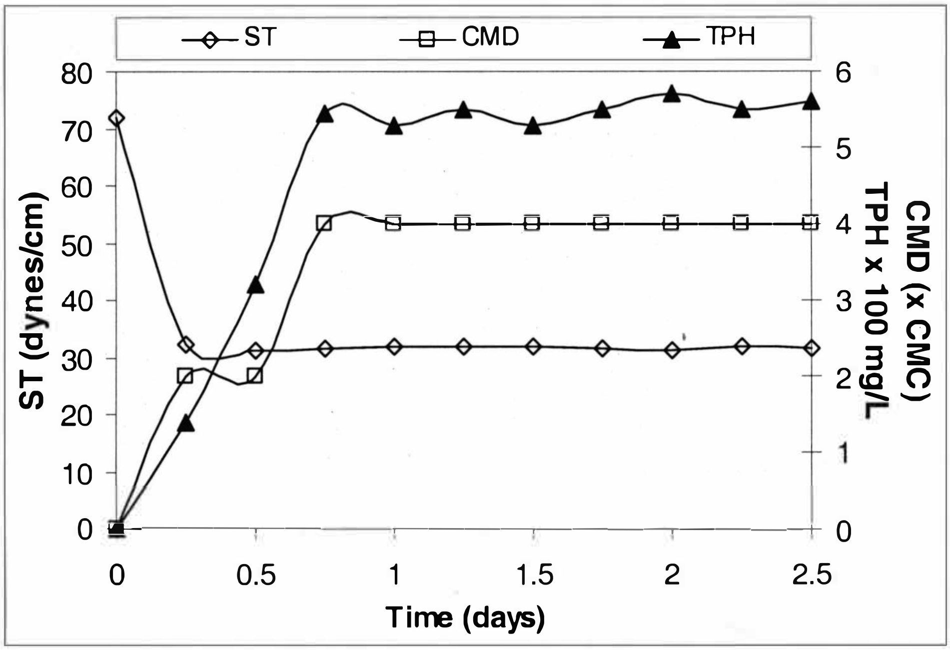

Figure C-1: Time profile for CaO_2 MF treatment of autoclaved soil.

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