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### DOTTORATO DI RICERCA IN INGEGNERIA AMBIENTALE



# EVALUATION OF FENTON-LIKE PROCESS FOR MTBE CONTAMINATED GROUNDWATER TREATMENT THROUGH LAB-SCALE AND PILOT-SCALE TESTS

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## XXVI CICLO

# Evaluation of Fenton-like process for MtBE contaminated groundwater treatment through lab-scale and pilot-scale tests

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"C'è una verità elementare, la cui ignoranza uccide innumerevoli idee e splendidi piani: nel momento in cui uno si impegna a fondo anche la Provvidenza allora si muove. Infinite cose accadono per aiutarlo, cose che altrimenti mai sarebbero avvenute... Qualunque cosa tu possa fare, o sognare di poter fare, incominciala. L'audacia ha in sé genio, potere, magia... Incomincia adesso." (W. Goethe)

"Bisogna vederle agire davanti ai nostri occhi queste sostanze che sembrano morte, mentre nel loro intimo sono pur sempre pronte all'azione; bisogna osservare con interesse come si cercano, si attirano, si afferrano, si distruggono, si divorano, si consumano e poi, sciolto il più stretto dei legami, riemergono in una forma diversa, nuova, inaspettata..."

(W. Goethe)

## ABSTRACT

Groundwater contamination by organic compounds is a widespread problem worldwide. Particularly, organic compounds from petroleum products (e.g., gasoline, diesel, fuel oil) are frequently detected in groundwater as a consequence of accidental spills occurring from pipelines and aboveground storage tanks (AST) or underground storage tanks (UST). Making reference to contamination detected at petrol stations or hydrocarbon storage sites, these organic contaminants may typically include benzene, toluene and xylene isomers if the source of contamination is a spill from a gasoline tank. The BTEX fraction and the light hydrocarbons fraction (HC<12) may often undergo aerobic biodegradation reactions, that may lead to their natural attenuation with time. A different behaviour is generally observed for oxygenates, which are usually added to commercial unleaded gasoline as octane enhancers to improve combustion efficiency, reduce vehicle exhaust emissions and improve air quality in order to increase the octane number of unleaded gasoline. These compounds, include methyl tert-butyl ether (MtBE), ethyl tert-butyl ether (EtBE), tert-amyl methyl ether (TAME) and alcohols (e.g., ethanol or tert-butyl alcohol (TBA)). They are frequently detected in groundwater plumes as they typically travel farther and faster in groundwater with respect to hydrocarbons and are typically much less biodegradable, thus leading to their accumulation in sites contaminated by gasoline spills. Oxygenates result in fact an environmental challenge both for the fate and transport behaviour and for resistance to biodegradation but also to the available clean-up technologies. In particular, MtBE is by far the most used oxygenate in European gasoline resulting in a diffuse contamination in several EU countries. MtBE has therefore become an important environmental priority in the management of contamination problems. The treatment of MtBE contaminated groundwater, particularly by In-Situ techniques, is a challenging task. Application of traditional techniques may in fact be limited by the physico-chemical and structural properties of MtBE: for instance, the effectiveness of Air Sparging may be limited by the relatively low value of the Henry's constant that will limit the partitioning of the compound in the vapour phase. Recently, In Situ Chemical Oxidation (ISCO) has been identified as one possible attractive cost-effective method for the remediation of MtBE contaminated groundwater. Nevertheless, its efficiency on MtBE oxidation is still debated, especially when the extent of mineralization to CO<sub>2</sub> and water is considered.

This Ph.D. thesis was thus focused on the evaluation of the performance of In Situ Chemical Oxidation to groundwater contaminated by MtBE. Namely, the investigated treatment was based on the application of the Fenton-like process, that relies on the use of hydrogen peroxide catalysed by iron minerals present in the soil, with the addition of chelating agents to extract the iron catalyst and potassium monobasic phosphate (KH<sub>2</sub>PO<sub>4</sub>) to stabilize the oxidant. This goal was achieved by performing both lab-scale column tests and by designing and performing a pilot-scale field test on a site contaminated by MtBE. The column scale tests allowed on the one hand to select the best operating conditions of the Fenton-like process and on the other hand to assess the extent of MtBE oxidation and mineralization, showing that up to 95% of the oxidised MtBE was actually mineralized. This result was obtained by performing a mass balance from the MtBE disappeared and the carbon dioxide evolved and was basically confirmed by the absence of the intermediate compounds in the outlet solutions from the column.

The design of the pilot-scale treatment was performed following an approach based on the combination of numerical and experimental modelling, allowing to define the layout of the injection wells and to predict the propagation of hydrogen peroxide. The pilotscale field results confirmed the effective propagation of hydrogen peroxide in the target area. The radius of influence of the oxidant was in line with the one predicted by the numerical simulation performed assuming that only the more permeable layer of the aquifer, where probably most of MtBE contaminated groundwater should be present, was available for oxidant propagation. As far as the MtBE removal is concerned, the ISCO application allowed to meet the clean-up goals in most of the treated area. A mass balance performed on the basis of the MtBE data in groundwater and on CO<sub>2</sub> and VOC data in the off-gas allowed to demonstrate that most of MtBE was actually mineralized. This result was supported by the evidence that no accumulation of reaction intermediates was noticed, whereas the concentration of TBA, i.e. a potential byproduct of MtBE oxidation, was actually reduced after the ISCO treatment. Thus summarising, the results obtained in this research support the feasibility of ISCO based on the Fenton-like process for MtBE treatment in contaminated groundwater and provide new insights on the oxidation of this compound and on the design strategy of ISCO.

## Sommario

Il problema della contaminazione delle acque di falda da composti organici rappresenta una criticità ambientale di grande attualità e rilievo. In particolare, i composti organici provenienti da prodotti petroliferi (benzina, gasolio, olio combustibile) sono frequentemente rilevati nelle acque sotterranee a seguito di sversamenti accidentali che si verificano da tubazioni e serbatoi di stoccaggio superficiali e sotterranei. In riferimento alla contaminazione rilevata nelle stazioni di servizio o nei siti di stoccaggio degli idrocarburi, tali contaminanti organici sono tipicamente benzene, toluene e xilene, se la fonte di contaminazione è una fuoriuscita accidentale da un serbatoio di benzina. Le frazioni di BTEX e di idrocarburi leggeri (HC<12) spesso subiscono reazioni di biodegradazione aerobica, che ne favoriscono il processo di attenuazione naturale. Un comportamento diverso viene generalmente osservato per i composti ossigenati, i quali vengono di solito aggiunti alla benzina senza piombo per aumentare il numero di ottano e migliorare l'efficienza di combustione, ridurre le emissioni di scarico dei veicoli e migliorare la qualità dell'aria. Questi composti, che includono il metil ter-butil etere (MtBE), l'etil ter-butil etere (ETBE), il metil terz-amile etere (TAME) e gli alcoli (etanolo o alcool ter-butilico (TBA)), hanno la capacità di diffondersi facilmente negli acquiferi dando origine a pennacchi di contaminazione molto estesi e, essendo meno biodegradabili degli idrocarburi, si accumulano facilmente nei siti contaminati da fuoriuscite di benzina. I composti ossigenati rappresentano, quindi, una sfida ambientale per il loro "destino" (trasporto e trasformazione) e per la loro resistenza alla biodegradazione e refrattarietà alle tradizionali tecnologie di risanamento. In particolare il MtBE è di gran lunga il composto ossigenato maggiormente utilizzato nelle benzine con conseguente contaminazione diffusa delle acque superficiali e sotterranee in diversi paesi dell'Unione Europea. Il trattamento delle acque sotterranee contaminate da MtBE, in particolare mediante il ricorso a tecnologie in-situ, è impegnativo. L'applicazione delle tradizionali tecnologie di bonifica può infatti essere limitata dalle proprietà fisicochimiche e strutturali del composto; ad esempio, l'efficacia dell'Air Sparging può essere limitata dal valore relativamente basso della costante di Henry che riduce la ripartizione del composto in fase vapore. Recentemente, l'Ossidazione Chimica In Situ (ISCO) è stata identificata come una delle possibili tecniche convenienti per la bonifica delle acque sotterranee contaminate da MtBE.

Nonostante questo tipo di formulazione sia già stata applicata a diversi contaminanti organici, la sua efficacia di rimozione nei confronti del MtBE è dibattuta. Infatti, una delle preoccupazioni principali quando si applica il processo Fenton alle acque contaminate da MtBE è data dal fatto che il contaminante possa non subire completa mineralizzazione a  $CO_2$  e acqua, con seguente formazione ed accumulo di composti intermedi quali alcool tert-butilico (TBA), acetato di metile, tert-butile formiato (TBF), e acetone.

Il dottorato di ricerca è stato quindi incentrato sulla valutazione delle prestazioni del processo di Ossidazione Chimica In Situ per il trattamento di acque sotterranee contaminate da MtBE. Nello specifico, il trattamento oggetto di studio è stato basato sull'applicazione del processo Fenton-like. Questo processo si differenzia dalla classica configurazione di Fenton per l'utilizzo di perossido di idrogeno catalizzato da minerali di ferro naturalmente presenti nel suolo, per il ricorso ad agenti stabilizzanti (fosfato di potassio monobasico) allo scopo di aumentare la permanenza dell'ossidante nel sottosuolo, nonché per l'impiego di agenti chelanti al fine di estrarre il ferro dal suolo e mantenerlo in soluzione, eliminando così la necessità di acidificare le acque sotterranee.

L'obiettivo del lavoro è stato raggiunto sia mediante l'esecuzione di prove in colonna in scala di laboratorio su un sistema suolo-acqua artificialmente contaminato da MtBE, sia progettando ed eseguendo un test in scala pilota su un sito precedentemente utilizzato per lo stoccaggio di combustibile e contaminato principalmente da MtBE. In particolare le prove in colonna hanno consentito da un lato di selezionare le migliori condizioni operative del processo Fenton-like e dall'altro di valutare il tasso di ossidazione e mineralizzazione del MtBE, dimostrando che il 95% del MtBE ossidato risulta effettivamente mineralizzato. Tale risultato è stato ottenuto eseguendo un bilancio di massa a partire dai dati di concentrazione del MtBE misurati in ingresso ed in uscita dal sistema colonna, confrontato poi con la quantità di anidride carbonica sviluppata in seguito al processo di ossidazione e misurata attraverso l'utilizzo di sensori on-line. La completa mineralizzazione del contaminante è stata sostanzialmente confermata anche dall'assenza di composti intermedi a seguito dell'analisi gascromatografica delle soluzioni in uscita dalla colonna.

In merito alla progettazione del trattamento in scala pilota, l'esecuzione ha seguito un approccio basato sulla combinazione di modellazione numerica e sperimentale,

#### Sommario

permettendo di definire la disposizione dei pozzi di iniezione e di prevedere la propagazione del perossido di idrogeno. I risultati di campo hanno confermato l'effettiva propagazione del perossido di idrogeno nell'area d'interesse. Il raggio di influenza dell'ossidante è risultato in linea con quello previsto dalla simulazione numerica che è stata eseguita assumendo che solo lo strato più permeabile della falda, dove probabilmente è presente la maggiore quantità di acque contaminate da MtBE, fosse disponibile per la propagazione dell'agente ossidante. Per quanto riguarda la rimozione del MtBE, l'applicazione ISCO ha consentito di raggiungere gli obiettivi di bonifica nella maggior parte della zona trattata. Anche in questo caso il bilancio di massa, eseguito sulla base dei dati del MtBE presente nelle acque sotterranee e dei dati di CO<sub>2</sub> e VOC misurati negli off-gas prodotti nel corso del trattamento, ha consentito di dimostrare che gran parte del MtBE si è effettivamente mineralizzato. Questo risultato è stato inoltre validato dall'assenza di intermedi di reazione, e considerando che la concentrazione di TBA, potenziale sottoprodotto di ossidazione del MtBE, risulta effettivamente ridotta dopo il trattamento ISCO. Quindi, riassumendo, i risultati ottenuti in questa ricerca supportano la fattibilità degli interventi di Ossidazione Chimica In situ basati sul processo Fenton-like per il trattamento di acque sotterranee contaminate da MtBE e forniscono nuove prospettive sull'ossidazione di questo composto e sulle strategie di progettazione degli interventi ISCO.

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## INTRODUCTION

### AIMS AND CONTENTS OF THIS THESIS

The presence of oxygenates in groundwater systems is an increasing environmental concern. These compounds, which include methyl tert-butyl ether (MtBE), ethyl tertbutyl ether (EtBE), tert-amyl methyl ether (TAME) and alcohols (e.g., ethanol or tertbutyl alcohol (TBA)) are added to gasoline as octane enhancers and are frequently found in contaminated sites as a result of gasoline spills. Due to their physico-chemical properties and poor biodegradability, they are a challenge for clean-up. In Situ Chemical Oxidation (ISCO) has been identified as a possible attractive cost-effective option for contaminated soils and groundwater remediation by organic compounds. Despite the ISCO based on Fenton processes is a proven technology option for the treatment of groundwater contaminated by many organic compounds, yet its effectiveness towards oxygenated organic compounds is debated. Namely, one of the main concern when applying the Fenton's process to MtBE contaminated water is that the contaminant may not undergo complete mineralization to CO<sub>2</sub> and water, whereas the oxidation can lead to the formation and accumulation of intermediate compounds, such as tert-butyl alcohol (TBA), tert-butyl formate (TBF), methyl acetate and acetone (Burbano et al., 2005; Siedlecka et al., 2007; Hwang et al., 2010). However, most of the available labstudies on this topic were carried out on water system whereas the influence of the soil that as known can lead to a generation of a stronger pool of reactive species, is still poorly investigated in the literature. Also the field-scale evidence supporting the efficiency of MtBE removal by ISCO and its capacity of achieving MtBE complete mineralization is still quite limited. For instance, the analysis of field-scale ISCO application carried out by Krembs et al. (2010) with reference to the US market in the period from 1996 through 2007, showed that MtBE was among the target contaminants in 7% of the more than 200 sites assessed. Despite the data reported by Krembs et al. (2010) show very high MtBE removal efficiency by ISCO, the reference sites are still poorly representative (6 sites only) suggesting the importance of testing its performance through a pilot-scale field test before designing and implementing the full-scale treatment. This conclusion is reinforced by the fact that the use of pilot testing also appears to have a positive impact on the results of ISCO remediation in some situations, specifically in sites characterized by heterogeneous hydrogeology (Krembs et al., 2010). The goal of this thesis was to assess the performance of ISCO based on a Fenton-like process, for the treatment of MtBE contaminated groundwater, with specific focus on the evaluation of the extent of contaminant mineralization. This goal was achieved by performing lab-scale column tests on soil-water systems and a pilot-scale field test.

The column tests were performed on artificially MtBE-contaminated soil-water system, using different oxidant and MtBE concentrations; the performances of the process were assessed by analysing pH, hydrogen peroxide and MtBE concentrations in the outlet solutions. In addition, in order to provide further lines of evidence of the oxidation performance and with the aim of identifying indirect parameters, for the monitoring of the chemical oxidation process, carbon dioxide and oxygen were measured in the outlet gas stream by on-line sensors allowing to assess the extent of unproductive consumption of the oxidant and MtBE mineralization, respectively.

The pilot-scale test was designed and performed for assessing the feasibility of an In Situ Fenton-like process to a site formerly used for fuel storage and contaminated by MtBE. This study was conducted in different steps in order to determine the design of pilot-scale treatment. First of all a lab-scale feasibility test, aimed at selecting the best operating conditions was performed. In this way a Fenton-like process was selected, where hydrogen peroxide is catalysed by naturally occurring iron minerals, using chelating agents (i.e. ethylenediaminetetraacetic acid - EDTA or sodium citrate) to enhance the extraction of iron from soil and avoid the precipitation of the sparingly soluble Fe<sup>3+</sup>. In addition, in order to increase the lifetime of hydrogen peroxide in the subsurface, potassium monobasic phosphate was used as stabilizing agent. Subsequently a modelling step was carried out, aimed to evaluate the radius of influence of the oxidant and to design the pilot-scale layout and operating conditions. Finally a pilot test was performed, followed by field testing of treatment efficacy. This feasibility study was carried out following the indications provided by the Italian protocol on ISCO (APAT, 2005) and more recently integrated by Baciocchi et al. (2014).

The present Ph.D. thesis is structured as follows: Chapter 1 reports a discussion on the properties of oxygenated compounds, particularly MtBE, and of possible removal

### Introduction

techniques available in the literature, followed by a general overview on the fundamentals and main applications of In Situ Chemical Oxidation processes. In particular, the attention is focused on hydrogen peroxide, and its main features were explained, based on the available and updated literature; hence the application of Fenton process, modified Fenton reagent (MFR) and Fenton-like is introduced and discussed. In Chapter 2 the study carried out to evaluate the influence of the soil on MtBE oxidation and the effect of the MtBE removal and mineralization was described and the main results were reported. Chapter 3 presents the main findings achieved in the different design steps of the pilot-scale feasibility study and those obtained from the pilot-scale tests were discussed in detail, with specific reference to the monitoring phase. Finally in Chapter 4 the most interesting findings achieved in this study are summarized and discussed.

# CHAPTER 1

# IN SITU CHEMICAL OXIDATION (ISCO) FOR MTBE REMOVAL FROM GROUNDWATER

## MTBE GROUNDWATER CONTAMINATION AND CLEAN-UP OPTIONS

Oxygenates, which include Methyl tert-Butyl Ether (MtBE), Ethyl tert-Butyl Ether (EtBE), Tert-Amyl Methyl Ether (TAME) and alcohols (e.g. ethanol or tert-butyl alcohol - TBA), are usually added to commercial unleaded gasoline as octane enhancers to improve combustion efficiency, reduce vehicle exhaust emissions and improve air quality (EFOA, 2005). MtBE is by far the most used oxygenate compound in European gasoline: a recent survey showed that the average MtBE concentration in EU 27 commercial gasoline is 5.4%, against 0.9% of EtBE and 0.2% of TAME (Concawe, 2012). One of the drawbacks related to oxygenates addition to fuels is that this class of contaminants is being detected more and more in groundwater affected by gasoline spills occurring in refineries, fuel storage sites and petrol stations. For this reason, it is not found only in groundwater plumes resulting from localized primary sources, but a diffuse presence of MtBE in groundwater concentration has also been detected in several EU countries, with concentrations ranging between 0.01 and 1.0 µg/L (Concawe, 2012). These are clearly much lower than the odor/taste threshold values (20-40 µg/L) and the screening values set by national authorities (e.g. 40 µg/L in Italy), but are indicative of the ubiquity of this poorly biodegradable compound in the environment. Furthermore, since U.S. EPA (2009) has identified this compound as a possible human carcinogen, MtBE has become an important environmental priority in the management of contamination problems. Oxygenates result in fact an environmental challenge both for the fate and transport behaviour and for resistance to the available clean-up technologies. In particular, more than other fuel components, MtBE is characterized by a relatively high solubility and low value of the Henry's constant resulting in the potential for a wide distribution in the environment and specifically in groundwater (Concawe, 2012). Besides, owing in part to its molecular structure (Fayolle et al., 2001), MtBE has been shown to generally resist biodegradation (Shih et. al., 2004), even though different authors reported the biodegradation of this compound by microcosms from different origins (Okeke and Frankenberger Jr, 2003; Fayolle et al., 2003; Hyman, 2013). It is generally accepted that MtBE and TBA can be degraded aerobically by both naturally occurring and/or cultured microorganisms, for instance for

the containment of MtBE plumes by establishing an oxygen-enriched reactive zone (termed bio-barrier) down-gradient the source of contamination (Johnson et al., 2009). Nevertheless, the details of the biological processes and the factors controlling the rate of MtBE and TBA degradation remain the subject of research and debate (ITRC, 2005). Similarly other traditional remediation technologies failed in cleaning up oxygenates contaminated sites. For instance, the effectiveness of Air Sparging to MtBE treatment is limited by the relatively low value of the Henry's constant that controls the partitioning of the compound to the vapour phase (ITRC, 2005). Although pump-and-treat could be a more effective technology for MtBE removal, it is well known that this is a long term energy-intensive option.

# IN SITU CHEMICAL OXIDATION (ISCO) - DEFINITION AND BACKGROUND

In Situ Chemical Oxidation, also referred to as ISCO, is a remediation technology that has been applied to a wide range of volatile and semivolatile hazardous contaminants, including hydrocarbons, solvents, BTEX (Benzene, Toluene, Ethylbenzene, Xylene), NAPL (Non-Aqueous Phase Liquid) source zones, fuels, and pesticides. Chemical Oxidation is a promising innovative process for degrading an extensive variety of hazardous compounds in remediation of soil at waste disposal and spill sites (Goi et al., 2006). Chemical oxidation uses chemicals called oxidants, to help change harmful contaminants into less toxic ones. It is commonly described as "in situ" because it is conducted in place, without having to excavate soil or pump out groundwater for aboveground clean-up. Oxidants most frequently used in chemical oxidation include potassium permanganate (KMnO<sub>4</sub>), persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), ozone (O<sub>3</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) which is typically mixed with an iron catalyst and other amendments, leading to the formulation of the so called Fenton's Reagent. Chemical oxidation is a process in which the oxidation state of a substance is increased. In general, the oxidant is reduced by accepting electrons released from the transformation-oxidation, of target and non-target reactive species. Oxidation of non-target species, including reduced inorganics in the subsurface, also involves the loss of electrons; however, the main target during ISCO involves organic chemicals. Oxidation of organic compounds may include oxygen addition, hydrogen abstraction (removal), and/or withdrawal of electrons with or without the withdrawal of protons. (Huling and Pivetz, 2006). The main objective of chemical oxidation is to transform undesirable chemical species into species that are harmless or naturally present in the soil (water, carbon dioxide, hydrogen ion, chloride ion). ISCO is usually used to treat soil and groundwater contamination in the source area where contaminants were originally released. The source area may contain contaminants that have not yet dissolved into groundwater. Typically, ISCO application is conducted with the injection in the field of the oxidant by means of wells until the source of contamination. Generally, the oxidants are injected with a sufficient number of points/wells in order to have a correct overlap of effective zones where the oxidant is in contact with the target contaminants (ITRC, 2005). Site-specific conditions and parameters, in conjunction with oxidant-specific characteristics, must be carefully considered to determine whether ISCO is a viable technology for deployment relative to other candidate technologies, and to determine which oxidant is most appropriate.

In situ chemical treatment offers several advantages over conventional treatment technologies. This technology does not generate large volumes of waste that must be disposed of and/or treated and is also implemented over a much shorter time frame (ITRC, 2005). An attractive advantage of ISCO is the short period of time it takes to complete the remediation, this in contrast to a number of alternative soil remediation techniques. The time needed for an ISCO remediation depends on the amount of pollution, the polluted soil volume, the oxidant and the rate at which the oxidant can be injected.

In oxidative treatment systems, different reactions can potentially occur, including acid/base reactions, adsorption/desorption, dissolution, hydrolysis, ion exchange, oxidation/reduction, precipitation, etc. (Huling and Pivetz, 2006). In environmental systems there is a wide array of reactants and conditions that influence reaction rates and pathways that vary from site to site. Often, numerous reactions are required to achieve innocuous end products, and many of the reaction intermediates are never identified. All of the ISCO technologies are based on the oxidative power of specific chemicals (oxidants) and the strength of the oxidants can be compared based on their standard reduction potential  $E_0$  (V) as shown in Table 1.1.

Oxidant	Reactions	Standard reduction Potential E <sub>0</sub> (V)	
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	$H_2O_2 + H^+ + e^- \rightarrow OH^- + H_2O$	1.78	
Catalysed hydrogen peroxide (Fe <sup>2+</sup> + H <sub>2</sub> O <sub>2</sub> )	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\scriptscriptstyle\bullet} + OH^{\scriptscriptstyle\bullet}$	2.8	
Persulfate (S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> )	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{}$ or	2.01	
	$S_2O_8^{2-} + 2Fe^{2+}$ (or heat) $\rightarrow 2 \text{ SO}_4^{-\bullet} + 2Fe^{3+}$	2.01	
Activated persulfate (SO4 <sup>-</sup> •)	$2SO_4 \stackrel{\bullet}{\rightarrow} 2H_2O \rightarrow 2HSO_4 \stackrel{\bullet}{\rightarrow} + 2OH \bullet$	2.6	
Permanganate (MnO <sub>4</sub> <sup>-</sup> )	$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 (s) + 2H_2O$	1.68	
	$O_3+2H^++2e^- \rightarrow O_2+2H_2O$	2.07	
Ozone (O <sub>3</sub> )	$O_3 + OH^{\scriptscriptstyle -} \to O_2 + HO_2 \bullet$		
Oxygen (O <sub>2</sub> )	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	
Chlorine (Cl <sub>2</sub> )	$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	

**Table 1.1.** Common oxidants and most important oxidant reactions with Standard reduction Potential (Huling and Pivetz, 2006).

The reduction potential, however, is not an exhaustive parameter for predicting the treatment efficiency, since the site-specific conditions may significantly influence the whole process (ITRC, 2005). Four major factors determine whether success will be obtained in the field; kinetics, thermodynamics, stoichiometry, and contact between oxidant and contamination (Bennedsen, Ph.D. Thesis, 2011). Specifically, the longevity of the reagent into the soil matrix depends on its kinetic decomposition. To estimate this factor is necessary to consider several parameters such as temperature, pH, reagent concentration, catalysts, the organic matter naturally present in the soil and the scavengers, or substances able to consume the oxidant unproductively. Some chemical reactions between the reagent and the target pollutants, although thermodynamically favoured, may not occur in field due to factors and substances present in the area to be treated. The reagent to be injected should be adequately dosed according to the specific Soil Oxidant Demand (SOD) in order to avoid the development of secondary chemical reactions in presence of excess/defect of oxidant. Soil Oxidant Demand refers to the consumption of an oxidant due to reactions that are unrelated to degradation of the contaminants of concern. A SOD measurement is a direct estimate of the oxidant consumption by organic and inorganic components in the matrix, soil or water. To ensure that the oxidation is effective, the reagent must be in contact with the contaminant; this occurs through a homogeneous distribution of the reagent solution within the area to be treated. In addition, the propagation of the oxidant, is closely related to the decomposition reactions of the reagent within the soil. Finally, it is worth noting that, during an ISCO treatment, the monitoring phase is a key step. The monitoring phase is aimed to analyse the efficacy of ISCO process by observation of propagation of the reagent and the possible mobilization of metals in groundwater as well as contaminants desorbed from soil and to verify if the ISCO system meets basis of design and performance specifications.

### IN SITU FENTON'S OXIDATION (ISFO)

Fenton's oxidation based on the use of hydrogen peroxide and iron (II) salt (Fenton's reagent) is one of the most common application of Advanced Oxidation Technologies (AOTs) in environmental applications (Rastogi et al., 2009). This chemical oxidation approach is recognized as one of the most powerful oxidizing reactions available and can be used to destroy a wide variety of biorefractory organic compounds in aqueous waste, soils, and groundwater, which are resistant to conventional treatment technologies (Lu et al., 2010).

### **Fenton and Related Reactions**

Hydrogen peroxide is a strong oxidant widely used for the remediation of contaminated soil and groundwater, with a large number of in situ applications (Ciotti, Ph.D. Thesis, 2009). The classic Fenton's process is based on the reaction in the aqueous phase between hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and an appropriate catalyst, usually iron sulphate (FeSO<sub>4</sub>), at acidic pH conditions, which leads to the generation of a pool of radicals (Kiwi et al., 2000). The conventional Fenton's reaction is initiated by adding H<sub>2</sub>O<sub>2</sub> resulting in nearly stoichiometric generation of the hydroxyl radicals (OH<sup>+</sup>) (Venny et al., 2012), according to the classic interpretation of Haber and Weiss (Haber and Weiss, 1934; Merz and Waters, 1949). Several studies in the literature have shown that the OH<sup>+</sup> radical acts as the primary reactive species which oxidises organic pollutants (Xu et al., 2011). The hydroxyl radicals break the hydrocarbon bonds of common petroleum constituents such as BTEX (Benzene, Toluene, Ethylbenzene, and Xylene) as well as polycyclic aromatic hydrocarbons (PAHs) and methyl tertiary butyl ether (MtBE) (US.EPA Chemical Oxidation, 2004). Fenton's reaction is a complex mechanism which involves, during Fenton transformation, a large number of reactions (Kang and Hua,

2005; Venny et al., 2012). These include radical initiation (Eq.1.1 and 1.2), radical propagation (Eq.1.3-1.6) and termination (Eq.1.7-1.9) reactions.

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

$$\tag{1.1}$$

$$Fe^{3+} + H_2O_2 \to Fe^{2+} + H^+ + HO_2^{\bullet}$$
 (1.2)

$$HO_2^{\bullet} \leftrightarrow O_2^{-\bullet} + H^+ \tag{1.3}$$

$$O_2^{-\bullet} + Fe^{3+} \to Fe^{2+} + O_2$$
 (1.4)

$$O_2^{-\bullet} + Fe^{2+} + 2H^+ \to Fe^{3+} + H_2O_2$$
(1.5)

$$O_2^{-\bullet} + HO_2^{\bullet} \to HO_2^{-} + O_2 \tag{1.6}$$

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

$$\tag{1.7}$$

$$OH^{\bullet} + H_2O_2 \to H_2O + HO_2^{\bullet} \tag{1.8}$$

$$OH^{\bullet} + OH^{\bullet} \to H_2O_2 \tag{1.9}$$

The hydroxyl radicals (OH<sup>•</sup>) generated through the reaction (1.1) react with hydrogen peroxide leading to further propagation reactions that generate several other reactive oxygen species, including the superoxide radical anion ( $O_2^{-}$ ) and the hydroperoxide anion ( $HO_2^{-}$ ), (Smith et al., 2006). Therefore, the oxidative properties of a Fenton's system is the result of the combined activities of the different radical produced and is not strictly correlated to just one radical species (Ciotti et al., 2009). Hydrogen peroxide also participates in non-productive reactions (i.e. those that do not lead to hydroxyl radicals formation) involving some metals such as manganese and copper, and enzymatic catalysts such as catalase or peroxidase (Huling et al., 2001).

### The main factors affecting efficiency and effectiveness of oxidation

The effectiveness of Chemical Oxidation treatments based on the Fenton's reaction is influenced by many factors often related to the chemical and physical characteristics of the matrix. The pH performs one of the most important roles during the Fenton treatment, it has a strong effect on hydrogen peroxide chemistry and effectiveness. In fact, it provides information about the activity of hydrogen ions (H<sup>+</sup>) and hydroxyl ions (OH<sup>-</sup>) present in the system (Venny et al., 2012). It is well known, that the optimum conditions for the reaction occurs under relatively low pH conditions (pH of 3 to 4). The

higher pH, the lower the speed of reaction and thus the degradation process efficiency. The reason is the loss of iron ions in solution caused by their coagulation in the form of ferric hydroxide (Fe(OH)<sub>3</sub>), high pH values also causes an excessive decomposition of hydrogen peroxide to oxygen and water and thus its lifetime is not sufficient to produce the required amount of hydroxyl radicals (Petigara et al., 2002; Mikutta et al., 2005). Moreover, the consumption of hydrogen peroxide does not imply a consequent production of OH• radicals because hydrogen peroxide may decompose according to reactions that do not involve the production of radicals. These unproductive reactions involve for example, the organic matter and inorganic constituents naturally present in the soil (Huling et al., 2001). The natural organic matter may reduce the effectiveness of the Fenton's reaction by competing with contaminants for hydroxyl radicals or catalysing the decomposition of hydrogen peroxide. De Laat et al. (2004) demonstrated the rate of the H<sub>2</sub>O<sub>2</sub> reaction with ferrous ions is influenced by the presence of inorganic ions. The rate of decomposition of H<sub>2</sub>O<sub>2</sub> in the presence of sulphate ions was more rapid than in the presence of perchlorate anion. In contrast, the presence of chloride in reaction mixture did not change the rate of H<sub>2</sub>O<sub>2</sub> decomposition. Therefore, the Fenton's oxidation is influenced by the presence of inorganic anions in solution. Siedlecka et al. (2007) showed that in the case of the chloride and dihydrophosphate ions the MtBE oxidation is clearly inhibited, instead the addition of sulphate or perchlorates influences the reaction to a much smaller extent. The anions suppress MtBE decomposition in the following sequence:  $ClO_4^- < SO_4^{2-} < Cl^- < H_2PO_4^-$ . The efficiency of in situ Fenton applications is also influenced by temperature. Namely, an increasing of temperature can lead to an higher hydrogen peroxide disproportionation into oxygen and water  $(H_2O_2 \rightarrow H_2O + 0.5 O_2)$  which can further enhance VOC emissions during the treatment (ITRC, 2005) and that may represent a risk for human health and safety hazard (Mecozzi et al., 2006).

### Modified Fenton Reagent (MFR) and Fenton-like

In the classic Fenton's reaction, hydrogen peroxide reacts with Fe<sup>2+</sup> to form the hydroxyl radical OH<sup>•</sup>. One of the main drawback of the application of classic Fenton's reagent is that the Fe<sup>3+</sup> produced is only sparingly soluble, especially at neutral pH, so that high concentrations of ferric oxyhydroxides precipitates are generated when stoichiometric quantities of Fe<sup>2+</sup> are used (Kwan and Voelker, 2002). As discussed before this limitation is overcome in the classic Fenton process by acidifying the soil to the optimal pH value between 3 and 4 (Watts et al., 1990). However, this is often not an easy task to be achieved especially in soil-water systems where the buffer capacity of the soil can be relevant. The Modified Fenton's process (MFR) was developed with the goal of achieving the in situ treatment of soil and groundwater contamination using Fenton's chemistry while avoiding the negatives need of acidification. Sun and Pignatello (1992) among others have shown that using chelating agents allows Fenton's reactions to proceed at circumneutral pH by minimizing the precipitation of iron which may eliminate the need to acidify groundwater. The MFR uses high hydrogen peroxide concentrations while maintaining the system at neutral pH using proper iron ligands (Watts et al., 2005). Modified Fenton reagent (MFR) is fundamentally different from the classic Fenton's reagent because the higher  $H_2O_2$  concentrations used may lead to the generation of non-hydroxyl radical reactive species, that can promote enhanced desorption and degradation of recalcitrant compounds from the soil. During this process, the hydroxyl radicals generated by the principal radical reaction (1.1) react with the hydrogen peroxide giving rise to a variety of reactions that propagate with the production of non-hydroxyl radicals such as perhydroxyl radical (HO<sub>2</sub>), superoxide radical anion  $(O_2^{-})$  and hydroperoxide anion  $(HO_2^{-})$  (Quan et al.,2003; Watts and Teel, 2005).

The non-hydroxyl radicals are favourably formed at high hydrogen peroxide dose (> 1%) or high pH values (> 11) (Yeh et al., 2008). The hydroxyl radicals are species characterized by a high reactivity and their subsequent rapid consumption, while non-hydroxyl radical, which unlike the first are characterized by a lower reactivity, have a more extended persistence and a more progressive consumption. Another formulation of the Fenton's reagent is represented by the so-called Fenton-like process. This process is based on the idea of using chelating agents and naturally occurring iron minerals for

catalysing the decomposition of hydrogen peroxide (Watts and Dilly, 1996). The concept of using naturally occurring minerals as iron source was first investigated by Watts et al. (1990), whereas Kakarla and Watts (1997) and more recently Watts and Teel (2005) addressed the issue of  $H_2O_2$  stabilization using phosphate salts. The hydrogen peroxide lifetime was also investigated by Baciocchi et al. (2003) through batch reactors and later using column tests (Baciocchi et al., 2004). Watts and Teel (2005) among others have demonstrated that in many cases Fenton's reactions are more stoichiometrically efficient when iron and manganese minerals are used as catalyst, suggesting that the injection of soluble forms of iron may not be needed for In-Situ treatments.

### Organic/inorganic stabilizers, chelating agents and iron

The hydrogen peroxide lifetime is typically short in the subsurface. For this reason, it is often desirable to improve its delivery and to increase its contact with the contaminants. In order to increase the hydrogen peroxide lifetime in the subsurface it is common to add proper chemical amendments, called stabilizers. Several formulations have been developed to stabilize hydrogen peroxide, trying to reduce its rapid decomposition in the presence of transition elements, metal oxyhydroxides, and soil surfaces (Ciotti, Ph.D. Thesis, 2009). Phosphates are most commonly used in bioremediation formulations because it is not only an inorganic stabilizer, but also a bacterial nutrient. Phosphates appear to inhibit the hydrogen peroxide decomposition reactions that are catalysed by mineral surfaces, possibly by affecting the surface charge or redox potential at the mineral surface (Watts et al., 1999). Phosphates can also act as radical scavengers because they may quench hydroxyl radicals and terminate radical chain reactions (Aggarwal et al., 1991). Anyhow, Watts et al. (1999) showed that the hydrogen peroxide formulation stabilized with phosphate decomposed more slowly with higher hydroxyl radical production, than the unstabilized hydrogen peroxide. Both low pH and presence of phosphates were shown to promote the stability of hydrogen peroxide and to slow its decomposition. Watts et al. (2007) also showed that citrate, malonate and phytate are effective to stabilize hydrogen peroxide. These stabilizers are able to decrease hydrogen peroxide decomposition rates; particularly it was also demonstrated that the phytate increase the hydrogen peroxide half-life as much as 50 times in the presence of subsurface solids, compared to malonate and citrate maintaining a significant portion of the reactive oxygen species activity.

As already discussed before, the application of Fenton's reaction at neutral pH is made possible by using chelating agents. The efficiency of the Fenton's reaction greatly decreases with increasing pH because the solubility of ferric ions (converted from ferrous ions by hydroxyl radicals) declines at higher pH (above pH 3). The decline in reactivity is due to precipitation of ferric ions as an oxyhydroxide complex that leads to the disappearance of iron ions from the water phase where the Fenton's reaction takes place (Nam et al., 2001). Chelating agents allow to maintain an adequate dissolved transition metal concentration also at neutral pH conditions. Chelating agents are also used to extract the transition metals of the soil used as catalyst in the Fenton-like process (Vicente et al., 2011). The chelate is capable of binding ferrous and ferric iron, allowing to control the concentrations of Fe(II) and Fe(III) in solution. This limits the amounts of Fe(II) and Fe(III) available for reaction with H<sub>2</sub>O<sub>2</sub>, thus controlling the rate of hydroxyl radical generation (Lewis et al., 2009). Examples of chelating agents that have been used for chelated metal activation are: amino polycarboxylic acids where they belong ethylenediaminetetraacetic (EDTA), NTA (nitrile triacetic acid), PDA (pyridine dicarboxylic acid) (Sun and Pignatello, 1992); L- ascorbic acid (ASC), gallic acid (GAL), citric acid (CIT), sodium citrate mono-hydrate (CITRm), sodium citrate 2hydrate (CITRt) (Vicente et al., 2011); cyclodextrines, amino-poly-acetic acids (Siegrist et al., 2011).

### APPLICATION OF ISCO TO MTBE OXIDATION

Recently, in situ chemical oxidation (ISCO) has been identified as one possible attractive cost-effective methods for the remediation of MtBE contaminated groundwater (Liang et al., 2011). Typically, ISCO is performed using oxidant formulations based on hydrogen peroxide (Watts and Stanton, 1999; Watts et al., 2002; Baciocchi et al., 2003; Watts and Teel, 2005), permanganate (De Souza et al., 2009), persulfate (Kislenko et al., 1996; Liang et al., 2008a; Liang et al., 2008b; Liang and Lee, 2008; Romero et al., 2010), peroxymonosulfates (Rastogi et al., 2009), or a combination of them. The growing interest in the treatment of MtBE using this technology is

demonstrated by the large number of laboratory and field studies available in recent literature aimed to assess the applicability of ISCO to MtBE using different oxidant formulations. As far as the Fenton's treatment is concerned, Siedlecka et al. (2007) and later Hwang et al. (2010) have investigated the influence of inorganic anions and other radical scavengers on the effectiveness of the Fenton's treatment of waters contaminated with MtBE. Burbano et al. (2005, 2008) have assessed the capability of Fenton's reagent to degrade MtBE and the resulting oxidation by-products, whereas more recently Innocenti et al. (2014) reported the successful field application of a Fenton-like process for the treatment of a site formerly used for fuel storage. The applicability of persulfate has been investigated by Huang et al. (2002) who studied the kinetics of MtBE oxidation by heat-assisted activation at various pH, temperature, oxidant concentration and ionic strength levels. Later, Huling et al. (2011) have investigated the effectiveness of persulfate to treat MtBE contaminated water using different methods of activation showing that thermal-activation was more effective than either alkaline-activation or  $H_2O_2$ -persulfate binary mixtures. More recently, Liang et al. (2011) have demonstrated at lab-scale the effectiveness of passive persulfatereleasing barrier to treat MtBE contaminated groundwater. As far as permanganate is concerned, Damm et al. (2002) have investigated the kinetics of MtBE oxidation in batch systems showing that the oxidation rate was 2-3 orders of magnitude lower than the one of other advanced oxidation processes. Furthermore, a combination of different advanced oxidation processes for MtBE treatment has also been tested (Mezyk et al., 2009). For instance, Safarzadeh-Amiri (2001) has reported the effectiveness of MtBE degradation using a combination of ozone and hydrogen peroxide. This result was later confirmed by Mitani et al. (2002) who have compared the degradation rates of MtBE using ozone or a combination of ozone and hydrogen peroxide showing that the latter was more effective and markedly increased the rate and degree of degradation of this compound. Finally, the combination of ultraviolet (UV) radiation with hydrogen peroxide (e.g. Stefan et al., 2000; Hu et al., 2008) and ozone (e.g. Graham et al., 2004), well as photocatalytic TiO<sub>2</sub> oxidation and H<sub>2</sub>O<sub>2</sub> oxidation (Xu et al., 2006; Hu et al., 2008) are also widely studied in literature. More recently, Gonzalez-Olmos et al. (2013) have highlighted that hydrophobic Fe-zeolites can be regarded as promising materials for the removal of MtBE from water, since they allow the combination of efficient adsorption and oxidative degradation of MtBE by hydrogen peroxide. All these studies indicate that MtBE can be degraded with radical-driven oxidation processes.

### **MTBE MINERALIZATION AND BY-PRODUCTS FORMATION**

Fenton's oxidation produces a variety of reactive intermediates that attack and degrade organic contaminants. Ideally these reactions lead to complete mineralization of the contaminants to carbon dioxide and water. However, in real systems the organic contaminants require multiple oxidation steps, and therefore multiple attacks by radicals before being completely mineralized (Siegrist et al., 2011). Therefore, one of the main concern when applying a Fenton's process to MtBE is that the contaminant may not undergo complete mineralization to CO<sub>2</sub> and water, whereas the oxidation can stop to intermediate compounds (Hong et al., 2007):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$$
(1.10)

$$OH + MTBE \rightarrow intermediates$$
 (1.11)

$$OH + intermediates \rightarrow final degradation products$$
 (1.12)

Figure 1.1. describes two MtBE oxidation pathways in the presence of hydroxyl radicals. Both of these start with the H-abstraction generated by the OH<sup>•</sup> radical from the carbon of the methoxy group of MtBE (pathway I) or from any carbon atom from methyl or tert-butyl groups (pathway II) (Burbano et al., 2008). In both cases (see Fig.1.1), the resulting carbon-centered radicals react with oxygen and form peroxyl radicals (Hong et al., 2007).



Figure 1.1. Mechanism of MtBE degradation with 'OH, (a) Pathway I, (b) Pathway II (Burbano et al.,2008).

These radicals subsequently dimerize to form tetroxides which undergo a series of further transformations that lead to the formation of different intermediates, including tert-butyl formate (TBF), tert-butyl alcohol (TBA), methyl acetate and acetone (Burbano et al., 2008; Hong et al., 2007; Xu et al., 2004; Burbano et al., 2005; Hwang et al., 2010).

# CHAPTER 2

# FENTON-LIKE COLUMN TESTS

This chapter is partially taken from:

Piscitelli D., Zingaretti D., Verginelli I., Gavasci R., Baciocchi R. (2014). Lines of evidence of MtBE mineralization by Fenton-like column tests. Submitted to the Journal of Hazardous Materials.

### BACKGROUND

In Situ Chemical Oxidation (ISCO) has been identified as a possible attractive costeffective option for the remediation of MtBE contaminated groundwater (Liang et al., 2011). The growing interest in the treatment of MtBE using this technology is demonstrated by the large number of laboratory and field studies available in the recent literature aimed to assess the applicability of ISCO to MtBE using different oxidant formulations. These studies suggest that MtBE can be effectively degraded by radicaldriven oxidation processes. As far as the Fenton's treatment is concerned, in the classic Fenton's reaction, these radicals are produced by the reaction of hydrogen peroxide with  $Fe^{2+}$ , which specifically leads to the formation of hydroxyl radical OH':

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH + OH^-$$
(2.1)

In this system Fe<sup>2+</sup> is added and consequently the system needs to be acidified in order to keep the iron in solution. The Fenton-like process differs from the classic formulation for the use of naturally occurring iron and manganese minerals in subsurface environment as well as relatively high concentrations of H<sub>2</sub>O<sub>2</sub> in solution. The concept of using naturally occurring minerals as iron source was first investigated by Watts et al. (1990), whereas Kakarla and Watts (1997) and more recently Watts and Teel (2005) addressed the issue of H<sub>2</sub>O<sub>2</sub> stabilization using phosphate salts. Hydrogen peroxide lifetime was also investigated by Baciocchi et al. (2003) through batch reactors and later using column tests (Baciocchi et al., 2004). More recently, Vicente et al. (2011) have also addressed the effect of chelating agent on H<sub>2</sub>O<sub>2</sub> stabilization. One of the main concern when applying the Fenton's process to MtBE contaminated water is that the contaminant may not undergo complete mineralization to CO<sub>2</sub> and water, whereas the oxidation can lead to the formation and accumulation of intermediate compounds, such as tert-butyl alcohol (TBA), tert-butyl formate (TBF), methyl acetate and acetone (Hwang et al., 2010; Burbano et al., 2005). The operating conditions of the Fenton's process (e.g. oxidant concentrations) have been found to affect the extent of oxidation and mineralization of MtBE. For instance, Burbano et al. (2008) investigated the extent of MtBE degradation at different H<sub>2</sub>O<sub>2</sub> to MtBE molar ratios, finding out that a 20:1 molar ratio was the minimum one required to achieve complete MtBE removal; nevertheless complete MtBE mineralization was never observed, even increasing the molar ratios up to 200:1. In addition, Siedlecka et al. (2007) showed that inorganic

anions can significantly affect the efficiency of Fenton-like system to MtBE and the extent of intermediates formation. However, most of the available lab-studies on this topic were carried out in batch water systems whereas the influence of the soil, that as known can lead to the generation of a stronger pool of reactive oxygen species (Schmidt et al., 2011), is still poorly investigated in the literature. In this work we investigate the application of a Fenton-like process to a soil-water system artificially contaminated by MtBE with the goal of assessing its performance in terms of MtBE removal and mineralization. To this end, column tests using different oxidant and MtBE concentrations were performed and the effectiveness of the oxidant system was assessed by analysing pH, hydrogen peroxide and MtBE concentrations in the outlet solutions. In addition, in order to provide further lines of evidence of the oxidation performance, carbon dioxide and oxygen were also monitored in the outlet gas stream by on-line sensors allowing to assess the extent of unproductive consumption of the oxidant and MtBE mineralization, respectively.

### **MATERIALS AND METHODS**

#### Reagents

Hydrogen peroxide (30% w/w solution), methyl tertiary butyl ether (99.8%), tert-butyl alcohol (99%), tert-butyl formate (99%), methyl acetate (98%), acetone (99.5%), titanium (IV) oxysulfate, sodium persulfate (>98%), potassium permanganate (>99%), sulphuric acid (96%), potassium iodide (>99.5%), sodium thiosulfate (> 98%), potassium monobasic phosphate (KH<sub>2</sub>PO<sub>4</sub>) and sodium chloride were purchased from Sigma–Aldrich. Ethylenediaminetetraacetic acid disodium salt dihydrate – EDTA (99%) from Sigma Aldrich was used as chelating agent. Fluorobenzene (99%) was used as internal standard and was purchased by Sigma Aldrich. All solutions employed in this work were prepared with deionized water.

### Soil Characterization

The soil used in this study was collected in an area located in the centre of Italy. The particle size fraction below 2 mm was characterized and used for the different ISCO tests. Total carbon (TC) and inorganic carbon (IC) content of the soil were measured using a Shimadzu TOC VCPH analyser equipped with a SSM-5000A solid sampler

(CSN EN 13137, 2001). Total organic carbon (TOC) content was determined from the difference between TC and IC data. The soil oxidant demand (SOD) was measured using both sodium persulfate (iodometric titration with sodium thiosulfate) (Kolthoff and Stenger, 1947; Haselow et al., 2003) and potassium permanganate (Haselow et al., 2003; Standard Methods, 1998). Table 2.1 summarizes the main chemical and physical properties of the analysed soil. The obtained SOD value suggests that the unproductive consumption of the oxidant through reaction with natural soil reductants is quite limited (Baciocchi et al., 2014).

Parameter	Units	Value	
SOD (using KMnO <sub>4</sub> )	(mg/kg)	4.7	
SOD (using Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> )	(mg/kg)	2.0	
TC	(%)	0.03	
IC	(%)	< 0.01	
TOC	(%)	0.03	
Fe	(mg/kg)	29700	
Mn	(mg/kg)	800	
Cl	(mg/kg)	9.8	
SO4	(mg/kg)	53.8	

Table 2.1. Soil characterization.

The chlorides and sulphates content was measured on the eluate obtained from a 24 hours leaching test performed on the soil sample applying a liquid to solid ratio (L/S) equal to 10 l/kg (UNI EN 12457-2, 2004). The chlorides content was then determined by titration with AgNO<sub>3</sub> and with colorimetric indicator (ISO 9297, 1994), whereas the sulphates content was determined by turbidimetric method using a UV-VIS spectrophotometer (APHA Standard Methods, 1992). As can be seen in Table 2.1, the measured values of sulphates and chlorides are quite low suggesting that their detrimental effect on the oxidation would be quite limited (Baciocchi et al., 2014).

Total Fe and Mn content in soil were determined by acid extraction (US EPA 3050B Method, 1996) and successive detection by an Agilent 710-ES inductively coupled plasma optical emission spectrometer ICP-OES (ISO 11885, 2007). Based on this analysis the iron and manganese content of the soil resulted equal to 29700 and 800 mg/kg respectively, indicating that the Fenton-like process can be successfully applied.

### **Preliminary batch tests**

Before performing the column tests, preliminary batch tests were carried out in order to select the best operating conditions in terms of potassium monobasic phosphate dosage. To this end, different batch tests were performed in 50 ml glass vials sealed with Teflon-lined screw caps on 20 g of air-dried soil adding a volume of hydrogen peroxide and stabilizer (potassium monobasic phosphate) needed to achieve soil saturation. The soil-water system was thoroughly mixed by means of a Vortex shaker (Heidolph Reax 1DR), set at 1000 rpm for few minutes and then left reacting. At the end of each test, the vial content was centrifuged and hydrogen peroxide concentration in the supernatant was analysed following the procedure described below. These batch experiments were performed for different reaction times. The collected data were then used to estimate the kinetics of hydrogen peroxide decomposition assuming a pseudo-first order kinetic:

$$C = C_0 \cdot e^{-k \cdot t} \tag{2.2}$$

Where  $C_0$  is the initial hydrogen peroxide concentration (%wt), t the reaction time (h) and k the pseudo-first order kinetic rate constant (h<sup>-1</sup>).

### **Column tests**

The Fenton-like column tests were carried out in a glass column, characterized by an inner diameter of 4.5 cm and a height of 40 cm. The experimental setup, represented in Fig. 2.1, is made up by a peristaltic pump (Gilson Miniplus3), which ensures the reagent flows, two sensors for measuring oxygen and carbon dioxide concentration in the outlet gas stream, a gas flow meter and a data acquisition system. Namely, carbon dioxide concentration was measured by AGM 1010 CO<sub>2</sub> sensor (concentration range 0-10%), oxygen concentration was measured using an Apogee Instruments SO-200 operating in the concentration range of 0-100% and the gas flow rate was measured by ADM Agilent 2000E flow meter (capacity range 0.1- 1000 ml/min).


Figure 2.1. Schematic representation of the experimental layout.

The column tests were performed using the operating conditions reported in Table 2.2. Namely, in the Control test the soil was first saturated with deionized water and then treated with stabilized  $H_2O_2$  solutions. In this way, the effect of the natural soil reductants on  $H_2O_2$  degradation could be investigated. In the Fenton test, the soil was first saturated with a MtBE solution and then treated with stabilized  $H_2O_2$  solution in order to assess the extent of MtBE removal and mineralization, as well as the combined influence of soil reductants and other process on the  $H_2O_2$  degradation. The Fenton (EDTA) test was similar to the Fenton one, except for the saturation step, that was performed with a solution of MtBE and chelating agent, that was left in the column for 24 h before injecting the oxidant. Finally the Washing test was performed by saturating the soil column with a MtBE solution, followed by its washing with deionized water. The Washing test was used as reference to quantify the effect of dilution and displacement on the MtBE removal obtained in the Fenton and Fenton (EDTA) tests.

Test	H2O2 (% wt)	[MtBE] <sub>in</sub> (mg/l)	Q (ml/min)	KH2PO4:H2O2 (mol/mol)	EDTA (mmol/kg)	Replicates (n.)
Control (a)	2	-	0.7	1:30	-	2
Fenton (a)	2	6	0.7	1:30	-	3
Fenton (EDTA) (a)	2	6	0.7	1:30	10	2
Washing (a)	-	6	0.7	-	-	2
Control (b)	6	-	0.7	1:30	-	2
Fenton (b)	6	30	0.7	1:30	-	3
Fenton (EDTA) (b)	6	30	0.7	1:30	10	2
Washing (b)	-	30	0.7	-	-	2

 Table 2.2. Operating conditions of the different tests carried out.

In each test the column was packed with 200 g of soil and the remaining space was filled up with layers of laboratory sand and glass spheres in order to obtain a uniform and well distributed flow. All tests were performed using a 0.7 ml/min flow rate that corresponds to a Darcy velocity of approximately 0.65 m/day, chosen in order to evaluate the dilution effects for relatively high permeable layers (e.g. sandy soils). Based on the experience already gained on ISCO by Baciocchi et al. (2010; 2014) and Innocenti et al. (2014) two different H<sub>2</sub>O<sub>2</sub> concentrations were tested i.e. 2% wt and 6% wt. The amount of the stabilizer ( $KH_2PO_4$ ) used in the column tests was selected based on the results of the preliminary batch tests. As reported in Table 2.2, for the Fenton, Fenton (EDTA) and Washing experiments, two different MtBE solutions of 6 mg/l and 30 mg/l were tested. It is worth noting that, all the solutions were fed in the column upward in order to achieve a uniform flow field and to minimize the risk of preferential flow paths or uncontrolled gravity-induced drainage. The outlet liquid was sampled every hour and then pH, H<sub>2</sub>O<sub>2</sub>, MtBE and its degradation by-products were analysed as described in analytical methods. In addition, during each column test, gas flow rate, CO<sub>2</sub> and O<sub>2</sub> concentrations were monitored in the outlet gas at 20 seconds intervals using the online sensors described above and the data were recorded using a data acquisition card (OB-LOG - Module data-logger 8) connected to a data acquisition system (Software Labview for the flow meter, Alarm Manager for  $O_2$  and Advanced Gasmitter for CO<sub>2</sub>).

#### **Analytical methods**

The pH of each collected sample was measured with a Eutech Instruments pH700 pHmeter. Hydrogen peroxide concentration in the feed solution and in the samples collected at the soil column outlet was measured using an UV-VIS spectrophotometer TU-18805 Double Beam after colour development with titanium sulphate technique (Schumb et al., 1955). H<sub>2</sub>O<sub>2</sub> concentration was measured in duplicate to obtain an average value. MtBE, TBA, TBF, Methyl Acetate and Acetone in the feed solution and in the water samples collected at the soil column outlet were measured by headspace gas chromatography-mass spectrometry detection (GC-MS) with fluorobenzene as internal standard. For headspace analysis, 10 ml samples were stirred for 40 min at 70 °C in 20 ml headspace vials containing 5 g NaCl to increase vapour phase concentration by the salting-out effect. The headspace gas (250 µl) was injected (split 1:10) with an autosampler (AOC-5000 plus) into a Shimadzu GC/MS (GC\_QP2010SE) equipped with a TR-5MS column (30 m x 0.25 mm ID x 0.25 um film thickness: 5% Phenyl (equiv) Polysilphenylene – siloxane). Helium (0.9 ml/min) was used as carrier gas. Initial oven temperature was 35 °C, which was held for 3 min, and then ramped to 180 °C (at a 30 °C/min rate) and maintained for other 2 min. The operating MS settings were as follows: Ionization voltage, 0.87kV; interface temperature, 230°C; detector temperature, 200°C (Shin and Kim, 2009). The selected ions monitoring (SIM) acquisition mode was used and the ions fragments selected were: 73 (MtBE), 96 (fluorobenzene), 43 (Methyl acetate), 58 (Acetone), 59 (tert-Butanol, TBA; tert-Butyl formate, TBF). The MtBE concentration was measured in triplicate to obtain an average value.

#### Interpretation of the experimental results

#### CO<sub>2</sub> and O<sub>2</sub> production from on-line measurements

The overall amount of oxygen,  $N_{O2,p}$  (mmol), and carbon dioxide,  $N_{CO2,p}$  (mmol), produced during each experiment was estimated on the basis of the on line measurements applying the following equations:

$$N_{O_2,p} = \frac{\sum_{i}^{n} [O_2]_i \cdot Q_i \cdot \Delta t}{V}$$
(2.3)

$$N_{CO_2,p} = \frac{\sum_{i=1}^{n} [CO_2]_i \cdot Q_i \cdot \Delta t}{V}$$
(2.4)

where  $[O_2]$  and  $[CO_2]$  are the oxygen and carbon dioxide concentrations acquired by the sensors (% vol) respectively, at each time interval, Q is the outlet gas flow measured by the flow meter (ml/s),  $\Delta t$  indicates the acquisition interval of the sensor (s), V (ml/mmol) is the gas molar volume calculated at the tested operating conditions and n is the number of data acquired by the sensor during each test.

#### $O_2$ and $CO_2$ stoichiometric production estimated from off-line measurements

In order to assess the extent of  $O_2$  and  $CO_2$  production, the stoichiometric amount expected assuming complete  $H_2O_2$  decomposition and MtBE and organic carbon mineralization were calculated.

The amount of oxygen expected assuming  $H_2O_2$  stoichiometric disproportionation  $(H_2O_2 \rightarrow H_2O + 0.5O_2)$ ,  $N_{O2,s}$  (mmol), was calculated as follows:

$$N_{O_{2,s}} = \frac{\left[H_2 O_2\right]_{in} \cdot Q \cdot t - \sum_{i}^{n} \left[H_2 O_2\right]_{out} (t_i) \cdot \Delta V(t_i)}{2}$$
(2.5)

where Q is the flow rate of solution injected in the column (l/h), t the injection duration (h),  $[H_2O_2]_{in}$  the hydrogen peroxide concentration injected in the column (mM),  $[H_2O_2]_{out}$  the hydrogen peroxide concentration in the outlet stream (mM),  $\Delta V(t_i)$  the volume sampled during each time interval (l), n the number of samples collected and  $t_i$  the time interval (h).

Similarly, the CO<sub>2</sub> produced assuming complete mineralization (C<sub>5</sub>H<sub>12</sub>O + 7.5O<sub>2</sub>  $\rightarrow$  5CO<sub>2</sub> + 6H<sub>2</sub>O) of the consumed MtBE, N<sub>CO2,s</sub> (mmol), was calculated applying the following mass balance equation:

$$N_{CO_{2,s}} = 5 \cdot \left( \left[ MtBE \right]_{in} \cdot V_{sat} - \sum_{i}^{n} \left[ MtBE \right]_{out} (t_{i}) \cdot \Delta V(t_{i}) \right)$$
(2.6)

where  $V_{sat}$  (1) is the volume of the MtBE solution needed to saturate the column, [MtBE]<sub>in</sub> is the MtBE concentration of the inlet stream (mM) and [MtBE]<sub>out</sub> is the concentration of MtBE in the outlet stream (mM). Furthermore the carbon dioxide resulting from the oxidation of the organic carbon of the soil, N<sub>CO2,OC</sub> (mmol), was estimated as:

$$N_{CO_{2,oc}} = (OC_{in} - OC_{fin}) \cdot \frac{M_{soil}}{12}$$
(2.7)

where  $OC_{in}$  is the initial organic carbon measured in the soil (g/g),  $OC_{fin}$  the organic carbon in the soil at the end of the test (g/g) and  $M_{soil}$  the amount of soil used in each test (g).

#### **RESULTS AND DISCUSSION**

#### **Preliminary batch tests**

Fig. 2.2a reports the decomposition kinetics of hydrogen peroxide obtained using different initial  $H_2O_2$  concentrations (1 % wt, 2 % wt and 3 % wt) without adding the stabilizer. This figure clearly shows that, independently from the initial oxidant concentration used, without adding the stabilizer, the hydrogen peroxide lifetime (here defined as the time required to achieve a reduction of 90% of the initial  $H_2O_2$  concentration) was below 6 hours.



**Figure 2.2.** Kinetics of  $H_2O_2$  decomposition: (a) tests performed using different initial hydrogen peroxide concentrations without adding  $KH_2PO_4$ ; (b) tests performed for an initial oxidant concentration of  $H_2O_2$  =1% using with different stabilizer:  $H_2O_2$  molar ratios. "k" represents the kinetic rate constant obtained by the best fitting of experimental data using a pseudo-first order kinetic model.

The same figure also shows that the  $H_2O_2$  decomposition kinetics for the three tested concentration follow the same trend, confirming that the  $H_2O_2$  decomposition can be described by a pseudo-first order kinetic model (Siegrist et al., 2011). In order to increase the  $H_2O_2$  lifetime, for one of the initial concentration tested (i.e. 1 % wt), further tests were carried out by adding different amounts of the stabilizing agent (see Fig. 2.2b). Making reference to this figure, it can be noticed that the addition of KH<sub>2</sub>PO<sub>4</sub> significantly increases the H<sub>2</sub>O<sub>2</sub> lifetime. Namely, it can be observed that H<sub>2</sub>O<sub>2</sub> lifetime is shown to increase up to 10 hours for a 1:50 KH<sub>2</sub>PO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> ratio and up to 16 hours for 1:30 KH<sub>2</sub>PO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> molar ratio, whereas no significant differences were observed at higher potassium monobasic phosphate dosages. Based on these results, a 1:30 KH<sub>2</sub>PO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> molar ratio was selected as the operating condition to be used in the column tests carried out. Making reference to this figure it can be also noticed that the obtained k values are not so far from the median value of 0.2 h<sup>-1</sup> reported by Petri et al. (2011) who have analysed 139 rate constants available in the literature for catalysed hydrogen peroxide applications.

#### **Column tests**

#### Concentration of hydrogen peroxide and pH variation

Fig. 2.3 reports the values of the hydrogen peroxide concentrations measured in the outlet solutions collected in the Fenton, Fenton (EDTA) and Control tests for the tested  $H_2O_2$  concentrations, i.e. 2 % (Fig. 2.3a) and 6 % (Fig. 2.3b).



**Figure 2.3.** Concentration of hydrogen peroxide measured in the column outlet during tests with (a) 6 mg/l MtBE and 2%  $H_2O_2$  and (b) 30 mg/l MtBE and 6%  $H_2O_2$ . In the figures the average  $H_2O_2$  values are reported together with vertical error bars indicating the standard deviation of the different experiments carried out.

As expected, for both the hydrogen peroxide concentrations tested, the values measured in the outlet stream, are significantly lower than those measured in the feed solution, indicating a relevant decomposition of the oxidant in the column. Furthermore, looking at the different results reported in Fig. 2.3, it can be noticed that the Fenton and Fenton (EDTA) tests, led to a hydrogen peroxide consumption similar to the one observed in the control tests. This suggests that the effectiveness of the oxidation process cannot be evaluated only measuring the hydrogen peroxide concentration over time. In addition, the same figure shows that, especially for the tests carried out using the Fenton reagent without adding the chelating agent (EDTA), the residual oxidant concentrations at the end of the tests are slightly higher (about 20%) than the ones measured in the control tests.

The pH measured in the outlet stream during the different tests (Control, Fenton, Fenton (EDTA)) is reported in Fig. 2.4 together with the one corresponding to the Washing test added as reference.



**Figure 2.4.** pH measured in the column outlet during tests with (a) 6 mg/l MtBE and 2%  $H_2O_2$  and (b) 30 mg/l MtBE and 6%  $H_2O_2$ . In the figures the mean pH values are reported together with vertical error bars indicating the standard deviation of the different experiments carried out.

It can be observed that in the latter test, the pH was always in the range of pH=8.5-9; in the case of the tests carried out feeding hydrogen peroxide only (i.e. Control test) the pH drops down at the end of the test to pH=8 in the case of the inlet  $H_2O_2$  concentration of 2% (Fig. 2.4a) and to pH=7 for 6%  $H_2O_2$  concentration (Fig. 2.4b). In the Fenton and Fenton (EDTA) tests, it can be observed that in both cases, in the early stages of the test the pH trend follows the same trend of the Control test, whereas toward the end of the

tests the pH drops down to values of 5-6. These results suggest that the higher  $H_2O_2$  stability observed in the Fenton and Fenton (EDTA) tests is probably related to the lower average pH values observed in these tests, probably due to the dissolution of  $CO_2$  in water, that may lead to higher  $H^+$  concentrations in water.

#### MtBE oxidation

As described above, the MtBE concentration in the water samples collected at the column outlet was measured at regular intervals for the entire duration of each test, allowing to estimate the cumulative mass of MtBE leaving the column in each test. Fig. 2.5 reports the ratio between the cumulative mass of MtBE leaving the column in the outlet stream and the initial mass injected in the column as a function of the applied liquid to solid ratio (L/S).



**Figure 2.5.** Percentage of cumulative outgoing MtBE mass normalized with respect to the initial contaminant mass injected in the column (average values) for tests performed with (a) 6 mg/l MtBE and 2%  $H_2O_2$  and (b) 30 mg/l MtBE and 6%  $H_2O_2$ . In the figures the mean values are reported together with vertical error bars indicating the standard deviation of the different experiments carried out.

It can be noticed that in the early stages of the test, i.e. for a L/S ratio lower than 0.5 l/kg, all the tests follow basically the same trend that is driven by the displacement of the contaminant present in the column. The effect of oxidation starts to become relevant for higher L/S ratios. Namely, for the Washing tests, the MtBE release continues to increase achieving the almost complete washout of the contaminant injected. On the contrary, in the Fenton and Fenton (EDTA) tests, the amount of MtBE released remains lower than 60% and 45% of the quantity of the MtBE injected in the column, respectively. This suggests that, despite the relatively high flow rate applied, a relevant

amount of the injected MtBE was oxidised. Furthermore, these results indicate that the addition of EDTA catalyses the oxidation process making the reaction more effective and leading to a consequent higher MtBE removal. In order to assess if the oxidation observed in the different tests corresponds also to a complete MtBE mineralization, the presence of typical MtBE by-products (i.e. TBA, TBF, acetone and methyl acetate) was investigated by GC-MS. As can be seen from the chromatograms shown in Fig. 2.6b, that correspond to the different samples collected during one of the performed Fenton (EDTA) tests, the only peaks that were detected are associated to MtBE and the internal standard (i.e. fluorobenzene) whereas the peaks of the specific MtBE by-products were not observed (see the reference chromatograms in Fig. 2.6a), thus suggesting a rather complete mineralization of MtBE.



**Figure 2.6.** (a) Reference chromatograms for MtBE and its degradation products; (b) Chromatogram of MtBE and fluorobenzene (PhF) at different stages of the Fenton (EDTA) test performed with 6 mg/l MtBE and 2%  $H_2O_2$ .

Similar results were also obtained for the other experiments carried out. These results hence suggest that after a contact time of 3 hours (i.e. the residence time of hydrogen

peroxide in the column) the oxidant seems to be able to complete the degradation pathway of MtBE. These findings are slightly different from the ones obtained for example by Siedlecka et al. (2007) and Burbano et al. (2008) who observed a slight MtBE by-products formation for all the tested operating conditions. This presumably could be due on the one hand, to the longer reaction time used here (i.e. 3 hours instead of 1-1.5 hours applied in the above cited works) and, on the other hand, to the presence of the soil that, differently from a simple water system, leads to a generation of a stronger pool of reactive oxygen species (Schmidt et al., 2011) which could result in a more efficient oxidation system.

#### Production of oxygen and carbon dioxide

The concentrations of oxygen and carbon dioxide measured with the online sensors during the different tests are reported in Fig.2.7 and Fig.2.8, respectively.



**Figure 2.7.** Oxygen concentrations (average values) measured with the online sensor in the gas stream line during tests with (a) 6 mg/l MtBE and 2%  $H_2O_2$  and (b) 30 mg/l MtBE and 6%  $H_2O_2$ .

Making reference to Fig. 2.7, it can be noticed that the oxygen concentration progressively increases during the oxidant injection reaching concentrations up to 90% v/v in both Control and Fenton tests. Obviously, for the Washing test the oxygen concentration remains constant and equal to its concentration in air for the entire experiment duration. Fig. 2.7 also shows that in the Control test the maximum oxygen concentration achieved at the end of the oxidant feeding, is higher than the one measured in the Fenton test (with or without EDTA). This observation is in agreement

with the  $H_2O_2$  decomposition data (Fig. 2.3), where the oxidant was observed to be more stable during the Fenton tests than in the Control one, showing a lower unproductive disproportionation of hydrogen peroxide. Furthermore, Fig. 2.7 shows that in the case of the tests conducted with EDTA, oxygen production starts already after an hour from the beginning of  $H_2O_2$  injection, confirming that the chelating agent significantly catalyses the  $H_2O_2$  decomposition. Besides, these results indicate that the maximum oxygen concentration observed in the test obtained using EDTA was quite lower than the maximum ones observed in the other tests, suggesting a lower unproductive disproportionation of the oxidant.

As far as the carbon dioxide production is concerned (Fig. 2.8), the obtained results show that in this case the presence of the contaminant, in the Fenton and Fenton (EDTA) tests, led to a CO<sub>2</sub> production significantly higher than the one measured in the case of the Control and Washing tests. This result provides a further line of evidence that MtBE was at least partially mineralized. This is also confirmed by the fact that for higher MtBE concentrations (Fig. 2.8b) the maximum CO<sub>2</sub> concentration was significant higher (i.e. 1.7% in Fig. 2.8b vs. 1% Fig. 2.8a for the Fenton (EDTA) test). Also in this case, the test carried out using the chelating agent (EDTA), shows that this formulation leads to a faster and higher carbon dioxide production, indicative of a more efficient oxidation process.



**Figure 2.8.** Carbon dioxide concentrations (average values) measured with the online sensor in the gas stream line during tests with (a) 6 mg/l MtBE and 2%  $H_2O_2$  and (b) 30 mg/l MtBE and 6%  $H_2O_2$ .

#### Mass Balance

The extent of unproductive oxidant consumption was assessed by comparing the oxygen measured with the on-line sensor with the stoichiometric value expected assuming that all the consumed hydrogen peroxide is transformed to oxygen according to Eq. (2.5).



**Figure 2.9.** Comparison between the average values of oxygen measured with the online sensor and the ones calculated by applying a mass balance to hydrogen peroxide assuming a complete disproportionation in tests performed with (a) 6 mg/l MtBE and 2%  $H_2O_2$  and (b) 30 mg/l MtBE and 6%  $H_2O_2$ . In the figures the mean values are reported together with vertical error bars indicating the standard deviation of the different experiments carried out.

The results of this comparison, reported in Fig. 2.9, show that only a small amount of the oxidant consumed underwent complete disproportionation. In particular, it can be noticed that the measured values are significantly lower than the ones obtained assuming a stoichiometric decomposition to oxygen of hydrogen peroxide. This is particularly true in the tests carried out with the chelating agent where the measured values are less than 10% of the values obtained assuming complete disproportionation of the consumed oxidant. Once again, the oxidant system seems to be more stable in the presence of the contaminant (see Fenton vs. Control test in Fig. 2.9a) and at higher oxidant concentrations (see Fig. 2.9b vs. Fig. 2.9a).

Similarly, in order to assess the extent of MtBE mineralization, the cumulative  $CO_2$  amount produced, estimated from the online sensor data using Eq. (2.4), was compared with the values calculated assuming that all the oxidised MtBE was subject to complete transformation to  $CO_2$  (i.e. complete mineralization). The obtained results are reported in Fig. 2.10. Making reference to the comparison performed for the Control tests, it can be seen that in both the operating conditions (i.e.  $H_2O_2$  at 2% and 6%) the amount of

 $CO_2$  measured was significantly lower than the one expected (Eq. 2.7) assuming complete mineralization of the initial organic carbon of the soil (TOC = 0.03%). This result indicates that for the Fenton and Fenton (EDTA) tests the contribution to the overall carbon dioxide production due to the mineralization of the soil organic carbon can be considered negligible. The other comparisons reported in Fig. 2.10 show that in the other tests carried out, the CO<sub>2</sub> measured with the online sensor almost equals the one calculated from the mass balance. In particular, making reference to the average values obtained in the different tests, the CO<sub>2</sub> measured with the online sensors was slightly lower than the one obtained from the mass balance indicating that the fraction of MtBE mineralized by the tested oxidant system was around 85% (Fenton tests) and 95% (Fenton (EDTA) tests) of the oxidised one. Once again the best performances were observed in the tests carried out using EDTA. Hence, these data demonstrate that most of the MtBE was surely mineralized.



**Figure 2.10.** Comparison between the average values of carbon dioxide measured with the online sensor and the ones calculated by applying a mass balance to MtBE assuming its complete mineralization in tests performed with (a) 6 mg/l MtBE and 2%  $H_2O_2$  and (b) 30 mg/l MtBE and 6%  $H_2O_2$ . In the figures the mean values are reported together with vertical error bars indicating the standard deviation of the different experiments carried out.

# CHAPTER 3

# PILOT-SCALE FEASIBILITY STUDY OF ISCO APPLICATION

This chapter is partially taken from:

Innocenti I., Verginelli I., Massetti F., Piscitelli D., Gavasci R., Baciocchi R. (2014). Pilot-scale ISCO treatment of a MtBE contaminated site using a Fenton-like process. Science of The Total Environment, Vol. (485–486), 726–738.

#### BACKGROUND

In the last decades remediation of groundwater contaminated by oxygenates (ethers and alcohols) has become a key environmental issue in most of advanced countries. Ether oxygenates include methyl tert-butyl ether (MtBE), ethyl tert-butyl ether (EtBE), tertamyl methyl ether (TAME), diisopropyl ether (DIPE), whereas alcohol oxygenates are ethanol (EtOH), methanol (MeOH), isopropyl alcohol (C<sub>3</sub>H<sub>8</sub>O), isobutyl alcohol (C<sub>4</sub>H<sub>10</sub>O) tert -butyl alcohol (TBA) (Deeb et al., 2003). These compounds, commonly known as "oxygenates", are almost exclusively used as a fuel additive in motor gasoline improving the combustion and limiting the production of unburned products such as carbon monoxide (EFOA, 2005). Among these, MtBE (methyl tertiary-butyl ether) is currently one of the most widely used fuel oxygenate (Concawe, 2012). Due to the physico-chemical and structural properties of MtBE, which reduce the efficacy of conventional groundwater clean-up technologies (e.g. Air Sparging), in situ chemical oxidation (ISCO) has become, in recent years, one of the attractive remedial alternatives for MtBE contaminated groundwater (Liang et al., 2011). In particular, in literature are reported several ISCO applications for MtBE degradation using different oxidant formulations based on hydrogen peroxide (Hwang et al., 2010; Siedlecka et al., 2007), persulfate (Huling et al., 2011; Liang et al., 2011; Huang et al., 2002) and potassium permanganate (Damm et al., 2002). Apart from permanganate, whose application is ideally suited to the remediation of groundwater contaminated by chlorinated solvents, catalysed hydrogen peroxide has been among the most widely applied oxidants through the well-known Fenton's process, where H<sub>2</sub>O<sub>2</sub> reacts with a proper catalyst leading to the generation of a pool of strongly oxidizing radicals. One of the main drawback of the application of classic Fenton's reagent is that the  $Fe^{3+}$  produced is only sparingly soluble, especially at neutral pH, so that high concentrations of ferric oxyhydroxides precipitates are generated when stoichiometric quantities of Fe<sup>2+</sup> are used (Kwan and Voelker, 2002). A possible option to overcome this limitation is to acidify the soil to the optimal pH value between 3 and 4 (Watts et al., 1990). However, this is often not an easy task to be achieved. A possible alternative, which is the one adopted in this work, is represented by the so-called Fenton-like process. This process is based on the idea of using chelating agents and naturally occurring iron minerals for catalysing the decomposition of hydrogen peroxide (Watts and Dilly, 1996). Watts and Teel (2005)

among others have demonstrated that in many cases Fenton's reactions are more stoichiometrically efficient when iron and manganese minerals are used as catalyst, suggesting that the injection of soluble forms of iron may not be needed for In-Situ treatments. In addition, Sun and Pignatello (1992) among others have shown that using chelating agents allows Fenton-like reactions to proceed at circumneutral pH by minimizing the precipitation of iron which may eliminate the need to acidify groundwater. The capacity of Fenton's reagent to degrade MtBE and the resulting oxidation by-products was assessed by Burbano et al. (2005, 2008) who have performed lab-scale tests at 2000 µg/L maximum concentration, achieving an almost complete mineralization, although small concentrations of TBA, tert-butyl formate (TBF), methyl acetate and acetone were still detected and quantified. Siedlecka et al. (2007) have investigated the effect of inorganic anions and other radical scavengers on the effectiveness of the Fenton's treatment of waters contaminated with MtBE showing that chlorides, phosphate ions, sulphates and perchlorates can significantly influence the oxidation rates of this compound. Nevertheless, the field-scale evidence supporting the efficiency of MtBE removal by ISCO and its capacity of achieving MtBE complete mineralization is still quite limited. The analysis of field-scale ISCO application carried out by Krembs et al. (2010) with reference to the US market in the period from 1996 through 2007, showed that MtBE was among the target contaminants in 7% of the more than 200 sites assessed. In this work a pilot-scale feasibility study, aimed at assessing the In-Situ applicability of a Fenton-like process to a site formerly used for fuel storage and contaminated by MtBE, was carried out. Namely, the tested Fenton-like process consisted in using H<sub>2</sub>O<sub>2</sub> catalysed by naturally occurring iron minerals and chelating agents (ethylenediaminetetraacetic acid, EDTA or sodium citrate), to enhance the extraction of iron from soil and avoid the precipitation of the sparingly soluble  $Fe^{3+}$ . In addition, in order to increase the lifetime of hydrogen peroxide in the subsurface, potassium monobasic phosphate was used as stabilizing agent. The feasibility study reported in this work was carried out following the indications provided by the Italian protocol on ISCO (APAT, 2005) and more recently integrated by Baciocchi et al. (2014). Namely, the design strategy, previously tested in an hydrocarbon contaminated site (Baciocchi et al., 2010), was based on a lab-scale feasibility test, aimed at selecting

the best operating conditions, and a modelling step, aimed to evaluate the radius of influence of the oxidant and to design the pilot-scale layout and operating conditions.

### **MATERIALS AND METHODS**

#### Reagents

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30% w/w solution), Sodium persulphate (> 98%), Potassium permanganate (> 99%), Sulphuric acid (96%) and Potassium Monobasic Phosphate (KH<sub>2</sub>PO<sub>4</sub>) were purchased from Carlo Erba. Ethylenediaminetetraacetic acid disodium salt dihydrate – EDTA (99%) and sodium dihydrogen citrate (98%) from Sigma Aldrich were used as chelating agents. Solid-phase micro-extraction fiber (PDMS/DVB) was purchased by Supelco. All solutions were prepared with Reverse Osmosis (RO) water purified with a deionizing system (Zeener Power I Human Corporation).

#### **Analytical methods**

#### Lab-scale tests

Hydrogen peroxide concentration was measured by iodometric titration (Schumb et al., 1955). MtBE concentration at the lab-scale was determined by Headspace Solid Phase Micro Extraction (HS-SPME) coupled with analysis by GC-FID (Dron et al., 2002), using a manual 65 µm poly(dimethylsiloxane)-divinylbenzene (PDMS/DVB) SPME fiber.

#### **Pilot-scale tests**

The samples collected during the pilot-scale test were analysed by an accredited laboratory analysis using the following analytical methods. Hydrogen peroxide concentration was measured by iodometric titration. MtBE concentration was determined by headspace coupled with analysis by GC-FID (ISO method 11423, 1997). TBA concentration was measured by purge and trap coupled by GC-MS (U.S. EPA method 5030C, 2003; U.S. EPA method 8260C, 2006). Total Petroleum Hydrocarbons (TPH) were determined using headspace coupled with analysis by GC-FID (ISO method 11423, 1997) for C<12 and solvent extraction coupled with analysis by GC-FID (ISO 9377-2, 2000) for C>12. The chlorides and sulphates content was measured by ion

chromatography (U.S. EPA method 9056A, 2007). Total Fe and Mn content in soils were determined by acid extraction and successive detection by an inductively coupled plasma mass spectrometry ICP-OES (ISO method 17294-2, 2003). Total organic carbon (TOC) content of the soil was measured using a TOC analyser equipped with a solid sampler.

During the pilot-scale test for each well the pH, Redox Potential (ORP), groundwater temperature (T) and electrical conductivity (EC) were monitored In-Situ using a multi-parametric sensor. In addition, the concentrations of oxygen ( $O_2$ ) and carbon dioxide ( $CO_2$ ) were measured in the off-gas line system using a portable gas analyser. The concentrations of volatile organic compounds (VOC) were monitored using a portable PID (photoionization detector).

#### Site description

The site of concern is a former fuel storage area located in central Italy, dismissed since about 10 years. The main contaminant of concern in the site is MtBE that is found in groundwater at concentrations around 4000  $\mu$ g/L. Groundwater contamination also includes hydrocarbons (TPH). The stratigraphy of the site consists of a 2-3 meters backfill layer followed by a 3-4 meters low permeability layer that confines the main aquifer, located approximately 5-7 meters below ground. The groundwater flow and direction is affected by a pump and treat system acting as hydraulic barrier along the south-east border of the site. Fig. 3.1 reports a plan view of the contaminated site, completed with the indication of the former position of tanks and other facilities that have been demolished and removed.



**Figure 3.1.** Plan view of the site with indication of the area of ISCO application. In this figure is also indicated the former position of tanks and other facilities, that have been demolished and removed. The same figure also reports the isopiestic curves corresponding to the groundwater in the main aquifer.

The same figure also reports the isopiestic curves corresponding to the groundwater in the main aquifer, which is extremely heterogeneous, being characterized by layers with different hydro-geological properties. Namely, the general aquifer lithology consists of fine sands with some discontinuous low permeable lenses. The iron content of the soil, which as described above will be used as a catalyst of the oxidation process, is found in the site at concentrations around 20 g/kg. The fraction of organic carbon in soil ( $f_{oc}$ ), which can lead to an unproductive oxidant consumption, is in the range between 0.0005 and 0.001  $g_{oc}/g_{soil}$ .

#### Characterization of the area selected for the pilot-scale test

The characterization of the area selected for the pilot-scale test was conducted, on the one hand, to collect soil and groundwater samples used for the different batch tests described below and on the other hand, to evaluate the hydro-geological parameters to be used for the modelling and design of the treatment. To this end, soil samples were collected in the area representative of the one selected for the pilot-scale test with surveys that extended down to the depth at which the contamination was found during

the site characterization. In addition, since the site was characterized by an heterogeneous stratigraphy, soil samples from each horizon were collected. This was crucial to assess, through the lab-scale tests, the behaviour of the oxidant in contact with the soil matrix corresponding to each horizon.

Based on this characterization, it was found that in the area selected for the pilot-scale test, the aquifer is located approximately 5.5 meters below ground and it is characterized by an upper and lower loamy sand layer (USDA classification system) of approximately 2-3 m thickness (soil layer 1 and soil layer 3, respectively) and a middle soil layer (approximately 1-2 m thickness) with a silt loam texture (soil layer 2). From the analysis carried out in the soil samples collected at different depths, an iron content of 20.2 g/kg was measured in soil layer 1, 12.5 g/kg in soil layer 2 and 22.2 g/kg in soil layer 3. The manganese content of soil, which can also catalyse the oxidation process, was of 1.2 g/kg in soil layer 1, 0.28 g/kg in soil layer 2 and 0.77 g/kg in soil layer 3. The collected groundwater samples were analysed for iron and manganese content resulting in an average value of 2.3 mg/L and 7.2 mg/L, respectively. These samples were also analysed for chlorides and sulphates content, which may act as scavengers of the oxidizing species, obtaining average values of 124 mg/L and 11 mg/L, respectively, which indicate that this detrimental effect should be quite limited (Baciocchi et al., 2014).

#### **Design of the pilot-scale test**

As described above, the design of the pilot-scale ISCO test was based on a combination of experimental and numerical modelling, following the approach outlined in Baciocchi et al. (2014) and previously applied by Baciocchi et al. (2010). A lab-scale feasibility test was performed first, allowing to select the most suitable operating conditions in terms of chelating agent and stabilizer dosages. These information, coupled with field data on the hydrogeological characteristics of the site, were used as input for the numerical simulation of the pilot-scale ISCO test, which allowed to assess the radius of influence of the oxidant and to support the definition of the pilot-scale test configuration in terms of number and position of the injection and monitoring wells, injection duration and injection flow rates.

#### Lab-scale tests

Before performing the batch tests, the soil samples collected from the site were tested for the oxidant demand (SOD), which provides a preliminary fast assessment of nonproductive oxidant consumption due to the different reactions that can occur between the subsurface media and the oxidant. Following the approach outlined by Haselow et al. (2003), the SOD average value estimated for the different soil samples was around 7 gKMnO<sub>4</sub>/kg of soil, with all measurements below 10 gKMnO<sub>4</sub>/kg.

Lab-scale experiments were carried out in agreement with the guidelines for application of ISCO technologies issued by the Italian Environmental Agency (APAT, 2005) in order to evaluate the applicability of a Fenton-like system for the site of concern. To this end, batch tests were performed at 6% H<sub>2</sub>O<sub>2</sub> concentration using different types and concentrations of amendments. i.e. two chelating agents (ethylenediaminetetraacetic acid, EDTA and sodium citrate) and a stabilizer (potassium monobasic phosphate). The hydrogen peroxide concentration of 6% was selected based on the experience already gained on ISCO by Baciocchi et al. (2010) who observed a significant gas production for concentrations of H<sub>2</sub>O<sub>2</sub> higher than 6%, which could lead to a reduction of the oxidant propagation in the subsoil, as well as additional problems in the management and monitoring of the pilot-scale test. The tests were carried out on different soil samples, representative of the different soil layers of the aquifer. The different batch tests were performed in 50 mL glass vials sealed with Teflon-lined screw caps on 20 g of air-dried soil samples collected from the site and with the amount of contaminated water, also collected from the site, needed to achieve soil saturation. First, the chelating agent (EDTA or sodium citrate) was added to the soil-water system and thoroughly mixed by means of a Vortex shaker (Heidolph Reax 1DR), set at 1000 rpm for few minutes. After 24 hours, required in order to extract the iron from the soil, hydrogen peroxide and the stabilizer (potassium monobasic phosphate) were then added, in different amounts, once again by mixing with a Vortex shaker and then left reacting. Repeating the same batch experiment for different reaction times allowed to assess the kinetics of hydrogen peroxide decomposition. At the end of each test, the vial content was centrifuged and the supernatant was analysed following the procedure described above.

#### Numerical modelling

To assess the potential effectiveness of ISCO at the field scale and to provide design guidance about the pilot-scale system, in this work the numerical FEFLOW software version 5.3 (Finite Element subsurface FLOW) was used. This software allows to simulate 2-D and 3-D fluid flow, mass and heat transport problems in a saturated media, in unsaturated media and also in variable saturation media (WASY, 2008). The simulations were performed in order to evaluate, for different operating conditions, the expected oxidant distribution in groundwater. To this end, the following main settings were used:

- 2-D modelling;
- Triangular discretization (Tmesh method);
- Saturated media (groundwater);
- Transient conditions (flow and transport);
- Automatic time stepping schemes based on backward Euler method;
- No heat transport;
- Dirichlet (1<sup>st</sup> kind, by defining at the borders of the model domain the hydraulic head values measured in the field) and Neumann boundary conditions (2<sup>nd</sup> kind, by defining at the lateral borders of the model domain no inflow/outflow of water).

Namely, in order to estimate for different operating conditions (e.g. injection flow rates) the expected radius of influence (ROI), preliminary simulations were carried assuming a single injection well and using the data available from the site characterization and from the lab-scale tests.

#### Monitoring plan of the pilot-scale test

The results obtained from the lab-scale tests and from the numerical modelling were then used to design the pilot-scale system and to define the layout of the injection system and the operating conditions. In this framework, the monitoring plan, aimed to assess the actual In-Situ applicability and effectiveness of the selected process, was also designed. To this end, before and after the oxidant injection, groundwater samples were collected from the monitoring wells and analysed for MtBE, TBA and TPH. In addition, during the pilot test the actual distribution of the oxidant in the subsurface together with pH, Redox Potential (ORP) and groundwater temperature were also monitored. Finally, in order to better assess the oxidant efficiency and the reaction chemistry, during the whole duration of pilot-test VOC,  $O_2$  and  $CO_2$  were also analysed in the off-gas collecting system.

## **RESULTS AND DISCUSSION**

#### Lab-scale feasibility test

As discussed above, the lab-scale tests were carried out on different soil samples, representative of the layers of the aquifer, using different types and concentrations of amendments (chelating and stabilizing agents). The tests performed using hydrogen peroxide without adding the stabilizer showed for the different soil layer tested a poor stability of hydrogen peroxide, with lifetime, i.e. the time required to achieve a 0.1%  $H_2O_2$  concentration, typically below 5 hours. Fig. 3.2 reports the results corresponding to 6% initial  $H_2O_2$  concentration, together with the best fit curve obtained assuming a pseudo-first order kinetic model (Siegrist et al., 2011).



**Figure 3.2.** Kinetics of  $H_2O_2$  decomposition: (a) tests performed on the different soil layers with  $KH_2PO_4$ :  $H_2O_2 = 1 : 20$  and EDTA = 5 mmol/kg; (b) tests performed on the soil layer 2 with different stabilizer :  $H_2O_2$  molar ratio and EDTA = 5 mmol/kg; (c) tests performed on the soil layer 2 with different EDTA concentrations and  $KH_2PO_4$ :  $H_2O_2 = 1 : 5$ ; (d) tests performed on the soil layer 2 with EDTA and sodium citrate concentration of 5 mmol/kg and  $KH_2PO_4$ :  $H_2O_2 = 1 : 10$ . Lines provide best fitting of experimental data with a pseudo-first order kinetic model (C = C<sub>0</sub> e<sup>-kt</sup>) where "k" represents the kinetic rate constant.

These results show that the addition of the stabilizing agent (KH<sub>2</sub>PO<sub>4</sub>) allows to significantly increase the H<sub>2</sub>O<sub>2</sub> lifetime. Namely, making reference to Fig. 3.2a it can be noticed that for a 1:20 KH<sub>2</sub>PO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> ratio the H<sub>2</sub>O<sub>2</sub> lifetime is shown to increase up to 11 and 16 hours for soil layer 1 and 3, respectively, but only to 8 hours for soil layer 2. Based on the available characterization data, this difference can be attributed to the finer soil texture of layer 2 with respect to the other two layers. Hence, a further optimization step was carried out focusing on the soil layer 2 that was found to be characterized by the worst performance in terms of H<sub>2</sub>O<sub>2</sub> stability. Fig. 3.2b reports the decomposition

kinetics of H<sub>2</sub>O<sub>2</sub> for this soil layer obtained by adding different amounts of KH<sub>2</sub>PO<sub>4</sub>. Making reference to this figure, it can be noticed that the H<sub>2</sub>O<sub>2</sub> lifetime is shown to increase from 8 hours, using a 1:20 stabilizer/ $H_2O_2$  molar ratio, up to more than 24 hours, at a 1:5 ratio, confirming the expected role of KH<sub>2</sub>PO<sub>4</sub> in stabilizing the hydrogen peroxide. Another issue addressed was the effect on the oxidant stability of the chelating agents (EDTA or sodium citrate) that, as described before, will be used in the pilot-scale test to enhance the extraction of iron from soil and avoid the precipitation of the sparingly soluble iron. Fig. 3.2c, where the results corresponding to different amounts of EDTA for a given stabilizer/ $H_2O_2$  molar ratio (1:5) are reported, shows that the addition of the chelating agent does not have any relevant effect on the stability of hydrogen peroxide. This is clearly observed by comparing, for instance, the decomposition kinetics obtained using 5 mmol/kg of EDTA and those performed without adding any EDTA. A similar behaviour was also observed in the tests performed using sodium citrate as chelating agent. Fig. 3.2d reports, for instance, the H<sub>2</sub>O<sub>2</sub> decomposition kinetics obtained using a 1:10 stabilizer/H2O2 molar ratio and a 5 mmol/kg concentration of EDTA or sodium citrate, showing that the decomposition kinetics are actually the same for the two chelating agent used confirming what already observed in Fig. 3.2c for a different stabilizer/H<sub>2</sub>O<sub>2</sub> molar ratio.

Based on these results, the operating conditions selected for the pilot-scale application were as follows: 6%  $H_2O_2$  concentration and 1:5  $KH_2PO_4$  /  $H_2O_2$  molar ratio. As the batch tests showed similar performance for the two chelating agents considered, the choice of the chelating agent to be used in the pilot test was left to the site manager, who later opted for EDTA.

#### **Preliminary numerical simulations**

As discussed above, numerical simulations with the commercial software FEFLOW were performed in order to assess the propagation of the oxidant in the subsurface and to evaluate its ROI (radius of influence, defined in this specific case as the distance at which  $H_2O_2$  concentration drops to 1%). These preliminary simulations have been performed on an area, corresponding to the site portion selected to perform the pilot-scale In–Situ test, shown in Fig. 3.1, assuming to inject the oxidant through a single well. The input parameters and conditions, summarized in Table 3.1, were taken from

the results of the lab-scale experimental tests and field-scale tests performed to obtain an hydrogeological characterization of the site.

Parameter	Units	Value	
Injection flow rate	m³/day	2 - 10	
Hydrogen peroxide concentration	%wt	6	
Aquifer trasmissivity	m²/s	$5  imes 10^{-4}$	
Aquifer thickness	m	2 - 4	
Hydraulic gradient (with P&T in operation)	%	3	
Porosity	-	0.353	
$H_2O_2$ decomposition rate constant (1 <sup>st</sup> order)	) h <sup>-1</sup>	0.11	
H <sub>2</sub> O <sub>2</sub> injection time	h	15	

Table 3.1. Input parameters and conditions used in FEFLOW simulations.

The injection duration of 15 hours was selected after some preliminary simulations aimed to estimate the time required, after the beginning of oxidant's injection, to achieve steady-state conditions corresponding to the maximum ROI. It is worth pointing out that, as the tests performed on the site revealed a relevant anisotropy with important variations of the local values of hydraulic conductivity, different simulations have been performed using an average value of the hydraulic conductivity and assuming, either that all the aquifer thickness (4 m) is available for the oxidant flow or that the oxidant migrates only in the more permeable layers (2 m). The results obtained from these preliminary simulations (reported in Table 3.2) showed that, depending on the adopted injection flow rate, the expected ROI is in the range between 1.2 and 5.5 m. These values are generally slightly lower than the average ROI measured in ISCO applications, that according to Krembs et al. (2010) is equal to 4.8 m (15 feet). Table 3.2 also reports the maximum increase of the hydraulic head ( $\Delta h$ ) expected during the treatment in correspondence of the injection wells, that looks acceptable even operating at the higher flow rates tested. This value was estimated neglecting the effect possibly induced by the gas production occurring from hydrogen peroxide disproportionation.

Conditions simulated with FEFLOW	ROI (m)	O <sub>2max</sub> (m <sup>3</sup> /h)	Δh (m)
$Q=10\ m^3/day$ for 15 h (k = 0.11 h^-1; thickness 4 m)	2.5 - 4	9	0.6
$Q = 2 \text{ m}^3/\text{day}$ for 15 h (k = 0.11 h <sup>-1</sup> ; thickness 4 m)	1.2 – 2.5	1.8	0.15
$Q=10\ m^3/day$ for 15 h (k = 0.11 h^-1; thickness 2 m)	3.3 - 5.5	9	0.6
$Q = 2 \text{ m}^3$ /day for 15 h (k = 0.11 h <sup>-1</sup> ; thickness 2 m)	1.5 - 3.5	1.8	0.15

**Table 3.2.** Results of the FEFLOW modelling for  $H_2O_2$  injection. The maximum oxygen flux ( $O_{2max}$ ) was estimated assuming the stoichiometric disproportionation of hydrogen peroxide ( $H_2O_2 \rightarrow H_2O + 0.5 O_2$ ).

The values of the maximum oxygen flux ( $O_{2max}$ ), estimated assuming the stoichiometric disproportionation of H<sub>2</sub>O<sub>2</sub>, also reported in Table 3.2, suggest that such a relevant gas production could further increase the water head.

#### Configuration of the pilot test and injection scheme

Based on the results obtained from the simulations of the single well injection, and taking in account the number and size of the injection pumps already available from another test site, the configuration reported in Fig. 3.3 was assumed for the pilot-scale test.



**Figure 3.3.** Layout of the pilot test. The red circles represent the injection wells whereas the blue ones the wells used for the monitoring of the oxidant and contaminant concentration. In the same figure an indication of the main groundwater (GW) direction is also reported.

This configuration consists of three injection wells positioned at a 3 meter distance one from each other, plus a number of monitoring wells. Injection and monitoring wells extend to a depth of about 10 meters below ground, with the screened section located between 5.5 and 9.5 meters below ground. The designed configuration has been then tested using the software FEFLOW. The conditions used for the simulations are once again those reported in Table 3.1, with injection flow rate equal to 2 or 10 m<sup>3</sup>/day per well and assuming once again either a 4 m or 2 m aquifer thickness available for oxidant migration. Fig. 3.4 shows the maximum hydrogen peroxide plume estimated after 15 hours of injection: namely Fig. 3.4a and 3.4b correspond to the simulations performed assuming an injection flow rate of 10 m<sup>3</sup>/day per well. In both cases reported in Fig. 3.4, the H<sub>2</sub>O<sub>2</sub> ROI of each injection well is sufficiently high to allow for an effective overlapping of the three H<sub>2</sub>O<sub>2</sub> plumes; clearly, the propagation of the oxidant is increased at higher injection flow rates (Fig. 3.4a and Fig. 3.4c and Fig. 3.4c).



**Figure 3.4.** Hydrogen peroxide distribution after 15 hours injection simulated with FEFLOW: (a)  $Q = 10 \text{ m}^3/\text{day}$ , groundwater thickness = 4 m; (b)  $Q = 2 \text{ m}^3/\text{day}$ , groundwater thickness = 4 m; (c)  $Q = 10 \text{ m}^3/\text{day}$ , groundwater thickness = 2 m; (d)  $Q = 2 \text{ m}^3/\text{day}$ , groundwater thickness = 2 m.

#### Pilot test set-up and operation

The pilot-scale test was performed in the area shown in Fig. 3.1. The pilot-scale configuration adopted is the one reported in Fig. 3.3, with three injection wells located at the corner of a triangle and twelve monitoring wells. All wells were 4" HDPE wells, except for three already existing wells, which were made of PVC and were used for monitoring purpose only. In analogy to the simulation conditions, all wells extended 9.5 meters below ground with a screened section between 5.5 and 9.5 meters. Based on preliminary tests performed in the site, the maximum feasible injection flow rate was 2-3 m<sup>3</sup>/day per well. New soil and groundwater samples were also collected after borehole execution: iron concentration in the soil was between 17 and 35 g/kg, whereas the MtBE concentration in groundwater was between 2000 and 5000  $\mu$ g/L, excluding two

outliers characterized by lower and higher values. These values, that confirmed what already obtained during the site characterization, are well above the clean-up goal for the target area that, based on site-specific risk assessment, was equal to 98  $\mu$ g/L. The pilot-scale tests consisted of two-steps: first, a 20% wt. EDTA solution (chelating agent) was injected at 3 m<sup>3</sup>/day for 10 hours; then, the following oxidant formulation, corresponding to the one selected after the lab-scale feasibility test, was injected at 2 m<sup>3</sup>/day per well for 16 hours: 5.8 wt% H<sub>2</sub>O<sub>2</sub>, 5.8 wt% KH<sub>2</sub>PO<sub>4</sub>. Finally, it is worth mentioning that all wells were connected to a vapour extraction unit and fed to a vapour treatment unit before discharge to the atmosphere, thus allowing to avoid gas accumulation in the wells and in the subsurface.

#### **Pilot test results**

The pilot-scale results, reported in Fig. 3.5, show the hydrogen peroxide contour lines after 6 hours (Fig. 3.5a) and 11 hours (Fig. 3.5b) of  $H_2O_2$  injection, respectively.



**Figure 3.5.** Results of the pilot-scale test: (a)  $H_2O_2$  (% wt) contour lines after 6h injection; (b)  $H_2O_2$  (% wt) contour lines after 11h injection; (c) Redox potential (mV) contour lines after 6h injection; (d) Redox potential (mV) contour lines after 11h injection; (e) pH contour lines after 6h injection; (f) pH contour lines after 11h injection. Blank areas indicate a zero value. Axis scale in m.

The  $H_2O_2$  propagation is still very limited at shorter injection times (Fig. 3.5a), with a ROI of each injection well between 0.5 and 1.0 meters and no overlapping of the  $H_2O_2$  plumes produced by the three injection wells OC4, OC13 and OC9. After 11 hours injection, the  $H_2O_2$  plumes overlapped, allowing to achieve a quite good and homogeneous distribution of the oxidant, with an area of influence of about 6 m

diameter, particularly extended along the groundwater flow direction eastward. It is worth pointing out that H<sub>2</sub>O<sub>2</sub> concentration remained rather low around the monitoring well OC2, located between the injection wells OC4 and OC10, as also expected by the modelling results reported in Fig. 3.4. Nevertheless, it is worth pointing out that the size of the area of influence after 11 hours (Fig. 3.5b) was much larger than the one predicted by the model at the same injection flow rate (i.e.  $2 \text{ m}^3/\text{day}$ ) assuming that all the aquifer thickness is available for the oxidant flow (Fig. 3.4b). On the other hand, the field H<sub>2</sub>O<sub>2</sub> propagation was similar to the one predicted by the model, assuming that the oxidant migrates only in the more permeable layers (Fig. 3.4d). Based on these results, it looks possible that only the more permeable layers of the aquifer were actually interested by H<sub>2</sub>O<sub>2</sub> flow. Unfortunately, vertical profiles of hydrogen peroxide or MtBE distribution, that could eventually confirm such hypothesis, were not collected neither before or during the field-scale test. The area of influence of the hydrogen peroxide has been also confirmed by measurements of redox potential (Fig. 3.5c and 3.5d) and pH (Fig. 3.5e and 3.5f). Namely, in wells where hydrogen peroxide was measured to be greater than 1 %, ORP values were observed to increase up to +170 mV (see Fig. 3.5d and Fig. 3.6-3.13).

Well: OC14	Trend							t (h	)					
Well. OC 14	rrenu	2	4	6	8	10	12	14	16	18	22	26	30	34
REDOX (mV)		26	60.7	19.5	44.2	88.3	108.1	93.2	72.8	69.9	41.2	40.6	34.2	22.2
рН		6.2	5.5	6.3	5.9	5.1	4.8	5.1	5.4	5.4	6.0	5.8	6.0	6.4
Т (°С)		22.4	21.3	20.0	23.3	22.9	24.4	26.6	25.2	23.6	21.9	20.3	19.8	23.6
EC (mS)		3.5	2.6	22.3	33.1	21.0	11.8	9.2	6.6	6.1	4.2	4.4	4.0	4.4
O <sub>2</sub> (%)		20.8	21.8	20.9	20.9	29.4	29.4	28.4	20	23.4	21.9	21.9	20.9	ND
CO <sub>2</sub> (%)		0.35	0.5	0.4	0.8	0.82	0.9	0.92	0.91	0.24	0.5	2.1	3.5	ND
VOC (ppm)		ND	8.5	1	9	6.4	8.9	8.7	4.6	4.8	3.8	ND	ND	ND

Figure 3.6. Parameters monitored in Well OC14 during the pilot-scale test.

Well: OC2	Trop	d							t (h	)					
Well. 002	iren	iu	2	4	6	8	10	12	14	16	18	22	26	30	34
REDOX (mV)	$\sim$		76.2	42.6	47.4	61.3	77.7	75	55.1	64.1	66.2	50.7	50.6	39.4	13.2
рН	$\sim$	1	5.8	5.9	5.9	5.6	5.3	5.3	5.7	5.6	5.5	5.8	5.8	6.0	6.5
т (°С)	$\sim \sim$		21.9	23.8	24.3	23.1	21.0	22.0	23.6	30.3	22.8	22.8	20.4	20.2	23.0
EC (mS)	$\sim$		2.4	4.7	6.5	14.0	10.4	4.9	2.8	13.4	1.9	5.7	4.1	2.5	1.7
O <sub>2</sub> (%)			20.9	20.9	20.9	20.9	22.4	19.8	20	20.1	20.1	20.1	20.1	20.9	ND
CO <sub>2</sub> (%)			0.13	0.25	0.16	0.16	0.18	0.25	0.32	0.35	0.4	2	2.9	4.5	ND
VOC (ppm)	$\mathcal{M}$		2.2	10.1	17.6	8.5	6.5	9.2	9.8	4.5	3.6	5.2	ND	ND	ND

Figure 3.7. Parameters monitored in Well OC2 during the pilot-scale test.

	Tre	and							t (h	)					
Well. 000		-nu	2	4	6	8	10	12	14	16	18	22	26	30	34
REDOX (mV)	$\mathcal{M}$		41.4	39.9	43.6	66.9	101.1	97.4	71.3	66.9	74.2	45.2	43.3	48.1	35.3
pН	$\sim$	الد با	5.9	6.0	6.0	5.5	4.8	4.9	5.4	5.5	5.4	5.9	5.8	5.8	6.1
T (°C)	$\sim \sim$		23.1	23.7	24.4	22.7	21.8	22.2	24.4	28.9	23.3	21.6	20.7	19.7	23.5
EC (mS)	$\nearrow$		1.5	4.3	8.6	10.5	15.0	12.4	10.5	19.0	8.7	3.2	6.6	5.4	6.7
O <sub>2</sub> (%)			20.9	20.9	20.9	22.2	22.3	20	20.1	20.1	20.1	20.1	20.1	20.9	ND
CO <sub>2</sub> (%)			0.13	0.25	0.16	0.16	0.18	0.25	0.4	0.35	0.4	2.4	2.95	3.3	ND
VOC (ppm)	$\square$		0.1	0.6	9.9	8.6	9.1	9.8	10	7.5	6.5	5.2	ND	ND	ND

Figure 3.8. Parameters monitored in Well OC8 during the pilot-scale test.

Well: OC10	Trend		_	_			_	t (h	)	_				_
Well. OCTO	rrenu	2	4	6	8	10	12	14	16	18	22	26	30	34
REDOX (mV)		52.8	25.7	34.5	73.4	127	95.4	81.5	72.5	79.6	54.2	55.1	54.1	40.7
рН		5.7	6.2	6.1	5.4	4.4	5.0	5.3	5.4	5.3	5.7	5.7	5.7	6.0
т (°С)		23.0	20.5	20.6	22.0	22.1	23.5	27.3	24.5	25.8	22.0	20.6	20.1	29.1
EC (mS)		2.6	1.5	18.3	11.5	28.8	11.7	10.8	7.6	8.5	6.5	5.5	6.3	5.5
O <sub>2</sub> (%)		21.6	21.6	22.4	27.7	29.7	27.1	20.2	20.9	20.9	21.9	20.9	20.9	ND
CO <sub>2</sub> (%)		0.65	0.6	0.55	0.8	0.85	0.85	0.86	0.9	0.9	1.6	3.15	3.25	ND
VOC (ppm)		0.5	8.2	10.1	11. <b>2</b>	9.2	9.3	10.1	4.4	4.5	5.8	ND	ND	ND

Figure 3.9. Parameters monitored in Well OC10 during the pilot-scale test.

Well: OC11	Tre							t (h	)						
Well. OCTI			2	4	6	8	10	12	14	16	18	22	26	30	34
REDOX (mV)	$\searrow$	. here	51.2	25.5	35.3	65.7	120.7	94.6	81.6	63.9	74.1	53.7	58.6	55.5	33.1
рН	$\sim$	li ani	5.8	6.2	6.0	5.5	4.5	5.0	5.2	5.6	5.3	5.7	5.6	5.7	6.1
T (°C)	$ \$		21.6	21.3	20.7	22.1	21.6	23.6	25.2	24.9	23.6	21.3	20.5	20.0	27.7
EC (mS)	$\mathcal{M}$	L	2.2	1.6	18.8	7.7	22.6	11.0	10.1	6.9	5.1	5.0	5.8	6.0	4.2
O <sub>2</sub> (%)	$\sim$		20.4	21.6	22.5	29.9	29.9	28.1	20.1	21.6	21.6	20.9	20.9	20.9	ND
CO <sub>2</sub> (%)			0.75	0.7	0.65	0.9	0.95	0.95	0.96	0.84	0.65	1.7	2.6	3.25	ND
VOC (ppm)			8.3	9	9.5	10.2	9.3	9.4	5.6	4.8	5.2	5.3	ND	ND	ND

Figure 3.10. Parameters monitored in Well OC11 during the pilot-scale test.

#### Pilot-scale feasibility study of ISCO application

Well: OC5	Tre	and							t (h	)					
Well. 005		ena	2	4	6	8	10	12	14	16	18	22	26	30	34
REDOX (mV)	$\sim$		27	50.5	19.5	59.3	68.2	92.5	60.9	58.5	60.5	42.7	49.7	39.8	-5
pН	$\sim$	ور مار	6.2	5.8	6.4	5.7	5.5	5.0	5.6	5.6	5.6	5.9	5.8	6.0	6.8
т (°С)	$\sim$	╺┛┙╹╻	22.2	22.1	23.0	26.3	22.1	22.4	27.9	24.3	21.2	26.4	21.1	20.1	21.8
EC (mS)	$\Lambda$		2.8	3.9	47.4	8.8	8.6	11.9	<mark>6.1</mark>	3.9	2.7	11.8	8.1	4.1	2.1
O <sub>2</sub> (%)			20.9	20.9	20.9	20.9	20.9	22	20.9	28.1	22	22.1	22.1	22.3	ND
CO <sub>2</sub> (%)	$\square$		0.12	0.14	0.12	0.12	0.12	0.12	0.14	0.12	0.08	0.16	2.2	3.25	ND
VOC (ppm)	$\square$		ND	ND	0.2	0.5	6.4	7.2	10.8	4	5.4	4.1	ND	ND	ND

Figure 3.11. Parameters monitored in Well OC5 during the pilot-scale test.

Well: OC3	Vell: OC3 Trend		_		_		_	t (h	)			_		
Well. 000	rrenu	2	4	6	8	10	12	14	16	18	22	26	30	34
REDOX (mV)		20.3	68	3.9	88.4	90	165.9	63.3	61.5	62.1	41.4	40.7	25.8	12.5
рН		6.6	5.6	6.7	5.0	5.0	4.2	5.6	5.6	5.5	5.1	6.0	6.2	6.5
Т (°С)		23.4	25.1	21.9	23.3	20.8	24.3	28.3	25.5	24.9	23.3	20.9	19.7	25.7
EC (mS)		2.2	14.4	67.2	30.4	26.5	41.8	15.4	22.4	19.0	17.7	3.4	6.8	12.4
O <sub>2</sub> (%)		20.9	20.9	21.6	21.6	21.6	22.3	20.9	20.9	20.9	20.9	20.9	20.9	ND
CO <sub>2</sub> (%)		0.05	0.03	0.09	0.05	0.05	0.26	0.22	0.23	0.08	2.1	2.9	3.15	ND
VOC (ppm)		0.1	7.3	10.8	9.1	5.2	8.6	9	6.5	4.2	3.5	ND	ND	ND

Figure 3.12. Parameters monitored in Well OC3 during the pilot-scale test.

Well: OC6	Tre	and							t (h	)					
Wen. 000			2	4	6	8	10	12	14	16	18	22	26	30	34
REDOX (mV)	L~~		89.8	45.5	47.5	65	63.1	92.9	74.2	66.7	75.7	51.8	53.8	39.9	34
рН	r~	le al	5.1	5.9	5.8	5.5	5.6	5.1	5.4	5.5	5.3	5.8	5.7	5.9	6.2
T (°C)	$\sim \sim$		20.1	25.0	24.0	22.5	22.1	21.9	26.1	28.4	23.7	24.3	21.4	19.5	25.2
EC (mS)	$\Lambda_{\sim}$		5.6	7.3	80.3	16.8	9.8	7.5	9.9	19.1	7.6	11.2	6.8	5.3	5.2
O <sub>2</sub> (%)	<u> </u>		20.6	20.6	21.6	29.4	29.9	28.1	21.6	21.6	21.6	21.6	20.9	20.9	ND
CO <sub>2</sub> (%)	$\square$		0.03	0.15	0.06	0.06	0.08	0.15	0.22	0.25	0.3	1.9	2.8	5	ND
VOC (ppm)	$\sum$		ND	0.1	11.4	9.5	8.9	9.9	6.9	6.4	5.6	4.5	ND	ND	ND

Figure 3.13. Parameters monitored in Well OC6 during the pilot-scale test.

On the other hand, the pH was found to decrease as a result of the injection (down to pH = 4), because the solution of hydrogen peroxide is acidic due to additives and stabilizers used in the synthesis phase of the reagent. Fig. 3.14a reports the MtBE concentration of the samples collected at the wells used in the monitoring phase after the chelating agent injection and at the end of the  $H_2O_2$  injection; these data were used to build the corresponding MtBE contour lines, reported in Fig. 3.15a and 3.15b, respectively.



**Figure 3.14.** Results of the pilot-scale test: (a) MtBE concentrations ( $\mu$ g/L) after chelating agent injection and after H<sub>2</sub>O<sub>2</sub> injection; (b) TBA concentrations ( $\mu$ g/L) after chelating agent injection and after H<sub>2</sub>O<sub>2</sub> injection; (c) TPH concentrations ( $\mu$ g/L) after chelating agent injection and after H<sub>2</sub>O<sub>2</sub> injection. For illustration purposes only, the concentrations lower than the detection limit (DL) were substituted with the DL limit (DL=0.2  $\mu$ g/L for MtBE, DL = 2  $\mu$ g/L for TBA, DL = 25  $\mu$ g/L for TPH).



**Figure 3.15.** Results of the pilot-scale test: (a) MtBE ( $\mu$ g/L) contour lines after chelating agent injection; (b) MtBE ( $\mu$ g/L) contour lines after H<sub>2</sub>O<sub>2</sub> injection; (c) TBA ( $\mu$ g/L) contour lines after chelating agent injection; (d) TBA ( $\mu$ g/L) contour lines after H<sub>2</sub>O<sub>2</sub> injection; (e) TPH ( $\mu$ g/L) contour lines after chelating agent injection; (f) TPH ( $\mu$ g/L) contour lines after H<sub>2</sub>O<sub>2</sub> injection. Blank areas indicate a zero value. Axis scale in m.

The injection of the solution containing the chelating agents caused already a slight reduction of MtBE concentration (average initial value 4000  $\mu$ g/L), in particular around the injection wells OC4, OC9 and OC13, due to dilution (Fig. 3.14a and 3.15a). After H<sub>2</sub>O<sub>2</sub> injection, MtBE was almost completely removed from the area of intervention
with reduction of MtBE concentrations up to 99% (Fig. 3.14a and Fig. 3.15b). Among the 13 monitoring wells samples, eight were below the clean-up target of 98  $\mu$ g/L and other two below 200 µg/L. The higher residual MtBE concentration was detected in wells OC2 and OC5; comparing this result with the H<sub>2</sub>O<sub>2</sub> contour lines reported in Fig. 3.5b, it can be observed that these wells were also poorly influenced by  $H_2O_2$ . Thus, it can be concluded that the effectiveness of ISCO was controlled by the oxidant delivery and not by the kinetics of degradation. The oxidation of MtBE was also confirmed by the relevant increase of CO<sub>2</sub> concentration in the off-gas collected at the monitoring wells during the ISCO treatment (see Fig. 3.6–3.13). Nevertheless, it is well known that the MtBE oxidation pathway may lead to the formation of by-products and reaction intermediates, such as TBA, TBF, methyl acetate and acetone (Burbano et al., 2008). For this reason, one of these alcohols (TBA) was also included in the monitoring plan. It is worth noting that TBA was selected as indicator of potential by-products formation since some studies (e.g. see Siedlecka, et al., 2007) have shown that this alcohol is typically the major by-product detected during MtBE oxidation. Fig. 3.14b reports the TBA concentration measured at the monitoring wells after the chelating agent injection and at the end of the  $H_2O_2$  injection, that were used also in this case to build the corresponding iso-concentration curves, reported in Fig. 3.15c and 3.15d, respectively. As reported in Fig. 3.14b and Fig. 3.15c, TBA was detected already after the injection of the chelating agent, thus showing that this compound was already present in the groundwater of the site before injecting the oxidant. Looking at Fig. 3.14b and comparing the iso-concentration curves reported in Fig. 3.15c and 3.15d, it is clear that the ISCO treatment allowed to reduce substantially also the TBA concentration in most of the monitoring wells, thus allowing to exclude its accumulation as by-product of ISCO. The higher residual TBA concentration was also in this case detected in wells OC2 and OC5, as in the case of MtBE and can be explained once again with the poor influence of hydrogen peroxide in these wells. Although the treatment was mainly aimed to test the ISCO effectiveness towards MtBE and fuel oxygenates, as the site was also characterized by hydrocarbons contamination, this class of contaminants was also included in the monitoring plan. The results obtained are in this case reported for each well after the injection of the chelating agent and of the oxidant in Fig. 3.14c, whereas the iso-concentration curves built with these data are shown in Fig. 3.15e and 3.15f,

respectively. The ISCO treatment was effective also with respect to Total Petroleum Hydrocarbons (TPH), with high removal efficiencies especially in those wells more influenced by  $H_2O_2$  propagation. Also in this case, the higher residual TPH concentration was detected in wells OC2 and OC5.

### **Mass Balance**

In order to better assess the effectiveness of the process, a mass balance for the different contaminants involved in the treatment, was carried out. To this end, the amount of carbon dioxide produced during the treatment was calculated, based on the measurements performed in the off-gas collection system. This was done starting from the flow rate of each off-gas extraction well (approximately  $1.5 \text{ m}^3/\text{h}$ ) and the corresponding CO<sub>2</sub> concentration measured at different time intervals (see Fig. 3.6-3.13). The estimated amount of CO<sub>2</sub> produced resulted equal to approximately 78 moles within the whole duration of the test. Next, based on the measured groundwater concentrations of MtBE, TBA and TPH before and after ISCO (Fig. 3.14 and Fig. 3.15), and on the volume of the aquifer involved in the treatment (Fig. 3.16), the mass of the contaminants disappeared was calculated (see Table 3.3). In Table 3.4 the data used for the estimation of the volume of the aquifer involved in the treatment are reported.



**Figure 3.16.** Data used for the estimation of the volume of the aquifer involved in the treatment. (a) MtBE after chelating agent injection; (b) MtBE after  $H_2O_2$  injection; (c) TBA after chelating agent injection; (d) TBA after  $H_2O_2$  injection; (e) after chelating agent injection; (f) TPH after  $H_2O_2$  injection.

Table 3.	<b>3.</b> C	Compariso	on of	$CO_2 r$	neasured	in the	e off-gas	line s	ystem a	and (	$CO_2$	measu	red by	apply	ing a
mass bal	ance	of the di	fferen	t cont	aminants	after	and befo	ore the	treatme	ent. V	W= v	vater; `	W+S=	water+	soil.
With the	bold	values an	e indi	cated	the sum	of MtE	BE, TBA	and T	PH.						

Compound	Initial Mass(g)		Mass after ISCO(g)		Mass removed(g)		Calculated CO <sub>2</sub> (mol)		Measured CO <sub>2</sub> (mol)
	W	W+S	W	W+S	W	W+S	W	W+S	
MtBE	169	171	26.1	26.4	143	145	8.1	8.2	78
ТВА	184	185	41.2	41.3	143	143	7.7	7.7	
ТРН	108	1499	24.7	343.9	83	1155	5.8	79.8	
Total	461	1855	92	412	369	1443	22	96	

 Table 3.4. Chemical parameters of the contaminants of concern.

Chemical of Concern	MW (g/mole)	Solubility (mg/L)	Koc (L/kg)
MTBE	88.1	4.80E+04	1.2E+01
TBA	74.1	2.35E+05	4.2E+00
>6-8 C aliphatics (TPH)	100	5.40E+00	4.0E+03
>8-10 C aliphatics (TPH)	130	4.30E-01	3.2E+04
>10-12 C aliphatics (TPH)	160	3.40E-02	2.5E+05
>12-16 C aliphatics (TPH)	200	7.60E-04	5.0E+06
>16-21 C aliphatics (TPH)	270	2.50E-06	6.3E+08
>7-8 C aromatics (TPH)	92	5.30E+02	1.4E+02
>8-10 C aromatics (TPH)	120	6.50E+01	1.6E+03
>10-12 C aromatics (TPH)	130	2.50E+01	2.5E+03
>12-16 C aromatics (TPH)	150	5.80E+00	5.0E+03
>16-21 C aromatics (TPH)	190	6.50E-01	1.6E+04

From the mass of the contaminants disappeared, it was then possible to predict the stoichiometric amount of  $CO_2$  produced, assuming complete mineralization of the contaminants, i.e. that their removal was due to oxidation, rather than to other effects (e.g. dilution, volatilization):

$$CO_2 = \gamma_i \cdot \frac{M_{in,i} - M_{out,i}}{MW_i} \tag{3.1}$$

where  $M_{in,i}$  and  $M_{out,i}$  are the mass of each contaminant before and after the treatment, MW<sub>i</sub> the molecular weight of the i-th compound and  $\gamma_i$  is the CO<sub>2</sub> stoichiometric molar ratio which can be calculated based upon the following oxidation reactions: MtBE

$$C_5 H_{12} O + \frac{15}{2} O_2 \to 5 C O_2 + 6 H_2 O$$
 (3.2)

$$C_4 H_{10} 0 + 6 O_2 \to 4 C O_2 + 5 H_2 0$$
 (3.3)

TPH

TBA

$$C_n H_m + \left(n + \frac{m}{4}\right) O_2 \rightarrow n C O_2 + \frac{m}{2} H_2 O \tag{3.4}$$

The results obtained applying Eq. (3.1) are reported in Table 3.3. Making reference to this table, it can be noticed that the measured carbon dioxide is much higher than the one calculated assuming stoichiometric conversion to CO<sub>2</sub> of the contaminants removed from groundwater (i.e. 22 vs. 78 mols). This difference may suggest that a relevant part of the measured CO<sub>2</sub> was produced from the oxidation and mineralization of a fraction of the mass of contaminant sorbed to the organic carbon of the soil. To test this assumption, the mass of the contaminants disappeared from the saturated soil was estimated based on the volume of the aquifer involved in the treatment and on the concentrations of MtBE, TBA and TPH in the soil before and after ISCO. The latter ones (C<sub>s</sub>) were calculated from the dissolved phase concentration (C<sub>w</sub>) measured before and after ISCO treatment, assuming linear equilibrium partitioning between the sorbed and the dissolved phase:

$$C_s = C_w \cdot K_{oc} \cdot f_{oc} \tag{3.5}$$

where  $k_{oc}$  (L/kg) is the organic carbon-water sorption coefficient (see Table 3.4) and  $f_{oc}$  (g/g) the fraction of organic carbon in soil (equal to 0.001 g/g in the area of concern). For petroleum hydrocarbons, the speciation available from the site characterization (Aliphatics C5-C8 = 84.5%, Aromatics C9-C10 = 6.2%, Aliphatics C9-C18 = 7.6%, Aliphatics C19-C36 = 0% and Aromatics C11-C22 = 1.7%) was also used.

Next, by applying once again Eq. (3.1), the expected carbon dioxide produced assuming complete oxidation of the total mass of the contaminants (now in both soil and water) present in the treated area was calculated. The results, again reported in Table 3.3, clearly show that in this case the expected produced  $CO_2$  is in line with the value measured in the off-gas line system (96 vs. 78 mols). The observed difference between

calculated and measured CO<sub>2</sub> could be due to the fact that the calculated CO<sub>2</sub> was estimated assuming equilibrium partitioning of the contaminants between the liquid and the solid phase. This assumption is probably not completely satisfied, so that the residual mass of contaminants in the soil phase could be higher than the estimated one, reported in Table 3.3. Besides, it is worth pointing out that for this assessment the contribution to the overall carbon dioxide production due to the mineralization of the soil organic carbon was considered negligible. This assumption does not imply that the soil oxidant demand (SOD) is negligible but, on the contrary, that this unproductive consumption is mainly due to reactions of the oxidant with naturally occurring Mn(II), Fe(II) and S(-I,-II) rather than to the ones that can occur with the soil organic matter.

In the same way, based on the volatile organic compounds (VOC) concentrations measured in the off-gas collection system, the amount of mass lost by stripping during the ISCO treatment was calculated. Namely, knowing the flow rate of each off-gas extraction well and the concentration measured at the different time intervals (see Fig. 3.6-3.13), the overall amount of VOC produced was calculated. In this case, the total amount of vapours measured in the off-gas collection system was equal to approximately 0.1 moles. This suggests that the losses due to volatilization were quite limited and within approximately 1% of the mass removed after the treatment.

In conclusion, given the different uncertainties (e.g. vertical contaminants distribution, amount of contaminants sorbed to the organic carbon of the soil, further by-products formation a part from TBA) these results of course do not constitute a conclusive proof of the removal rate due to oxidation but provide, however, a quite robust line of evidence that a large amount of the contaminants mass present in the treated area has been oxidized by ISCO up to complete mineralization. These results are also in line with the more recent ones obtained by our group, where the efficiency of Fenton-like processes to oxidize MtBE was assessed through dynamic column tests (Piscitelli et al., Submitted to the Journal of Hazardous Materials).

## Environmental compatibility and side-effects of the ISCO treatment carried out

In this section, some typical side-effects of an ISCO treatment based on a Fenton-like process are briefly discussed for the pilot test carried out.

### Fe and Mn mobilization

The use of EDTA leads to a temporary increase of the concentration of some metals in groundwater, that may exceed the maximum concentration level allowed in groundwater bodies. This effect is clearly shown in Figure 3.17 that reports the concentrations of Fe and Mn measured in the different monitoring wells after the chelating agent injection during the pilot-scale test. The Fe and Mn concentrations were observed to increase from the values measured before the EDTA injection (around 2.3 mg/L and 7.2 mg/L, respectively) up to concentrations of 100 mg/L. Nevertheless, these concentrations decreased considerably at the end of the oxidant injection, dropping down in almost all the monitoring wells to the values detected before the treatment. This suggests that this side-effect for the specific case is limited in time and does not represent a potential long-term environmental concern.



**Figure 3.17.** Results of the pilot-scale test: (a) Fe concentrations (mg/L) after chelating agent injection and after  $H_2O_2$  injection; (b) Mn concentrations (mg/L) after chelating agent injection and after  $H_2O_2$  injection.

#### Gas production

Another possible side-effect related to Fenton applications is that a fraction of hydrogen peroxide can undergo disproportionation reactions, leading to a potential significant

oxygen production (Watts et al., 1999). In addition, the oxidation reaction may enhance the desorption of volatile organic compounds present in solution creating a potentially explosive atmosphere (Baciocchi et al., 2014). For these reasons, as described above, all wells were connected to a vapour extraction unit and fed to a vapour treatment unit. In addition, oxygen, carbon dioxide and VOC concentration in each off-gas extraction well were monitored during the whole duration of the pilot-scale test. The results, showed that the oxygen production in this specific case was quite limited with an increase of concentrations up to a maximum value of 30%. Finally, as already highlighted before, the VOC production was not very significant and almost limited to the first hours of treatment.

## Thermal and pH effects

Exothermic disproportionation of hydrogen peroxide reaction can also lead to a temperature increase during the treatment (Siegrist et al., 2011). In this specific case, during the treatment an increase of  $+10^{\circ}$ C was observed in some wells, even though at the end of the treatment the temperature returned in nearly all cases to the values observed before the oxidant injection (typically 20-22°C). As far as the pH is concerned, a similar trend to the one described for temperature was observed. Namely, as already discussed above, the pH was found to decrease down to pH = 4 as a result of the oxidant injection but at the end of the treatment in nearly all monitoring wells a rapid rebound to the background values between 6 and 7 was observed.

### Implications for the full-scale application and cost estimation

The obtained results suggest that the ISCO treatment based on a Fenton-like system may be, from a technical viewpoint, a suitable option for the remediation of the contaminated groundwater for this specific site. Table 3.5 reports a summary of the results obtained from the pilot-scale test, which could be used for the design of the full-scale treatment.

Namely, in this table the main design parameters, such as the radius of influence (ROI), the number of pore volumes delivered, the oxidant and chelating agent dose are reported. It is interesting to note that these values are quite in line with the median values reported by Krembs et al. (2010) for catalysed hydrogen peroxide (CHP) applications.

Parameter	Units	Value
Number of injection wells	-	3
Flow rate for each injection well	m <sup>3</sup> /day	2
Duration of injection	h	16
Radius of Influence (ROI) observed <sup>a</sup>	m	2 - 5
Area treated	m <sup>2</sup>	85
Number of pore volumes delivered <sup>b</sup>	-	0.07
Fenton's reagent dose	$g_{\rm ox}/kg_{\rm soil}$	2.3
EDTA dose	$g_{\rm EDTA}/kg_{\rm soil}$	7.5

 Table 3.5.
 Summary of the design parameters of the pilot-scale test carried out.

<sup>a</sup> Defined in this specific case as the distance at which  $H_2O_2$  concentration drops to 1%.

<sup>b</sup> Assuming that the oxidant has migrated only in the more permeable layer (i.e. thickness of 2 m).

In particular, Krembs et al. (2010) report a ROI of 4.8 m (15 feet), an oxidant dose of  $1.2 \text{ g}_{ox}/\text{kg}_{soil}$  and a number of pore volumes delivered equal to 0.073. Finally, in Table 3.6 the overall costs estimated for the pilot-scale tests resulting from the costs of reagents, construction of the wells, monitoring and sampling and the personnel costs are reported.

**Table 3.6.** Estimation of the total and unit costs of the pilot-scale test carried out. R= Reagents, C = Construction of the injections system, M = monitoring, O&M = Operation and Maintenance. With the bold values are indicated the total costs considering the reagents and the constructions of the monitoring wells only (R + C) or including also the costs of Monitoring and Operation and Maintenance (R + C + M + O&M).

Activity/reagent		Unit cost	Amount	Costs (€)
$H_2O_2$ (solution at 16%)	R	0.5 €/L	1450 L	725 7500
KH <sub>2</sub> PO <sub>4</sub> (solution at 20%)	R R	4 €/L 1.6 €/kg	1875 L 1160 kg	1856
Plant installation & commissio	ning C	20,000 -	1 -	20,000
Injection wells installation	С	1000 €/each	3 -	3000
Monitoring wells installation	М	1000 €/each	10 -	10,000
Sampling and chemical analysi	is M	1000 €/each	26 -	26,000
Personnel costs	O&M	100 €/h	144 h	14,400
Total (R + C)		195 €/m <sup>3</sup> soil		33,081
Total $(R + C + M + O\&M)$		491 €/m <sup>3</sup> soil		83,481

It is worth noting that the values shown in the table do not represent the actual costs spent for the pilot test carried out but rather an assessment based on the prices of the Italian market. Making reference to this table, it is quite evident that in this specific case the overall costs were quite high and mainly due to the large number of monitoring wells realized (approximately 40% of the total cost). On the contrary, the calculated unit costs considering only the reagents and the construction of wells (equal to  $195 \notin m_{soil}^3$ ) are not so far from the median value of about 125  $\notin$ /m<sup>3</sup><sub>soil</sub> reported by Krembs et al. (2010) for CHP applications, also considering that they were estimated based on a pilotscale application without including any economy of scale. In addition, since ISCO is a remediation technology preferably applied to the mass reduction of contaminants in highly-contaminated areas more than plume treatment, the costs of the full-scale application could be eventually reduced by combining it, especially in the areas mainly characterized by an hydrocarbon contamination, with other remediation strategies such as e.g. natural attenuation or enhanced bioremediation. Sutton et al. (2011) among others have, in fact, clearly highlighted how coupling ISCO and bioremediation, when properly implemented, can provide more extensive, rapid, and cost-effective treatment than either chemical or biological techniques alone.

# CONCLUSIONS

This Ph.D. work was focused on the application of In Situ Chemical Oxidation, specifically using the Fenton-like process, to MtBE treatment in contaminated groundwater. Despite this kind of technology is already applied for many organic contaminants, yet its effectiveness towards oxygenated organic compounds, such as MtBE, is debated. In fact one of the main concern when applying the Fenton's process to MtBE contaminated water is that the contaminant may not undergo complete mineralization to CO<sub>2</sub> and water, whereas the oxidation can lead to the formation and accumulation of intermediate compounds, such as tert-butyl alcohol (TBA), tert-butyl formate (TBF), methyl acetate and acetone. Moreover most of the available lab-studies on this topic were carried out on water system whereas the influence of the soil that as known can lead to a generation of a stronger pool of reactive species is still poorly investigated in the literature.

This thesis was then aimed to assess the performance of the Fenton-like process for MtBE oxidation in soil-water systems, with particularly interest in evaluating the extent of mineralization of the contaminant that can be achieved. This result was achieved by performing this assessment first at lab-scale, through column tests in soil water systems and then at pilot-scale, by elaborating the results of a field ISCO treatment.

As to the column tests, the obtained results allowed to provide some insights and evidence about different issues related to this remediation option. In particular, the obtained results showed that hydrogen peroxide was quite stable with a disproportionation of only 10% with respect to the oxidant consumed. This was observed by comparing the hydrogen peroxide residual concentrations in the outlet solutions with the oxygen measured by the online sensor in the outlet gas stream. In addition, it was found that around 40% of the MtBE injected in the column was oxidized using the Fenton-like process whereas the remaining part was displaced by washing out due to the high flow rate selected for the dynamic test. A further improvement of the MtBE removal was achieved by preliminary feeding in the column a chelating agent (EDTA) that allowed to enhance and accelerate the Fenton-like process leading to a MtBE oxidation extent higher than 60%. As far as the degradation products are concerned, the different analysis carried out on the outlet solutions showed that no by-products (e.g. TBF and TBA) were detected, demonstrating the efficiency of the tested oxidant system to treat MtBE contaminated groundwater up to a complete mineralization. This was also confirmed by comparing the amount of carbon dioxide measured by the online sensor connected to the outlet gas stream of the column, with the one calculated assuming that all the mass of disappeared MtBE was completely mineralized by ISCO. Based on this comparison it was possible to estimate that using a stabilized hydrogen peroxide solution at 6% wt. and EDTA as chelating agent, around 95% of the disappeared MtBE mass was mineralized. This study also allowed us to identify the indirect parameters such as oxygen (O<sub>2</sub>) and the carbon dioxide (CO<sub>2</sub>), for the monitoring of the Chemical Oxidation Process, based on the use of Fenton-like process in contaminated groundwater, in order to evaluate the evolution of the treatment in progress.

As to the pilot-scale ISCO treatment of a MtBE contaminated site by the Fenton-like process, the design of the pilot-scale treatment was performed following an approach based on the combination of numerical and experimental modelling, allowing to define the layout of the injection wells and to predict the propagation of hydrogen peroxide. The pilot-scale field results confirmed the effective propagation of hydrogen peroxide in the target area (around 75 m<sup>2</sup> using 3 injection wells). The radius of influence of the oxidant was in line with the one predicted by numerical simulation performed assuming that only the more permeable layer of the aquifer, where probably most of MtBE contaminated groundwater should be present, was available for oxidant propagation. As far as the MtBE removal is concerned, the ISCO application allowed to meet the cleanup goals in an area of 60 m<sup>2</sup>. Besides, the concentration of TBA, i.e. a potential byproduct of MtBE oxidation but already present in the site before the treatment was performed, was actually reduced after the ISCO treatment. The removal of TPH from the target area was also relevant. Given that the pilot-scale treatment was performed in a very limited portion of the site, surrounded by contaminated groundwater and characterized by an hydraulic barrier that induced a rather high groundwater velocity (around 1 m/day), long term monitoring, usually applied for proving the effectiveness of the ISCO treatment, was not feasible in this case. Nevertheless, a mass balance based on the amount of contaminants disappeared and of CO<sub>2</sub> and VOC produced, provided a clear line of evidence that a large amount of the mass of contaminants present in the

#### Conclusions

treated area was actually oxidized by ISCO up to complete mineralization, allowing to exclude major effects due to dilution or volatilization.

The results of both column and pilot-scale tests demonstrated that In Situ Chemical Oxidation using the Fenton-like process is effective for MtBE treatment in contaminated groundwater, allowing to achieve fairly complete mineralization of the compound. This result is surely an improvement with respect to previous studies dealing with MtBE oxidation in water systems. We can then argue that the apparently better performance observed can be ascribed to the operating conditions adopted in the Fenton-like process (e.g. higher  $H_2O_2$  concentrations) and to the presence of heterogeneous catalysts in the soil, that probably induced the formation of a more reactive pool of oxidizing radicals.

# PUBLICATIONS AND SUPPORTING DOCUMENTATION

## **Publications**

- Innocenti I., Verginelli I., Massetti F., Piscitelli D., Gavasci R., Baciocchi R., Pilot-scale ISCO treatment of a MtBE contaminated site using a Fenton-like process, Sci Total Environ, Volume (485–486) (2014) 726–738.
- Piscitelli D., Zingaretti D., Verginelli I., Gavasci R., Baciocchi R., Lines of evidence of MtBE mineralization by Fenton-like column tests, Submitted to the J Hazard Mater (2014).

## Proceedings

- R. Baciocchi, L. D'Aprile, I. Innocenti, F. Massetti, D. Piscitelli, I. Verginelli, Towards a National protocol for the application of In-Situ Chemical Oxidation, In: Proceedings of SIDISA 2012, Sustainable Technology for Environmental Engineering, 9TH Edition, 26-29 Giugno 2012, Milano.
- Remediation Technologies: Poster "Ossidazione chimica in situ", 19-21 settembre 2012, Ferrara.
- R. Baciocchi, R. Gavasci, I. Innocenti, F. Massetti, D. Piscitelli, I. Verginelli, Pilot scale ISCO treatment of a MtBE contaminated site, In: 12<sup>th</sup> International UFZ-Deltares Conference on Groundwater-Soil-Systems and Water Resource Management, 16-19 Aprile 2013 Barcelona.
- I. Verginelli, D. Piscitelli, D. Zingaretti, R. Baciocchi, Evaluation of Fenton-like process for MtBE contaminated groundwater treatment through lab-scale column tests, In: Proceedings of SIBESA 2014, Simposio Italo-Brasiliano di Ingegneria Sanitaria-Ambientale, 12TH Edition, 19-21 Maggio 2014, Natal.

## Technical Reports

- R. Baciocchi, I. Verginelli, D. Piscitelli, F. Polli, C. Barreca, I. Innocenti (2012). Studio di fattibilità del trattamento mediante ISCO. Technical report produced for eni Refining & Marketing.
- R. Baciocchi, D. Piscitelli, I. Verginelli, D. Zingaretti (2013). Monitoraggio Interventi ISCO. Technical report produced for eni Refining & Marketing.

# LIST OF ABBREVIATIONS

AOPs	Advanced Oxidation Processes
APAT	Italian Environmental Agency
AST	Aboveground Storage Tanks
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
СНР	Catalysed Hydrogen Peroxide
$CO_2$	Carbon Dioxide
DL	Detection Limit
Eo	Standard Reduction Potential
EC	Electrical Conductivity
EDTA	Ethylenediaminetetraacetic Acid
EPA	Environmental Protection Agency
EtBE	Ethyl tert-Butyl Ether
FEFLOW	Finite Element Subsurface FLOW
GC-FID	Gas Chromatography- Flame Ionization Detector
GC-MS	Gas Chromatography- Mass Spectrometry
GW	Groundwater
HDPE	High-density Polyethylene
$H_2O_2$	Hydrogen Peroxide
HS-SPME	Headspace Solid Phase Micro Extraction
IC	Inorganic Carbon
ICP-OES	Inductively Coupled Plasma Mass Spectrometry
ISCO	In Situ Chemical Oxidation
KH <sub>2</sub> PO <sub>4</sub>	Potassium Monobasic Phosphate
KMnO <sub>4</sub>	Potassium Permanganate
MFR	Modified Fenton Reagent
MtBE	Methyl tert-Butyl Ether
NaCl	Sodium Chloride
NAPL	Non-Aqueous Phase Liquid
$Na_2S_2O_8$	Sodium Persulfate

Oxygen
Ozone
Redox Potential
Polycyclic Aromatic Compounds
POLY (dimethylsiloxane)-divinylbenzene
Fluorobenzene
Photoionization Detector
Poly (vinyl chloride)
Reverse Osmosis
Radius of Influence
Soil Oxidant Demand
Temperature
Tert-Amyl Methyl Ether
Tert-Butyl Alcohol
Tert-butyl Formate
Total Carbon
Total Organic Carbon
Total Petroleum Hydrocarbons
Underground Storage Tanks
Ultraviolet
Ultraviolet Visible Spectroscopy
Volatile Organic Compounds

# NOMENCLATURE Fenton-like column tests (Chapter 2)

Symbol	Parameter	Units
[CO <sub>2</sub> ]	Carbon dioxide concentration	% vol.
$[H_2O_2]_{in}$	Hydrogen peroxide concentration injected in the column	mM
$[H_2O_2]_{out}$	Hydrogen peroxide concentration in the outlet stream	mM
[MtBE] <sub>in</sub>	MtBE concentration in the inlet stream	mM
[MtBE] <sub>out</sub>	MtBE concentration in the outlet stream	mM
M <sub>soil</sub>	Amount of soil	g
N <sub>CO2,OC</sub>	Amount of carbon dioxide from the oxidation of organic carbon	mmol
$N_{\text{CO2},p}$	Amount of carbon dioxide produced during each experiments	mmol
$\mathbf{N}_{\text{CO2},s}$	Amount of carbon dioxide produced assuming complete MtBE	mmol
$N_{\text{O2,p}}$	Amount of oxygen produced during each experiments	mmol
N <sub>02,s</sub>	Stoichiometric amount of oxygen expected	mmol
[O <sub>2</sub> ]	Oxygen concentration	% vol.
$OC_{\text{fin}}$	Final organic carbon	$g_{oc}/g_{soil}$
OC <sub>in</sub>	Initial organic carbon	$g_{oc}/g_{soil}$
Q	Flow rate of solution injected in the column	l/h
$\mathbf{Q}_{i}$	Outlet gas flow	ml/s
t	Duration of injection	h
ti	Time interval	h
$\Delta t$	Acquisition interval	S
V	Gas molar volume	ml/mmol
$\mathbf{V}_{sat}$	Volume of MtBE solution	1
$\Delta V$	Sample volume	1

# PILOT-SCALE FEASIBILITY STUDY OF ISCO APPLICATION (CHAPTER 3)

Symbol	Parameter	Units
Cs	Sorbed phase concentration	g/m <sup>3</sup>
$C_{\rm w}$	Dissolved phase concentration	g/m <sup>3</sup>
$CO_2$	Stoichiometric amount of carbon dioxide produced	mol
$\mathbf{f}_{oc}$	Fraction of organic carbon in soil	g/g
K <sub>oc</sub>	Organic carbon-water sorption coefficient	L/Kg
M <sub>in,i</sub>	Mass of contaminant before treatment	g
M <sub>out,i</sub>	Mass of contaminant after treatment	g
$MW_i$	Molecular weight of compound	g/mol
$\gamma_i$	Carbon dioxide stoichiometric molar ratio	g/g

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# REFERENCES

Aggarwal P.K., Means J.L., Hinchee R.E, Formulations of nutrient solutions for in situ bioremediation, in: R.E. Hinchee, R.F. Olfenbuttel (Eds.), In Situ Bioreclamation, Butterworth, Boston MA (1991).

APAT. Protocol for ISCO application (2005).

APHA, Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 18th Ed. Washington, D.C., (1992).

Baciocchi R., Ciotti C., Cleriti G., Innocenti I., Nardella A., Design of in-situ Fenton oxidation based on the integration of experimental and numerical modelling., J Adv Oxid Technol 13(2) (2010) 153-161.

Baciocchi R., Boni M.R, D'Aprile L., Hydrogen peroxide lifetime as an indicator of the efficiency of 3-chlorophenol Fenton's and Fenton-like oxidation in soils, J Hazard Mater B 96 (2003) 305–329.

Baciocchi, R., Boni M.R., D'Aprile L., Application of H<sub>2</sub>O<sub>2</sub> lifetime as an indicator of TCE Fenton-like oxidation in soils, J Hazard Mater B 107 (2004) 97–102.

Baciocchi R., D'Aprile L., Innocenti I., Massetti F., Verginelli I., Development of technical guidelines for the application of In-Situ Chemical Oxidation to Groundwater remediation, J Clean Prod (2014) http://dx.doi.org/10.1016/j.jclepro.2013.12.016. [in press].

Bennedsen L.R., Activated Peroxygens for Remediation of Contaminated Soil and Groundwater, Ph.D. thesis (2011).

Burbano A.A., Dionysiou D.D., Suidan M.T., Richardson T.L., Oxidation kinetics and effect of pH on the degradation of MtBE with Fenton reagent, Water Res 39 (2005) 107–118.

Burbano A.A., Dionysiou D.D., Suidan M.T., Effect of oxidant-to-substrate ratios on the degradation of MtBE with Fenton reagent, Water Res 42 (2008) 3225–3239.

Ciotti C., Advanced oxidation processes (AOPs) as innovative technology for the remediation of contaminated sites, Ph.D.thesis (2009).

Ciotti C., Baciocchi R., Tuhkanen T., Influence of the operating conditions on highly oxidative radicals generation in Fenton's systems, J Hazard Mater 161 (2009) 402–408.

Concawe. Gasoline ether oxygenate occurrence in Europe, and a review of their fate and transport characteristics in the environment, Report no. 4/12. (2012).

CSN EN 13137, Characterization of waste - Determination of total organic carbon (TOC) in waste, sludges and sediments (2001).

Damm J.H., Hardacre C., Kalin R.M., Walsh K.P., Kinetics of the oxidation of methyl tert-butyl ether (MtBE) by potassium permanganate, Water Res 36 (2002) 3638–3646.

De Laat J., Truong G.L., Legube B., A comparative study of the effects of chloride, sulfate and nitrate ions on the rates of decomposition of  $H_2O_2$ , and organic compounds by Fe(II)/ $H_2O_2$  and Fe(III)/ $H_2O_2$ , Chemosphere 55 (2004) 715–725.

De Souza e Silva P.T, Da Silva V., De Barros Neto B., Simonnot M.O., Potassium permanganate oxidation of phenanthrene and pyrene in contaminated soils, J Hazard Mater 168 (2-3) (2009) 1269-1273.

Deeb R.A., Chu K.H., Shih T., Linder S., Suffet I., Kavanaugh C.M., Alvarez-Cohen L., MTBE and other oxygenates: environmental sources, analysis, occurrence, and treatment, Environ Eng Sci 20 (2003) 433–447.

Dron J., Garcia R., Millan E., Optimization of headspace solid-phase microextraction by means of an experimental design for the determination of methyl tert-butyl ether in water by gas chromatography-flame ionization detection, J Chromatogr A 963(2002) 259-264.

EFOA, MTBE Resource Guide, Version n.3, 2nd Revision. (2005)

Fayolle F., François A., Garnier L., Godefroy D., Mathis H., Piveteau P., Monot F., Limitations in MTBE biodegradation, Oil Gas Sci Technol 58(4) (2003) 497-504.

Fayolle F., Vandecasteele J.-P., Monot F., Microbialdegradation and fate in the environment of methyl tert-butyl ether and related fuel oxygenates, Appl Microbiol Biotechnol 56 (2001) 339–349.

Goi A., Kulik N., Trapido M., Combined chemical and biological treatment of oil contaminated soil, Chemosphere Vol 63 Issue 10 (2006) 1754–1763.

Graham J.L., Striebich R., Patterson C.L., Radha Krishnan E., Haught R.C., MtBE oxidation byproducts from the treatment of surface waters by ozonation and UV-ozonation, Chemosphere Vol 54 Issue 7 (2004) 1011–1016.

Gonzalez-Olmos R., Kopinke F.D., Mackenzie K., Georgi A., Hydrophobic Fe-Zeolites for Removal of MtBE from Water by Combination of Adsorption and Oxidation, Environ Sci Technol 47(5) (2013) 2353-2360.

Haber F., Weiss J. J., Proc. R. Soc. London, Ser. A 147(1934) 332-345.

Haselow J.S., Crimi M., Siegrist R.L., Tim J., Estimating the Total Oxidant Demand for In Situ Chemical Oxidation design, Wiley periodicals, (2003).

#### References

Hong S., Zhang H., Duttweiler C.M., Lemley A.T, Degradation of methyl tertiarybutyl ether (MtBE) by anodic Fenton treatment, J Hazard Mater Vol 144 Issues 1–2 1 (2007) 29–40.

Hu Q., Zhang C., Wang Z., Chen Y., Mao K., Zhang X., Xiong Y., Zhu M., Photodegradation of methyl tert-butyl ether (MtBE) by  $UV/H_2O_2$  and  $UV/TiO_2$ , J Hazard Mater 154 (2008) 795–803.

Huang K-C., Couttenye R.A., Hoag G.E., Kinetics of heat-assisted persulfate oxidation of methyl tert-butyl ether (MtBE), Chemosphere 49 (2002) 413–420.

Huling S.G., Arnold R.G., Sierka R.A., Miller M.R., Influence of peat on Fenton oxidation ,Water Res Volume 35 N.7 (2001) 1687-1694.

Huling S.G., Pivetz B.E., In-Situ Chemical Oxidation, EPA (2006).

Huling S.G., Ko S., Park S., Kan E., Persulfate oxidation of MtBE- and chloroformspent granular activated carbon, J Hazard Mater 192 (2011) 1484–1490.

Hwang S., Huling S.G., Ko S., Fenton-like degradation of MtBE: Effects of iron counter anion and radical scavengers, Chemosphere 78 (2010) 563–568.

Hyman M., Biodegradation of gasoline ether oxygenates, Curr Opin Biotech 24(3) (2013) 443–450.

Innocenti I., Verginelli I., Massetti F., Piscitelli D., Gavasci R., Baciocchi R., Pilotscale ISCO treatment of a MtBE contaminated site using a Fenton-like process, Sci Total Environ Volume (485–486) (2014) 726–738.

ISO 11885, Water quality- Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES), (2007).

ISO 9297, Water Quality. Determination of Chloride. Silver Nitrate Nitration with Chromate Indicator. Mohr's method, 1989. UNICHIM METHOD 931, (1994).

ISO method 11423. Water quality - Determination of benzene and some derivatives. (1997).

ISO method 17294-2. Water quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements (2003).

ISO method 9377-2. Water quality – determination of hydrocarbon oil index – Part 2: Method using solvent extraction and gas chromatography (2000).

ITRC (Interstate Technology & Regulatory Council). Overview of Groundwater Remediation Technologies for MtBE and TBA. MtBE-1. Washington, D.C.: Interstate Technology & Regulatory Council, MtBE and Other Fuel Oxygenates Team; (2005). Available on the Internet at http://www.itrcweb.org.

Johnson P.C., Bruce C.L., Miller K.D., Practical Approach to the Design, Monitoring, and Optimization of In Situ MtBE Aerobic Biobarriers, Ground Water Monit R, 30(1) (2009) 56-64.

Kakarla C., Watts R.J., Depth of Fenton-like oxidation in remediation of surface soil, J Environ Eng 123 (1997) 11–17.

Kang N., Hua I., Enhanced chemical oxidation of aromatic hydrocarbons in soil systems, Chemosphere 61 (2005) 909–922.

Kislenko V.N., Berlin A.A., Litovchenko N.V., Kinetics of the oxidation of organic substances by persulfate in the presence of variable-valence metal ions, Kinet Catal 37 (1996) 767-774.

Kiwi J., Lopez A., Nadtochenko V., Mechanism and kinetics of the OH-radical intervention during Fenton oxidation in the presence of a significant amount of radical scavenger (Cl<sup>-</sup>), Environ Sci Technol 34 (2000) 2162–2168.

Kolthoff J.M., Stenger V.A., Volumetric Analysis Titration Methods: Acid–Base, Precipitation and Complex - Formation Reactions, Second Revised Edition, Volume II, Interscience Publishers Inc New York (1947).

Krembs F.J., Siegrist R.L., Crimi M.L., Furrer R.F., Petri B.G., ISCO for Groundwater Remediation: Analysis of Field Applications and Performance, Ground Water Monit R. 30 (2010) 42-53.

Kwan W.P., Voelker B.M., Decomposition of hydrogen peroxide and organic compounds in the presence of dissolved iron and ferrihydrite, Environ Sci and Technol 36 (2002) 1467-1476.

Lewis S., Lynch A, Bachas L., Hampson S., Ormsbee L. and Bhattacharyya D., Chelate-Modified Fenton Reaction for the Degradation of Trichloroethylene in Aqueous and Two-Phase Systems, Environ Eng Sci Volume 26(4) (2009) 849-859.

Liang C., Huang C.F., Chen Y.J., Potential for Activated Persulfate Degradation of BTEX Contamination, Water Res 42 (2008a) 4091-4100.

Liang C., Lee I.L., Hsu I.Y., Liang C.P., Lin Y.L., Persulfate oxidation of trichloroethylene with and without iron activation in porous media, Chemosphere 70 (2008b) 426-435.

Liang C., Lee I.L., In Situ Iron Activated Persulfate Oxidative Fluid Sparging Treatment of TCE Contamination – A Proof of Concept Study, J Contam Hydrol 100 (2008) 91-100.

Liang S.H., Kao C.M., Kuo Y.C., Chen K.F., Application of persulfate-releasing barrier to remediate MTBE and benzene contaminated groundwater, J Hazard Mater 185 (2011) 1162–1168.

#### References

Lu M., Zhang Z., Qiao W., Guan Y., Xiao M., Peng C., Removal of residual contaminants in petroleum-contaminated soil by Fenton-like oxidation, J Hazard Mater 179 (2010) 604–611.

Mecozzi R., Di Palma L., Merli C., Experimental in situ chemical peroxidation of atrazine in contaminated soil, Chemosphere 62 (2006) 1481–1489.

Merz J. H.; Waters W. A. Discuss. Faraday Soc., 2 (1949) 179-182.

Mezyk S.P., Hardison D.R., Song W., O'Shea K.E., Bartels D.M., Cooper W.J., Advanced oxidation and reduction process chemistry of methyl tert -butyl ether (MtBE) reaction intermediates in aqueous solution: 2-Methoxy-2-methyl-propanal, 2-methoxy-2-methyl-propanol, and 2-methoxy-2-methyl-propanoic acid, Chemosphere. 77 (2009) 1352–1357.

Mikutta R., Kleber M., Kaiser K., Jahn R., Review: organic matter removal from soils using hydrogen peroxide, sodium hypochlorite and disodium peroxodisulfate, Soil science society of America journal 69 (2005) 120-135.

Mitani M.M., Keller A.A., Bunton C.A., Rinker R.G., Sandall O.C., Kinetics and products of reactions of MtBE with ozone and ozone/hydrogen peroxide in water, J Hazard Mater B89 (2002) 197–212.

Nam K., Rodriguez W., Kukor J.J., Enhanced degradation of polycyclic aromatic hydrocarbons by biodegradation combined with a modified Fenton reaction, Chemosphere 45 (2001) 11–20.

Okeke B.C., Frankenberger Jr. W.T., Biodegradation of methyl tertiary butyl ether (MTBE) by a bacterial enrichment consortia and its monoculture isolates, Microbiol Res 158 (2003) 99–106.

Petigara B.R., Blough N.V., Mignerey A.C., Mechanisms of hydrogen peroxide decomposition in soils, Environmental science and technology 36 (2002) 639-645.

Petri B.G, Watts R.J., Teel A.L., Huling S.G., Brown R.A, Fundamentals of ISCO using hydrogen peroxide, in: In Situ Chemical Oxidation for Groundwater Remediation, Springer New York 33-88 (2011).

Piscitelli D., Zingaretti D., Verginelli I., Gavasci R., Baciocchi R., Lines of evidence of MtBE mineralization by Fenton-like column tests, Submitted to the J Hazard Mater (2014).

Quan H.N., Teel A.L., Watts R.J., Effect of contaminant hydrophobicity on hydrogen peroxide dosage requirements in the Fenton-like treatment of soils, J Hazard Mater B 102 (2003) 277-289.

Rastogi A., Souhail R.A., Dionysios D.D., Effect of inorganic, synthetic and naturally occurring chelating agents on Fe(II) mediated advanced oxidation of chlorophenols, Water Res 43(2009) 684-694.

Romero A, Santos A., Vicente F., González C., Diuron abatement using activated persulphate: Effect of pH, Fe (II) and oxidant dosage, Chem Eng J 162(1) (2010) 257-265.

Safarzadeh-Amiri A.,  $O_3/H_2O_2$  treatment of Methyl.tert-butyl ether (MtBE) in contaminated waters, Water Res Volume 35 N. 15 (2001) 3706–3714.

Schmidt J.T., Ahmad M., Teel A.L., Watts R.J., Hydrogen peroxide stabilization in one-dimensional flow columns, J Contam Hydrol 126 (2011) 1–7.

Schumb W.C., Stratterfield C.N., Wentworth R.L., Hydrogen peroxide. American Chemical Society, Rienholt Publishing New York (1955).

Shih T., Rong Y., Harmon T., Suffet M., Evaluation of the Impact of Fuel Hydrocarbons and Oxygenates on Groundwater Resources, Environ Sci Technol 38 (2004) 42-48.

Shin H-S., Kim T-S., Analysis of tert-Butanol, Methyl tert-Butyl Ether, Benzene, Toluene, Ethylbenzene and Xylene in Ground water by Headspace Gas Chromatography-Mass Spectometry, Bull Korean Chem Soc 30 (12) (2009) 3049-3052.

Siedlecka E.M., Wieckowska A., Stepnowski P., Influence of inorganic ions on MTBE degradation by Fenton's reagent, J Hazard Mater 147 (2007) 497–502.

Siegrist R.L., Crimi M., Simpkin T.J., In Situ Chemical Oxidation for Groundwater Remediation, Springer Verlag (2011).

Smith B.A., Teel A.L., Watts R.J., Mechanism for the destruction of carbon tetrachloride and chloroform DNAPLs by modified Fenton's reagent, J Contam Hydrol 85 (2006) 229–246.

Standard methods for the examination of water and wastewater, 20th ed. American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington DC (1998).

Stefan M.I., Mack J., Bolton J.R., Degradation pathways during the treatment of methyl tert-butyl ether by the UV/  $H_2O_2$  process, Environ Sci Technol 34 (2000) 650–658.

Sun Y., Pignatello J.J., Chemical treatment of pesticide wastes. Evaluation of iron (III) chelates for catalytic hydrogen peroxide oxidation of 2,4-D at circumneutral pH, J Agric Food Chem 40 (2) (1992) 322–327.

#### References

Sutton N.B., Grotenhuis J.T.C., Langenhoff A.A., Rijnaarts H.H., Efforts to improve coupled in situ chemical oxidation with bioremediation: a review of optimization strategie, J Soils Sediments 11(1) (2011) 129-140.

U.S. EPA method 5030C. Purge-and-Trap for aqueous samples, (2003).

U.S. EPA method 9056A. Determination of inorganic anions by ion chromatography, (2007).

U.S.EPA method 8260C. Volatile organic compounds by gas chromatography/mass spectrometry (GC/MS), (2006).

UNI EN 12457-2, Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges, (2004).

US EPA 3050B Method, Acid digestion of sediments, sludges and soils, (1996).

US EPA. MTBE. http://www.epa.gov/mtbe/water.htm, (2009a).

US. EPA Chemical Oxidation, (2004).

Venny, Gan S., Ng H.K., Current status and prospects of Fenton oxidation for the decontamination of persistent organic pollutants (POPs) in soils, Chem Eng J 213 (2012) 295–317.

Venny, Gan S., Ng H.K., Inorganic chelated modified-Fenton treatment of polycyclic aromatic hydrocarbon (PAH)-contaminated soils, Chem Eng J 180 (2012) 1–8.

Vicente F., Rosas J.M., Santos A., Romero A., Improvement soil remediation by using stabilizers and chelating agents in a Fenton-like process, Chem Eng J 172 (2011) 689–697.

WASY. FEFLOW 5.3: User Manual. WASY GmbH Berlin, (2008).

Watts R.J., Finn D.D., Cutler L.M., Schmidt J.T., Teel A.L., Enhanced stability of hydrogen peroxide in the presence of subsurface solids, Journal of Contaminant Hydrology 91 (2007) 312–326.

Watts R.J., Dilly S.E., Evaluation of iron catalysts for the Fenton-like remediation of diesel-contaminated soils, J Hazard Mater 51(1) (1996) 209-224.

Watts R.J., Foget M.K., Kong S-H., Teel A.L., Hydrogen peroxide decomposition in model subsurface systems, J Hazard Mater B69 (1999) 229–243.

Watts R.J., Sarasa J., Loge F.J., Teel A.L., Oxidative and reductive pathways in manganese-catalyzed Fenton's reactions, J Environ Eng Volume 131 N. 1 (2005) 158-164.

Watts R.J., Stanton P.C, Howsawkeng J., Teel A.L., Mineralization of a sorbed polycyclic aromatic hydrocarbon in two soils using catalyzed hydrogen peroxide, Water Res 36 (17) (2002) 4283-4292.

Watts R.J., Stanton P.C., Mineralization of sorbed and NAPL-phase hexadecane by catalyzed hydrogen peroxide, Water Res 33 (1999) 1405-1414.

Watts R.J., Udell M.D., Rauch P.A., Leung S.W., Treatment of pentachlorophenolcontaminated soils using Fenton's reagent, Hazard Waste Hazard 7(4) (1990) 335–345.

Watts R.J., Teel A.L., Chemistry of Modified Fenton's Reagent (Catalyzed H<sub>2</sub>O<sub>2</sub> Propagations–CHP) for In Situ Soil and Groundwater Remediation, J Environ Eng 131 (2005) 612–622.

Xu X-R., Li H-B., Gu J-D., Simultaneous decontamination of hexavalent chromium and methyl tert-butyl ether by UV/TiO<sub>2</sub> process, Chemosphere .63 (2006) 254–260.

Xu J., Xin L., Huang T., Chang K., Enhanced bioremediation of oil contaminated soil by graded modified Fenton oxidation, J Environ Sci 23 (2011) 1873–1879.

Xu X-R., Zhao Z.-Y., Li X-Y., Gu J.-D., Chemical oxidative degradation of methyl tert-butyl ether in aqueous solution by Fenton's reagent, Chemosphere 55 (3) (2004) 73–79.

Yeh C.K-J., Hsu C-Y., Chiu C-H., Huang K-L., Reaction efficiencies and rate constants for the goethite-catalyzed Fenton-like reaction of NAPL-form aromatic hydrocarbons and chloroethylenes, J Hazard Mater 151 (2008) 562-569.