CHEMICAL OXIDATION TECHNIQUES FOR *IN SITU* REMEDIATION OF HYDROCARBON IMPACTED SOILS

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ABSTRACT: Increasing concerns over health and ecological impacts of contaminated sites are leading to the development of cost effective remediation techniques for reducing the mass, mobility and/or toxicity of contaminated soils and groundwater. Amongst these, *in situ* chemical oxidation techniques are evolving as an effective way of remediating contaminated soil. *In situ* chemical oxidation involves the introduction of chemical oxidants into subsurface soil and groundwater to destroy organic contaminants and has been applied at the field scale to a number of sites throughout North America. These have been found to be extremely effective in degrading a variety of contaminants including: chlorinated solvents such as perchloroethylene (PCE), trichloroethylene (TCE) and vinyl chloride (VC); and methyl-tert-butyl-ether (MTBE), polyaromatic hydrocarbons (PAH), benzene, toluene, ethylbenzene and xylene (BTEX) and others. This paper provides a general overview of *in situ* chemical oxidation technology by examining various oxidants and their reaction chemistry, the effect of geology and hydrogeology on oxidant performance, oxidant delivery methods and future research needs.

INTRODUCTION:

In situ chemical oxidation is an evolving technology that involves the introduction of chemical oxidants into subsurface soil and groundwater to destroy organic contaminants. This technology has promise when the contamination is amenable to mineralisation to carbon dioxide and water or oxidation to a relatively less harmful form that may then be suitable for subsequent treatment. Selection of oxidation as an appropriate technology and the oxidant is dependent on the nature and type of contaminant, the level of remediation required, viability of oxidant delivery, soil conditions and hydrogeology of the site.

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There are three main chemicals that have been used for *in situ* oxidation of organic contaminants in soil and groundwater: Hydrogen Peroxide/Fenton's reagent, permanganates (potassium and sodium) and ozone. In field applications, hydrogen peroxide/Fenton's reagent or ozone is commonly used in treating contamination in the vadose zone, whereas hydrogen peroxide/Fenton's reagent or permanganates are used for treatment in the saturated zone.[1] While there are a number of oxidants available, the aforementioned oxidants are favored due to their oxidizing power, non-toxicity, availability and low cost for commercial applications. Although each of these oxidants function to degrade contaminants, their reaction chemistry can be quite different. For commercial applications of *in situ* oxidation technologies a number of processes based on reaction chemistry and/or mode of delivery of oxidant, have been developed, some of which are patented.

Additionally, the reaction chemistry between the oxidant and the contaminant is a multi-step process involving the production of intermediates, which may impact the performance of the oxidant. Furthermore as the oxidants are generally non-selective, they also oxidize natural organic material present in the soil, increasing the total oxidant demand substantially.

OXIDANT-HYDROCARBON REACTION CHEMISTRY

Hydrogen Peroxide/Fenton's Reagent:

Hydrogen peroxide, when used alone in the oxidation of organic compounds has an oxidizing power relative to chlorine of 1.31.[2] When combined with iron (II) salts, Fenton-like reactions occur yielding hydroxyl radicals (OH•) with a relative oxidation power of 2.06. Iron (II) is naturally occurring in soil in the form of iron oxides, or can be added to the hydrogen peroxide as iron sulphate. The basic reaction is given as:[2,3]

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

There are also a number of subsequent reactions that can lead to the production of the perhydroxyl radical ($HO_2\bullet$) as well as the scavenging of OH•. Both hydrogen peroxide and the free radicals will oxidize contaminants of concern, though their reaction rates vary. Hydrogen peroxide alone and Fenton's reagent react with the longer chain carbon sources prior to oxidizing the lighter hydrocarbons[4] but Fenton's reagent reacts faster and is much more efficient[5] due to the genesis of free hydroxyl radicals. The hydroxyl radical rapidly reacts non-selectively by attacking and cleaving the carbon-hydrogen bonds of contaminant organic compounds and have been used to treat many organics such as chlorinated and non-chlorinated solvents, PAHs, esters, pesticides, VOCs, SVOCs, BTEXs, phenols and others.[2,3,6] Intermediate compounds formed as a result of the reaction with the hydroxyl radical can then be subsequently oxidized to carbon dioxide and water in the presence of excess oxidant.[7]

Oxidation reactions with hydrogen peroxide/Fenton's reagent are affected amongst others by pH, reaction time, temperature, catalysts and concentration[4] Efficacy of reaction is greatest in conditions of low pH and is minimized in moderate to high alkaline environments where the ferrous ion (Fe^{2+}) occurs as a colloidal solid that can reduce the permeability of the subsurface media and thereby lower the reaction efficiency.[6] In order to obtain the optimal pH range required, an acidic solution might be required, which could potentially have a detrimental effect on the surrounding ecosystem. Moreover, it is not always feasible to decrease the pH without excess acid addition due to buffering action of the soil.[8] The impact of hydrogen peroxide application on biological activity can be either way. It is possible that Fenton's reagent can adversely impact the microbial populations eliminating the feasibility of using bioremediation as a companion remediation technology[5] or the breakdown of hydrogen peroxide to oxygen can stimulate the aerobic biological activity.[6] Another factor in the use of this technology is the exothermicity of the Fenton's reaction that can result in the evolution of substantial amounts of gas and heat. As hydrogen peroxide can readily decompose to water vapor and oxygen, special care is required during the delivery process. The success of the treatment can further be affected by the presence of competing reactions by free radical (hydroxyl) scavengers such as carbonates, bicarbonates and organic matter present in the subsurface.[4,9]

Advantages of employing this form of oxidant in the treatment of contaminated soil and/or groundwater include: 1) low chemical cost; 2) relatively rapid reaction process; 3) application over a wide range of volatile and semi-volatile organics. As hydrogen peroxide has been applied in the field, there is a range of reliable information available that can be utilized in designing the appropriate remediation plan. [5,10]

Permanganates:

Permanganates are oxidants that have historically been used for treatment of drinking water and wastewater. The permanganate ion has a relative oxidizing power of 1.24.[2] Permanganate is typically provided as either $NaMnO_4$ or $KMnO_4$. Permanganates react with organic compounds producing manganese dioxide (MnO_2) as well as CO_2 and intermediate organic compounds.[6]

$$R + MnO_4^- \rightarrow MnO_2 + CO_2 \text{ or } R_{ox} + \text{others}$$

where, R = organic contaminant of concern
R_{ox} = oxidized intermediate organic compound

The permanganate ion is especially useful in oxidizing organics which have carbon-carbon double bonds, aldehyde groups or hydroxyl groups. A number of processes such as cleaving, hydroxylation, hydrolysis and others lead to production of intermediates and eventually to carbon dioxide and water.[3] Manganese dioxide (MnO_2) produced during the reaction does not pose environmental concerns as it occurs naturally in soils, though there is some concern with the precipitation of MnO_2 leading to a decrease in permeability.[3] As manganese exists in multiple valence states and mineral forms, numerous reactions can occur simultaneously and hence permanganate reactions tend to be effective over a wide pH range. Reaction with contaminants of concern can occur either by direct electron exchange or free radical advanced oxidation reactions: [2,7,11]

$MnO_4^- + H_2O \rightarrow MnO_4^{-2}$ (pH =12)
$MnO_4^- + H_2O \rightarrow MnO_4^{-2} + OH\bullet + H^+$ (pH = 9)
$4MnO_4^- + 4H^+ \rightarrow 3O_2 (g) + 2H_2O + MnO_2(s)$ (slightly acidic)
$2MnO_4^- + 3Mn^{+2} + 2H_2O \rightarrow 5MnO_2(s) + 4H^+$ (acidic conditions)
$MnO_4^- + 8H+ + 5e^- \rightarrow Mn^{+2} + 2H_2O$ (pH = 3.5)
$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2(s) + 4OH^-$ (3.5 < pH < 12)

Permanganate has been successfully utilized for the oxidation of alkenes, aromatics, phenols, PAHs, pesticides, some organic acids, aldehydes, amines, alcohols, ketones, chlorinated solvents (PCE, TCE), sulfides, MTBE and others.[3,5,6,11,12] Oxidation rate via permanganate is influenced by pH, temperature, solubility of the target contaminant and the concentration of each species.[2,9] Advantages in utilizing permanganates for oxidation of contaminants include the following: [3,5,6,13,14,15] 1) the oxidation reactions are not exothermic; 2) they are readily soluble and has a higher efficiency in water and soil treatment; 3) relatively safe to handle; 4) catalysts are not required; 5) pH control is not required; 6) the presence of free radical scavengers in the soil (e.g. carbonate, bicarbonate) has no adverse impact on performance; 7) neither the oxidants nor their by-products are toxic to the local microbial population allowing the use of bioremediation as a companion remediation technology; and 8) more persistent in the subsurface and therefore can migrate by diffusive processes to further regions within the contamination zone.

Two main difficulties associated in the use of permanganates are (1) regulatory concerns regarding the amount of dissolved manganese in an area, as well as the remaining purple color of unreacted permanganate in groundwater[3] and (2) the genesis of $MnO_2(s)$ precipitate which can occupy pore space reducing soil permeability and limiting further injection of aqueous oxidant into the contaminated zone.[1]

Even though permanganates are more expensive than hydrogen peroxide/Fenton's reagent[7], its ease of delivery to the contaminated zone, applicability over a wider pH range, higher level of treatability, reliability and high solubility makes remediation of contaminated soil and/or groundwater by permanganate cost effective.[14]

<u>Ozone:</u>

Ozone is a gas phase oxidizer with a relative oxidizing power of 1.77. Ozone is generated artificially on site by electric generators that produce a high-voltage discharge in air or oxygen.

$$O_2 + \text{Electric Current} \rightarrow O_3$$

Once introduced into the subsurface, the ozone gas can oxidize both organic and inorganic contaminants either directly with ozone molecules or through the generation of free-radical intermediates, such as hydroxyl radicals(OH•).[16] The types of contaminants oxidized by ozone gas are: aromatics, PAHs, chlorinated alkenes, pesticides, aliphatic hydrocarbons, phenols and chlorinated solvents.[3,5,6,9]

Ozone has been most widely used for vadose zone treatment but has also been used for the treatment of LNAPL accumulations in the capillary fringe, and injected into the subsurface along with air sparging for remediation in the saturated zone.[1] Ozone can be delivered to the contamination zone by injection through both vertical and horizontal wells. Closely spaced injection ports incorporating diffusion pipes that, as the ozone passes through, produce micro-sized bubbles with larger surface area that will rapidly travel through small pore spaces have been used.[4]

The problems associated with the use of ozone are related to its high reactive rate, instability, and short half-life.[9] These characteristics limit the distance over which the oxidant can be delivered; therefore to facilitate effective coverage closely spaced delivery points are required. As ozone is an unstable gas, it must be produced on-site. During treatment ozone can break complex organics to simpler ones making bioremediation more amenable. Additionally, oxygenation of the pore water would stimulate biodegradation. However, in high concentrations and at long residence times, ozone can be a sterilizing agent.[3] Ozone is effective around the natural pH range, but is most effective at an acidic pH.[13] As oxidation with ozone is an exothermic reaction, gas and heat can be evolved in the subsurface that could potentially result in genesis of particulates when fine-grain sediments are being treated.[9] Furthermore, ozone being a gas will escape through the surface if the geology of the site does not provide a means of natural containment, thus a geomembrane or clay cover to site should be applied to the treatment region as required.

The advantages of *in-situ* ozone oxidation of contaminants include the following: 1) greater ease of delivery; 2)on-site oxidant generation eliminates need for shipping, handling and storage of oxidant; 3)minimal degradation during injection; 4)breakdown of contaminants of concern to simpler compounds that can be easily degraded by bioremediation; 5)provides oxidation and biostimulation that can enhance bioremediation; 6) more rapid than biodegradation or vapor extraction technologies, thereby reducing remediation time and costs. [3,5,6,9]

The selection of ozone in comparison to permanganates or hydrogen peroxide is based primarily on the fact that is applied as a gas. Costs associated with the use of this oxidant include the cost of electric generators for on-site ozone production as well as the incorporation of vapor recovery and treatment technologies in cases where there is significant volatilization.

GEOLOGY AND HYDROGEOLOGICAL EFFECTS ON OXIDANT PERFORMANCE*:*

In situ chemical oxidation provides a useful means of performing mass contaminant reductions in a given area. The effectiveness of the process is dependent on the selection of an appropriate oxidant and delivery system for the site contaminants and site conditions. The most critical success factors are the effectiveness of, and the ability to control the oxidation reaction with the contaminants and the delivery of the reagents to the zone being treated. The physical setting of the site, site regulatory constraints, subsurface characterizations, safety considerations, presence and location of underground utility corridors, etc. must be thoroughly examined and characterized prior to design and implementation.

Site specific geochemical data are required to estimate the chemical dosage and to establish a baseline condition prior to treatment for efficiency evaluation and may vary depending upon the technology to be utilized. The required parameters are provided in Table 1. Some parameters are generic and are applicable to all three of the chemical oxidation technologies examined, while others are specific to a technology.

All In-Situ Chemical Oxidation Technologies	Contaminant delineation, volatile organic compounds, chemical oxygen demand, soil and/or groundwater pH, hydraulic conductivity, soil classification, groundwater gradient, vadose zone permeability, oxidation reduction potential, dissolved oxygen levels, groundwater depth and conductivity
Hydrogen Peroxide Fenton's Reagent	soil and/or groundwater iron content, soil and/or groundwater alkalinity
Potassium Permanganate	soil and/or groundwater manganese concentration, permanganate impurities
Ozone	vadose zone moisture content

Table 1: Parameters Required for In-Situ Chemical Oxidation Technology[1,2,3]

In addition to the above parameters, knowledge of the geologic and hydrologic characteristics of a site, the depth and thickness of the contaminated region and its permeability must be determined. For an efficient system, the physical and chemical heterogeneities within the site should be well characterized. Physical heterogeneities deal with variations in geological formations, layering, existing high permeable pathways along which the oxidant (and contaminants) can be transported.[14] Physical heterogeneities can be either natural or caused by human interventions such as presence of underground pipes. These will impact both the contaminant distribution as well as the oxidant delivery. Chemical heterogeneity such as the presence of reduced minerals and organic matter in groundwater, can consume the oxidants as they move through the subsurface, increasing the demand. Additionally, the generation of reaction products such as carbon dioxide as gas and manganese dioxide as solids can plug pores, and reduce the efficiency of oxidant delivery through the contaminant zone. The presence of other oxidizable contaminants can also pose concerns such as the oxidation of Cr(III) to Cr(VI).[4,14] Other chemical heterogeneities that can impact the effectiveness of the oxidant include the pH in the subsurface, presence of carbonates and bicarbonates and the amount and variability in the natural organic matter in the geological media.[14]

OXIDANT DELIVERY METHODS:

A number of methods exist for the delivery and recovery of fluid from the subsurface vadose and saturated zones at a contaminated site: Surface applications, injection probes, vertical/horizontal well flushing, soil mixing, soil fracturing and treatment walls.

Lance permeation involves the utilization of injection probes to deliver the appropriate oxidant into the contaminated zone. Monitoring wells established throughout the treatment area are used for tracking oxidant migration and for testing contaminant concentrations.[2,5] During injection, the reagents exit the probes via small perforations along its length, migrate outwards and create a zone of reactivity. Oxidant injection can be done in a horizontal or radial configuration.[5] Some of the problems associated with this method are those of subsurface obstructions, permeability and porosity variations, reaction rate of delivered reagent and contaminant concentrations. The main advantage of this treatment is that if contaminant concentrations are high, multiple deliveries of oxidant/retreatment to hotspot areas are possible. [2]

Recirculation (Vertical/Horizontal Flushing) involves the injection of the oxidant in one location of a contaminated zone while extracting groundwater at another.[5] Extracted groundwater can be amended with the oxidant and re-injected into the contaminant zone. In areas where oxidant delivery via vertical wells is impeded due to obstructions or the contaminant is isolated in thin saturated zones, horizontal wells are utilized. The advantages of recirculation include: 1) greater control of oxidant and contaminant migration; 2) higher volumes of oxidant solutions can be injected since fluid is simultaneously being extracted from the pores; and 3) potentially lower treatment costs.[2]

Soil mixing is performed in moderate to low permeability media in both the vadose and saturated zones.[2,6] For near surface applications, soil can be mixed utilizing the appropriate oxidant and simple construction equipment. For applications at greater depths deep soil mixing techniques are employed.[2]

For clayey and tight soils, soil fracturing may be necessary to create pathways to transmit the oxidant.[2]

Treatment walls consist of trenches filled with aggregate and a piping network used for oxidant delivery and are located downstream of the contaminant plume. Factors affecting this form of application include plume velocity and contaminant concentration, wall spacing, trench thickness, potential plugging and loss of hydraulic conductivity with the genesis of in situ solids (e.g. $MnO_2(s)$).[2]

TECHNOLOGY STATE OF THE ART:

The performance of chemical treatment technologies has been investigated by both laboratory and field studies/demonstrations in a variety of media. Details of a number of field applications have been provided in literature.[1,2,6] In Alberta, hydrogen peroxide has been used to oxidize hydrocarbons in impacted soils in areas with restricted access.[17] The reports from field applications have indicated significant success and it is expected that in the future as this technology matures and more answers are obtained it will become more widely accepted.

Even though successful application of in situ chemical oxidation treatments has been achieved and reported in literature, a better understanding of the different aspects of the technology is still necessary. The mechanisms of the reactions, the intermediate and final products generated need to be conclusively identified. Even though the generation of carbon dioxide is desired, not all hydrocarbons get converted to carbon dioxide as a result of the application. Additionally, there is an impact of carbon dioxide generation on the soil conductivity and volumetric changes.[18,19] Volumetric changes of soil can have implications when applying the technology to sites with superstructures. Xu (2003)[8] found that the hydraulic conductivity of hydrogen peroxide to be about 30 times lower than that of water, largely attributed to gas generation and reaction products, which block the pores. An uneven distribution of the oxidant even in a homogeneous environment, due to the precipitation of reaction products and gas generation causing micro level heterogeneity was also reported. Development of relationships between the amount of oxidant necessary and the soil organic matter along with the contaminant content would be quite useful in deciding the amount of oxidant necessary for a field application. The weathering of the contaminants and the kinetics of adsorption-desorption play a significant role in the performance of a particular oxidant. These areas also need further research to understand the process. From an engineering perspective, the oxidant delivery is quite a challenge. The use of pressure to inject the oxidant may cause fractures. In clayey soils, use of fracturing may be necessary which may then become the preferred paths for oxidant delivery. The use of an oxidant under pressure may cause the contaminant to get “flushed” instead of oxidized, requiring a good site monitoring plan to ensure success.

In conclusion, in situ chemical oxidation is an evolving technology. Efficiency combined with the speed of reaction, relatively low cost, reliability and simplicity make in-situ oxidation a viable remediation technology for the mass reduction of contaminants in soil and groundwater. It offers the advantages of being rapid, aggressive and non-selective to a variety of contaminants and concentrations. It provides the ability to treat and reduce mass contaminants in areas without disturbing above ground structures[17] and it can work alone or in conjunction with other technologies. With additional research and understanding, this technology has further promise.

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