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## CHEMICAL OXIDANTS FOR REMEDIATION OF CONTAMINATED SOIL AND WATER. A REVIEW

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**Abstract.** This review covers the main agents used for *in situ* and *ex situ* chemical oxidation of organic contaminants particularly oil products, in soil and water environments. Among them there are hydrogen peroxide, permanganate salts, ozone and sodium persulfate. The fields of application, as well as benefits and disadvantages of the mentioned agents use were described.

**Key words:** oxidation, remediation, soil, water, contaminants.

### 1. Introduction

The effective removal of antropogenous contaminants from contaminated soil is an essential problem because of environmental concerns. One of the major groups of organic contaminants, which cause harmful consequences, endanger natural environment and human health, is crude oil and oil products. It is explained by their ability to form toxic compounds in soils, superficial and ground water. The remediation from oil contaminations is especially difficult and most essential for enterprises and regions, involved in oil production.

An effective solution of this problem is *in situ* chemical oxidation, which is a technique used to remediate contaminated soil and groundwater systems and utilizes chemical agents capable of oxidizing organic contaminants (*i.e.* active chemical oxidants) [1-3]. Physico-chemical processes, which are able to destroy persistent contaminants, are affected less by environmental and contaminant factors. The oxidants used are readily available, and treatment time is usually measured in months (or even days) rather than years, making the process economically feasible. *In situ* chemical oxidation (ISCO) is accomplished by introducing the agents into the soil or aquifer at a contaminated site using injection and mixing apparatuses. Although chemical oxidation processes have been studied and publicized for decades, the use of

chemical oxidation for remediation applications is limited to the past decade. The effectiveness of oxidation depends upon the geological conditions, the residence time of the oxidant, the amount of oxidant used and the effective contact between oxidant and the contaminant(s).

Chemical oxidation offers several advantages over other *in situ* or *ex situ* remediation technologies: i) rapid treatment time and treatment of concentrated contaminants; ii) effectiveness for a diverse group of contaminants. Chemical oxidation has also some disadvantages: i) non-selective oxidation, *i.e.* the oxidant may react not only with the definite contaminants but with substances in the soil which can be readily oxidized, as well; ii) control of pH, temperature, and contact time is important to ensure the desired extent of oxidation; iii) the costs necessary for the implementation of this process are rather high.

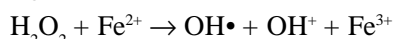
The main agents used in ISCO technologies are described below.

### 2. Chemical Oxidants

#### 2.1. Hydrogen Peroxide and Fenton's Reagent

Hydrogen peroxide ( $H_2O_2$ ) is a strong oxidant that can be injected into a contaminated zone to destroy organic contaminants. When injected to groundwater,  $H_2O_2$  is unstable, and reacts with organic contaminants and subsurface materials. It decomposes to oxygen and water within hours of its introduction into groundwater generating heat in the process [4]. The soil treatment with hydrogen peroxide has the potential for both *ex situ* and *in situ* applications. Most *ex situ* processes employ excavation followed by treatment and return of the soil to the site. *In situ* applications could involve surface application of the peroxide or injection into the soil [3]. Oxidation using liquid hydrogen peroxide in the presence

of native or supplemental ferrous iron ( $\text{Fe}^{2+}$ ) produces Fenton's Reagent:



This optimal reaction occurs under relatively low pH (e.g. pH = 2-4). Using a ferrous sulfate solution simultaneously adjusts aquifer pH and adds the iron catalyst needed for Fenton's Reagent. Because of the low pH requirement, Fenton's Reagent treatment may not be effective in limestone geology or sediments with elevated pH levels. In addition, the reaction between hydrogen peroxide and ferric iron can consume hydrogen peroxide, reducing the effectiveness of the oxidant dose. The same effect may also occur in soils with the high ferric iron content. The hydroxyl radicals break the petroleum hydrocarbon bonds of common petroleum constituents such as benzene, toluene and xylene, as well as aromatic hydrocarbons *etc.*

The remediation of contaminated soils is the most recent application of Fenton's process chemistry. Watts *et al.* [1] investigated pH optima, documenting the mineralization of pentachlorophenol through catalyzed hydrogen peroxide. Tyre *et al.* [5] determined the optimum conditions or the catalyzed-peroxide treatment of dieldrin, hexadecane, pentachlorophenol, and trifluralin in soils with various organic carbon contents. Their data suggest that mineral-catalyzed hydrogen peroxide treatment may provide the most efficient mechanism (*i.e.* the highest contaminant degradation rate per amount of hydrogen peroxide consumed). Watts *et al.* [2] also performed bench-scale treatment of soils contaminated with octachlorodibenzo-*p*-dioxin, destroying this highly-refractory contaminant with a dose of hydrogen peroxide excess.

The difficulty in addressing contamination in low permeability soils may be alleviated to some degree by controlled pneumatic or hydraulic fracturing of the soil. In any case, long term post-injection monitoring of contaminant levels in groundwater is critical in evaluating the success of putting Fenton's Reagent into contact with adsorbed contaminants. Controlled oxidation is increasingly being practiced using solid peroxides, pH modifiers, and catalysts which promote the generation of free radicals. This new approach moderates the rate of dissolution and peroxide generation, which in turn controls that rate of reaction between the peroxide and the petroleum contaminants.

The main advantage of hydrogen peroxide treatment is the speed at which cleanup can be achieved. Due to oxidation kinetics small sites can be possibly remediated in days or weeks. The main disadvantage of hydrogen peroxide treatment is the cost of the hydrogen peroxide. If the aim may be achieved in a much shorter time period compared to bioremediation, the cost of the peroxide may be offset by reduced labor and monitoring costs. Being highly reactive hydrogen peroxide is classified as a strong oxidant. The widespread availability of hydrogen peroxide

is another advantage. To weaken its potential for reactivity and decomposition, commercially available hydrogen peroxide is stabilized through the addition of stannites.

## 2.2. Permanganate

Permanganate salts are well-known oxidizing agents as they are commonly used in many water treatment applications at low concentrations [4-5]. As an oxidizer, permanganate has a unique affinity for destroying organic compounds containing carbon-carbon double bonds. The permanganate ion is strongly attracted to the negative charge associated with electrons in the *pi*-cloud of carbon-carbon double bonds of chlorinated alkenes and borrows electron density from the *pi*-bond, which disturbs the carbon-carbon double bond, thus forming hypomanganate diester. This intermediate product is unstable and further reacts by a number of mechanisms including hydroxylation, hydrolysis or cleavage. The final oxidation product is carbon dioxide, chloride salt and manganese dioxide. Other contaminants may be oxidized by free radical oxidation.

Although the reaction of the permanganate ion with contaminants is well understood, these reactions have not been commonly used for *in situ* remediation due to complications resulting from precipitate of manganese dioxide. Plugging of the soil matrix with  $\text{MnO}_2$  has been observed when permanganate salts are injected into the soils through injection wells or points, which results in the poor contact of the oxidant with the contaminants. However, the manganese dioxide precipitates are unstable as they are readily reduced by chemical or biological *in situ* processes to form soluble divalent manganese ions [15].

The reaction stoichiometry of permanganate salts in natural systems is rather complex. Due to its multiple valence states and mineral forms, manganese can participate in numerous reactions. The reactions proceed with a slower rate compared with the reactions of hydrogen peroxide or ozone, according to the second order kinetics. Depending on pH, the reaction can include destruction by direct electron transfer or free radical advanced oxidation. Permanganate reactions are effective over a pH range from 3.5 to 12. The stoichiometric reaction for the complete destruction of trichloroethylene by  $\text{KMnO}_4$  is given by



Permanganate as an oxidant is weaker than hydrogen peroxide. Its inability to oxidize benzene can lead to the early elimination of permanganate as a candidate for oxidation technology at petroleum cleanup sites.

However, permanganate has several advantages over other oxidants: i) oxidation of organics over a wider pH range; ii) reactivity over a prolonged period in the subsurface allowing the oxidant to permeate soil more effectively and contact adsorbed contaminants; iii) absence

of heat, steam and vapors or associated health and safety concerns.

As with other chemical oxidation technologies, the success of the permanganate use relies heavily on its ability to come into contact with the site contaminants. The delivery mechanism must be capable of dispersing the oxidant throughout the treatment zone. To accomplish this, permanganate may be delivered in a solid or liquid form in a continuous or cyclic application schedule using injection probes, soil fracturing, soil mixing, groundwater recirculation or treatment fences [15].

*In situ* permanganate reactions can yield low pH (*e.g.* pH = 3) and high Eh conditions (*e.g.* +800 mV), which can temporarily mobilize naturally occurring metals and metal contaminants which may also be present in the treatment area. The release of these metals from the aquifer formation, however, may be offset by sorption of the metals onto strongly sorbent MnO<sub>2</sub> solids that are precipitated as a by-product of permanganate oxidation.

Cr(OH)<sub>3</sub> in soils may be oxidized to hexavalent chromium, which may persist for some time. This may be dangerous if the aquifer is used for drinking water. Thus, regardless all advantages of the application of permanganate salts the questions remain about their efficiency as well as about MnO<sub>2</sub> that is generated, and the effect, which it may have on subsurface permeability and remediation performance.

### 2.3. Ozone

Ozone is a strong oxidant and can oxidize contaminants directly or through the formation of hydroxyl radicals. Like peroxide, ozone reactions are most effective in systems with acidic pH. The oxidation reactions proceed with extremely fast, pseudo first order kinetics. For decades it has been used in the wastewater industry acting as a disinfectant as well as a chemical oxidant, used to oxidize or destroy organic chemicals in the waste stream. Due to the ozone high reactivity and instability, O<sub>3</sub> should be produced on-site, and it requires closely spaced delivery points (*e.g.*, air sparging wells). The gas may be transferred to the dissolved phase on-site by sparging upgradient water with ozone. Groundwater which is extracted upgradient from the area to be treated may be amended with ozone, then re-injected or re-infiltrated into the subsurface. More commonly, gaseous ozone is injected or sparged directly into contaminated groundwater. *In situ* decomposition of the ozone can lead to beneficial oxygenation and biostimulation. The simplified stoichiometric reaction of ozone with TCE in water is given by equation:



The innovative *in situ* remedial technology using ozone is a form of chemical oxidation, which destroys organic contaminants leaving behind harmless end

products. *In situ* chemical oxidation becomes a desirable remedial alternative due to the potential for large cost savings as well as limited site disturbance.

Ozone is a strong oxidant with an oxidation potential about 1.2 times greater than hydrogen peroxide. It can be used to destroy petroleum contamination *in situ*. Delivery concentrations and rates vary, however, depending on the object and the type of contaminations and because of the high reactivity of ozone and associated free radicals [18].

The advantages of ozone application for ISCO are its reactivity and the wide range of substances, which can be treated; the disadvantages – the same high reactivity, which results in complications during its application and its distribution in soil after injection.

### 2.4. Sodium Persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>)

Activated persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) is an emerging oxidation agent which is used for *in situ* and *ex situ* destruction of a wide range of chemical contaminants. Field pilot or full-scale application of activated persulfate now has been performed at over sixty sites in more than twenty states, treating effectively chlorinated ethenes, chlorinated ethanes, chlorinated methanes, polyaromatic hydrocarbons, petroleum hydrocarbons, BTEX, MTBE *etc.* [14].

It has been demonstrated that such oxidants as sodium persulfate can be thermally activated to promote the formation of sulfate free radicals. A potential alternative to thermal activation is a chemical activation. Transition metal activators such as ferrous ion (Fe<sup>2+</sup>) can activate persulfate decomposition at ambient temperature (~293 K). The ferrous ion activated persulfate reaction requires activation energy of 12 kcal/mol, which is lower than the value of 33.5 kcal/mol required for thermal rupture of the O–O bond.

Researchers have used iron chelates as a catalyst in oxidation reactions to enhance their efficiency [7-9].

Citric acid is a natural multidentate organic complexing agent that is environmentally friendly, and readily biodegradable, and has the ability to extract toxic metals from contaminated soils and sediments [11]. Therefore, citric acid is often used in environmental applications and is recommended for application in combination with the source of ferrous ions for sodium persulfate activation.

Activated persulfate forms sulfate radicals, which are primary oxidizing agents. Sulfate radicals are one of the strongest oxidants available, with an oxidation potential of 2.6 V, as compared to the hydroxyl radical (2.7 V), the permanganate ion (1.4 V) and ozone (2.2 V), and are effective in oxidizing a broad range of chemical substances. In addition, the persulfate anion is also formed during oxidation, which itself is a strong oxidant (2.1 V), relatively stable and can persist in the subsurface for up

to several months before decomposing. Proper choice of activation chemistry can tailor the kinetics of radical formation, thus allowing the applicator to be flexible in balancing between persulfate distribution and speed of contaminant destruction. The soil oxidant demand for persulfate is reported to be less than that for hydrogen peroxide and permanganate, which makes this method more effective economically.

### 3. Combination of Bioremediation and Chemical Oxidation

One of the most promising modern approaches is the application of chemical oxidation methods not only for remediation of contaminated sites but also for stimulation of the biodegradation process.

However, there are some obstacles in introduction of the oxidants into the medium for microorganisms stimulation, *e.g.* toxic influence on microflora or oversaturation of soil with oxygen and naturally inhibition of aerobic and anaerobic microflora [16, 17].

#### 3.1. Oxygen Releasing Compounds

Various enhanced aerobic bioremediation approaches rely on oxygen releasing compounds. More commonly used oxygen releasing compounds include calcium and magnesium peroxides which are introduced to the saturated zone in solid or slurry phases. These peroxides release oxygen to the aquifer when hydrated by groundwater as the peroxides are ultimately converted to their respective hydroxides. Magnesium peroxide has been more commonly applied in industrial scales than calcium peroxide because of magnesium peroxide lower solubility and, consequently, prolonged release of oxygen. Magnesium peroxide formulations placed in the saturated zone during a short-term injection event can release oxygen to groundwater from four- to eight- months period. Significant quantities of magnesium peroxide are required due to stoichiometry and the fact that 90 % of the weight of the compound is not oxygen.

Many site-specific conditions must be considered before this technology can be devised and implemented. One such site-specific concern is the proximity of drinking water supply wells to the treatment area and how the injected oxygen or other nutrients may affect these wells. Another problem is the limited zone of oxygen releasing compounds influence while they are brought into a well. This method often provides the increased oxygen levels only up to twice the diameter of the well. Other factors such as contaminant composition and their properties, site geology and hydrology, *etc.* should be taken into account [16].

#### 3.2. Hydrogen Peroxide Infiltration

An additional benefit of hydrogen peroxide and Fenton's Reagent is the temporary increase of oxygen levels in and around the treatment area. The increased oxygen levels on the border of the treatment area can enhance naturally occurring aerobic biodegradation processes that reduce contaminant mass. While there may be a threat of inactivation or even elimination of hydrocarbon-degrading bacteria in the chemical oxidation treatment area, many studies have shown that soil cannot be readily sterilized by Fenton's Reagent and that microbial populations rapidly renewed after chemical oxidation treatment. Apart from enhancing aerobic biodegradation, reduced nitrogen and sulfur are oxidized to nitrates and sulfates which can be used by anaerobic microbes.

#### 3.3. Ozone Injection

Ozone injection is both a chemical oxidation technology and an enhanced aerobic bioremediation technology. Ozone is a strong oxidant with an oxidation potential greater than that of hydrogen peroxide. It is also effective in delivering oxygen to enhance subsurface bioremediation of petroleum-impacted areas.

Ozone is 10 times more soluble in water than is pure oxygen which favours objects saturation with oxygen. About one-half of dissolved ozone introduced into the subsurface degrades to oxygen within approximately 20 minutes. The dissolved oxygen can then be used as a source of energy by indigenous aerobic hydrocarbon-degrading bacteria. Because of its oxidization potential, injected ozone can also be toxic to indigenous aerobic bacteria and can actually suppress subsurface biological activity. However, this suppression is temporary, and a sufficient number of bacteria survive *in situ* ozonation to resume biodegradation. Furthermore, aerobic bacteria on the boarder of treatment zone actively grow and develop in well-aerated conditions as a result of ozone application [10].

## 4. Conclusions

A process that is designed to destroy organic contaminants present in a variety of phases without removing the contaminated material is known as *in situ* (or below-ground) chemical oxidation. The most commonly used oxidants include hydrogen peroxide ( $H_2O_2$ ), potassium permanganate ( $KMnO_4$ ), ozone ( $O_3$ ) and relatively new agent sodium persulfate. Chemical oxidants are introduced into a contaminated site using injection and mixing apparatus.

The cost of chemical oxidation processes with the aim of remediation of soil and water systems depends on the contaminant being treated, the effectiveness of recycling the oxidant *etc.*

Field tests have proven that *in situ* chemical oxidation is a viable remediation technology for contaminant reduction in source areas as well as for environment renewal. The potential benefits of *in situ* oxidation include the rapid and extensive reactions with various contaminants applicable to many bio-recalcitrant organics as well as water and subsurface environments. Also, *in situ* chemical oxidation can be tailored to a site and implemented with relatively simple, readily available equipment.

Some potential limitations exist including the requirement for handling large quantities of hazardous oxidizing chemicals due to the oxidant demand of the target organic chemicals and the unproductive oxidant consumption of the formation.

Further research and development is ongoing to advance the science and engineering of *in situ* chemical oxidation and to increase its overall cost effectiveness. Application of ISCO not only for oxidation purposes, but also for stimulation of bioremediation process is an exceedingly perspective modern way of successful remediation of environment.

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## ХІМІЧНІ ОКИСНИКИ ДЛЯ ОЧИЩЕННЯ ЗАБРУДНЕНИХ ГРУНТІВ І ВОДИ. ОГЛЯД

*Анотація.* Цей огляд присвячений основним реагентам, що використовуються у хімічному окисненні органічних забрудників *in situ* (безпосередньо на об'єкті) та *ex situ* (локалізовано), у першу чергу нафтопродуктів, у ґрунті та водних ресурсах. Серед них – пероксид водню, перманганати, озон і персульфат натрію. Розглянуто області застосування, а також переваги і недоліки використання зазначених реагентів.

*Ключові слова:* окиснення, очищення, ґрунт, водні ресурси, забрудники.