

IN SITU CHEMICAL OXIDATION OF CHLORINATED SOLVENTS

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INTRODUCTION

Interest in the use of innovative technologies for the in situ treatment of chlorinated solvent (VOCs) groundwater plumes has rapidly increased in recent years as an alternative to long term containment using established technologies such as pump and treat. One of the newest and fastest growing remediation technologies is In Situ Chemical Oxidation (ISCO).

Chemical oxidation uses chemicals called oxidants to destroy pollution in soil and groundwater. Chemical oxidation has been used for decades in the municipal and industrial water and wastewater treatment industry to destroy organic contaminants. ISCO is an attractive technology that has the potential to more rapidly and completely destroy chlorinated solvents in a cost effective way when compared to traditional approaches.

There are two critical issues with chemical oxidation:

- The reaction process. Does the reaction with the contaminant take place? What reaction products are formed?
- The application. Can sufficient oxidant be brought into contact for a long enough time to react with the contaminant(s)?

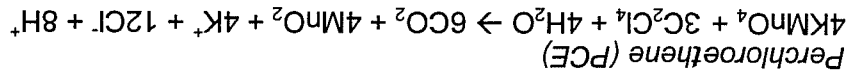
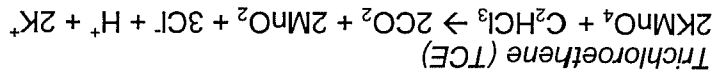
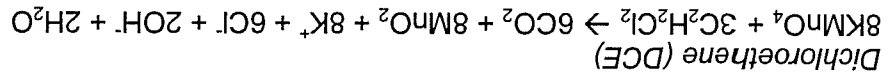
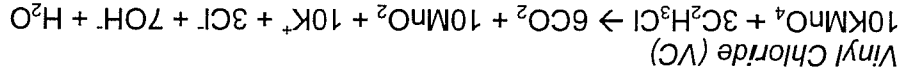
OXIDANTS

There are many oxidants that can be used. However, they are not all environmentally acceptable. To be used in an environmental setting, oxidants have to be non-hazardous and leave minimal hazardous or undesirable by-products. The oxidants that are mostly used are hydrogen peroxide, permanganate (potassium and sodium), persulfate (sodium) and ozone. An overview of the available oxidants is given in the table below.

Table 1: Overview of available oxidants

Oxidant	Formula	Equivalent Weight	Oxidation Potential	Available Forms
Hydrogen Peroxide	H ₂ O ₂	17 as H ₂ O ₂ 34 as HO [•]	1.77 2.76 (HO [•])	30 – 50% as H ₂ O ₂
Permanganate	MnO ₄ ⁻	52.6 K 47.3 Na	1.7	K – solid Na – 40% solution
Persulfate	S ₂ O ₈ ⁼	119 Na	2.01 2.5 (SO ₄ ^{•-})	Solid
Ozone	O ₃	24	2.07	Gas 3-5% Air 5-10% O ₂

The equations show that the more chlorines present, the less oxidant proportionately is required for reaction. It should be noted that the amount of permanganate required to treat a site is the sum of the stoichiometric requirement and the soil demand as permanganate reacts as well with naturally occurring soil organics. The soil demand in some cases may be several folds greater than the stoichiometric requirement.



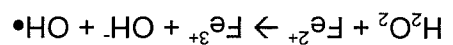
The balanced oxidation-reduction reactions of KMnO_4 with the various species of chlorinated ethenes can be written as follows:

Permanganate
There are two forms of permanganate, KMnO_4 and NaMnO_4 . Generally, potassium permanganate is used, as it is less expensive and more readily available. However, it is limited to about a 4-5% solution. For situations requiring high strength, sodium permanganate is used.

Peroxide is used amongst others for chlorinated VOCs – both ethenes as ethanes.

- It may significantly raise the cost;
 - When the decomposition reaction occurs, it generates heat and gas, which can strip organics from the groundwater causing an uncontrolled release of VOCs. If the VOCs are combustible, fire can result from the increase in temperature and O_2 ; and
 - The peroxide doesn't last. If there is soil contamination present it will often persist and re-contaminate the groundwater. This may result in multiple applications. Therefore, the usefulness of Fenton's reagent may be limited by low soil permeability, incomplete site delineation, and subsurface heterogeneities.
- There is a limit to the effectiveness of hydrogen peroxide or "Fenton's Reagent" as it may rapidly decompose. This leads to three undesirable effects:

The hydroxyl radicals ($\text{OH}\cdot$) serve as very powerful, effective, and nonspecific oxidizing agents.

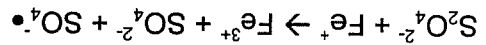


Hydrogen peroxide
Hydrogen peroxide is primarily used as a "modified Fenton's reagent." As such it is typically added with an acid (generally sulfuric) and ferrous iron. This process involves free radical generation and direct oxidation with hydrogen peroxide. The basic reaction is as follows:

Carbon dioxide (CO₂) exists naturally in the subsurface from biological processes and bicarbonate partitioning in the groundwater. Manganese dioxide (MnO₂) is a natural mineral already present in the soil. If the precipitation of MnO₂ in the soil is excessive, it can reduce the permeability of the soil and can thus limit injection capabilities.

Pernanganate is very effective against the chlorinated ethenes – PCE, TCE, DCE, and VC. However, it does not oxidize ethanes such as 1,1,1-TCA; 1,1- or 1,2-DCA. Persulfate is the newest of the chemical oxidants. It has a very high equivalent weight so proportionately more persulfate is required to oxidize a given mass of contaminant than is permanganate. However, persulfate has the advantage that it does not appear to react that readily with soil organics. As a result, when the total oxidant demand – both soil demand and stoichiometric demand – is considered, persulfate may be more efficient than permanganate.

Persulfate is potentially more reactive than permanganate with some contaminants and is more stable than peroxide. Its increased reactivity is due to the formation of sulfate radicals that behave similar to hydroxyl radicals. Sulfate radicals are formed by adding an iron catalyst or by adding heat. Under iron-catalyzed conditions, the sulfate free radicals (SO₄•) are produced as is shown in the equation below:



Persulfate reacts well with ethenes, and, at elevated temperatures (40-50° C), with ethanes such as 1,1,1-TCA; 1,1- or 1,2-DCA.

As it is a relatively new oxidant, it requires continued development work.

Ozone (O₃) is one of the strongest oxidants available for ISCO. Ozone is added as a gas. Ozone can oxidize organic contaminants in two ways, either with direct oxidation by ozone or by the generation of free radical intermediates.

Ozone is highly reactive and will oxidize most contaminants. The primary limitations of ozone are its low mass-delivery rate and its cost.

DESIGN CONSIDERATIONS

The application of ISCO requires a systematic approach. Site-specific geochemical data are required to estimate chemical dosage, to establish a baseline condition prior to treatment and to evaluate the effectiveness of treatment in soil and/or groundwater.

The following figure describes the process needed for successful application of ISCO. There are several stages. First, there is the selection of the proper oxidant. Second is the selection of the application method. Third is the combination of both into an ISCO design. This process can be iterative as there are often multiple options for oxidants and application methods. Feasibility testing is typically first conducted at the laboratory scale, and continuously with a pilot test in the field.

