TECHNICAL OUTREACH
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TOSC Program

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TOSC ENVIRONMENTAL BRIEFS FOR CITIZENS

Chemical Oxidation for Groundwater Remediation

What is chemical oxidation?
Oxidation is defined as a chemical process in which electrons are transferred from an atom, ion or compound. The *in-situ* (below ground) chemical oxidation process is designed to destroy organic contaminants either dissolved in groundwater, sorbed to (stuck to) the aquifer material, or present in their free phase (for examples, as gasoline). Oxidants most frequently used in chemical oxidation include hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), persulfate ($Na_2O_8S_2$) and ozone (O_3). Peroxone, which is a combination of ozone and hydrogen peroxide, is also used. Fenton's Reagent, hydrogen peroxide mixed with a metal (commonly iron) catalyst, can also be used. Table 2 summarizes some characteristics of the oxidants.

In-situ chemical oxidation (ISCO) can be accomplished by introducing chemical oxidants into the soil or aquifer at a contaminated site using a variety of injection and mixing apparatuses. Normally, vertical or horizontal injection wells are used to deliver chemical oxidants.

Ex-situ oxidation is accomplished by pumping groundwater from extraction wells and treating the groundwater above ground. In the recirculation approach, oxidants can be mixed with the extracted groundwater, which is subsequently pumped back into the aquifer through injection wells.

What are the advantages and disadvantages of chemical oxidation?
Chemical oxidation offers several advantages over other *in-situ* or *ex-situ* remediation technologies:

- The greatest advantages are the rapid treatment time and the ability to treat contaminants present at high concentrations.
- It is effective on a diverse group of contaminants.

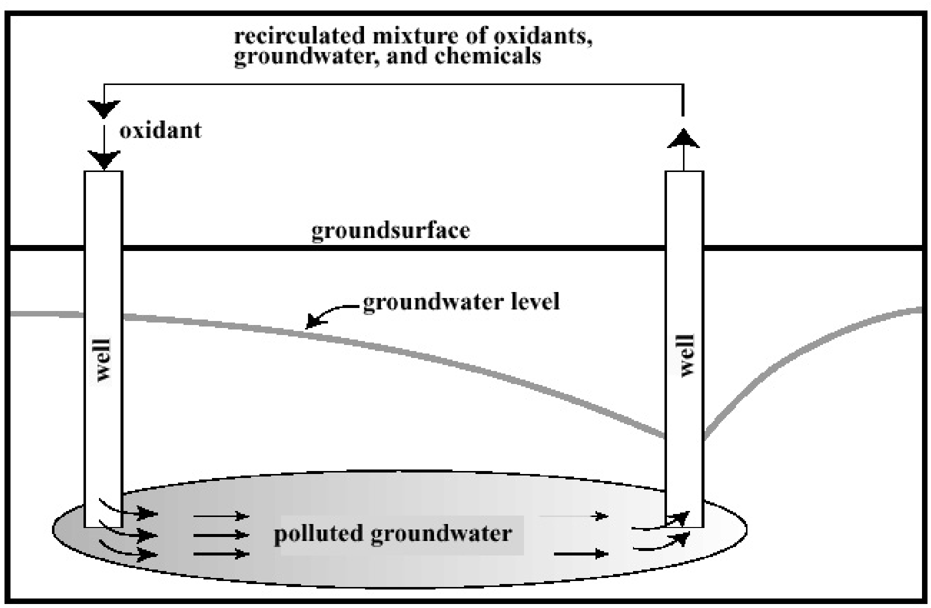

Fig. 1 — In-situ chemical oxidation system diagram.
(http://clu-in.org/download/citizens/oxidation.pdf)

Chemical oxidation also has some disadvantages. The disadvantages are as follows.

- Oxidation is nonselective. As such, the oxidant will not only react with the target contaminants but also with substances found in the soil that can be readily oxidized. In the case of ozone, ozone can react with water and decompose to oxygen. Oxygen production can lead to serious problems such as the development of high pressures below the ground surface and possible explosions.
- Control of pH, temperature, and contact time is important to ensure the desired extent of oxidation.
- Capital costs are typically high.
- Operating costs can also be high.

Where is chemical oxidation applicable?

Chemical Oxidation technology is applicable to sites with contaminants in the vadose zone or in aquifers. The vadose zone is the unsaturated region between the soil surface and water table. Chemical oxidation can be combined with traditional remediation technologies to achieve maximum clean-up results. Implementation of chemical oxidation technologies should only be undertaken after a complete contaminated site characterization (that is, the identification of contaminants and their concentrations, vertical and horizontal locations of contaminants and media—soils, groundwater, etc.—that are affected.)

What contaminants can be treated with chemical oxidation?

Common contaminants treated by chemical oxidation are amines, phenols, chlorophenols, cyanides, halogenated aliphatic compounds, mercaptans, and certain pesticides in liquid waste streams (for more on these particular contaminants, see the website www.envirotools.org). Soil slurries and sludge can also be treated. Oxidation effectiveness depends on the organic compound, as shown in Table 1.

Is chemical oxidation safe?

While the use of chemical oxidation can be quite safe if done properly, there are significant potential hazards. Most oxidants are corrosive. This means that they have the ability to burn the skin and wear away certain materials. They are highly reactive and, as such, have the potential to be explosive. Those handling the oxidants should wear protective equipment. Heat may also be generated by the reactions. This heat production will need to be controlled.

Oxidation Suitability	Compounds
High	Phenol, aldehydes, amines, some sulfur compounds
Medium	Alcohols, ketones, organic acids, esters, alkyl-substituted aromatics, nitro-substituted aromatic compounds, carbohydrates
Low	Highly halogenated hydrocarbons, saturated aliphatic compounds

Table 1. Suitability of Organic Compounds for Oxidation

How long does chemical oxidation take?

The time required to clean up a contaminated site using chemical oxidation is dependent on the reactivity of the contaminant with the oxidant, the size and depth of the contaminated zone, the speed and direction of groundwater flow and type of soils and the conditions present at the contaminated facility. Generally, chemical oxidation is more rapid than other treatment technologies. The time scale is usually measured in months, rather than years.

What is the cost of chemical oxidation?

The cost of chemical oxidation depends heavily on the nature of the contaminant being treated. Recycling the oxidant also plays a role in the cost. The Department of Energy estimates that the total cost for direct chemical oxidation using peroxydisulfate (thiosulfate), for example, is \$10.40/kg carbon destroyed, if the oxidant is recycled.

Summary

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 ($KMnO_4$), and ozone (O_3). Chemical oxidants are introduced into a contaminated site using a variety of injection and mixing apparatus.

There are advantages and disadvantages to chemical oxidation processes. Advantages are the range of contaminants that can be treated and chemical oxidation can be rapid in certain situations. The disadvantages include high costs, difficulty control chemical reactions and the oxidation is non-selective.

Sites with contaminant in the vadose zone are applicable for chemical oxidation technology. The contaminants that can be treated range from phenol to halogenated hydrocarbons.

The use of chemical oxidation can be quite safe. However, there are potential hazards including corrosive and highly reactive oxidants. The time to perform chemical oxidation is highly dependent on the contaminant and the oxidant reactivity. Some reactions can be very rapid or they can be slow.

There are several factors affecting the cost of the chemical oxidation process. These include the contaminant being treated and the effectiveness of recycling the oxidant.

Technology Features	Fenton's Reagent	Permanganate	Persulfate	Ozone
Physical State as injected	Liquid	Liquid	Liquid	Gas
Key Oxidant	OH^-	MnO_4^-	SO_4^{2-}	O_3 and OH^-
Oxidation Potential	2.8 V	1.7 V	2.5 V	2.07 V / 2.8 V
By-products	Fe(III), O_2, H_2O	Mn(VI)	Sulfate	Oxygen
Reagent Costs	Moderate	Moderate for $KMnO_4$; High for $NaMnO_4$	Moderate	Moderate
Subsurface Fouling	Possible	Yes, due to MnO_2 formation	No	No

Table 2. Characteristics of common oxidants.
(Adapted from: http://www.insituoxidation.com/pages/833738/)

For more information

Federal Remediation Technologies Roundtable (FRTR) (http://www.frtr.gov/matrix2/section4/4_40a.html)
FRTR was established in 1990 to bring together top federal cleanup program managers and other remediation community representatives to: Share information and learn about technology-related efforts of mutual interest, discuss future directions of the national site remediation programs and their impact on the technology market, interact with similar state and private industry technology development programs, and form partnerships to pursue subjects of mutual interest. For more info on FRTR see http://www.frtr.gov.

Environmental Protection Agency (http://clu-in.org/download/citizens/oxidation.pdf)
The Technology Innovation Program is an EPA program designed to provide information about innovative and site characterization technologies while acting as a forum for all waste remediation stakeholders. CLU-IN (or Clean up Information) Technology focuses on bundling information for particular technologies together so that they may be used in a variety of applications. Information is presented in a variety of categories such as Overview, Guidance, Application, Training, and Additional Resources. For more info on CLU-IN see http://clu-in.org.

Interstate Technology Regulatory Council (http://www.itrcweb.org/ISCO-1.pdf)
ITRC is a state-led coalition consisting of 40 states, the District of Columbia, multiple federal partners, industry participants, and other stakeholders. The coalition works cooperatively with industry and stakeholders to achieve regulatory acceptance of environmental technologies to break down barriers and reduce compliance costs, making it easier to use new technologies, and helping states maximize resources. For more info see http://www.itrcweb.org