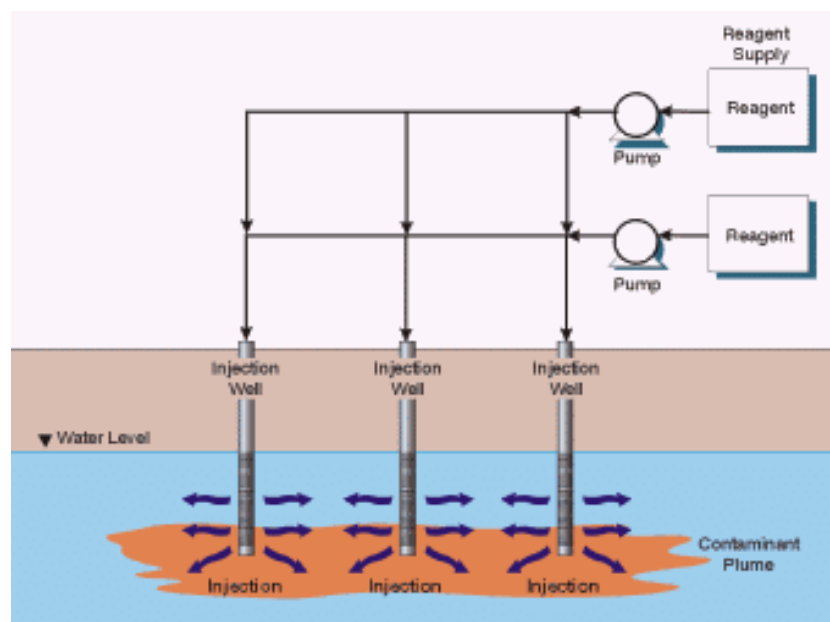


Chemical Oxidation Overview

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Chemical oxidation uses reagents to transform, degrade, or immobilize organic wastes. Chemical oxidizers have been used for decades in the waste-water industry for the treatment of carbon-containing (organic) compounds, such as petroleum hydrocarbons and chlorinated solvents, and numerous other contaminants.

In-Situ Chemical Oxidation (ISCO) relies on the destructive capacity of oxidants to chemically destroy the bonds of the hydrocarbons. Complete chemical oxidation of gasoline would produce carbon dioxide and water. Chemical oxidants work by producing free radicals, such as the hydroxyl radical, which oxidize the gasoline. Several commonly used chemical oxidants have been used for in-situ applications on gasoline and MTBE, including hydrogen peroxide, Fenton's Reagent (hydrogen peroxide with an iron catalyst, frequently performed at a low pH), sodium persulfate and ozone.



In Situ Chemical Oxidation Injection

In Situ Chemical Oxidation (ISCO) remedial process involves injecting an oxidizing agent, such as hydrogen peroxide (H_2O_2), activated sodium persulfate ($Na_2S_2O_8$), or other oxidant into the subsurface to destroy organic compounds. The by-products for complete mineralization of carbon-based compounds by most chemical oxidizers include carbon dioxide (CO_2), water (H_2O), and oxygen (O_2) as well as minor concentrations of nontoxic ions, salts, and acids.

Hydrogen Peroxide and Fenton's Reagent

Hydrogen peroxide (H₂O₂) is one of the most powerful oxidizers known. A stronger oxidizer than chlorine (Cl₂), hydrogen peroxide is also a natural metabolite of many organisms that use oxygen, a byproduct of the decomposition of the low concentration hydrogen peroxide. The autodecomposition can be represented overall as follows: 2H₂O₂ → 2H₂O + O₂. Pure hydrogen peroxide and its aqueous solutions are clear liquids resembling water. Unlike water, hydrogen peroxide has a slightly sharp and distinctive odor. Low concentrations (1% to 3%) of hydrogen peroxide are sold in drug stores as a mild antiseptic. Hydrogen peroxide is available commercially at aqueous concentration as high as 80%.

In the presence of a transition metal such as iron or copper, hydrogen peroxide reacts much more vigorously and aggressively than without the metal (acting as a catalyst). The reaction of iron-catalyzed hydrogen peroxide oxidation is called a "Fenton's Reagent" after its discoverer H.J.H. Fenton in 1894. Even after over 100 years of study and use in water treatment, *in-situ* remediation methods were slow to use Fenton's Reagent, owing to safety concerns. For *in-situ* remediation applications, Leetham et al. (2002), describe gasoline and MTBE destruction using Fenton's Reagent. For *in situ* remedial applications, naturally occurring iron in the soil or fill materials dramatically increases the oxidative strength of hydrogen peroxide. This increase in oxidation power is attributed to the production of hydroxyl radicals (OH•). In addition, a chain reaction is initiated, forming more radicals, which are very reactive and destroy chemical bonds of organic compounds. The iron is not destroyed but rather cycles between the iron(II) and iron(III) oxidation states, yielding the hydroxyl radical and other by-products (Suthersan, 2002). Frequently, when natural concentrations of iron are too low in the field, iron salts such as iron(II) sulfate are added. Iron(III) also improves the oxidizing power of H₂O₂, albeit at a reduced rate. In addition, pH adjustment using a strong acid such as sulfuric acid (H₂SO₄) or hydrochloric acid (HCl), is common since reactions of classic Fenton's Reagent is more rapid and efficient under low pH conditions (pH 2 to 4 is optimal).

Residual hydrogen peroxide not used in the oxidation process breaks down to water and oxygen in a matter of hours. In addition to the much simplified reaction described in Equation 1 there are also a large number of competing reactions including the free radical scavengers, most importantly, carbonate and hydrogen carbonate alkalinity that will greatly affect the overall reaction scheme. After the Fenton's Reagent has been completely depleted, the breakdown products of the spent hydrogen peroxide can serve as an oxygen source for microbes in the subsurface to enhance biodegradation of contaminants.



EQUATION 1

Where,

H₂O₂ = hydrogen peroxide

Fe²⁺ = iron(II) ion

Fe³⁺ = iron(III) ion

OH• = hydroxyl radical

O₂⁻ = peroxide ion

Classic Fenton's Reagent includes the use of a low to moderate concentration of hydrogen peroxide (1% to 30%), with iron addition at a pH of 2 to 4. Classic Fenton's Reagent is exothermic and can increase temperatures of aquifers, as well as produce steam, reaction foam, and generate subsurface pressures in the treatment area capable of moving or cracking paved surfaces when used with hydrogen peroxide in the 10% to 12% concentration range. Any deviation from the classic Fenton's Reagent, referred to as "modified Fenton's Reagent" includes the use of slurried solid peroxides and metallic or organo-metallic chelating catalysts, such as iron(II) EDTA to create a Fenton's Reagent at a neutral (pH 7) or higher pH.

Persulfate with Hydrogen Peroxide

Persulfate oxidation commonly uses sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) catalyzed by a chelated iron complex such as iron(II) EDTA at a neutral pH to produce sulfate radicals ($\text{SO}_4\bullet^-$) that attack most petroleum hydrocarbons and selected chlorinated solvents. Liang et al. (2004) describes persulfate *in situ* remediation. The reaction mechanism (Equation 2) associated with the persulfate ($\text{S}_2\text{O}_8^{2-}$) process is shown as follows:



Where,

$\text{S}_2\text{O}_8^{2-}$ = persulfate ion

$\text{SO}_4\bullet^-$ = sulfate radical

Heat, hydrogen peroxide (H_2O_2), and sodium hydroxide (NaOH) have also been used separately as activators for the persulfate. However, the by-product generated by injecting activated persulfate is long lasting sulfate (SO_4^{2-}). There is a secondary drinking water standard for sulfates of 250 mg/L.

Potassium permanganate (KMnO_4) lasts longer and can react in an environment with much higher pH compared to hydrogen peroxide. Permanganate has been well documented (Siegrist et al., 2001) for destruction of trichloroethene (TCE; C_2HCl_3) and other chlorinated solvents, but it is generally not used for petroleum hydrocarbons or methyl *tertiary*-butyl ether (MTBE) (Jacobs et al. 2000). For field use, potassium permanganate is shipped as a powder and is mixed with water creating a deep purple liquid. The solubility of potassium permanganate is strongly influenced by temperature. At 30° C, the solubility is more than 8%. The pH range is critical in being able to determine whether the oxidation reaction will be fast or slow. Equation 3 summarizes the permanganate reaction:



Ozone (O_3) is a powerful gaseous oxidizer that can be used to treat volatile organic compounds. Ozone is generated on-site because the gas is very difficult to store; therefore all the ozone gas that is generated must be injected into the subsurface or destroyed using an ozone destruction unit on the ozone generator. The ozone gas can be bubbled into closely spaced injection ports that release the bubbles into the aquifer for remediation. The smaller the bubbles, the more surface area and the faster they can travel through small pore spaces. Pumping the ozone gas through specially designed ozone diffusers can produce micro-bubbles. Advanced oxidation

processes refer to when ozone is catalyzed or enhanced by ultraviolet (UV) light, hydrogen peroxide, or other oxidizers, to increase the power of the ozone by producing more hydroxyl radicals. Treatability testing in the laboratory can evaluate the cost benefit of the different ozone enhancements prior to mobilizing into the field. Peroxone, a type of advanced oxidative process (AOP), uses hydrogen peroxide activated ozone to create the hydroxyl and perhydroxyl radicals (Equation 4). Ozone and peroxone can mineralize most petroleum hydrocarbons and chlorinated solvents into water and carbon dioxide.



EQUATION 4

Where,

O_3 = ozone

OH^\bullet = hydroxyl radical

HO_2^\bullet = perhydroxyl radical

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