Treatment of Contaminated Soils and Groundwater using ISCO

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1. Introduction

- The improper disposal of hazardous wastes has resulted in tens of thousands of contaminated sites in the United States and throughout the world.

- Methods for the cleanup of these sites have evolved over the past 25 years; the first approaches focused on the excavation of source areas and the pump-and-treat cleanup of groundwater.

1. Introduction

- Subsequently, bioremediation was the primary remediation process used throughout the 1980s and much of the 1990s.

- Tens of millions of dollars were spent on bioremediation research and many new advances were established in the areas of electron acceptor systems, reductive dehalogenation of chlorinated and fluorinated solvents, and the use of methanothrophs.

1. Introduction

- However, when controlled field experiments were performed at many bioremediation sites in the early 1990s, contaminants at the active bioremediation plots often degraded no faster than control plots.

- As a result, natural attenuation, or allowing the contaminants to degrade without addition of nutrients, terminal electron acceptors, or other active remedial process additions, often became the treatment method of choice.

1. Introduction

- However, monitored natural attenuation has numerous limitations. Years or decades may be required before site closure can be established, and responsible parties are liable until the contaminants are transformed to acceptable levels.

- Numerous other site remediation processes have been used for the saturated and unsaturated zones. Saturated zone technologies include air sparging and permeable reactive barriers, and common technologies for the unsaturated zone include soil vapor extraction and bioventing.

1. Introduction

- Like most remediation technologies, each of these has limitations, which generally fall into two categories:

(1) Reactivity with contaminants of concern

(2) Mass transfer of contaminants from the sorbed phase and dense nonaqueous phase liquids DNAPLs to the medium in which the reactive species exists, usually water.

1. Introduction

- In the 1990s, the first reports were published on in situ chemical oxidation ISCO, specialty companies had been established that offered ISCO services almost exclusively.

- In situ chemical oxidation is the delivery of strong chemical oxidants to the subsurface for the purpose of treating organic contaminants.

1. Introduction

- The first ISCO process that was investigated in laboratory research and developed at full scale was catalyzed H_2O_2 propagations CHP, commonly known as modified Fenton's reagent.

- Shortly following the initial use of Fenton's reagent, ozone sparging and permanganate treatment came into widespread use.

- In just the past few years, interest in another oxidant, persulfate, has provided yet another option for ISCO remediation.

1. Introduction

- Each of these four ISCO processes has advantages and shortcomings related to contaminant reactivity and stability of the oxidant source Table 1.

- Therefore, selection of the most effective process is essential to the success of an ISCO-based site cleanup.

- The purpose of this review is to provide practicing site managers with a synopsis of ISCO process chemistry for a better understanding of these important site remediation processes.

1. Introduction

Table 1. Characteristics of Four ISCO Technologies

Characteristic	CHP	Permanganate	Ozone	Persulfate
Contaminants amenable to treatment	All organic contaminants studied to date, including chlorinated alkenes and alkanes, PCBs, dioxins, PAHs, benzene derivatives	Chlorinated alkenes (e.g., TCE, PCE) Some aromatics with ring activating groups	Similar to CHP, but not thoroughly evaluated	All aromatics and alkenes
Oxidant stability	Low: H_2O_2 lasts hours to days in subsurface	High	Low	High
Reactivity with sorbed compounds	High	Not reported	Not studied	Not studied
Enhanced reactivity with DNAPLs	High	No	Not studied	Not studied

Note: ISCO=in situ chemical oxidation; TCE=trichloroethylene; PCE=perchloroethylene; CHP=catalyzed H_2O_2 propagations; PAH=polyaromatic hydrocarbon; PCB=polychlorinated biphenyl; and DNAPLs=dense nonaqueous phase liquids.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations Chemistry

- The use of modified Fenton's reagent, or catalyzed H_2O_2 propagations CHP, has become increasingly popular for the in situ and ex situ treatment of surface soils and the in situ remediation of the subsurface.

- The process is based on the catalyzed decomposition of hydrogen peroxide by soluble iron, iron chelates, or iron minerals to generate the strong oxidant hydroxyl radical OH· , as well as other reactive oxygen species.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations Chemistry

- CHP is very different from Fenton's reagent, which is a laboratory procedure in which dilute hydrogen peroxide is slowly added to a solution of excess iron II to generate hydroxyl radical (Walling 1975):

$$H_2O_2 + Fe^{2+} \rightarrow OH\cdot + OH^- + Fe^{3+} \quad k = 76\ M^{-1}\ s^{-1} \qquad (1)$$

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations Chemistry

Hydroxyl radical reaction

- The oxidant of interest in CHP has traditionally been hydroxyl radical, one of the strongest oxidants found in nature.

- The most common reactions of hydroxyl radical are electrophilic substitution to aromatic compounds and addition to alkenes.

- Another class of hydroxyl radical reactions is hydrogen abstraction from saturated compounds such as alkanes, a pathway that proceeds at a slower rate relative to electrophilic substitution and addition.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations Chemistry

Hydroxyl radical reaction

- The rate of reaction of hydroxyl radical with an organic compound C is described by the second-order rate expression:

$$-\frac{dC}{dt} = k[\mathrm{C}][\mathrm{OH}\cdot] \qquad (2)$$

- Chemicals that react very rapidly with hydroxyl radical are limited by the rate of diffusion of hydroxyl radical in water, which is $\approx 10^{10}\ M^{-1}\ s^{-1}$, rather than the rate at which it attacks the chemical.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations Chemistry

Hydroxyl radical reaction

- Second-order rate constants for the reactivity of hydroxyl radical with a number of important environmental contaminants are listed in Table 2.

Table 2. Second-Order Rate Constants for the Reactivity of Common Contaminants with Hydroxyl Radical

Compound	$k_{OH}\cdot(M^{-1}\,s^{-1})$
2,4,5-Trichlorophenoxy acetic acid	4.0×10^9
Pentachlorophenol	4.0×10^9
Benzene	7.8×10^9
Toluene	3.0×10^9
Nitrobenzene	2.9×10^9
2,4,6-Trinitrotoluene	4.3×10^8
Polycyclic aromatic hydrocarbons	1.0×10^{10}
Carbon tetrachloride	$<2\times10^6$
Chloroform	$\approx5\times10^6$
Tetrachloroethylene (PCE)	2.8×10^9
Trichloroethylene (TCE)	4.0×10^9
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)	4.0×10^9
Methyl tert-butyl ether (MTBE)	$(3.9\pm0.73)\times10^9$

Note: Sources are Chang and Young (2000); Haag and Yao (1992); and Schmelling et al. (1998).

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations Chemistry

Hydroxyl radical reaction

- Some general rules have been established for the reactivity of hydroxyl radical with organic contaminants. Rate constants $>10^9$ $M^{-1}s^{-1}$ are considered high enough to be effective for ISCO treatments, while rate constants $<10^8$ $M^{-1}s^{-1}$ are considered too low to be effective.

- The data of Table 2 show that almost all aromatic compounds, even those with a high degree of halogenation, react rapidly with hydroxyl radical.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations Chemistry

Hydroxyl radical reaction

- Chlorinated alkenes, such as trichloroethylene TCE and perchloroethylene PCE, also react rapidly.

- In contrast, alkanes exhibit relatively low reactivity with hydroxyl radical; in particular, chlorinated and fluorinated alkanes such as carbon tetrachloride, chloroform, hexachloroethane, and freons (e.g., 1,1,2-trichloro-2,2,1-trifluoroethane), are effectively nonreactive.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations Chemistry

Non-Hydroxyl radical Species

- With the high concentrations of hydrogen peroxide used for CHP ISCO (i.e., 2–20% [0.6–3.6 M]), hydroxyl radical generated in the Fenton's initiation reaction [Eq. 1] reacts with hydrogen peroxide to promote a series of propagation reactions:

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations Chemistry

Non-Hydroxyl radical Species

$$OH\cdot + H_2O_2 \rightarrow HO_2\cdot + H_2O \quad k = 2.7 \times 10^7\ M^{-1}\ s^{-1} \qquad (3)$$

$$HO_2\cdot \leftrightarrow O_2\cdot^- + H^+ \quad pK_a = 4.8 \qquad (4)$$

$$R\cdot + H_2O_2 \rightarrow ROH + OH\cdot \quad k = 10^6 - 10^8\ M^{-1}\ s^{-1} \qquad (5)$$

$$HO_2\cdot + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \quad k = 1.2 \times 10^6\ M^{-1}\ s^{-1} \qquad (6)$$

- Although the rate constant for reaction 3 is relatively low, these reactions become important when the concentration of hydrogen peroxide is high (e.g., 1%).

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations Chemistry

Non-Hydroxyl radical Species

- Therefore, the rates of generation of perhydroxyl radical (HO_2 ·) , superoxide radical anion (O_2·$^-$), and hydroperoxide anion (HO_2^-) become significantly greater at higher hydrogen peroxide concentrations.
  - Perhydroxyl radical: weak oxidant
  - Superoxide: weak reductant and nucleophile in aqueous systems
  - Hydroperoxide anion: a strong nucleophile

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations Chemistry

Non-Hydroxyl radical Species

- CHP reactions that generate hydroxyl radicals, superoxide, and hydroperoxide provide a mixture of oxidants, reductants, and nucleophiles that can degrade almost all organic contaminants.

- For example, carbon tetrachloride and hexachloroethane, which are unreactive with hydroxyl radical, are rapidly degraded in CHP systems through reactions with superoxide in the presence of sufficient hydrogen peroxide to provide a solvent effect.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations In Situ Chemical Oxidation

- Some of the important process parameters for CHP ISCO include the nature of the catalyst, the pH, and the hydrogen peroxide concentration. Soluble iron and iron chelates have been added as CHP.

- In addition, the iron oxide minerals naturally present in the subsurface serve as effective CHP catalysts.

- Soluble iron and iron minerals are most effective at acidic pH, and iron chelates are also effective at neutral pH regimes.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations In Situ Chemical Oxidation

- The pH of CHP systems is a very important process parameter. If iron minerals are used as the CHP catalyst, the pH must be maintained at less than 4.0.

- Reactions 1–5 are sensitive to oxidation-reduction conditions, and the acidic pH regime provides suitable redox conditions; in addition, the acidic conditions aid in maintaining soluble iron in solution.

- If iron chelates are used, the reactions can be conducted at neutral pH regimes.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations In Situ Chemical Oxidation

- Hydrogen peroxide concentrations in the 2–12% (0.6–3.6 M) range are typically used for ISCO applications, and the common practice in the field has been to increase the concentration of hydrogen peroxide when treatment has been unsuccessful.

- This practice often enhances treatment effectiveness, in part because the high hydrogen peroxide concentration provides a pool of the oxidant source.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations In Situ Chemical Oxidation

- More importantly, however, high hydrogen peroxide concentrations (>1% [0.3 M]) also promote propagation reactions that form reactive oxygen species other than hydroxyl radicals, such as perhydroxyl radicals, superoxide radical anions, and hydroperoxide anions, which have a significant role in CHP remediation.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations In Situ Chemical Oxidation

Enhanced Treatment of Sorbed Contaminants and Dense Nonapueous Phase Liquids

- A distinct advantage of CHP over other ISCO processes is the documented enhanced treatment of sorbed contaminants and DNAPLs.

- These contaminants are problematic because almost all reactants used in soil and groundwater remediation e.g., bacteria, hydroxyl radical, reductants exist in the aqueous phase.

- Therefore, sorbed contaminants must desorb or dissolve into the aqueous phase before transformation can occur.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations In Situ Chemical Oxidation

- As the contaminants are degraded in the aqueous phase, a concentration gradient increases between the sorbed phase and the aqueous phase, driving subsequent desorption or dissolution.

- Such treatment is referred to as desorption- or dissolution-limited, and can require years or even decades for site cleanup.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations In Situ Chemical Oxidation

- However, CHP has the potential to treat sorbed contaminants and DNAPLs significantly more rapidly than the rate of desorption or dissolution.

- In some cases, the rate of sorbed contaminant or DNAPL destruction can be up to 100 times faster than the rate of desorption- or dissolution-limited treatment.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations In Situ Chemical Oxidation

- For example, Watts and Stanton 1999 showed that hexadecane sorbed to a silty loam soil was treated to 90% in 24 h, although no measurable desorption occurred in control reactions over 5 days.

- These results have also been seen in the field; rapid treatment of sorbed contaminants and DNAPLs has been demonstrated in numerous field studies

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations In Situ Chemical Oxidation

Hydrogen Peroxide Stability

- Although CHP is a universal treatment system that degrades any organic contaminant studied to date, it is characterized by a significant shortcoming: high rates of hydrogen peroxide decomposition in surface soils and the subsurface.

- The half-life of hydrogen peroxide varies substantially in ISCO applications, ranging from a few hours to 10 days at its uppermost limit.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations In Situ Chemical Oxidation

Hydrogen Peroxide Stability

- Soil organic matter SOM may affect hydrogen peroxide stability; however, the reactions between SOM and hydrogen peroxide are complex and not well studied.

- SOM is destroyed by hydrogen peroxide; however, SOM does not appear to have a significant effect on hydroxyl radical activity.

2. Modified Fenton's Reagent (Catalyzed H_2O_2 Propagation)

Catalyzed H_2O_2 Propagations In Situ Chemical Oxidation

Hydrogen Peroxide Stability

- Therefore, hydrogen peroxide stability is the primary factor that determines well spacing at CHP treatment sites.

- The rate of hydrogen peroxide decomposition should be used in conjunction with the pore water velocity to determine the radius of influence for injection wells. If the hydrogen peroxide decomposition rate is slow, well centers are typically 25–30 feet (7.6–9.1 m); rapid hydrogen peroxide decomposition dictates injection wells on 5–10 foot (1.5–3.0 m) centers.

3. Permanganate

Permanganate Chemistry

- Permanganate has become a popular ISCO reagent in the past ten years, and is often the oxidant of choice for groundwater contaminated with TCE or PCE.

- Permanganate MnO_4^- is a highly oxidized form of manganese, Mn (VII), that serves as a selective chemical oxidant. It can be purchased as the salt of a number of cations, but the most commonly used for ISCO are potassium permanganate and sodium permanganate.

3. Permanganate

Permanganate Chemistry

- Potassium permanganate is a crystalline solid that contains other salts and trace quantities of heavy metals (e.g., chromium, copper, and zinc) and is usually dissolved in water prior to use.

- Sodium permanganate is available as a 40% wt/wt liquid, and does not contain as many heavy metal impurities as potassium permanganate.

3. Permanganate

Permanganate Chemistry

- The water solubility of permanganate is dictated by its associated cation and by the water temperature.

- Because of the low water temperatures that may exist in the subsurface, the maximum permanganate concentration used is in the range of 20–40 g/L.

- The rate of potassium permanganate dissolution in water is a function of temperature, size of the $KMnO_4$ crystals, the extent of agitation, and the final concentration.

3. Permanganate

Permanganate Chemistry

- The thermodynamically stable form of manganese in water is manganese oxide MnO_2, not permanganate.

- As a result, when permanganate is reduced in water during its oxidation of organic substrates, solid manganese dioxide is formed, which then catalyzes the subsequent reduction of more permanganate.

3. Permanganate

Permanganate Chemistry

- However, the rate of permanganate reduction in water in the absence of oxidizable organics is relatively slow. In addition, permanganate solutions are most stable at neutral pH, and the rate of reduction increases above a pH of 10 and below a pH of 3.

3. Permanganate

Permanganate Chemistry

- Potassium permanganate has been used in a range of industrial and environmental applications. The mechanism of permanganate oxidation is often dictated by the pH of the reaction medium.

- The most common reaction pathway for environmental applications pH of 3.5–12 is a three-electron transfer with subsequent formation of manganese dioxide.

3. Permanganate

Permanganate Chemistry

- In the presence of organic compounds susceptible to oxidation, the three electrons are transferred from the organic contaminant.

- For example, the oxidation of chlorinated alkene solvents (e.g., TCE and PCE) is based on the well-established alkene-permanganate reaction in which permanganate adds to the C=C double bond to form a cyclic hypomanganate (V) ester intermediate.

3. Permanganate

Permanganate Chemistry

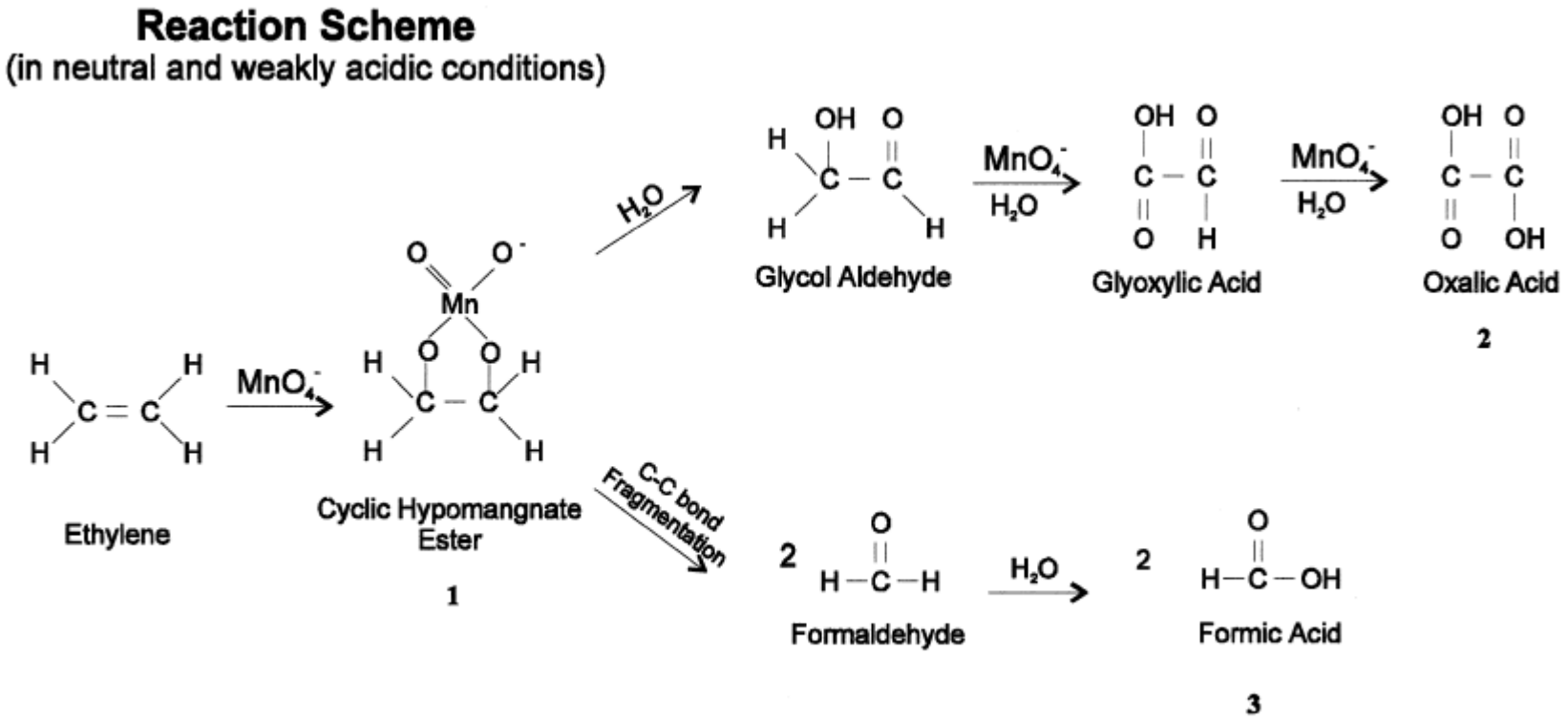


Fig. 1. Reaction scheme. The oxidation of ethylene in a neutral to weak acidic condition.

3. Permanganate

Permanganate Chemistry

- Reactions that follow include oxidation at low pH to form a cyclic hypomanganate (VI) ester with subsequent degradation to carbonyl compounds and the reduction of Mn (VII) to MnO_2 or Mn (III).

3. Permanganate

Permanganate In Situ Chemical Oxidation

- Because permanganate is highly reactive with alkenes, the most common use of permanganate for ISCO is for the oxidation of chlorinated ethenes, such as TCE and PCE; it is also effective in oxidizing the dichloroethylene (DCE) isomers (e.g., 1,2-cis-DCE and 1,2-trans-DCE), vinyl chloride, phenols, and some polyaromatic hydrocarbons (PAHs) (e.g., naphthalene and phenanthrene).

3. Permanganate

Permanganate In Situ Chemical Oxidation

- However, permanganate is ineffective in oxidizing chloroalkanes (e.g., TCA), benzene, and other aromatic compounds with a low degree of ring activation (e.g., chlorinated aromatics).

- The associated cation of permanganate potassium or sodium does not significantly influence the rate and mechanism of permanganate oxidation, but the permanganate concentration does.

3. Permanganate

Permanganate In Situ Chemical Oxidation

- For example, in the oxidation of 480 mg/L TCE, almost no TCE oxidation occurred with 8.7 mg/L of permanganate; however, degradation to undetectable concentrations occurred over 1800 min with 1,300 mg/L permanganate, and over 100 min with 8,740 mg/L permanganate.

- Although increasing the permanganate dose can increase the rate of contaminant oxidation, increasing the permanganate dose far in excess of what is needed for contaminant oxidation may be counterproductive: The rate of permanganate reduction will also be increased, possibly due to decomposition of the permanganate by MnO_2 solids.

3. Permanganate

Permanganate In Situ Chemical Oxidation

Natural Oxidant Demand

- Consumption of permanganate in ISCO is not only related to the oxidation of contaminants of concern (CoCs) and reduction by MnO_2 particles; permanganate is also rapidly consumed by NOM and reduced organic and inorganic species, which compete with CoCs for permanganate and are referred to as the natural oxidant demand NOD.

- The presence of reduced compounds can increase the required oxidant dose and alter the kinetics and extent of treatment.

3. Permanganate

Permanganate In Situ Chemical Oxidation

Natural Oxidant Demand

- If [MnO_4^-]>>[TCE]+[NOD], both demands are satisfied; however, if [MnO_4^-]<[TCE]+[NOD], treatment will not be complete.
- Oxidant dosage requirements resulting from NOD range from 2–100 mg MnO_4^- /mg total organic carbon.
- However, dosage requirements are highly variable and not easily predictable; therefore, treatability studies are usually required to assess the extent of NOD and its potential effect on permanganate remediation processes.

4. Ozone

Ozone Chemistry

- Although ozone-based treatment has the potential to provide rapid treatment of contaminated soils and groundwater, its use lags behind that of CHP and permanganate.

- Ozone has traditionally been used alone or with hydrogen peroxide or hydroxide ions, which increases the hydroxyl radical formation rate and dissociates some contaminants (i.e., phenols) into their ionic forms, which are usually more readily oxidized.

4. Ozone

Ozone Chemistry

- Two mechanisms are involved in the ozone treatment of organic contaminants. Ozone can oxidize some compounds directly, usually via the attack of O3 on unsaturated carbon-carbon bonds to form an ozonide intermediate.

- Other compounds are oxidized only by hydroxyl radicals Table 2, which are formed through initiation reactions, such as the reaction of ozone with hydroxide ion or hydrogen peroxide Hoigne and Bader 1976; Beltran 2003:

4. Ozone

Ozone Chemistry

$$O_3 + OH^- \rightarrow O_2^{\cdot -} + HO_2^{\cdot} \quad (7)$$

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \quad (8)$$

$$O_3 + HO_2^- \rightarrow OH^{\cdot} + O_2^{\cdot -} + O_2 \quad (9)$$

- In soils and groundwater some transition metals may also act as initiators. Hydroxyl radical generation during ozone-based ISCO processes may be promoted by soil constituents such as soil organic matter, carboxylic acids, and some alcohols, but may be inhibited by other common constituents such as carbonates and tertiary alcohols.

4. Ozone

Ozone In Situ Chemical Oxidation

- Ozone has been shown to be an effective ISCO process Nelson and Brown 1994, and has been shown to be transported within soil matrices.

- Although ozone is used as the primary oxidant in some processes, such as water and wastewater disinfection, ISCO applications generally rely on the use of ozone as an advanced oxidation process, acting primarily through hydroxyl radical-mediated oxidations.

4. Ozone

Ozone In Situ Chemical Oxidation

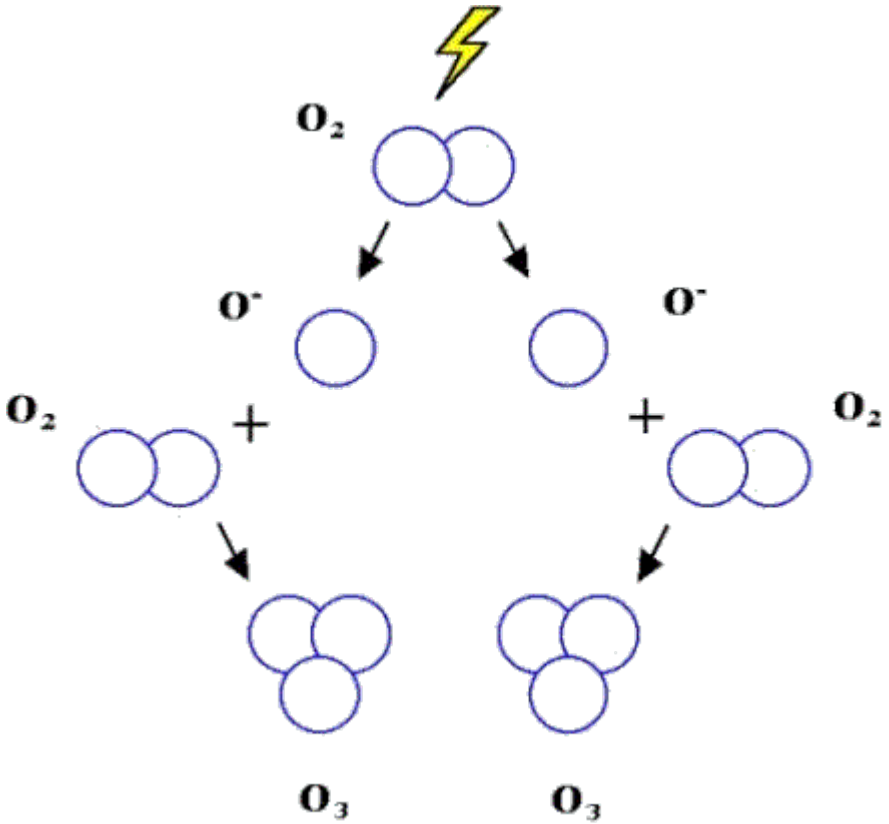
Equipment

- A corona discharge generator is typically used to generate ozone on-site for ISCO processes.

- Oxygen or dry air is passed between two tube electrodes with opposite charges, yielding ozone at 2–5% from dry air or 4–10% from pure oxygen by weight.

4. Ozone

Ozone In Situ Chemical Oxidation



- Principle of Corona discharge ozone generator

4. Ozone

Ozone In Situ Chemical Oxidation

Ozone Delivery

- The solubility of ozone is typically 5–30 mg/L in clean water, and is affected by the nature of the carrier gas and characteristics of the water.

- Ozonation differs from other ISCO reagents in that the oxidant source is present in the gas phase and must be transferred into the aqueous phase. Furthermore, it is present at only 2–10% in the gas phase, increasing the mass transfer problem.

4. Ozone

Ozone In Situ Chemical Oxidation

Scavenging

- Both ozone and hydroxyl radical are nonselective oxidants.

- They react with many soil and subsurface constituents, including organic carbon and metals, such as iron and manganese, carbonates, hydrogen sulfide, and bacteria.

5. Persulfate

Persulfate Chemistry

- Persulfate peroxydisulfate is the newest chemical oxidant to be used for ISCO, having received attention over just the past few years.

- Persulfate is a sulfate peroxide with the structure:

$$[O_3S - O - O - SO_3]^{2-}$$

5. Persulfate

Persulfate Chemistry

- Persulfate has been used in a number of industrial applications.

- It is used as an initiator for olefin polymerization, the manufacture of polyacrylonitrile, and the emulsion polymerization of vinyl chloride, styrene-butadiene, vinyl acetate, and acrylic esters.

- Perhaps the most common use of persulfate is in the total organic carbon TOC analysis of water.

5. Persulfate

Persulfate Chemistry

- Commercial instruments employ ultraviolet UV-catalyzed or heat-induced persulfate oxidation to promote the conversion of most organic compounds to carbon dioxide.
- Similar to the decomposition of hydrogen peroxide by CHP reactions, various initiators transform persulfate into radical species.
- The auto decomposition of persulfate is slow at temperatures 20°C and initiators, such as heat and UV light, are usually involved in its decomposition.

5. Persulfate

Persulfate Chemistry

- Transition metals, which are important in soil and groundwater systems, also initiate the decomposition of persulfate through a one-electron transfer reaction analogous to the Fenton initiation reaction. Initiation reactions result in the formation of sulfate radicals:

$$S_2O_8^{2} + Fe^{2+} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + Fe^{3+} \qquad (10)$$

- In addition, hydroxyl radicals OH· are generated during persulfate propagation reactions:

$$SO_4^{\cdot -} + H_2O \rightarrow OH\cdot + HSO_4^{-} \qquad (11)$$

5. Persulfate

Persulfate Chemistry

- Sulfate radicals and hydroxyl radicals are strong oxidants that can potentially oxidize many common groundwater contaminants.
- Sulfate radical, like hydroxyl radical, is a strong oxidant, with E=2.6 V.
- It oxidizes organic contaminants through three mechanisms:

(1) hydrogen abstraction

(2) addition and substitution reactions with alkenes and aromatic compounds

(3) electron transfer from carboxylate groups.

5. Persulfate

Persulfate In Situ Chemical Oxidation

- Although persulfate has been employed extensively for many industrial applications and some environmental applications, the use of persulfate for soil and groundwater remediation has received minimal attention.

- However, the use of persulfate as an agent for ISCO appears to have advantages; for example, unlike hydrogen peroxide, it has the potential for migrating tens of meters downgradient from the point of injection.

- Bench-, pilot-, and full-scale applications of persulfate remediation have recently been described.

Thank you !!!