

# **TECO Networking Conference**

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**In situ chemical oxidation (ISCO)**  
**technology for remediation of pesticide**  
**contaminated soil and groundwater**



**TECO Project**

*Technological Eco-Innovations for the Quality Control  
and the Decontamination of Polluted Waters and Soils*

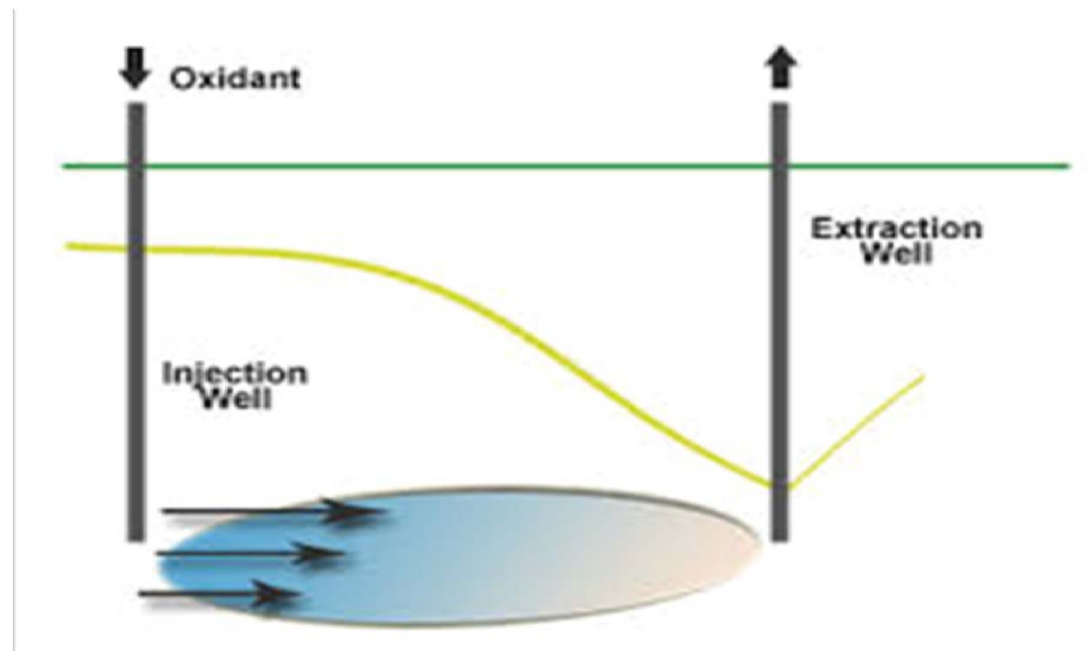
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## **In-situ Chemical Oxidation (ISCO) remediation**

- **Chemical Oxidation uses chemicals called “Oxidants” to help in change harmful contaminants in to less toxic ones.**
- **A technique whereby an oxidant is introduced into the subsurface to chemically oxidize organic contaminants changing them to harmless substances.**



**Fig. 1 Schematic diagram of In-situ Chemical Oxidation (ISCO) Remediation**

## **ISCO remediation**

- **Rapidly emerging technology**
- **Still subject of academic research as well as applied routinely as a commercialized process**
- **Several options for selection of oxidant chemicals**
- **Requires good understanding of contaminant and site characteristics to ensure effective treatment**

**ISCO technology is most often deployed in source zones characterized by**

- **moderate to high contaminant concentrations in groundwater,**
- **significant sorbed contamination,**
- **the potential presence of residual, separate-phase contamination.**

**e.g. LNAPL or DNAPL droplets or ribbons**

## ISCO Process:

- ❖ In situ chemical oxidation (ISCO) involves the **injection** or **direct mixing** of reactive chemical oxidants into groundwater and soil for the primary purpose of rapid and complete contaminant destruction.

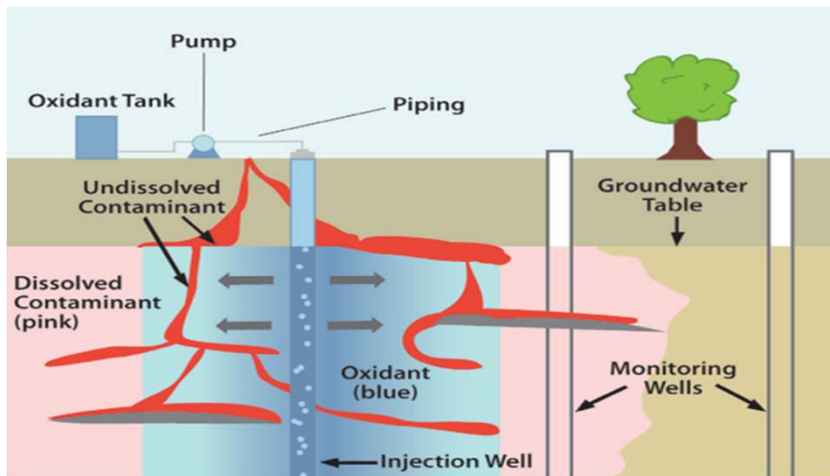


Fig.2 Injection of Oxidant



Fig. 3 Direct mixing of Oxidant

## When is ISCO Applicable

- Organic Contaminants
  - PAHs, Pesticides, Chlorinated Solvents, Petroleum Hydrocarbons, others
- Some Contaminants Require More Aggressive Oxidant Chemicals
- Screening Level Evaluation Needed to Assess Site Feasibility and Appropriate Oxidant Chemicals.

# The most common oxidants used in the ISCO processes are:

## ▶ Permanganate

- Potassium permanganate ( $\text{KMnO}_4$ )
  - Crystalline solid
- Sodium permanganate ( $\text{NaMnO}_4$ )
  - Concentrated liquid

## ▶ Ozone

- $\text{O}_3$  (gas)

## ▶ Peroxide (Fenton's Reagent)

- $\text{H}_2\text{O}_2$  and ferrous iron react to produce radicals
- More accurately catalyzed peroxide propagation (i.e., modified Fenton's reagent)

## Emerging Oxidants

### Persulfate

- ▶ Sodium persulfate - most commonly used
- ▶ Potassium persulfate - very low solubility
- ▶ Persulfate anions ( $S_2O_8^{2-}$ ) dissociate in water
- ▶ Oxidative strength greatly increased with addition of heat or a ferrous salt (Iron II)
  - Attributed to production of sulfate free radical ( $SO_4^{-\bullet}$ )

### Other oxidants – solid peroxides

- ▶ Magnesium peroxide ( $MgO_2$ )
- ▶ Calcium peroxide ( $CaO_2$ )
- ▶ Sodium percarbonate ( $Na_2CO_3 \cdot 3H_2O_2$ )



- **Persulfate is an increasingly popular ISCO reagent because it is significantly more stable than hydrogen peroxide, providing the potential for transport from the point of injection to contaminants in lower permeability regions of the subsurface.**

► Chain Initiation Reactions (Me is a metal ion; R is an organic compound):



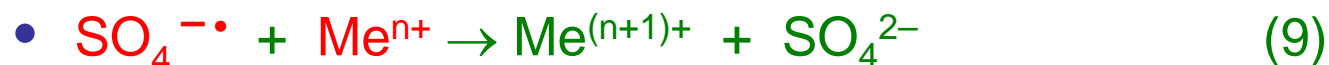
**Catalyzed Persulfate:**



► Chain Propagation Reactions:



► Chain Termination Reactions (excess metal/catalyst):



- Remediation of pesticide contamination is of significant interest at both **manufacturing and application sites** due to their toxicity and regulatory limits in water and soil.
- Organochlorine pesticides (OCPs) are the important group of pesticides concern due to their ***persistent nature*** and adverse effect on natural environment and human health.
- Although the *ban and restriction on use* of these pesticides in developed countries, still using them **for agricultural and public health purposes** due to their low cost and versatility in controlling various insects (Tanabe 1994).
- For instance, it is evident from investigations carried out in India at various locations and found their **occurrence of OCPs in groundwater** (Shukla 2006; Sivasankaran 2007), **soil, and air** (Pillai 1986).

## Literature review on pesticide remediation

Many technologies for pesticide treatment and/or removal have been reported that include: **adsorption, filters, biological treatment, and advanced oxidation processes.**

- A triolein-embedded composite **adsorbent** has been used for selective removal of organochlorine pesticides such as aldrin, heptachlor epoxide, dieldrin and Endrin (Ru 2007).
- Solar **photocatalytic degradation** of aldrin in aqueous systems was reported (Bandala 2002) using titanium dioxide (TiO<sub>2</sub>) which is mostly suitable for the surface and wastewater treatment.

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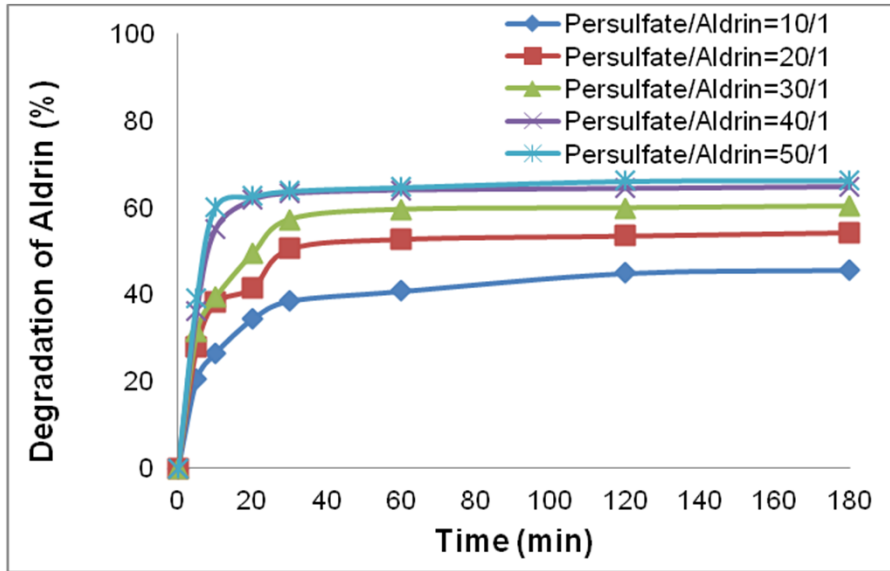
## Literature review Continued.....

- **Advance oxidation process (AOPs)** such as Fenton, UV/Fenton, UV/H<sub>2</sub>O<sub>2</sub>, UV/Fe<sup>2+</sup> systems have been applied for degradation of aldrin adsorbed on activated carbon (Kusvuran 2004).
- However, AOPs showed less degradation due to the phenyl group in the activated carbons reacted with OH· radicals.
- Consequently, cost-effective and reliable remediation of pesticide contaminated aquifer systems is continuous to be sought ***to provide eco-friendly technological solutions.***
- It has been observed that **chemical oxidation** is a promising method for *in situ* degradation and removal of *chlorinated pesticides.*

# ISCO remediation of Organochlorine Pesticides – OCPs e.g. Aldrin

- Aldrin is a priority toxic pollutant and has been found in at least 207 of 1613 of the most serious hazardous waste sites recognized by USEPA on the National Priorities List (ASTDR 2002).
- It is also included in the list of Persistent Organic Pollutants (POPs) during the United Nations Environment Program (UNEP) Stockholm Convention on POPs ([www.pops.int](http://www.pops.int)).
- Aldrin should not increase the concentration of 0.03  $\mu\text{g/L}$  in drinking water as per the WHO (2003) guide line values.
- In view of its widespread occurrence in surface, ground water and regulatory drinking water guidelines has motivated interest to find environmental friendly solutions for the treatment and/or remediation of aldrin residues from contaminated aquifers.

# Degradation of Aldrin aqueous solutions (with or without Activator)



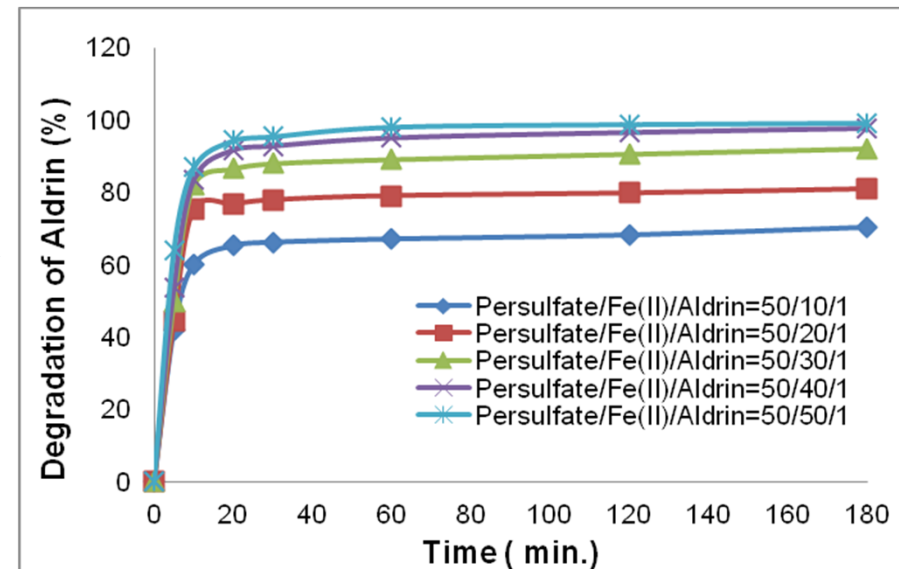
**Fig. 4** Effect of persulfate on aldrin degradation.  
 $[Aldrin]_0 = 0.001 \mu M$ ;  $[PS]_0 = 0.01 \sim 0.05 \mu M$ ;  
 initial  $pH = 6.5$ ; reaction time = 180 min.



This study demonstrated that aldrin degradation occurring almost instantaneously and then very slowly increased

**Fig. 5** Effect of initial  $Fe^{2+}$  dosage on aldrin degradation during ferrous ion activated persulfate oxidation.

$[Aldrin]_0 = 0.001 \mu M$ ;  $[PS]_0 = 0.05 \mu M$ ;  
 $[Fe^{2+}]_0 = 0.01 \sim 0.05 \mu M$ ; initial  $pH = 6.5$ ;  
 reaction time = 180 min



## Effect of oxidant and activator concentration

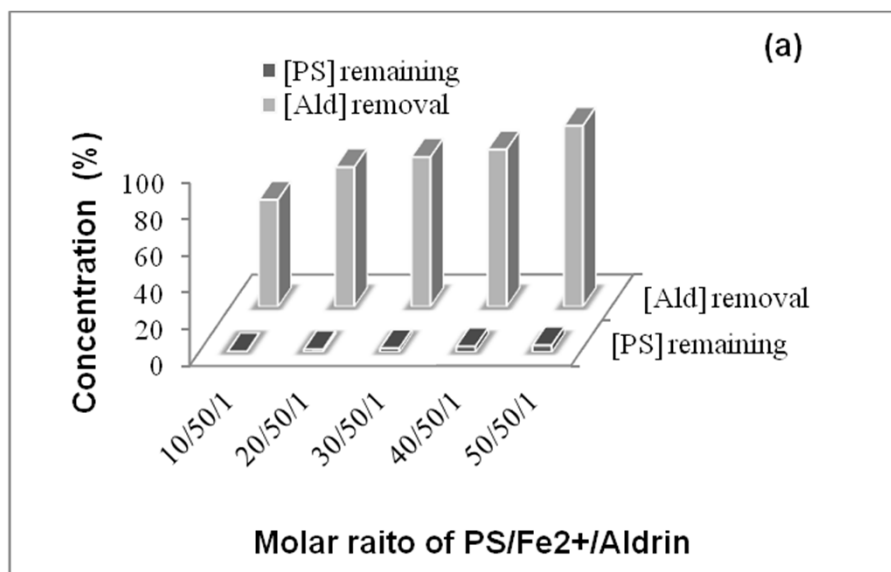
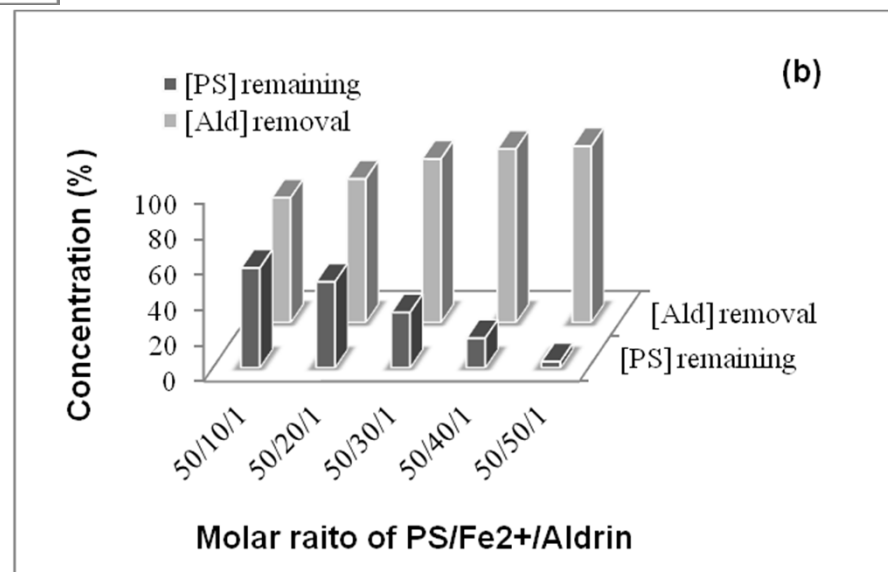


Fig.6 Aldrin removal and persulfate remaining in the ferrous ion activated oxidation system.

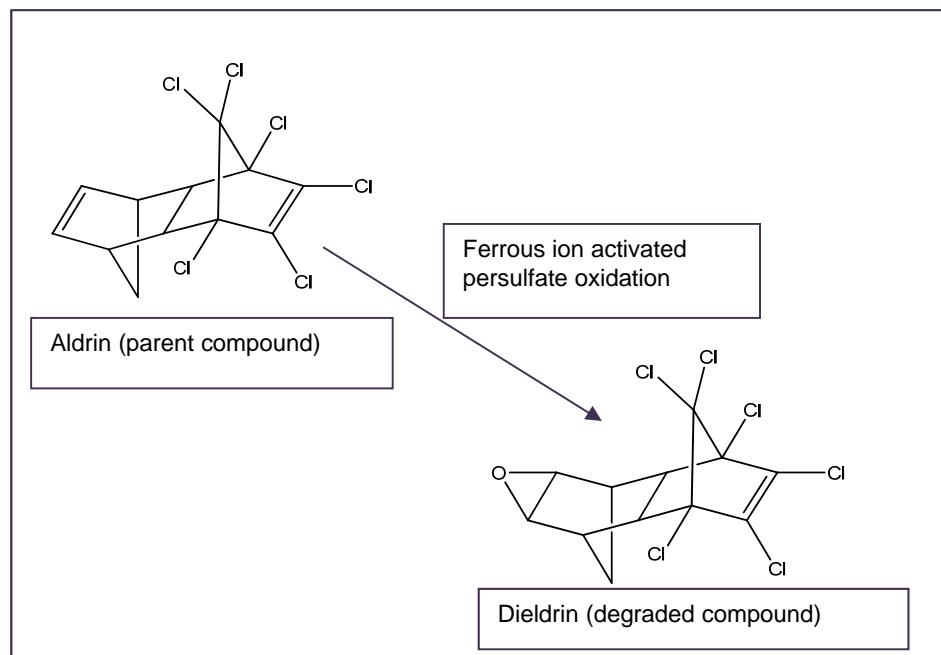
**Increase of persulfate concentration**  $[PS]_0 = 0.01 \sim 0.05 \mu\text{M}$ ;  
 $[Fe^{2+}]_0 = 0.05 \mu\text{M}$ ; initial  $pH = 6.5$ ; reaction time = 180 min.

Persulfate decomposed gradually with increase of  $Fe^{2+}$  content. Typically it is assumed that increase of  $Fe^{2+}$  concentration should produce more sulfate radicals, thereby increases aldrin degradation.



**Increase of ferrous ion concentration**  $[PS]_0 = 0.05 \mu\text{M}$ ;  $[Fe^{2+}]_0 = 0.01 \sim 0.05 \mu\text{M}$ ; initial  $pH = 6.5$ ; reaction time = 180 min.





In biological systems of soils, plants, and animals, aldrin converts rapidly to **dieldrin** by microsomal oxidation (epoxidation) reaction (ASTDR 2002; Lichtenstein 1959). Further, it is conceptualized that dieldrin may further degrade to **photodieldrin, diol and keto forms, monodechlorodieldrin** compounds (Bandala 2006).

In this study, along with the parent compound (i.e. aldrin) its degradation compound, dieldrin is identified through GC-MS spectral comparison.

Even though only one degraded product (dieldrin) is identified in this work, which is more toxic than the parent compound (aldrin).

The dehalogenated products as reported in various biological systems may not formed in this work.

This might be expected due to the **instantaneous degradation** of aldrin with ferrous ion activated persulfate oxidation process.

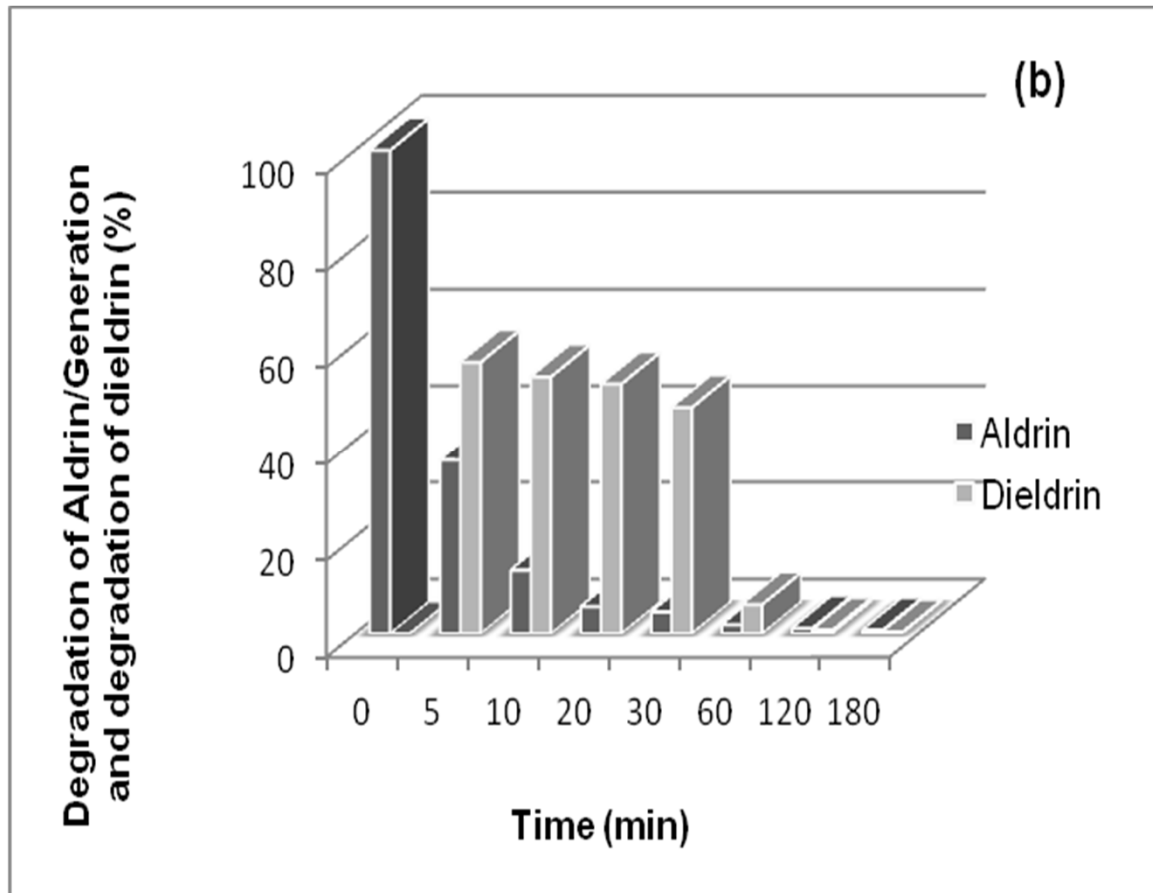


Fig. 8 Degradation of aldrin, and formation of degraded product (dieldrin) and its degradation

## *Advantages and Disadvantages of ISCO*

### ★ **Advantages**

- Fast Treatment (weeks to months)
- Temporary Facilities
- Treatment to Low Levels (ND in some cases)
- Effective on Some Hard-to-Treat Compounds

### ★ **Disadvantages**

- Requires Spending “Today’s” Money to Get Fast Cleanup
- Involves Handling Powerful Oxidants, and Carries Special Safety Requirements

# **Combination System Strategies:**

**ISCO with ISCO**

**ISCO with Mass Transfer Technologies**

**Bio with ISCO**

# ISCO with ISCO

- ▶ Multiple ISCO technologies are sometimes used in concurrent or sequential fashion to take advantages of the unique properties of each
- ▶ Sequential example
  - Permanganate following persulfate or peroxide
- ▶ Concurrent example
  - Persulfate with hydrogen peroxide
    - Peroxide reduces soil oxidant demand (SOD)
    - Multi-radical attack
    - Peroxide desorbs and dissolves mass/persulfate is persistent

## ISCO with Mass Transfer Technologies

- ▶ Mass transfer technologies limited in their effectiveness because they must rely on the natural flow and inefficient desorption of the contaminants of concern from the soil
- ▶ ISCO enhances mass transfer from soil to groundwater by breaking down natural organic matter (NOM) (and sorption sites) and increasing temperature (peroxide co-addition)

## Bio with ISCO

- ▶ Usually **microorganisms are inactive** / dormant **before remediation** due to toxic concentrations
- ▶ ISCO reduces toxicity and supplies essential chemicals (e.g., O<sub>2</sub> for aerobic microbes)
- ▶ Rebound in microbial populations increases biodegradation of organic contaminants/byproducts
- ▶ ***It is very difficult to render a site biologically inactive.*** Even those with anaerobic bacteria

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