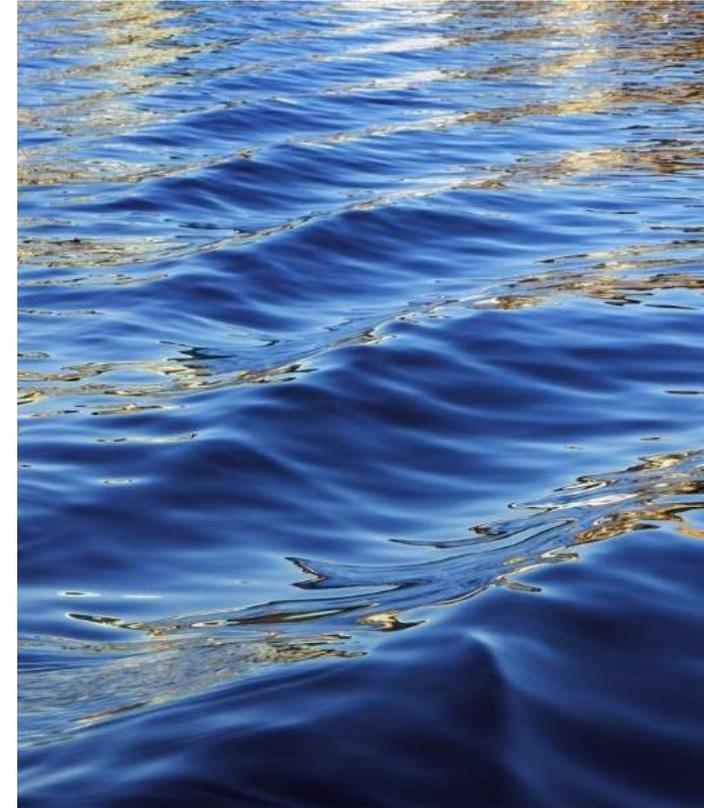




In-Situ Chemical Oxidation

DOUG HAMILTON, PRINCIPAL HYDROGEOLOGIST
ACV ENVIRO



Who am I (or where did I come from)?

- BS-Geology, BA-Geography Water Resources, MS-Geochemistry
- Handex – mid-1980's to 1990 – hey day of environmental assessment and remediation
- TPH Technology – 1990 to 2007 – started my own environmental consulting/contracting company. By mid-1990's, smaller companies were being gobbled up by large consulting firms, major oil and industrial companies were selecting national account holders rather than smaller regionally-selective consultants. Sink or swim, TPH transitioned into TPH Industries and began supplying industrial services, as well as continuing traditional assessment/remediation services. Ultimately, we sold by mid-2000's to Clean Venture.
- Clean Venture – 2007 to 2017 – was a leading industrial maintenance and waste management company serving Mid-Atlantic region since early 1990's. By 2017, the owner wanted to retire and sold company.
- ACV Enviro – 2017 to present.



What have I done?

- 30+ years in environmental assessment and remediation, construction dewatering, waste management and industrial reclamation.
- > 1000 soil and groundwater remediation systems.
- > 2000 site assessments and Remedial Investigations/Feasibility Studies (RI/FS, or pilot test).
- > 200 dewatering projects with flows > 2000 gpm – many with water treatment requirements
- > 800 remediation programs from Atlanta, GA to Wapakoneta, OH to Cheektowaga, NY to Boston, MA. Most in Maryland, District of Columbia, Delaware, Virginia, Pennsylvania & NJ.
- All Kinds of Chemicals
 - Petrochemicals – gasoline, fuel oils, jet fuels, LNAPLs (stuff that floats on water)
 - Chlorinated Solvents – dry cleaner solvents, PCE, TCE, DCE, Methylene Chloride, DNAPLs (stuff that sinks in water)
 - Heavy Metals including Hexavalent Chromium, Cadmium, Arsenic, Mercury, Lead, Copper and Zinc
- All Kinds of Environments
 - Fractured bedrock environments
 - Stratified sand and clay environments
 - Glacial till and glacial washout environments
 - Military, industrial, urban, suburban and rural locations
- All Kinds of Clients



What is ISCO?

- ISCO is the injection of liquid or gas into the subsurface that causes oxidation and can result in the direct destruction of an organic contaminant.
- This process can also result in the indirect decrease of organic contamination by increasing the dissolved oxygen in the groundwater, which enhances biodegradation.
- Oxidation = chemical reaction characterized by the loss of one or more electrons from an atom or molecule.
- When an atom (or molecule) combines with oxygen, it tends to give up electrons to the oxygen in forming a chemical bond.
- Carbon (in the form of organic carbon) and manufactured hydrocarbons are common substances readily oxidized.



Why ISCO?

- Despite nearly **four decades of effort**, contamination of groundwater with organic pollutants remains a significant threat to drinking water supplies, as well as cause potential impacts to humans and/or the environment.
- Attempts to employ ex-situ treatment are often expensive including **high capital expenditures and may take decades** to complete.
- Bioremediation and physical isolation (excavation) are difficult to use at many complex sites.
- As a result, environmental remediation experts are increasingly using ISCO as a fast approach for contaminant remediation.

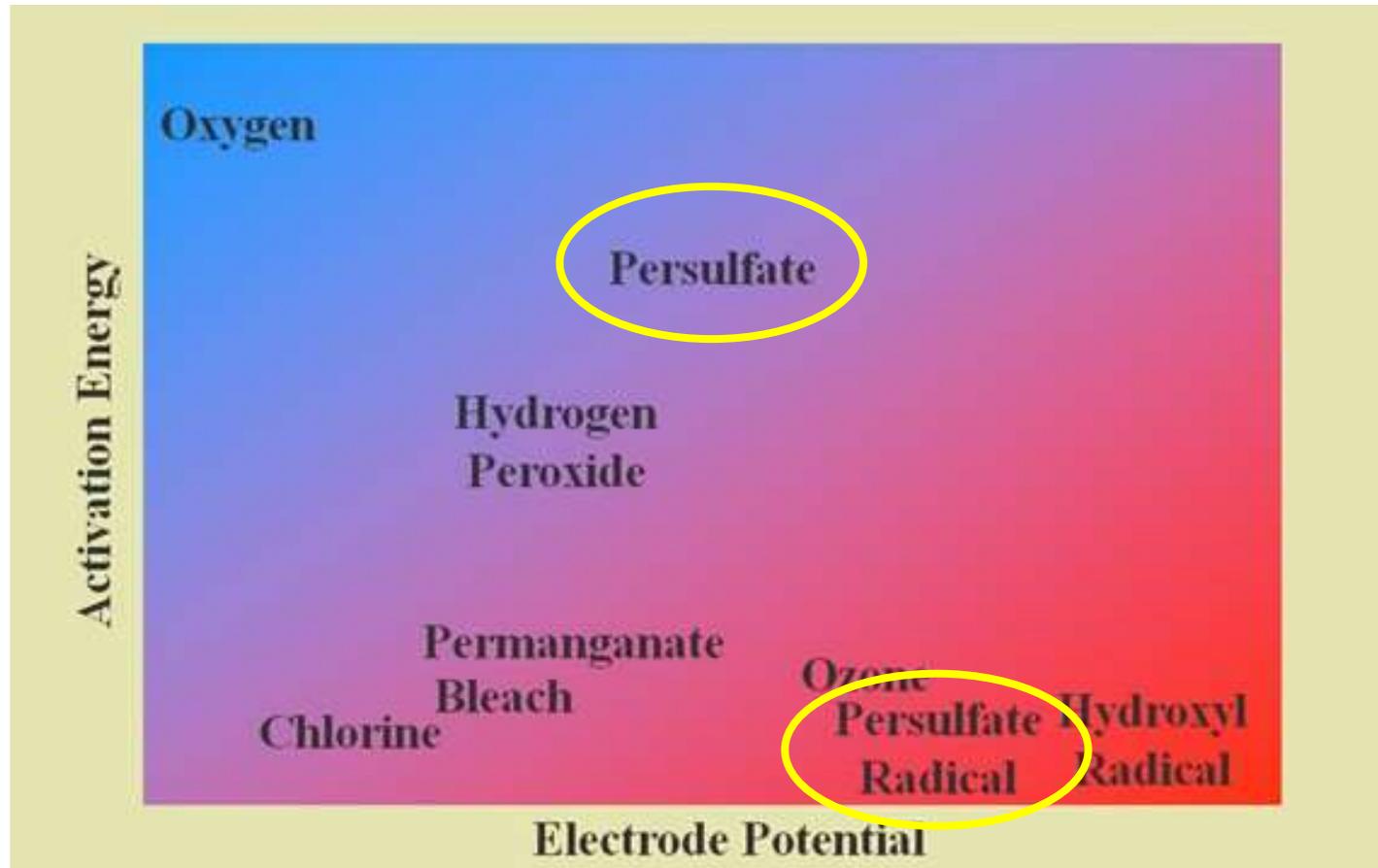


Which ISCO is best?



Oxidant	Oxidation Potential (v)	Oxidant Strength (Chlorine = 1)
Hydroxyl Radical (HO [•]) [*]	2.8	2.0
Sulfate Radical (SO₄^{•-})^{**}	2.5	1.8
Ozone (O ₃)	2.1	1.5
Sodium Persulfate (Na₂S₂O₈²⁻)	2.0	1.5
Hydrogen Peroxide (H ₂ O ₂)	1.8	1.3
Permanganate (MNO ₄ ⁻)	1.7	1.2
Oxygen (O ₂)	1.2	0.9
*This radical is formed when Ozone and Hydrogen Peroxide decompose		
**This radical is formed during activated sodium persulfate reactions		

Which ISCO is best?

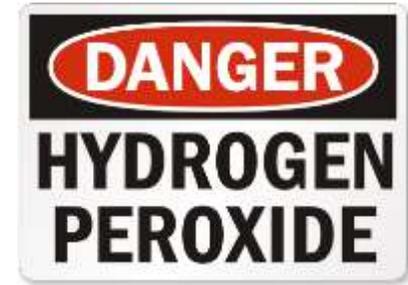


Which ISCO is best?

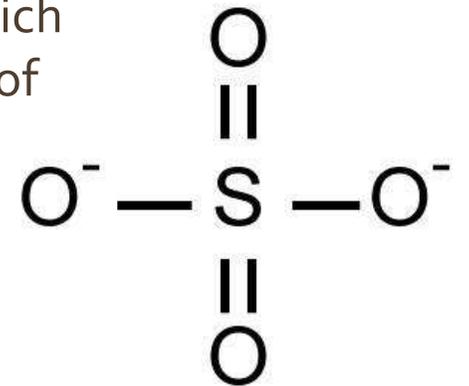
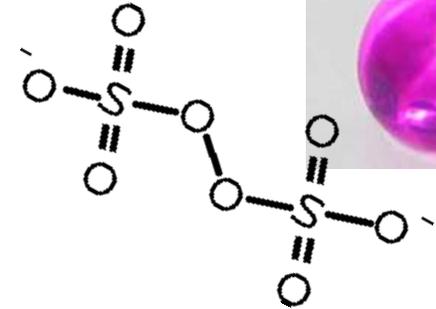
Oxidant	Amenable VOC's	Reluctant VOCs	Recalcitrant VOCs	Limitations
Peroxide, Old Fenton's	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA	DCA, CH ₂ Cl ₂	TCA, CT, CHCl ₃	Stability (25-95% decomp/hr), low pH
Peroxide, New Fenton's	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA	DCA, CH ₂ Cl ₂ , TCA, CT, CHCl ₃		Stability (10-50% decomp/hr)
Potassium Permanganate	PCE, TCE, DCE, VC, TEX, PAH	MTBE, TBA	TCA, CT, B, CHCl ₃ , DCA, CB, CH ₂ Cl ₂	Soil oxidant demand
Sodium Permanganate	PCE, TCE, DCE, VC, TEX, PAH	MTBE, TBA	TCA, CT, B, CHCl ₃ , DCA, CB, CH ₂ Cl ₂	Soil oxidant demand
Sodium Persulfate, Fe	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA	DCA, CH ₂ Cl ₂ , CHCl ₃	TCA, CT	Stability (10-25% decomp/wk), low pH
Sodium Persulfate, Base	All VOCs			Stability (10-25% decomp/wk), NaOH costs
Sodium Persulfate, Heat	All VOCs			Stability (10-50% decomp/day), low pH, heating costs
Ozone	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA		DCA, CH ₂ Cl ₂ , CHCl ₃ , TCA, CT	Mass Delivery, Volatilization



Which ISCO is best?



- ISCO has been used for over three decades – early uses included **Permanganate** (MnO_4^-) or **Hydrogen Peroxide** (H_2O_2), both of which have **drawbacks** including clogging soil pores (permanganate) and creation of and reactivity with hydroxyl radicals that are self-limiting.
- **Persulfate** ($\text{S}_2\text{O}_8^{2-}$) is now a very popular choice of ISCO oxidant.
- The formation of radicals from persulfate is **Persulfate Activation**
 - heat/activator
- $\text{S}_2\text{O}_8^{2-} \xrightarrow{\text{heat/activator}} 2\text{SO}_4^{\cdot-}$ this **sulfate radical** is similarly oxidative as the hydroxyl radical (HO^\bullet) produced from H_2O_2 – but is more selective toward electron-rich organic contaminants, and the half-life of persulfate in an aquifer is orders of magnitude longer than peroxide or permanganate.



Activated Sodium Persulfate ($\text{Na}_2\text{S}_2\text{O}_8$)

- Sodium Persulfate is the most common persulfate salt used for ISCO applications.
- ISCO process consists of the dissociation of persulfate salt to persulfate anion.

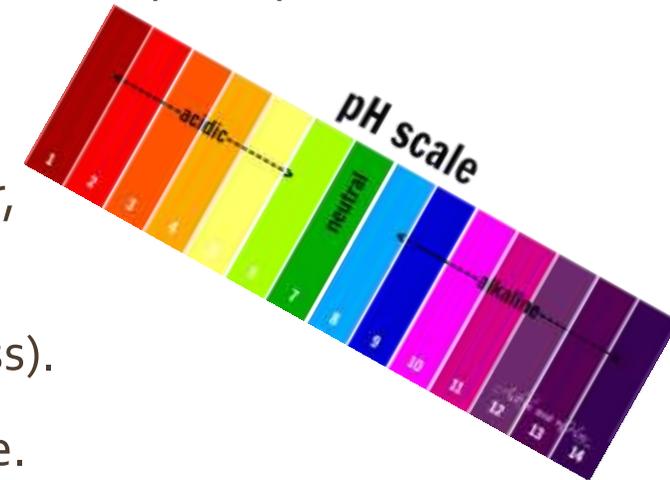
heat/activator

- $\text{S}_2\text{O}_8^{2-} \xrightarrow{\text{heat/activator}} 2\text{SO}_4^{\bullet-}$
- **Persulfate** ($\text{S}_2\text{O}_8^{2-}$) anion is more powerful than hydrogen peroxide, although the hydroxyl radicals (HO^{\bullet}) generated during hydrogen peroxide applications are kinetically faster in destroying Chemicals of Concern (COCs).
- Because persulfate anion is kinetically slower, its reaction with **Natural Organic Material (NOM)** is also lower.
- The addition of heat, ferrous iron salt/chelated ferric iron (Activator), hydrogen peroxide or sodium hydroxide (caustic soda) significantly increases the oxidative strength of the persulfate anion with the creation of sulfate radicals. The sulfate radical is kinetically faster than the persulfate anion.



Activated Sodium Persulfate Advantages/Disadvantages

- Because the persulfate reaction with COCs is kinetically slower than with hydroxyl radicals, further distribution of the oxidant is possible prior to decomposition.
- Sodium persulfate has the potential to lower the pH in groundwater, although many soils have the capacity to buffer this low pH.
- Persulfate has the ability to degrade soft metals (e.g. copper or brass).
- Low pH can cause metals to be mobilized within the treatment zone.
- As with all ISCO applications, the increase of NOM (natural organic material) reduces the volume of contaminants that can be oxidized per volume of oxidant.



Site Characterization

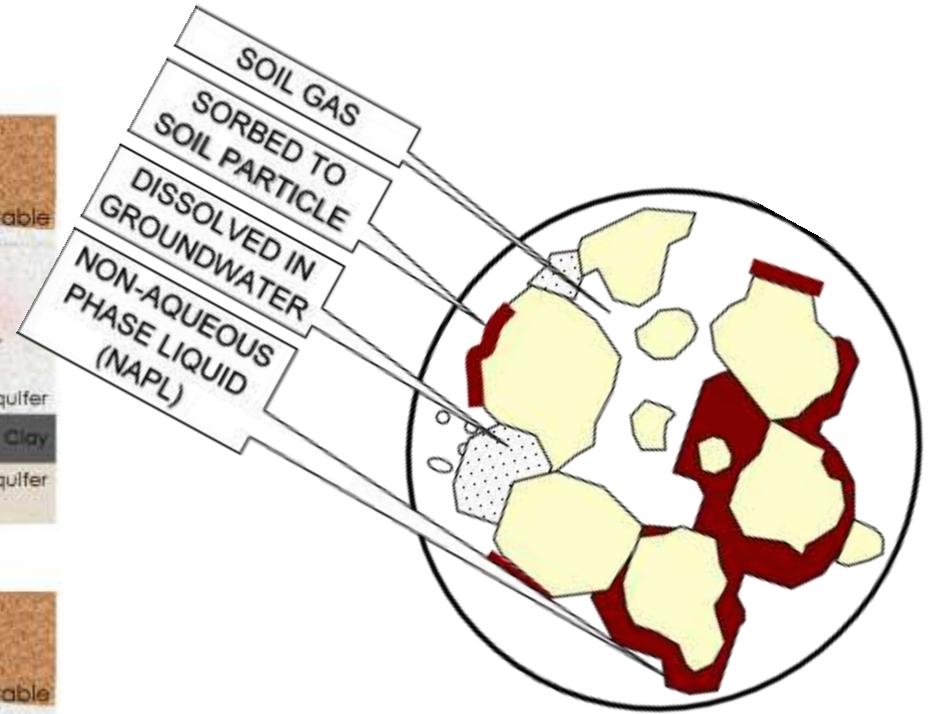
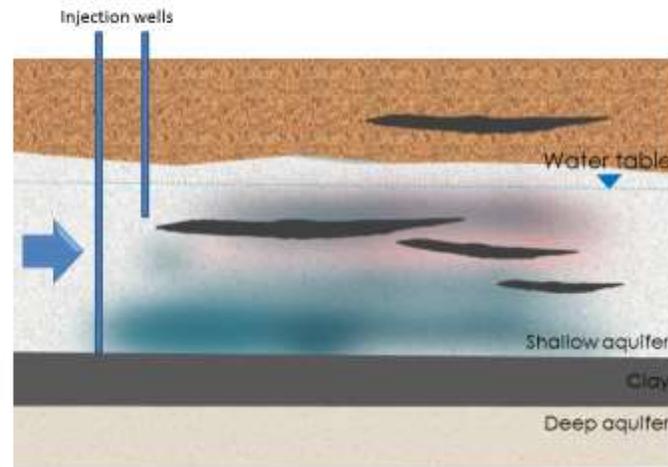
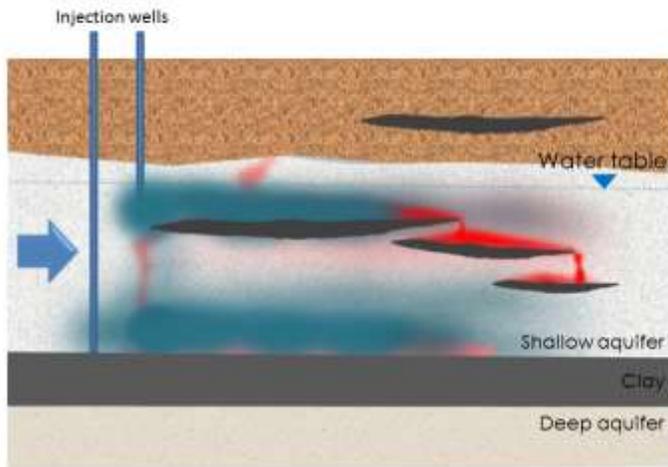
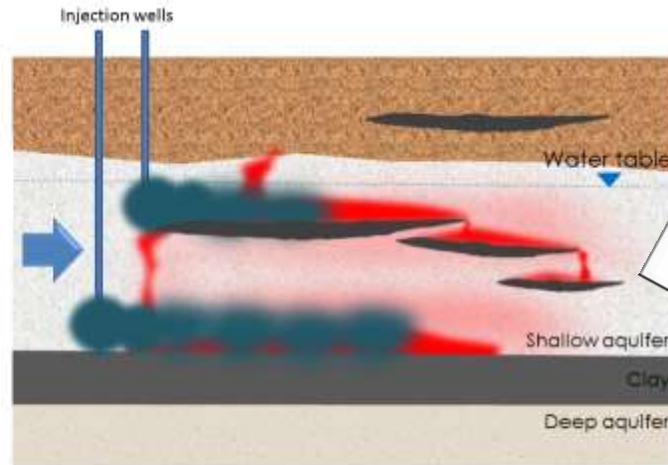
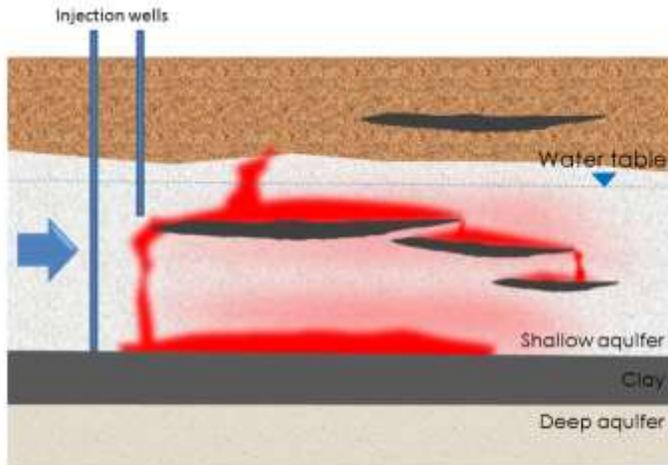
- The most important factor in remediation success is completion of an adequate site characterization.
- Understanding of the geology, stratigraphy, hydrogeology, aquifer geochemistry –pH, ORP, DO, soil effective porosity (soil permeability), hydraulic conductivity, soil heterogeneity
- Migration pathways, groundwater flow direction
- Identification of surface/subsurface structures (utilities) & potential receptors
- If the location/mass of the contamination is not properly identified, leaching of chemicals to groundwater will continue to occur (after ISCO) and dissolved concentrations will not decrease in a timely manner. During ISCO, LNAPL or sorbed-phase contaminants may change to dissolved phase.
- Successful oxidation is dependent on the reaction rate and effective distribution of the oxidant. Reaction rates are dependent on temperature, pH, chemical concentrations, reaction byproducts, NOM.



Site Characterization

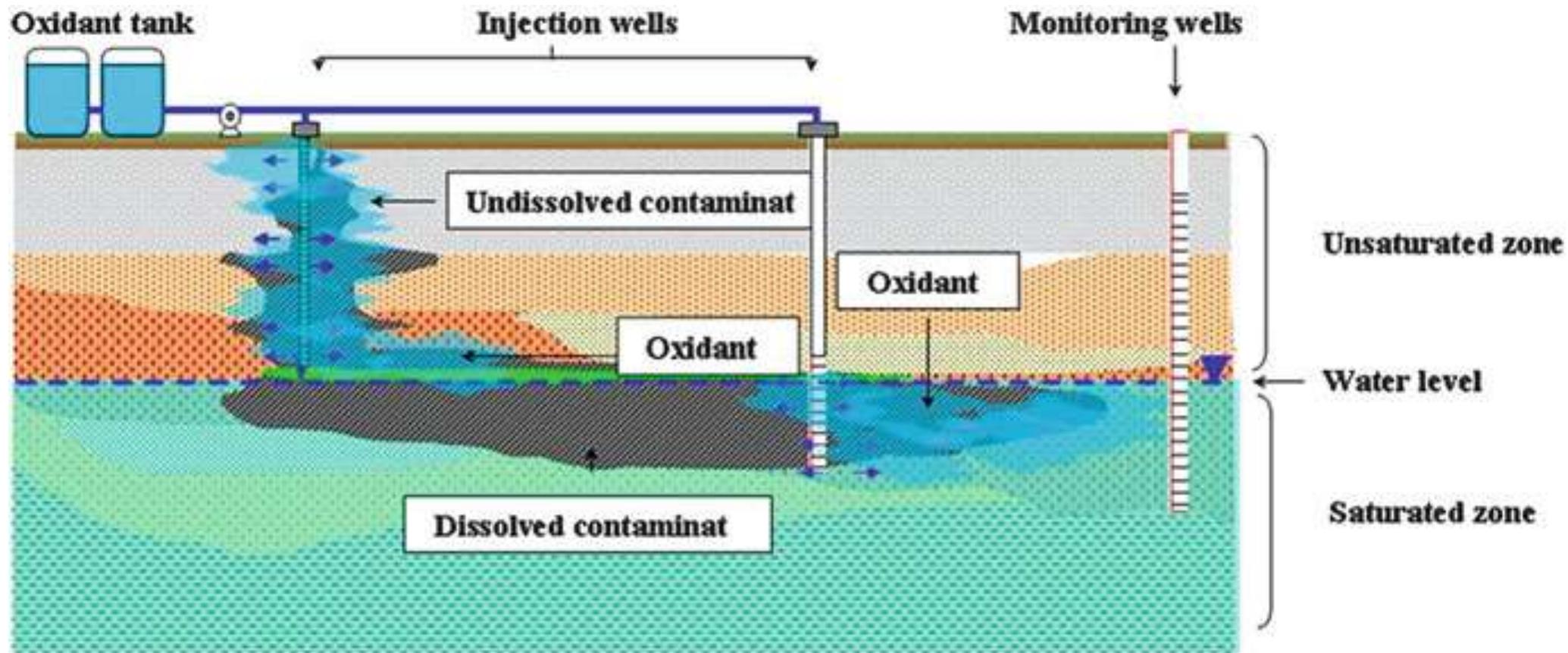
- Total Oxidant Demand = contaminant load (all phases) + NOM + natural chemical/physical components of soil and groundwater that consume oxidant
- Metals concentrations - Iron, Chromium and Selenium can be oxidized and mobilized by ISCO.
- Characterization should include analyzing As, Ba, Cd, Cr, Cu, Fe, Pb and Se, and Fe⁺²
- Anion (chloride, sulfate, nitrate) and Cation (calcium, sodium, magnesium, potassium & manganese)

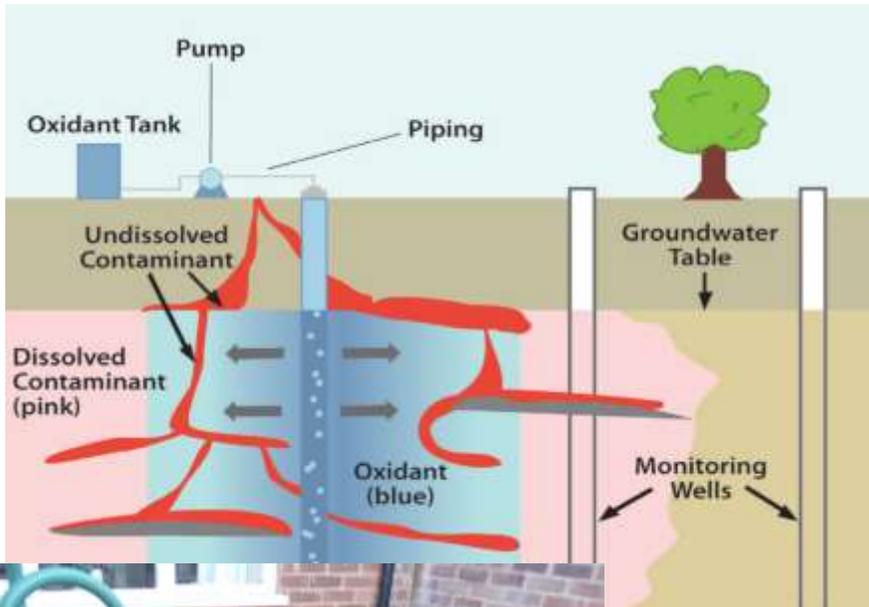
Site Characterization



How is ISCO performed?

- Injection of sodium persulfate at 12% to 25% solution in water
- Addition of activator
 - iron catalyst (ferrous salts or chelated ferric iron, Iron-EDTA.) at 150 to 600 mg/l of Fe in the groundwater treatment zone
 - Sodium Hydroxide (25% solution) to raise treatment zone groundwater pH to 10.5
 - Total Alkaline Demand = natural demand from soil and groundwater + neutralization of generated acid
 - Sodium Hydroxide (Caustic Soda) is caustic
 - Hydrogen Peroxide (8% solution) – typically 3 gallons 8% Peroxide per gallon of 20% sodium persulfate
 - Peroxide is reactive and can be highly exothermic





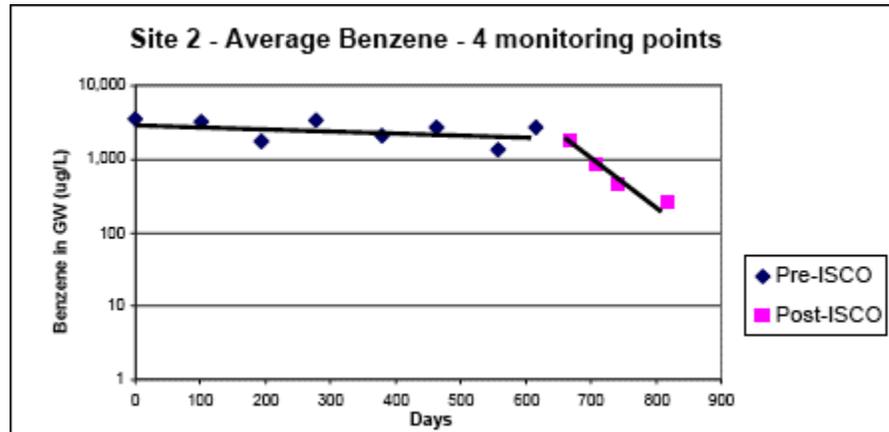
What things change during ISCO?

- Monitoring points should be installed (if not already) at varying distances from ISCO injection points.
- Groundwater – increases (mounding)
- Contaminant concentration – may decrease (destruction) or increase (desorption)
- Oxidation-Reduction Potential (ORP) – decreases
- pH – decreases
- Dissolved Oxygen – generally increases
- Temperature – increases
- Oxidant-specific characteristics – such as oxidant coloration or by-product (sulfate concentration with activated persulfate injection)

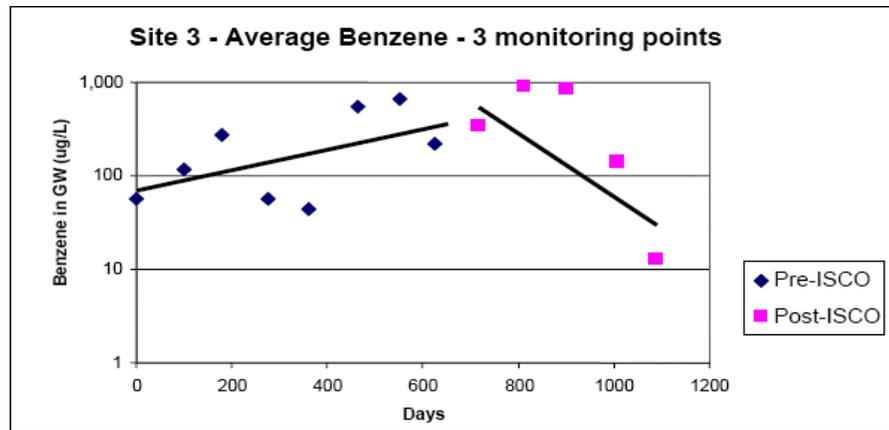
organic
sediments
aquifer
oxidation
carbon
soil
groundwater
nitrate
denitrification
dissolution
DNAPL
marine
humic
natural
surface
nonaqueous
phase
source
pyrite
degradation
chemical
reduction
pyrolysis
water
soils
rates
acid
coastal



Good ISCO – Not So Good ISCO

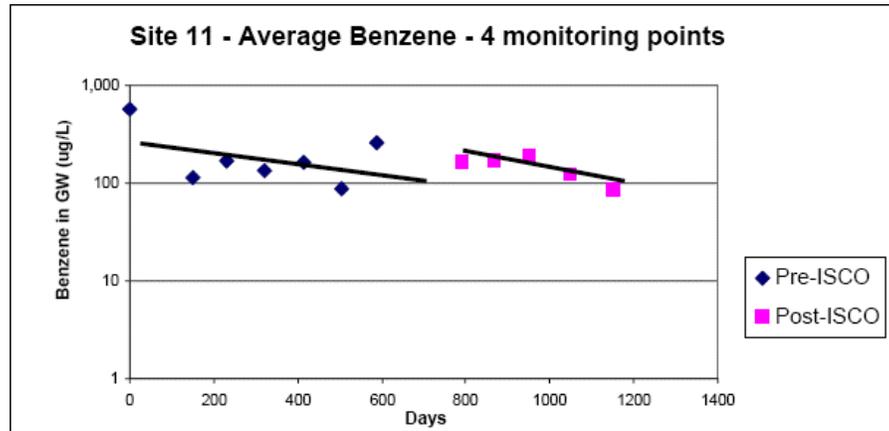


- Natural attenuation was occurring prior to ISCO.
- Significant reduction in Benzene after ISCO.
- **ISCO successful.**

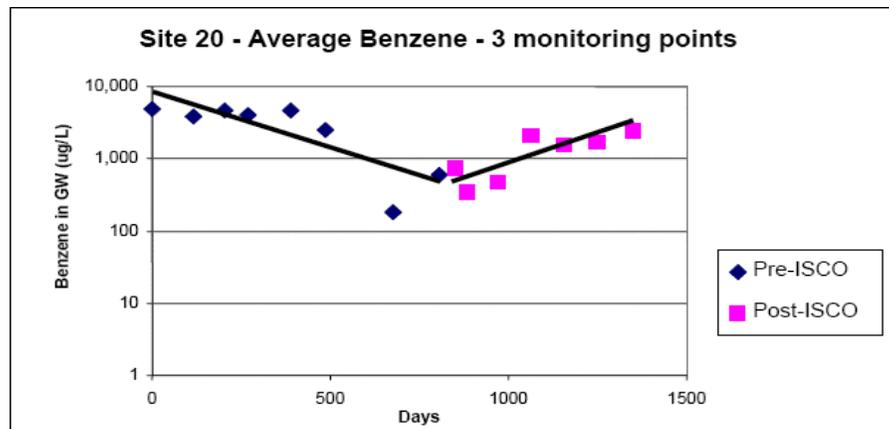


- Season fluctuations and no identified natural attenuation were occurring prior to ISCO.
- ISCO appears to have caused initial desorbing of contamination from soil to dissolved phase, followed by destruction.
- **ISCO successful.**

Good ISCO – Not So Good ISCO



- Natural attenuation was occurring prior to ISCO.
- Post-ISCO trendline is similar to natural attenuation.
- **ISCO not successful.**



- Natural attenuation was occurring prior to ISCO.
- Following ISCO, desorption occurred releasing contaminants to groundwater to the extent that destruction of the dissolved phase contamination was not possible.
- **ISCO not successful.**

Limitations

- Handling of strong oxidizers – health & safety issue
- ISCO enhances desorption of contaminants into vapor and dissolved phases. This may allow contaminant mobilization beyond the monitoring area.
- Contaminant concentrations often rebound, and multiple injection events are necessary.
- It is difficult to deliver oxidant into heterogeneous geology. It is nearly impossible to deliver oxidant into low permeability soils.
- Oxidants tend to react quickly, which greatly limits radius of influence. Closely-spaced injection points with low volume injections are usually best.
- Soil with high oxidant demand will consume oxidant more readily requiring larger volumes of oxidant.
- ISCO rarely remediates the entire contaminant area – residual contaminants typically need additional treatment, monitoring and/or risk assessment.
- Reductions in soil permeability are common.
- Metals can be mobilized by changes in their oxidation state.