CHEMICAL OXIDATION VS. CHEMICAL REDUCTION- CHOOSING THE RIGHT APPLICATION

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Overview

The objectives of this talk are to provide:

- An overview of chemical oxidation vs. reduction
- Discuss use of common oxidants & reductants
- Application methods
- Comparisons of oxidants/reductants
- Application considerations

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Chemistry Overview

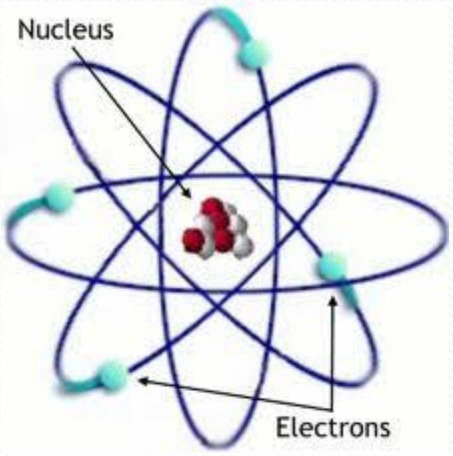
- Oxidation-reduction (redox) reactions involve electron transfer
- One half of the reaction shows an electron loss (oxidation)
- Opposite side of the reaction shows a net gain (reduction)

Oxidation of TCE using Sodium Permanganate

$$2NaMnO + C_2HCl_3 \longrightarrow 2CO_2 + 2MnO_2 + 3Cl^- + H^+ + 2Na^+$$

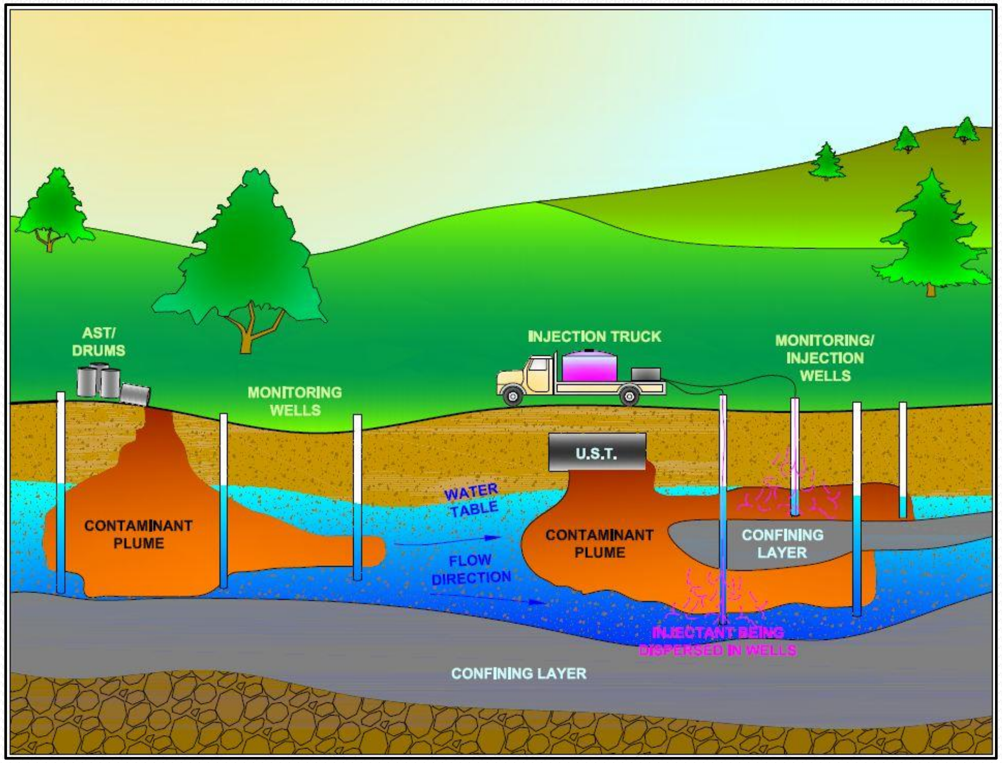
Reduction of TCE using Zero-Valent Iron

$$3Fe^0 + 3H^+ + C_2HCl_3 \longrightarrow 3Fe^{+2} + 3Cl^- + C_2H_4$$



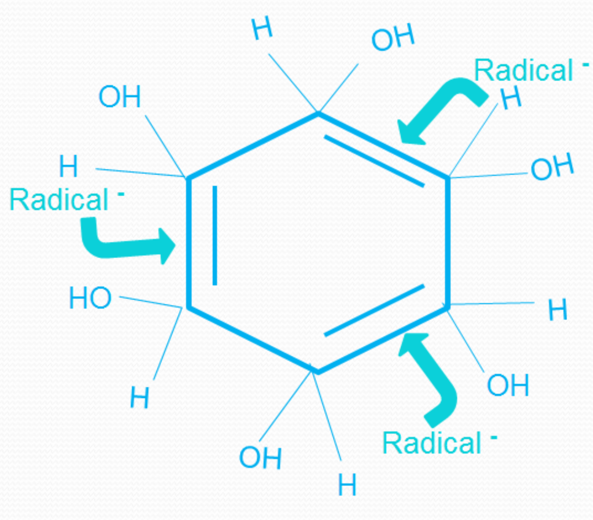
Subsurface Application of Redox Chemistries

- Applications using chemical oxidation- In-situ Chemical Oxidation (ISCO)
- ISCO utilized since mid-1980s, now a go-to-method
- In-situ remediation using chemical reduction is referred to as ISCR
- ISCR initial development with zero-valent metals in the 1970s, now an emerging method
- ISCR treatment is abiotic- different from reductive de-chlorination (bioremediation)

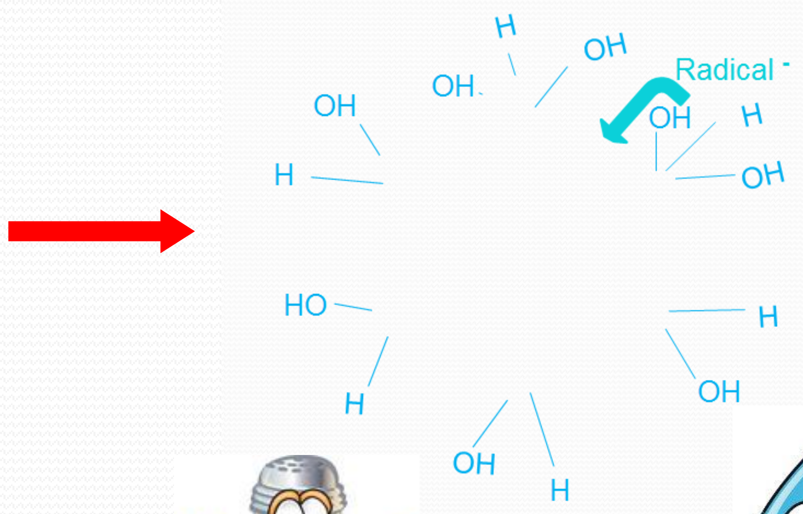


In-Situ Chemical Oxidation (ISCO)

- Chemical Oxidation involves breaking bonds and inserting oxygen
- End products are carbon dioxide, water, and harmless salts
- Treatment works on contact- *needs full oxidant contact for success*
- Desorption from soil matrix to groundwater is required



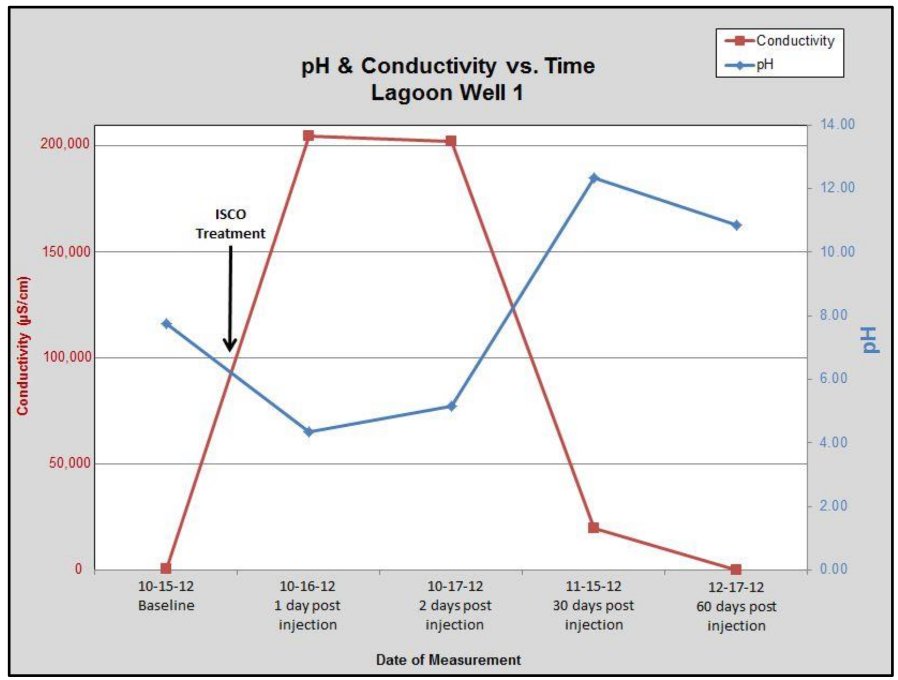
Typical Aromatic Contaminant



Oxidant Descriptions

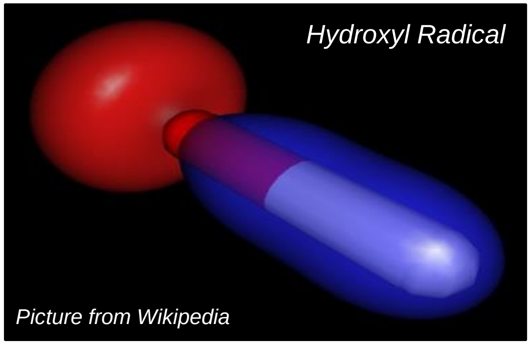
Different oxidants include:

- Fenton's Reagent/CHP
- Sodium Persulfate
- Sodium and Potassium Permanganate
- Calcium Peroxide/Modified Fenton's



Oxidant Descriptions

Fenton's Reagent/Catalyzed Hydrogen Peroxide (CHP)

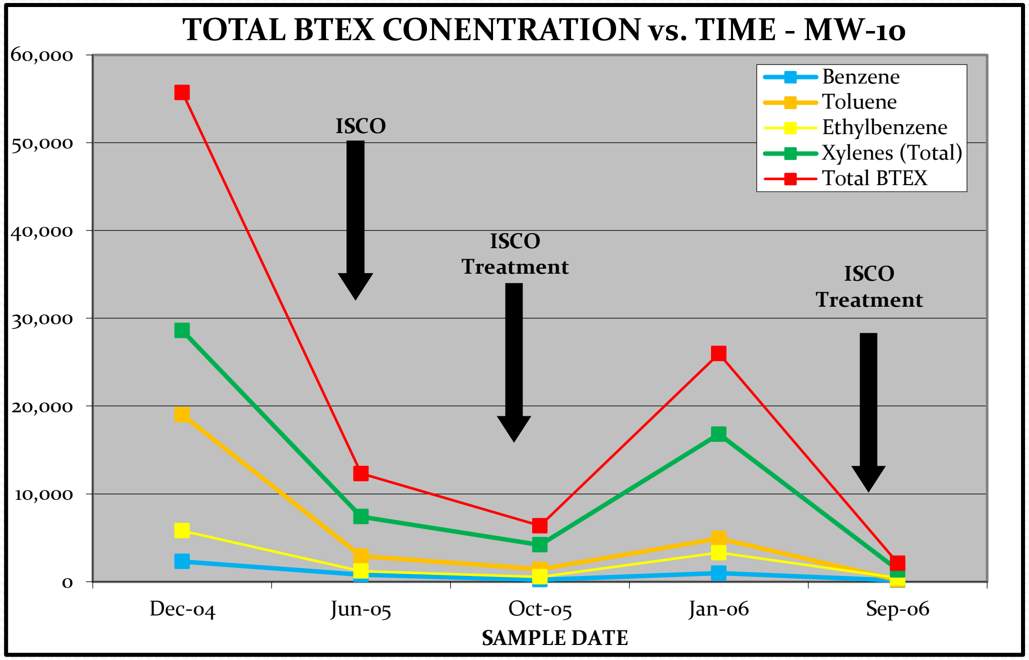


- Fenton's Reagent, developed in 1895 by H.J.H. Fenton, who combined hydrogen peroxide with an iron salt producing hydroxyl radicals (**$OH^{\cdot -}$**)
- Basic reaction: **$H_2O_2 + Fe^{+2} \rightarrow OH^{\cdot -} + OH^{-} + Fe^{+3}$**
- CHP or Modified Fenton's relies on iron chelation
- Cost effective/rapid oxidation/breaks down soil structure
- Effective on a wide range of compounds/NAPL treatment
- Easily combined with mechanical extraction/fixed based systems

Fenton's/CHP Case Study

Auto Dealer, Dalton, GA

- Site was an active auto dealer with two petroleum release areas
- Free product detected in 22 wells, up to 1.4 feet in thickness
- CHP oxidation selected using naturally occurring iron



- A second treatment using potassium permanganate performed to treat vinyl chloride
- Treatment resulted in rapid removal of free product and BTEX reduction resulting in a NFA

Oxidant Descriptions

Sodium Persulfate

- Versatile oxidant/long persistence in subsurface/ low natural oxidant demand
- Direct oxidation of sodium persulfate produces the following reaction:

$$S_2O_8^{-2} + 2H^+ + 2e^- \rightarrow 2HSO_4^{-}$$

- Oxidation enhanced using catalysts to release sulfate radicals:

$$S_2O_8^{-2} + \text{activator} \rightarrow SO_4^{\cdot -} + (SO_4^{\cdot -} \text{ or } SO_4^{-2})$$

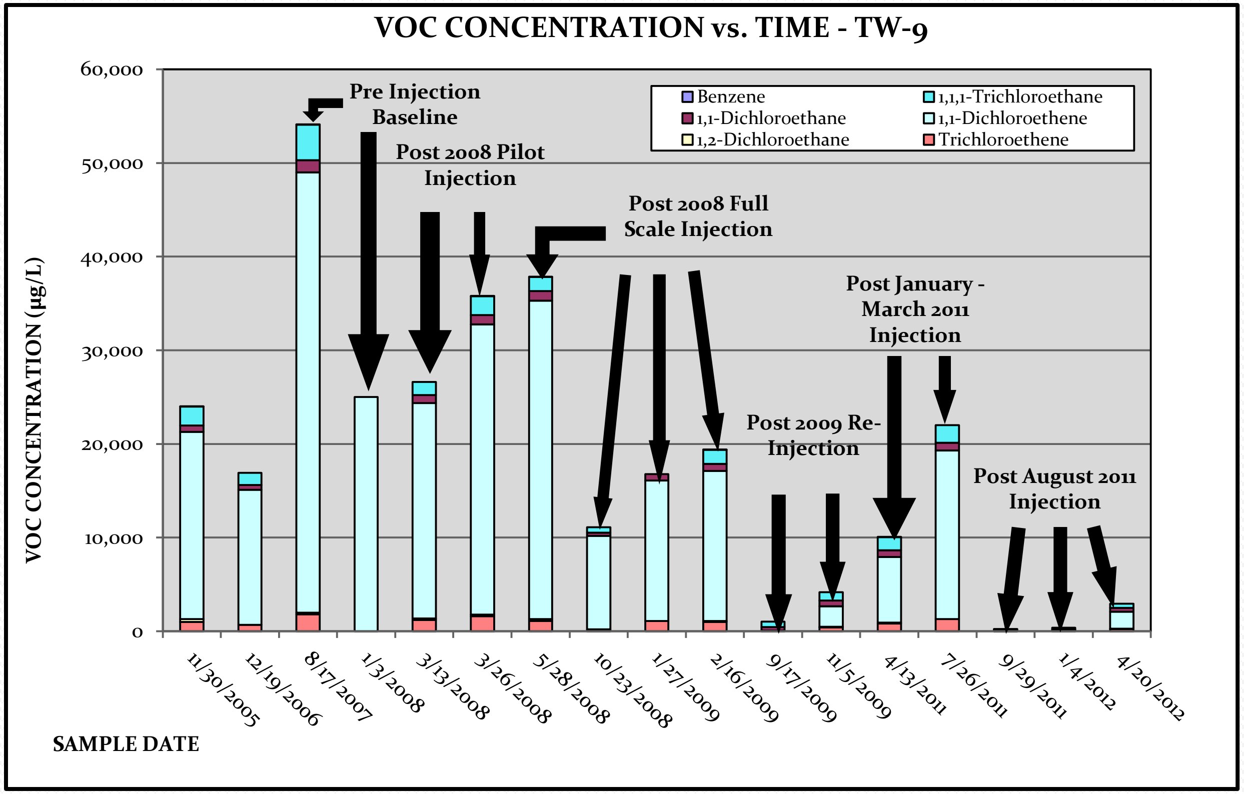
- Catalysts include: heat, metal catalysts (iron), H_2O_2, and pH buffers
- Sulfate radicals comparable in oxidant strength to $OH^{\cdot -}$
- Successful on a variety of organics/less exothermic reaction than CHP
- Combination with oxygen release agents produces ISCO-aerobic bioremediation “treatment train”

Sodium Persulfate Case Study

RCRA/VRP Site, Opelika, AL

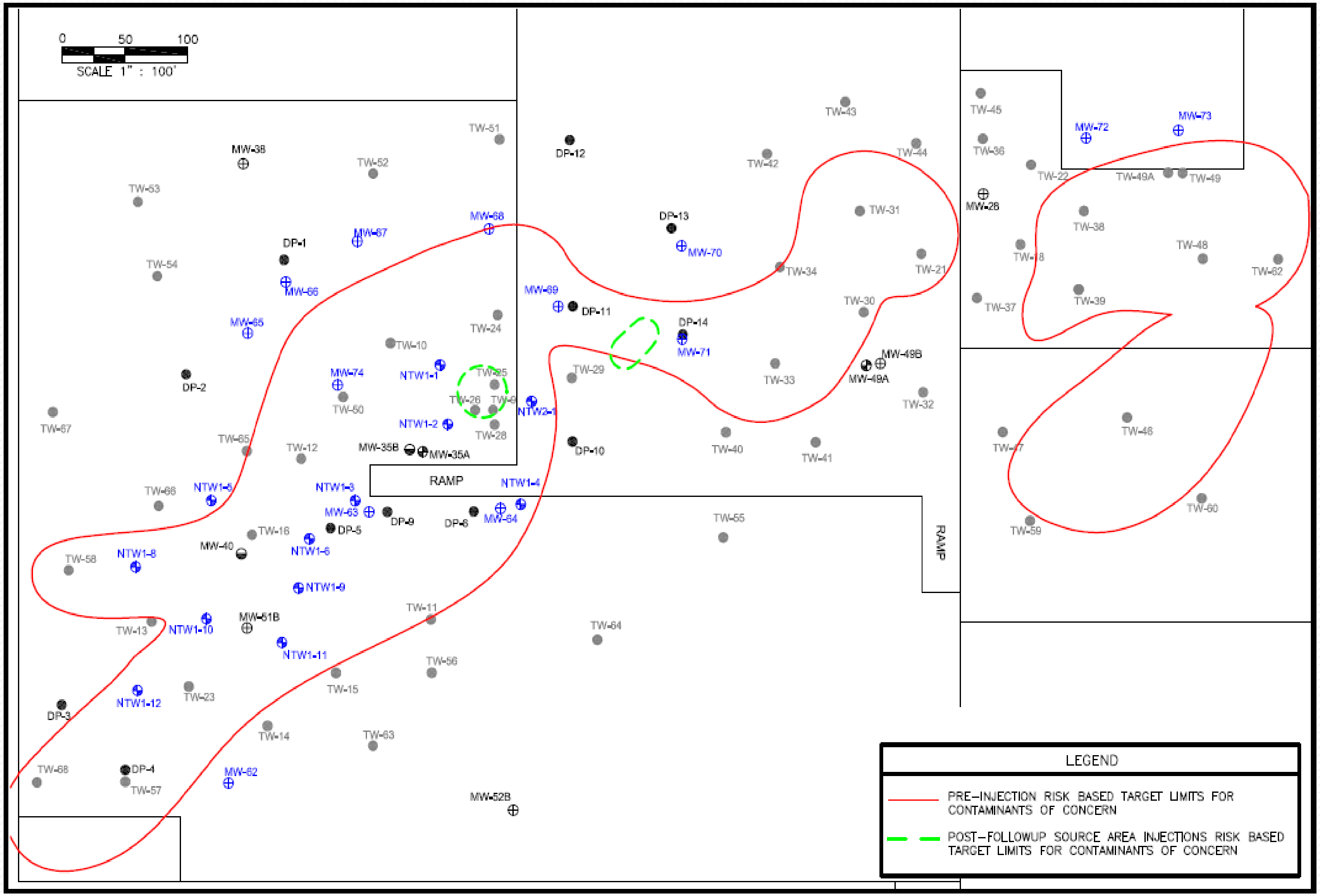
- Industrial site utilized as a German camp during WWII, converted to a fitness equipment manufacturer who discharged chlorinated solvents
- Site contained a large VOC plume covering 3.5 acres beneath a warehouse, source area contained VOC concentrations in excess of 50,000 ppb
- ISCO using sodium persulfate was utilized into over 900 injection wells

- First treatment showed a 70% reduction, additional smaller area treatments were conducted
- Confirmatory sampling results were conducted and results were BRL or below risk levels
- Received a NFA in 2014



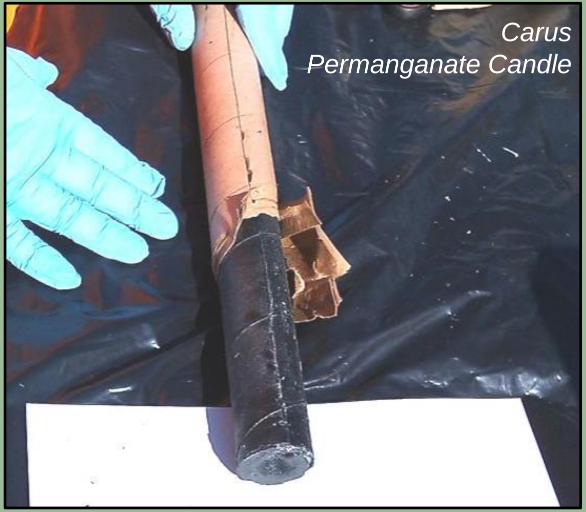
Sodium Persulfate Case Study

RCRA/VRP Site, Opelika, AL – cont.



Oxidant Descriptions

Sodium and Potassium Permanganate

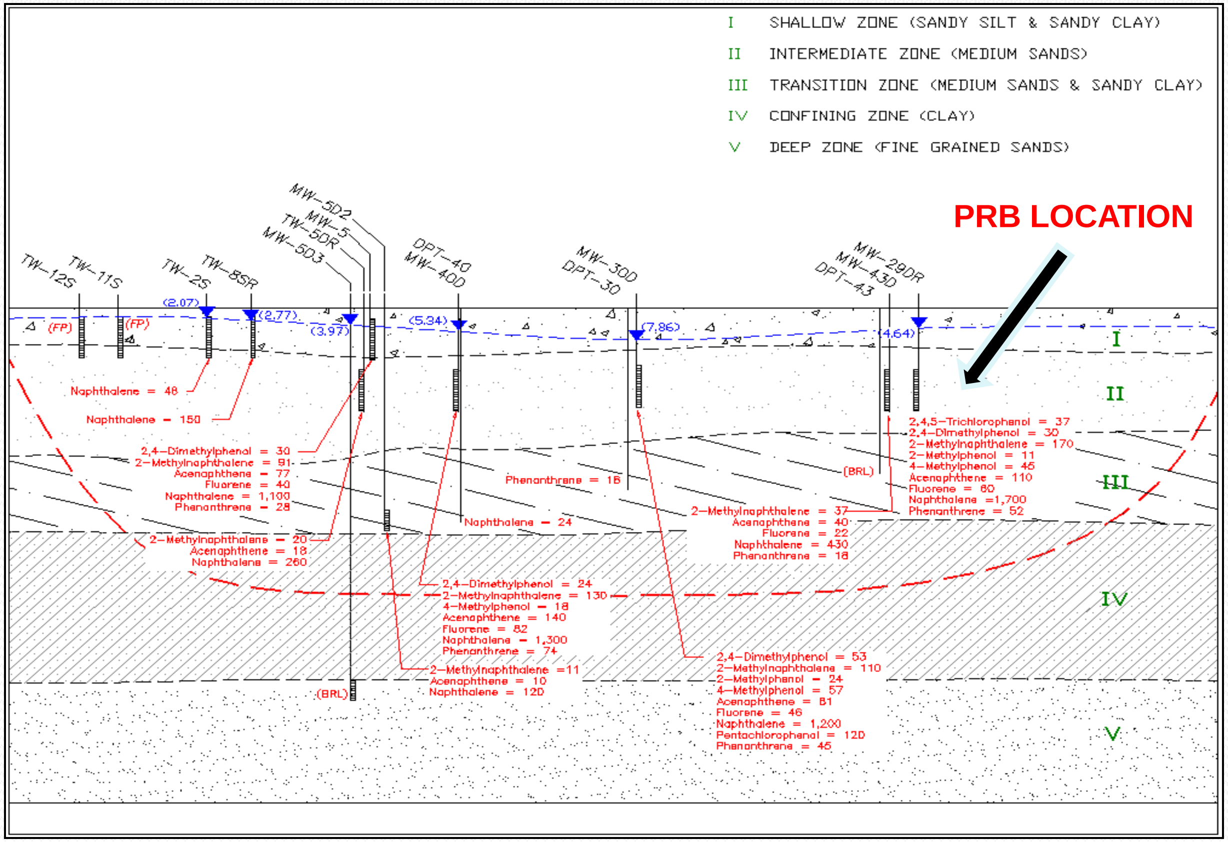


- Permanganate ion works well on chlorinated ethenes (PCE, TCE) and select VOCs/SVOCs
- Weaker oxidant but easy application
- Oxidation occurs without formation of radicals
- Long persistence in subsurface (up to a year)
- Purple color aids in determining positive contact/radius of influence
- New permanganate candles offer low cost PRB barrier treatment

Potassium Permanganate Case Study

B&M Wood Products, Manor, GA

- Site is an active wood treater with a release of PAHs (naphthalene) migrated off-site
- Treatability study showed potassium permanganate was an effective treatment option
- Planned construction this month of a potassium permanganate candle PRB
- Will include 30 points to 38 ft-bgs
- Each point will contain 15 paraffin wax candles
- Expected treatment duration is 5-8 years



Oxidant Descriptions

Calcium Peroxide

- Can be used as an oxidant and as a slow release bio-enhancer
- Typically contains hydrated lime (25%), releases DO at higher pH (10-12)

$$2\ CaO_2 + 2\ H_2O \rightarrow Ca(OH)_2 + O_2$$

- When pH drops <10 or 11, hydrogen peroxide is formed:

$$CaO_2 + 2H + Ca_2 + (aq) + 2H_2O_2$$

- Hydrogen peroxide reacted with an iron source produces Modified Fenton's:

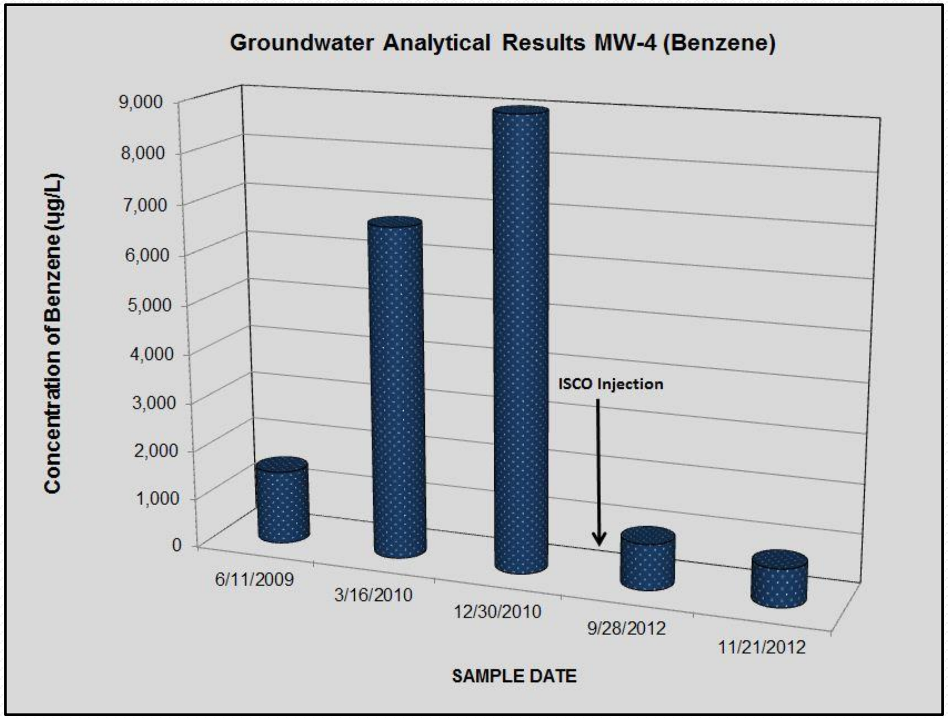
$$H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH^{\cdot -} + OH^-$$

- In-situ formation of hydroxyl radicals produces a controlled reaction

Calcium Peroxide Case Study

Former Gasoline Station, Atlanta, GA

- Former gasoline station operating as a Walgreens with BTEX contamination
- Highest benzene detected at 9,000 µg/L in MW-4 near the tank pit
- Soil over-excavation performed followed by ISCO in the source area
- Injected a 7.7% solution of alkaline activated sodium persulfate combined with 11% calcium peroxide
- Confirmatory sampling 24 and 80 days post injection indicated a significant reduction in benzene
- Site received a NFA

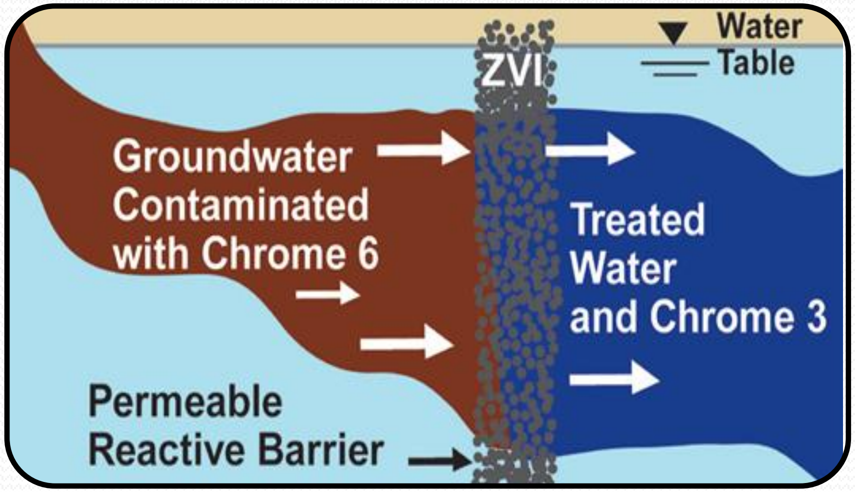


In-Situ Chemical Reduction (ISCR)

- ISCR involves the addition of electrons (often hydrogen) substituted for other ions
- Abiotic reactions usually result in less daughter product formation
- Selective treatment of chlorinated VOCs/SVOCs, metals, explosives, etc.
- Applied via direct injection and solid phase PRBs (goal of developing reducing zones)

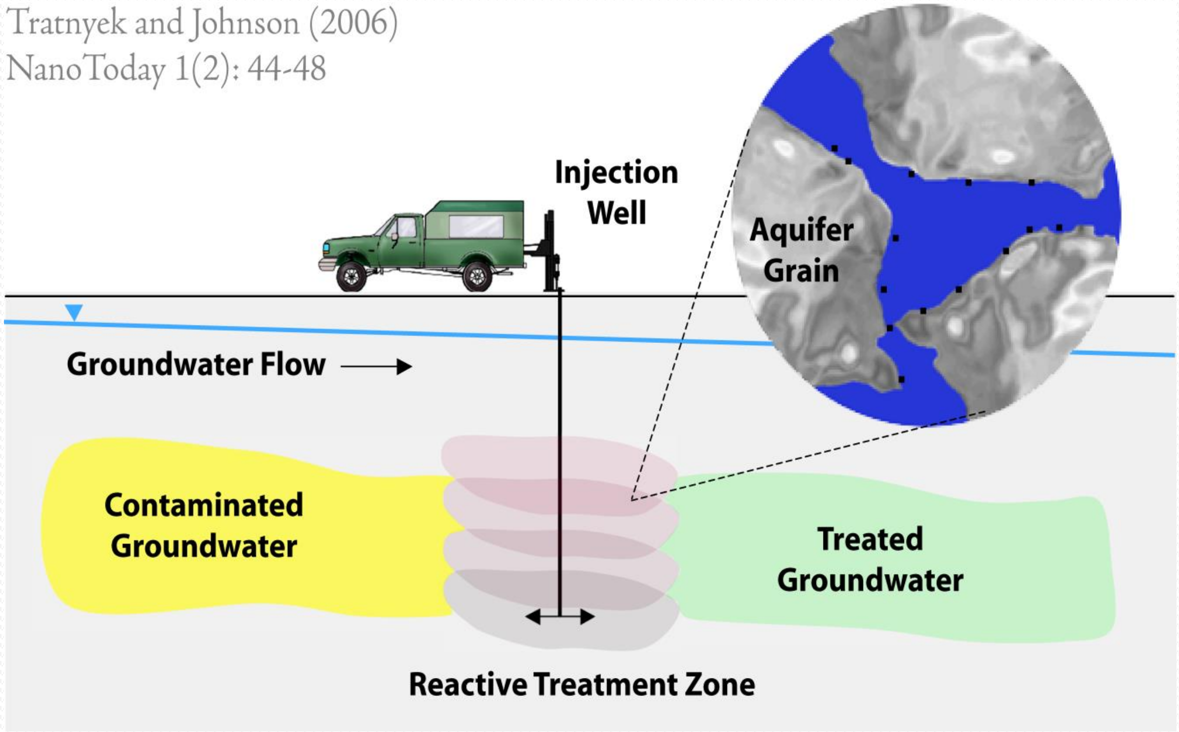
Examples:

- ZVI
- nZVI
- iron sulfides
- Polysulfides
- dithionates



Chemical Reductants

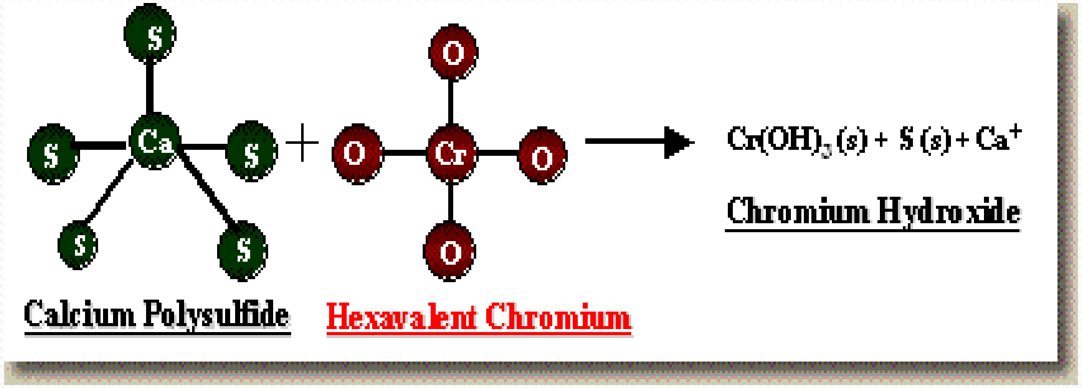
- Sulfide Salts (calcium polysulfide/sodium dithionate)
- Zero Valent Metals
- Polyphenol generated nZVI
- Iron Sulfide (BiRD®)



Chemical Reductant Descriptions

Calcium Polysulfide

- Calcium Polysulfide (CaS_X) is a strong bulk reductant producing a high pH (10-11) solution
- Originally developed for pest control industry (lime sulfur)
- Reduces metal oxy-hydroxides producing sulfides (FeS, ZnS, PbS, CuS), most often used for hexavalent chromium reduction
- Arsenic treatment using Calcium Polysulfide requires iron to precipitate arsenopyrite
- Low cost, application easily modified based on naturally occurring iron, pH



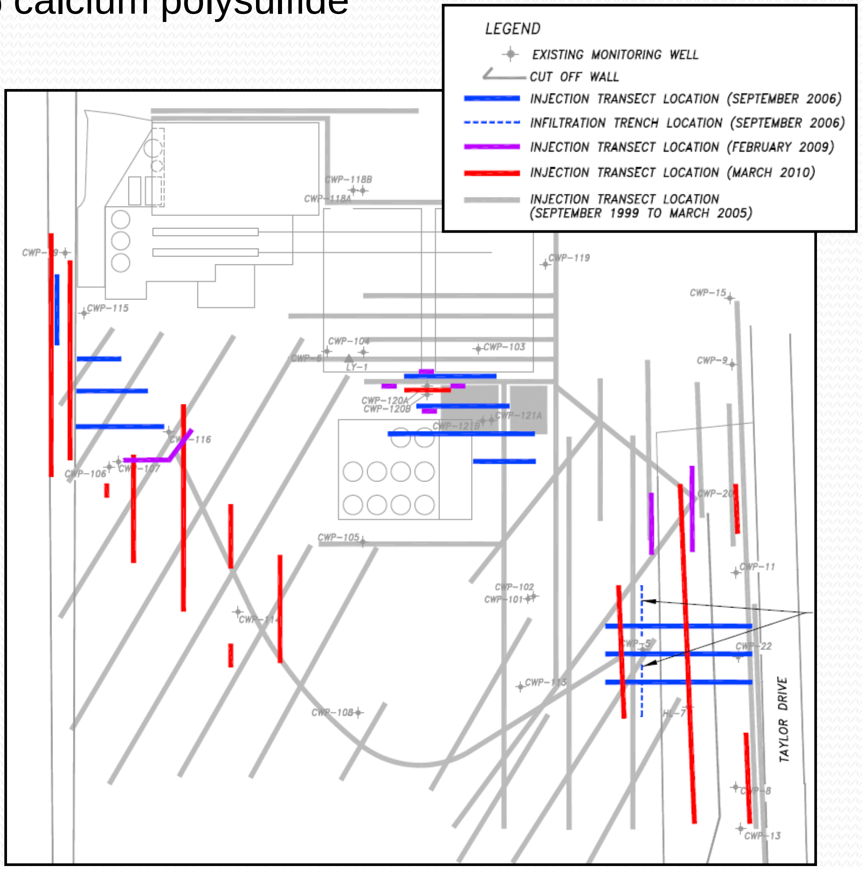
Calcium Polysulfide Case Studies

Morses Pond Culvert, MA

- Former paint factory that used chromium-laden pigment as fill material
- Over 1,000 yd³ soils impacted with hexavalent chromium along a steep embankment, shallow soil excavation/blending not feasible
- Installed 40 IWs, injected 56,800 gallons of 18% calcium polysulfide
- Wells spaced 10 ft apart with 5-foot ROI
- Concentrations pre-treatment as high 11,400 mg/kg, post treatment highest concentration was 5,600 mg/kg (treatment goal was <200 mg/kg)
- Total project cost was $119,719

Coast Wood Preserving, CA

- Wood preserving facility with CCA in groundwater, groundwater total chromium clean-up goal of 50 µg/L, soils 100 mg/kg
- 8 injections of calcium polysulfide have been conducted, also placed in soil excavations
- Chromium in well CWP-6 decreased from 28,000 µg/L to <50 µg/L 1 year after treatment



Coast Wood figure and data from US EPA, Fourth Five-Year Review Report, 2011. Morses Pond Culvert info from US EPA website, 2004 publication

Chemical Reductant Descriptions

Sodium Dithionate

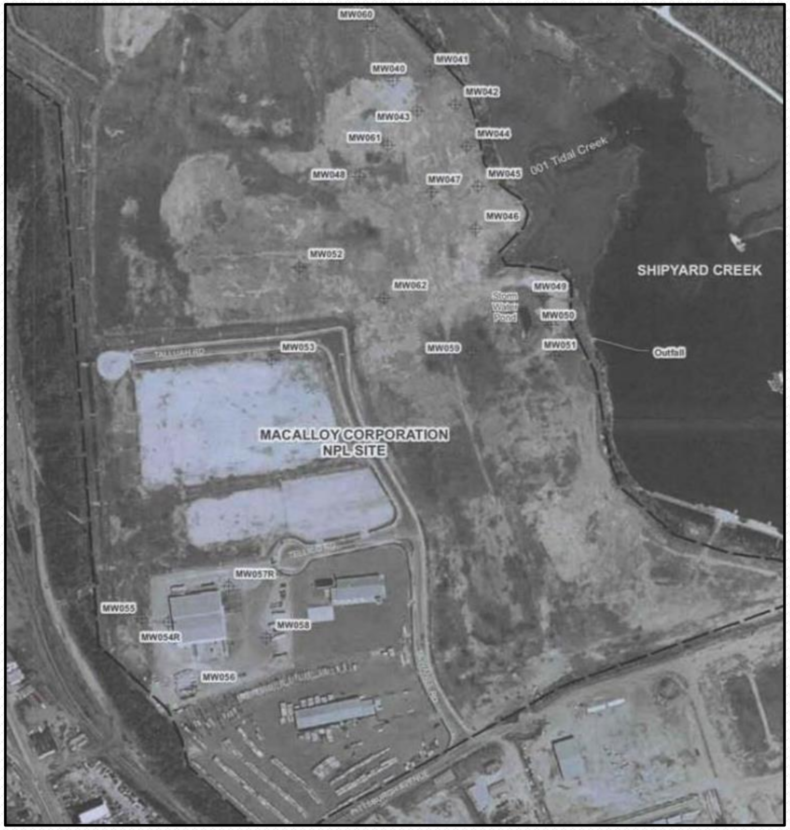
- Sodium Dithionate ($Na_2S_2O_4$) is a strong bulk reductant producing a high pH (10-11) solution
- Reduces metal oxy-hydroxides producing sulfides (FeS, ZnS, PbS, CuS), most often utilized for hexavalent chromium (Cr^{+6}) reduction
- Sodium Dithionite (or sodium hydrosulfite) primarily used in the textile/paper industries as a whitening agent
- Combined with naturally occurring iron for Cr^{+6} reduction
- Low cost, application easily modified based on naturally occurring iron, pH

Sodium Dithionate

Sodium Dithionate Case Study

Macalloy Corporation- Superfund Site

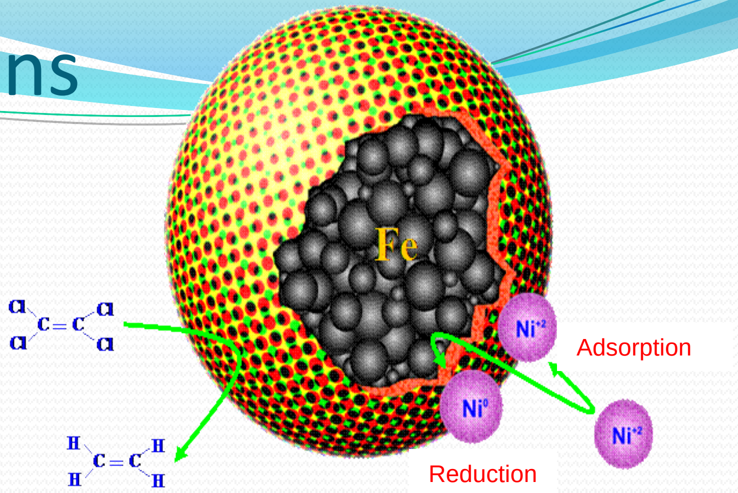
- Site was a ferrochromium alloy smelting plant from 1941-1998
- Groundwater contamination covered 20+ acres and contained hexavalent chromium (>10,000 µg/L), nickel, and zinc
- Sodium Dithionate (Sodium Hydrosulfite) injected with ferrous iron for treatment
- Pilot testing indicated the injectant provided in-situ treatment for up to 1,020 days
- Full scale system installed in 2005 including the use of injection wells and a PRB
- As of 2010, 19 of 23 wells had chromium levels < 100 µg/L (target clean up goal), with decreasing concentrations in the other 4 wells



Aerial and data taken from US EPA, First Five-Year Review Report, 2010

Chemical Reductant Descriptions

Zero-Valent Metals

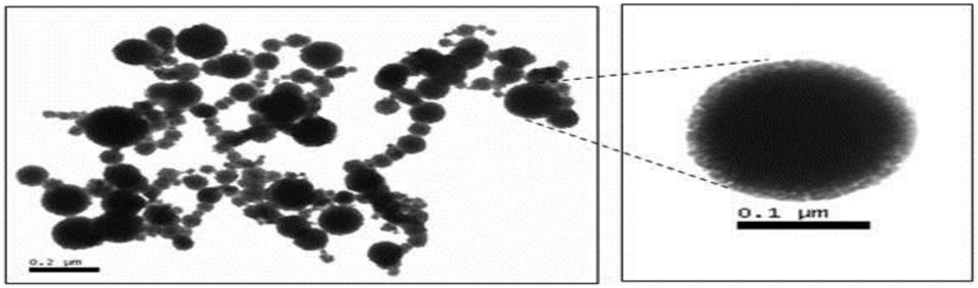


- Zero valent metals (primarily ZVI) are used to treat chlorinated hydrocarbons (select VOCs/SVOCs) and metals
- Chemical reduction occurs as iron oxidizes and hydrogen is released for chlorinated or metals reduction:

Reduction of PCE $4Fe^0 + 4H^+ + C_2Cl_4 \rightarrow 4Fe^{2+} + 4Cl^- + C_2H_4$

Reduction of Hexavalent Chromium $CrO_4^{2-} + Fe^0 + 8H^+ \rightarrow Fe^{3+} + Cr^{3+} + 4H_2O$

- Reduced metals typically precipitated as oxy-hydroxides
- Zero Valent Zinc with/without ZVI used for pentachlorophenol/phenols/PCB reduction
- ZVI electron transfer enhanced by combining palladium, nickel, or platinum catalysts
- Current research focused on nano-scale ZVI (1-100 nm diameter)



Pictures from Wikipedia

ZVI Case Study

East Helena, MT

- Former lead smelter with arsenic contamination in groundwater
- A pilot ZVI barrier installed 600 feet down-gradient from source area
- Study showed overall removal capacity of ZVI of 7.5 mg/gram iron
- Arsenic decreased from 20,000 µg/L to <0.01 µg/L within barrier
- Down-gradient concentrations still being evaluated
- Construction costs were $325,000

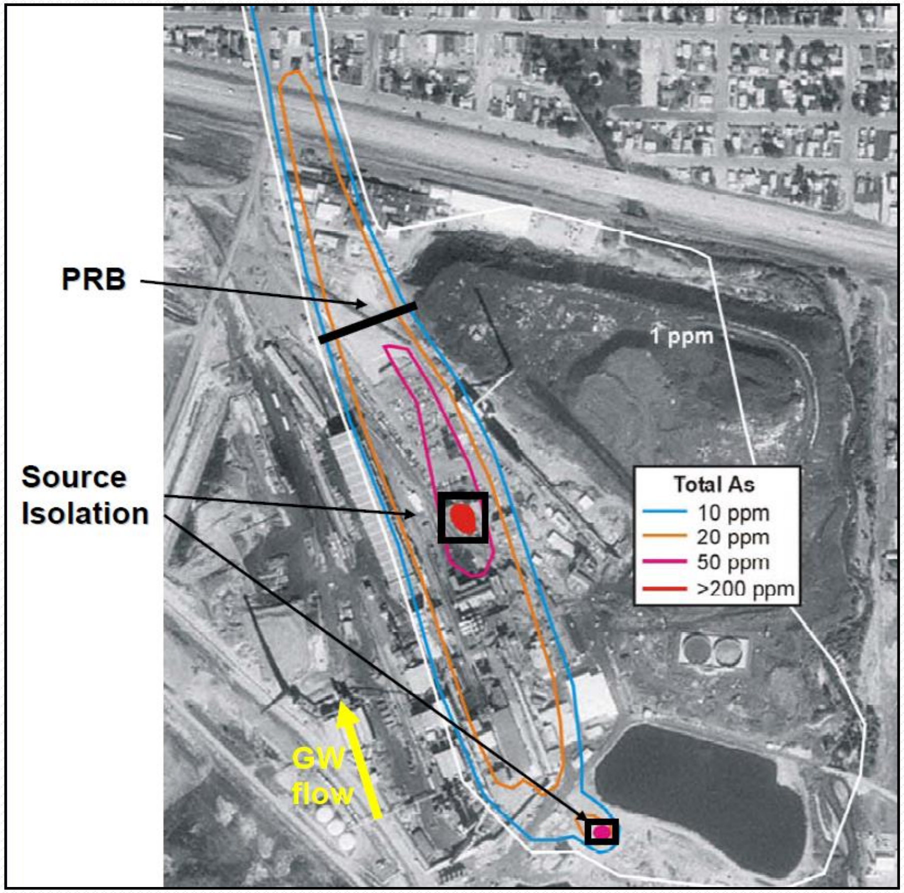
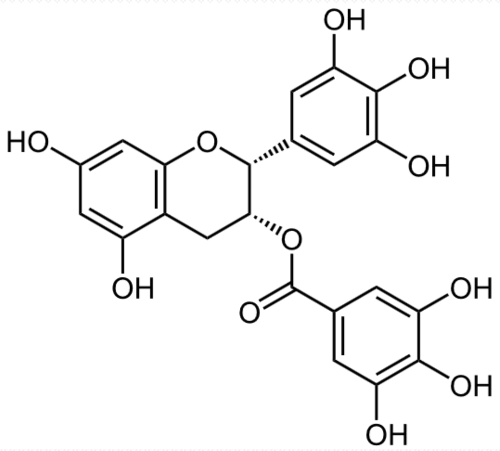


Figure and data taken from US EPA, East Helena, ZVI Permeable Reactive Barrier Treatment of Arsenic in Groundwater, 2006

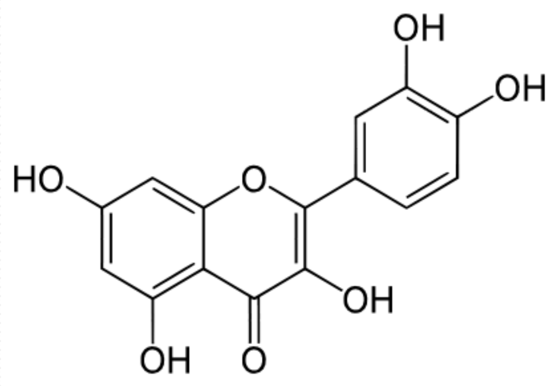
Chemical Reductant Descriptions

Polyphenol nZVI

- Produced by mixing Fe(II) or Fe(III) with natural source of polyphenols in water
- Polyphenols reduce ionic Fe to nZVI (10-100 nm particle size, amorphous)
- Sources of polyphenols: Sorghum Bran, Teas, Fruit Extracts, Fruit Wastes
- Polyphenol layer naturally caps/stabilizes nZVI particles
- Particles remain dispersed in water (do not aggregate)
- Chemically stable without special handling
- Can be produced *in situ* by co-injecting the reagents
- Same ISCR treatment applications as ZVI, but more mobile!
- Patent Issues??

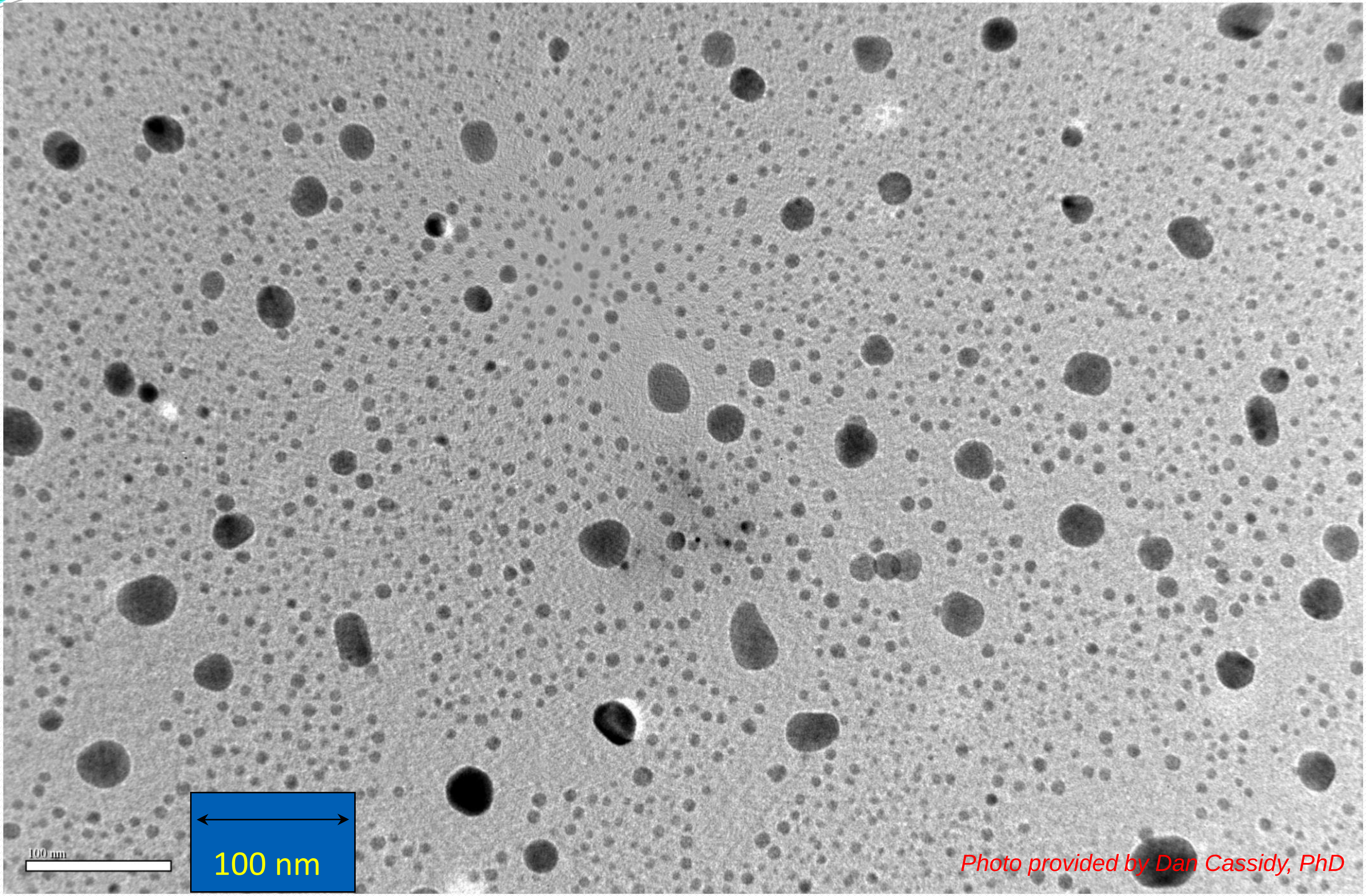


Polyphenols in Green Tea Extract
(*Camellia sinensis*)



Polyphenols in Sorghum Bran Extract
Flavonoids (e.g., *Quercetin*)

FE-SEM Images of Polyphenol nZVI made with Sorghum Bran Extract



Chemical Reductant Descriptions

BiRD®

- Biogeochemical Reductive Dechlorination (BiRD) patented process for treatment of chlorinated solvents/metals [Kennedy-US Patent Office #6,884,352 B1]
- BiRD® relies on engineered in-situ reactions using low cost carbon & sulfate sources reacted with natural occurring iron
- BiRD® reactions include 3 steps/phases that may occur simultaneously:

1) Biological: Supplied organic carbon + sulfate to stimulate common sulfate reducing bacteria (SRB):

$$CH_2O + ½\ SO_4^{2-} \rightarrow HCO_3 + ½\ HS^- (ag) + H_2O + H^+$$

2) Geochemical Step: HS- from SRB respiration reacts with native or supplied iron to produce FeS:

$$3HS^- + 2FeOOH_{(s)} \rightarrow 2FeS_{(s)} + S^o + H_2O + 3OH^-$$

3) Iron sulfides (FeS and FeS_2) reduce chlorinated compounds, similar to ZVI as shown in the chemical reaction below for TCE:

$$4/9FeS + C_2HCl_3 + 28/9\ H_2O \rightarrow 4/9\ Fe(OH)_3 + 4/9SO_4^{2-} + C_2H_2 + 3Cl^- + 35/9H^+$$

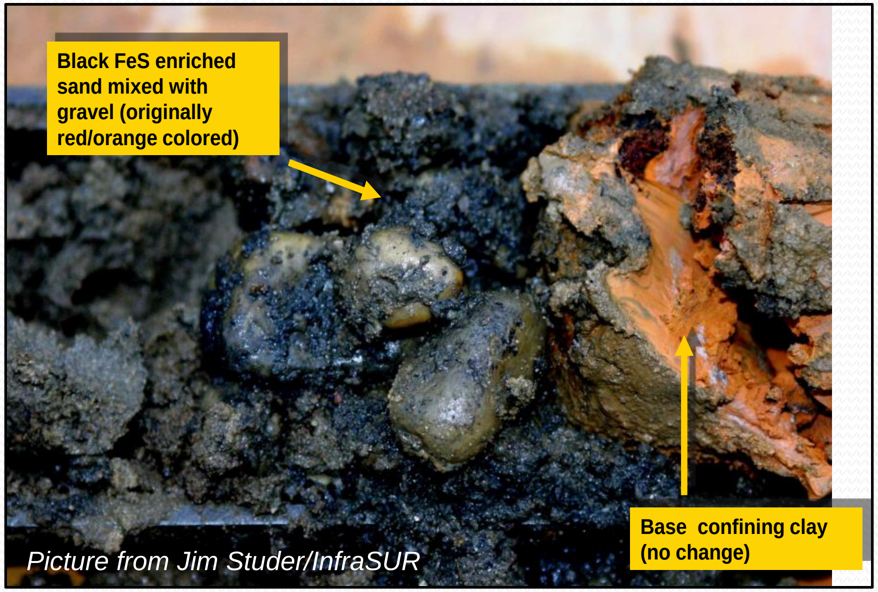
- FeS reduction usually begins within 2-3 weeks or sooner

Information provided by Jim Studer/InfraSUR, Biogeochemical Reductive Dechlorination of Chlorinated Solvent Plumes, October 2012

Chemical Reductant Descriptions
BiRD® cont.

Key benefits of BiRD® include the following:

- BiRD® reaction created using injectable liquids or solid reactants (PRB)
- FeS is formed in-situ, replacing iron oxide minerals, to create a natural flow-through barrier (minimizes concern over pore clogging from iron oxide precipitation)
- Daughter production is generally insignificant
- Reaction kinetics (e.g., half lives) can be less than those indicated for ZVI
- Cost for BiRD® is even less than bioremediation because:
  - Naturally occurring sulfate reducing bacteria and native iron minerals are usually present in most aquifer systems
  - Carbon sources used for FeS generation are inexpensive and almost completely consumed
  - Sulfate, iron, and other amendments, if required, are inexpensive
  - Bio-augmentation is not needed

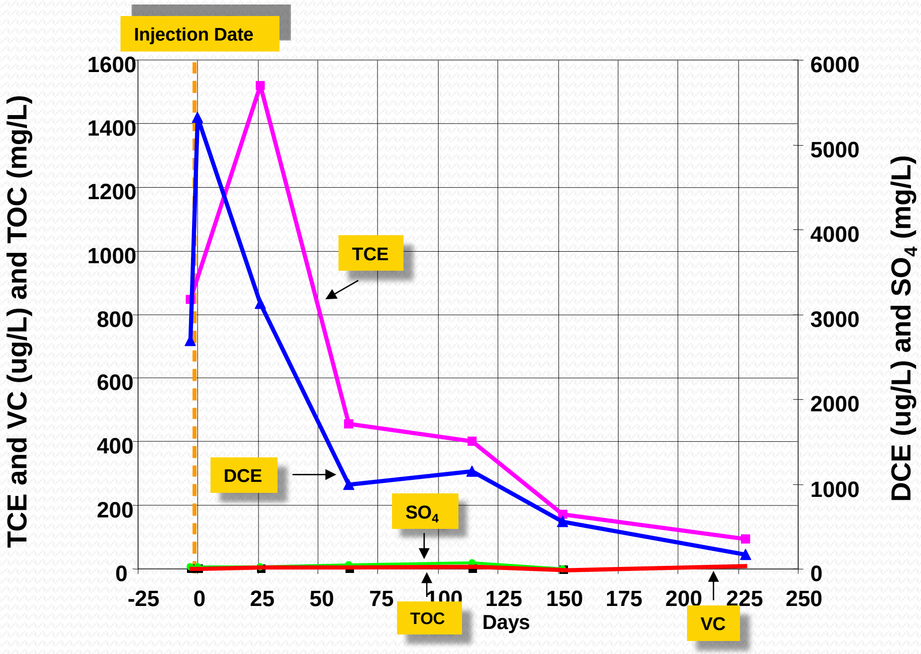


Picture from Jim Studer/InfraSUR

BiRD® Case Study

Dover Air Force Base, DE

- BiRD was tested next to bioremediation test plot at the Dover AFB National Test site
- BiRD was stimulated by injection of Mg SO4·7H2O (Epsom salt) and sodium lactate
- BiRD showed rapid, complete treatment of PCE, TCE, DCE with no daughter products
- Bio showed decreasing TCE, but increasing VC and DCE (no net treatment)



Jim Studer, 18th Annual FL Remediation Conference, Biogeochemical Reductive Dechlorination of Chlorinated Solvent Plumes, 2012

Application Methods

Injection (via direct push or injection wells)

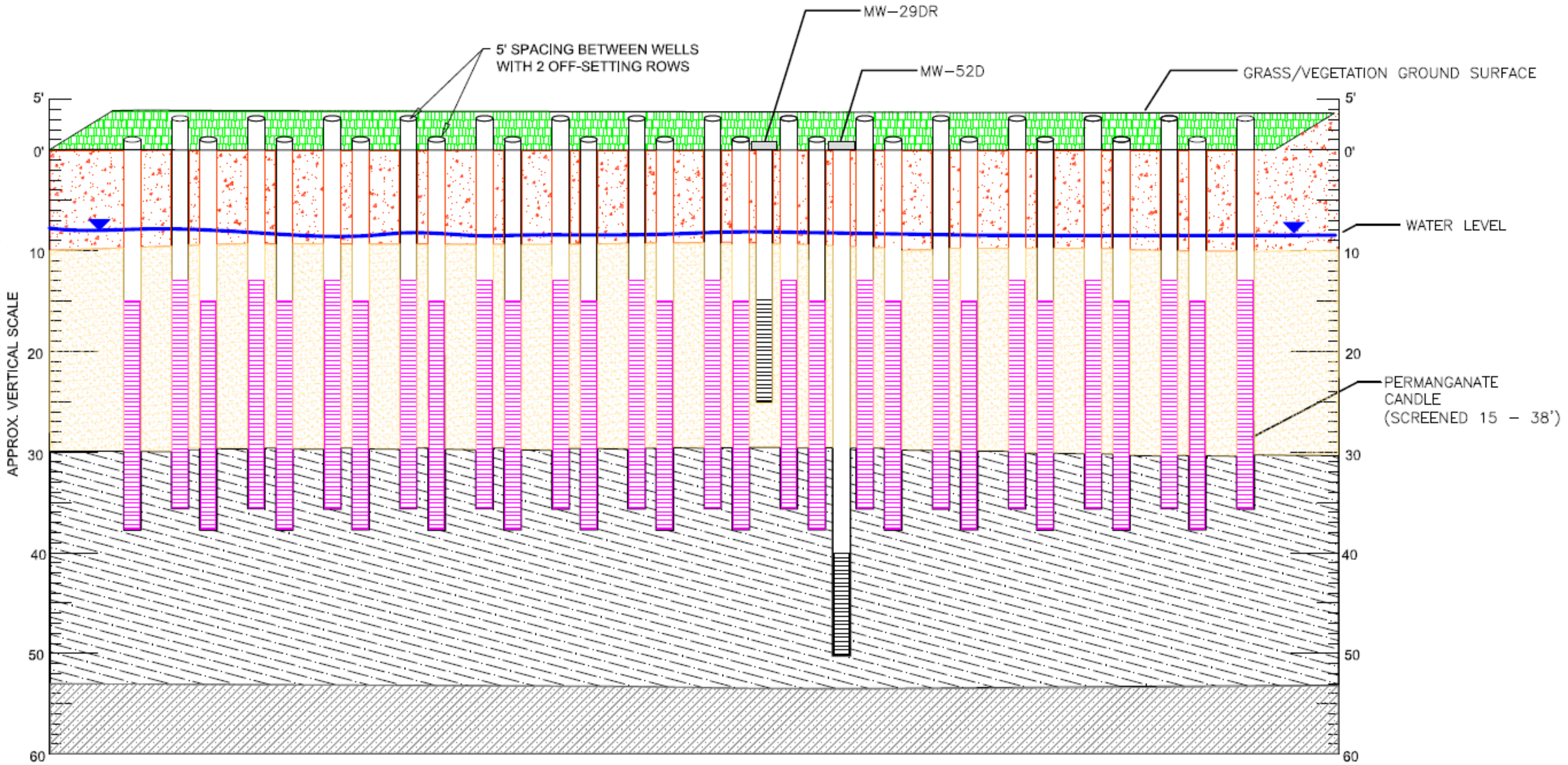
- Direct push allows higher pressure injection, targets discrete zones, may be difficult in "tight" formations/surfacing
- Injection wells with grout seals are better in "tight" formations, allows easier geochemical monitoring, facilitates multi-point injections, offers cost savings with multiple injections

Soil Blending (in-situ or ex-situ)

- In-situ utilizes excavators/augers and allows better contact, eliminates RCRA waste classifications, treats soils and groundwater, allows treatment of "tight" soils, "green friendly"
- Ex-situ involves removal prior to treatment, blending is performed using pug mills, lower cost alternative to hazardous waste landfilling

Application Methods- Permeable Reactive Barriers (PRBs)

- Permeable reactive barriers provide down-gradient plume treatment
- Properly constructed barriers can last 5-10 years or more
- Best suited for ISCR applications where reducing zones are developed
- Permanganate wax candles provide an oxidant PRB option

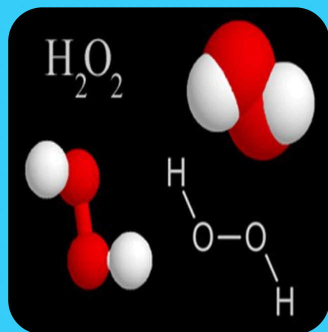


Oxidant Comparisons

Fenton's Reagent

- Hydroxyl radicals have high oxidation potential (2.6-2.8 eV)
- Can treat wide variety of organic compounds
- Fast reaction
- Ideally suited for soil blending
- Rapid desorption
- Difficult to inject

CHP/Modified Fenton's

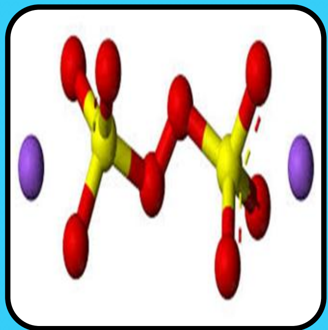


- Chelators slow decomposition and hydroxyl radical formation
- Limited radial influence- requires larger injection volumes
- Very useful for soil matrix desorption/ NAPL destruction
- Per pound least expensive oxidant

Calcium Peroxide

- Offers unique combination of ISCO (H_2O_2) + aerobic bioremediation
- No residual salt by-products
- Slurry- low solubility
- Limited ROI
- Higher cost- often combined with other oxidants

Sodium Persulfate

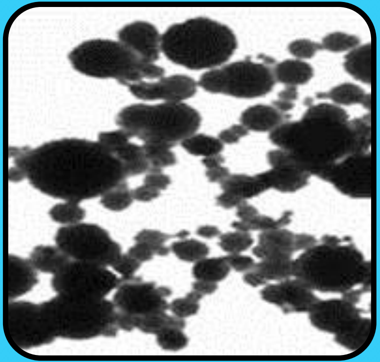


- Versatile, easy to inject
- Sulfate radicals comparable in oxidant strength to **OH**
- pH activation can be difficult to maintain
- Consider utilizing naturally occurring iron when feasible

Permanganate

- Selective oxidant
- No radical chemistry
- Excellent subsurface longevity
- Candles offer PRB option
- Less than calcium peroxide but higher than other oxidants
- Treatability study recommended

ISCR Comparisons



Calcium polysulfide and sodium dithionate: useful for metal reduction (hexavalent Cr), relatively inexpensive

(high DO, low pH, lack of iron affects cost)

Produces iron sulfides

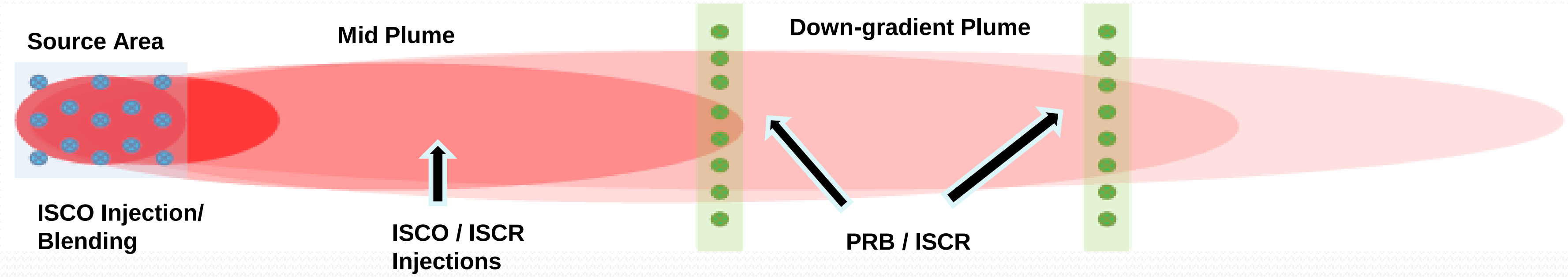
ZVI/Zero valent metals: treats chlorinated VOCs, select SVOCs, various metals, requires injection under high pressure, limited ROI, commonly used in PRB, rapid iron oxidation may limit permeability

nZVI: provides more subsurface mobility and reaction surfaces, polyphenol generated nZVI can be produced in-situ via liquid reagent injection, greater ROI & versatility

BiRD®: used for chlorinated VOCs and select metals, can create reaction using liquid injection or solid phase reactants in a PRB, similar reaction to ZVI but less concern of pore clogging/flow reduction, costs a fraction of ZVI

Application Considerations: ISCO vs ISCR

- ISCO reactions are generally faster than ISCR
- ISCR creates reactive reducing zones- direct chemical contact NOT required
- ISCO can treat NAPL/high dissolved plume areas
- Large plumes– ISCR more cost effective (less reductant needed)
- Lower concentration plume areas- ISCR preferred
- PRBs– ISCR usually better suited
- ISCR more pH dependent/natural geochemistry more of a factor
- Treatability testing aids in comparison and selection
- Consider a “zoned” treatment approach



Base diagram provided by FMC

You can close sites using ISCO/ISCR methods! Keep at it, and remember to:

- Start with a good estimate of clean-up mass and volume
- Choose the right chemistry and application (ISCO/ISCR)
- Treatability testing may be beneficial
- Design a “best-fit” strategy (“zoned” treatment approach)

Eden Remediation Services

Services We Offer

- Chemical Injections (ISCO/ISCR)
- Soil Blending (In-Situ/Ex-Situ)
- Enhanced Bioremedial Approaches
- Surfactant Applications

- Treatability Testing
- PRB Design and Implementation
- Remedial Design/System Optimization
- Rapid Closure Strategies