CHEMICAL OXIDATION VS. CHEMICAL REDUCTION-CHOOSING THE RIGHT APPLICATION

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The objectives of this talk are to provide:

- An overview of chemical oxidation/reduction
- Descriptions of various oxidants/reductants
- Comparisons of oxidants/reductants
- Application considerations
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**

\[ 2\text{NaMnO} + \text{C}_2\text{HCl}_3 \rightarrow 2\text{CO}_2 + 2\text{MnO}_2 + 3\text{Cl}^- + \text{H}^+ + 2\text{Na}^+ \]

**Reduction of TCE using Zero-Valent Iron**

\[ 3\text{Fe}^0 + 3\text{H}^+ + \text{C}_2\text{HCl}_3 \rightarrow 3\text{Fe}^{+2} + 3\text{Cl}^- + \text{C}_2\text{H}_4 \]
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)
What is In-Situ Chemical Oxidation?

- Chemical Oxidation involves breaking bonds of organic molecules with insertion of oxygen and/or removal of hydrogen.
- End products are carbon dioxide, water, and harmless salts.
- ISCO generally involves low to moderate pressure injections to treat contaminants in “smear zone” above/below the water table.

- Used for source area or small area (“spot” treatments) as well as larger plume sites.

- Treatment works on contact- *need full oxidant contact for success!* To reach target goals, desorption of contaminants from soil matrix into the groundwater is required.
Oxidant Descriptions

Different oxidants include:

- Fenton’s Reagent/CHP
- Sodium Persulfate
- Sodium and Potassium Permanganate
- Calcium Peroxide/Modified Fenton’s
Fenton’s Reagent, developed in 1895 by H.J.H. Fenton, who combined hydrogen peroxide with an iron salt producing hydroxyl radicals ($\text{OH}^{-}$).

Basic reaction: $\text{H}_2\text{O}_2 + \text{Fe}^{+2} \rightarrow \text{OH}^{-} + \text{OH}^{-} + \text{Fe}^{+3}$

- 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
- Can easily combine CHP with mechanical extraction
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:

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

Catalysts include: heat, metal catalysts (iron), H$_2$O$_2$, and pH buffers

Sulfate radicals comparable in oxidant strength to OH$^{-}$

Successful on a variety of organics/less exothermic reaction than CHP

Combination with oxygen release agents produces ISCO-aerobic bioremediation “treatment train”
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
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):

\[ 2 \text{CaO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{O}_2 \]

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

\[ \text{CaO}_2 + 2\text{H}^+ + \text{Ca}^{2+} (\text{aq}) + 2\text{H}_2\text{O}_2 \]

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

\[ \text{H}_2\text{O}_2 + \text{Fe}^{+2} \rightarrow \text{Fe}^{+3} + \text{OH}^- + \text{OH}^- \]

In-situ formation of hydroxyl radicals produces a controlled reaction.
**ISCR Description**

<table>
<thead>
<tr>
<th>ISCR involves the addition of electrons (often hydrogen) substituted for other ions</th>
<th>Abiotic reactions usually result in less daughter product formation</th>
<th>Used on chlorinated plumes, metals, explosives, etc., applied via direct injection and solid phase PRBs (goal of developing reducing zones)</th>
<th>Examples: ZVI, nZVI, iron sulfides, polysulfides, dithionites, etc.</th>
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</table>
Common ISRC Reagents

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

Tratnyek and Johnson (2006)
NanoToday 1(2): 44-48
Chemical Reductant Descriptions
Sulfide Salts (Calcium Polysulfide, Sodium Dithionate)

- **Calcium Polysulfide** ($\text{CaS}_x$) and **Sodium Dithionate** ($\text{Na}_2\text{S}_2\text{O}_4$) are strong bulk reductants that produce high pH (10-11) solutions.
- Reduces metal oxy-hydroxides producing sulfides ($\text{FeS}$, $\text{ZnS}$, $\text{PbS}$, $\text{CuS}$)
- Utilized for hexavalent chromium ($\text{Cr}^{6+}$) reduction
- Arsenic treatment using **Calcium Polysulfide** requires iron to precipitate arsenopyrite.
- **Sodium Dithionite** (or sodium hydrosulfite) primarily used in the textile/paper industries
- Combined with naturally occurring iron for $\text{Cr}^{6+}$ reduction
- Other contaminants treated include explosives/energenics (TNT, RDX)
- Low cost, application easily modified based on naturally occurring iron, pH.
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:

\[
\text{(Reduction of PCE)} - 4\text{Fe}^0 + 4\text{H}^+ + \text{C}_2\text{Cl}_4 \rightarrow 4\text{Fe}^{2+} + 4\text{Cl}^- + \text{C}_2\text{H}_4
\]

\[
\text{Reduction of Hexavalent Chromium} - \text{CrO}_4^{2-} + \text{Fe}^0 + 8\text{H}^+ \rightarrow \text{Fe}^{3+} + \text{Cr}^{3+} + 4\text{H}_2\text{O}
\]

- Reduced metals can be precipitated in a stable form or as iron oxyhydroxides.
- 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).
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)

![Polyphenol structure](image1.png)

### Polyphenols in Sorghum Bran Extract

Flavonoids (e.g., Quercetin)

![Polyphenol structure](image2.png)
FE-SEM Images of Polyphenol nZVI made with Sorghum Bran Extract

Photo provided by Dan Cassidy, PhD
Chemical Reductant Descriptions

**BiRD®**

- Biogeochemical Reductive Dechlorination (BiRD) patented process (InfraSUR) 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):

     \[
     \text{CH}_2\text{O} + \frac{1}{2} \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \frac{1}{2} \text{HS}^- (\text{ag}) + \text{H}_2\text{O} + \text{H}^+
     \]

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

     \[
     3\text{HS}^- + 2\text{FeOOH} (s) \rightarrow 2\text{FeS} (s) + S^0 + \text{H}_2\text{O} + 3\text{OH}^-
     \]

  3) Iron sulfides (FeS and FeS$_2$) reduce chlorinated compounds, similar to ZVI as shown in the chemical reaction below for TCE:

     \[
     \frac{4}{9}\text{FeS} + \text{C}_2\text{HCl}_3 + \frac{28}{9} \text{H}_2\text{O} \rightarrow \frac{4}{9}\text{Fe(OH)}_3 + \frac{4}{9}\text{SO}_4^{2-} + \text{C}_2\text{H}_2 + 3\text{Cl}^- + \frac{35}{9}\text{H}^+
     \]

- 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*
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 precipitates)
- 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
Application Methods – Injection

Direct Push Injection
- Target discrete zones
- Allows higher pressure injection (ZVI/slurries)
- Difficult in “tight” formations/surfacing
- Additional wells often needed for monitoring

Injection Wells
- Constructed with PVC, CPVC, Stainless Steel
- Grout seals – better in “tight” formations
- Easier geochemical monitoring
- Facilitates multiple point injection
- Cost savings with multiple injections
Application Methods - Soil Blending

- Ex-situ blending involves removal prior to treatment using augers, excavators, etc.
- Blending performed using pug mills
- Lower cost alternative to hazardous waste landfilling

- In-situ blending utilizes excavators or augers
- Better contact than injection
- Eliminates waste generation
- Treats soils AND groundwater together
- Allows treatment of “tight” soils
- “Green friendly” alternative to landfilling
Permeable reactive barriers provide down-gradient plume treatment
Properly constructed barriers can last 5-10 years or more prior to chemical replenishment
More suitable for ISCR applications
Permanganate wax candles provide an oxidant PRB option
Oxidant Comparisons

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Hydroxyl radicals</th>
<th>Chelators</th>
<th>Sodium Persulfate</th>
<th>Permanganate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>have high oxidation potential (2.6-2.8 eV)</td>
<td>slow decomposition and hydroxyl radical formation</td>
<td>offers unique combination of ISCO ($\text{H}_2\text{O}_2$) + aerobic bioremediation</td>
<td>Versatile, easy to inject</td>
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<td>Can treat wide variety of organic compounds</td>
<td>Limited radial influence - requires larger injection volumes</td>
<td>No residual salt by-products</td>
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<td>Very useful for soil matrix desorption/NAPL destruction</td>
<td>Slurry - low solubility</td>
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<td>Ideally suited for soil blending</td>
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<td>Difficult to inject</td>
<td>Per pound least expensive oxidant</td>
<td>Higher cost - often combined with other oxidants</td>
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Fenton's Reagent
- Hydroxyl radicals
- 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 ($\text{H}_2\text{O}_2$) + 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 $\text{OH}$
- 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
- **Calcium polysulfide and sodium dithionate**: useful for metals reduction (hexavalent chromium), relatively inexpensive (high DO, low pH, or lack of iron will affect cost)

- **ZVI/Zero valent metals**: allows reductive treatment of chlorinated VOCs / select SVOCs / various metals, requires injection under high pressure, limited ROI due to particle size, most commonly used in a PRB application, rapid iron oxidation may limit PRB permeability over time

- **nZVI**: provides more subsurface mobility and reaction surfaces, polyphenol generated nZVI can be produced in-situ via liquid reagent injection, more versatile product

- **BiRD®**: used to treat 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
Subsurface Remediation is Attainable!

Keep at it, and remember to:

- Start with a good estimate of clean-up mass and volume
- Choose the right chemistry (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