Benefits of Combining In Situ Chemical Oxidation with In Situ Stabilization: Synergies and Solutions

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SMART Remediation
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Benefits of Combining In-Situ Chemical Oxidation with In Situ Stabilization: Synergies and Solutions for Complex Sites

Presented by Jean Paré, P. Eng.

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Presentation Agenda

- Technology overview
  - In Situ Solidification-Stabilization
  - In Situ Chemical Oxidation
- Combined Remedy
  - Synergies and Benefits
- Reagent Blend
  - Match to site specific remedial goals
- Strategies and Applications
- Summary
About us

Canadian Company founded in 1988

- **Production and warehouses throughout Canada**
  - Quebec
  - Ontario
  - Alberta
  - British Columbia

- **Sectors of activity:**
  - Industrial and Municipal Potable & Waste Water
  - Contaminated Soil and Groundwater
  - Air, Odours and Atmospheric Emissions (Activated Carbon, filtering medias)
  - Process Water & Thermal Exchange Fluids (Glycols)
  - Drilling Fluids (Oil and Gas & Diamond exploration)
  - Aircraft De-icing Fluids

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Canadian leader in environmental expertise & specialized products

- Chemical Oxidation
- Chemical Reduction
- Co solvent-Surfactant soil Washing
- Enhanced Bioremediation
- Permeable Reactive Barrier Amendments
- Metals Stabilization

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Technologies In Situ – Key Drivers

- Remedial objectives - Time versus Money
- Access to the contaminant of concern (underground infrastructure, public utilities, building, road, etc.)
- Polishing step to meet low remedial objectives or Risk-Based Criteria
- Sustainable Development Contribution versus remote off-site disposal, environmental footprint, air emission from trucking, etc.
- Improvement of contaminant removal rate versus natural attenuation
Typical site remediation technique

- Dig & Haul
- Pump & Treat
- Soil Vapour Extraction under vacuum with or without air/steam injection
- Chemical Oxidation In Situ/Ex Situ
- Chemical Reduction In Situ/Ex Situ
- Monitored Natural Attenuation
- Enhanced Bioremediation
- Risk Analysis
- Stabilization /Solidification
- Soil Washing
- Phytoremediation
- Reactive Barriers
- Thermal degradation/desorption
- Activated Carbon Sorption Technology

In Situ Solidification-Stabilization (ISS)

- Contaminant *immobilization or mass flux reduction* (used for metals and organic leachable species)

- **Stabilization** - Decreases the hydraulic conductivity of soils

- **Solidification** - Compressive soil strength influenced by type and dose of reagents

- Applied via soil mixing/blending

ISS is commonly used to immobilize highly contaminated petroleum hydrocarbon sites (MGP sites, etc)
In Situ Chemical Oxidation (ISCO)

- In situ chemical oxidation (ISCO)
  - Powerful destructive remedial technology
  - Applied via injection, recirculation, backfill amendment, and soil mixing

Alkaline activated persulfate

- Thousands of successful applications
- Oxidative and reductive destructive pathways
  - Complex comingled plumes
- Minimized corrosivity on carbon steel equipment & underground infrastructure
- Little to no heat or gas evolution

ISCO works by establishing contact between a sufficient mass of activated persulfate and the mass of contaminant

ISCO applied via Soil Mixing

- ISCO with Soil Mixing
  - Establishes contact
  - More rapid treatment
  - Homogenizes soil and contaminant
    - Minimizes impact of heterogeneity
    - Low permeable soil

- Some sites have reported very soft soils post soil mixing

Courtesy of Bill Lang
Remedial Objective - Where to Use ISS and ISCO

- **Source zones**
  - Very highly contaminated sites (NAPL)
    - Petroleum hydrocarbon (MGP, etc.)
    - cVOC
  - Petroleum hydrocarbon (MGP, etc.)

- **To create hydraulic barriers**
  - Lower hydraulic conductivities observed in ISS with ISCO rather than ISS alone

- **Soil mixing application strategy**

- **Enhanced Site soil characteristics**

- **Balance contaminant destruction, solidification, and post application**

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**ISS & ISS-ISCO - Deployment Options**

![Deployment Options Diagram](#)
Technological Synergies of ISCO and ISS

Combining ISCO and ISS can make each technology better

ISCO benefits:
1. Alkalinity from ISS reagents can be used to activate Klozur SP
2. Soils can have their geotechnical characteristics enhanced with low amounts of ISS reagents

ISS benefits:
3. Contaminant destruction by ISCO can enhance stabilization from ISS
   • Helps the cementitious process
   • Less contaminant to immobilize = lower leachate concentrations
4. Less overall mass of reagents results in less excess soil generation
5. Better balance between hydraulic conductivity and compressive soil strength

Contaminant destruction and immobilization in single soil mixing application (combined remedy)
6. Saving project time and overall cost

ISCO Benefits - Alkaline activation

ISS reagents
• Portland cement (~65% CaO)
• Calcium hydroxide [Ca(OH)₂]
• Calcium oxide (CaO)
• Fly Ash (Class C & F)
• Blast furnace slag
• Lime kiln dust
• Cement kiln dust
• Pozzolans
• Bentonite

Activated Klozur persulfate reagents
• Klozur Sodium Persulfate (oxidant)
• Klozur Potassium Persulfate (oxidant)
• Alkaline activation*. One (or more) of the following:
  • 25% NaOH (typical for injections)
  • Calcium hydroxide [Ca(OH)₂]
  • Calcium oxide (CaO)

• Heat activation
  • CaO upon hydration releases heat

Common ISS reagents can activate Klozur SP

* PeroxyChem LLC ("PeroxyChem") is the owner of U.S. Patents No: 7,576,254 and its foreign equivalents. The purchase of PeroxyChem’s Klozur® persulfate includes with it, the grant of a limited license under the foregoing patent at no additional cost to the buyer.
Combining ISS and ISCO


ISS Benefits: Leachate Concentrations

• Contaminant leachate reduction
  • Greater reduction in leachate concentrations with Klozur SP and Portland cement than Portland cement only
  • ISCO preferentially reduced more soluble contaminants
  • Portland cement alone only preferentially reduced leachate concentrations of larger, less soluble compounds

**EVOLUTION - Combining ISS and ISCO**


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**ISS Benefits: Control of Soil Characteristics**

- ISS is typically used to achieve multiple remedial goals. For example:
  - Hydraulic conductivity (common $< 10^{-6}$ cm/sec)
  - Compressive soil strength (common 20-50 psi)

- Using ISS reagents alone may be difficult to achieve both hydraulic conductivity and compressive soil strength goals

- ISS with ISCO
  - ISS and persulfate dosage rates can be varied to better achieve both hydraulic conductivity and compressive soil strength goals
Optimizing Ratio of Reagents

• ISCO and ISS reagents can be combined for their mutual benefit

• The ratio of reagents can be adjusted to achieve site-specific remedial goals

ISS-ISCO Reagent Ranges

ISCO and ISS reagent doses can be varied to achieve a variety of remedial goals

Stabilization  Remedial Goals  Destruction

ISS  ISS with ISCO  ISCO-ISS  ISCO with ISS  ISCO

ISCO Reagents  ISS Reagents
Case Study 1 - Turtle Bayou

- ISCO and ISS are already being combined at several sites

- 2008 Turtle Bayou (URS-AECOM)
  - COCs: BTEX, cVOCs and PAHs
  - Klozur SP, hydrated lime, and Portland cement
    - 760,000 lbs Klozur SP
  - Met remedial goals
    - ISCO: 84% to 97% treatment
    - ISS: Stabilized soils

Lesson Learned: Chemical compatibility with reagents, and benefits of alkaline activated persulfate

**ISCO Benefits from ISS Soil Strength**

- ISCO applied with soil mixing and no ISS reagents may not have desirable post application soil characteristics
  - Low levels of ISS reagents can enhanced post application soil characteristics
    - Site specific (approximately 0.5 to 1.5% Portland cement)

<table>
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<th>Consistency</th>
<th>Unconfined Compressive Strength (UCS) Ranges</th>
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<tr>
<td></td>
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<tr>
<td></td>
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<td>Hard</td>
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Typical target range for “workable” soils
20-50 psi

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**Case Study 2 - Combining ISS and ISCO**


- Highly contaminated soils
  - >36,900 mg/Kg TPH
  - ~6,800 mg/Kg BTEX
  - ~13,400 mg/Kg Naphthalene (Nap)
  - ~16,900 mg/Kg 17 PAHs (not including Nap)

- Klozur SP: Portland Cement (PC) ratio (1:2 w/w)
  - CaO in PC facilitates persulfate activation

- ISCO:
  - Persulfate underdosed for complete treatment of TPH
  - Preferential treatment of soluble contaminants
Case Study 3 - Application
Strategy

Different reagent blends can be used at the same site

Example:
• Highly contaminated center
  • Stabilize: ISS, or ISS (with ISCO)
  • Treat and stabilize: ISCO with ISS

• Less contaminated outer ring:
  • ISS is balanced with ISCO to maximize reduction in hydraulic conductivity to create a hydraulic barrier

Salinity Parameters Aquifer Impact
(Persulfate Alkaline Activation with Hydrated Lime)

<table>
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<tr>
<th>Parameters (All unit in mg/l other than for SAR – no unit)</th>
<th>Blank</th>
<th>Alkaline (Hydrated Lime) Activated Sodium Persulfate</th>
<th>Alkaline (Hydrated Lime) Activated Potassium Persulfate</th>
<th>Alkaline (Hydrated Lime) Activated Ammonium Persulfate</th>
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<td>Sulfate</td>
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<td>13 000</td>
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Summary

• Blends of ISCO and ISS using soil mixing can be a powerful combined remedy
  • Degrades the contaminant
  • Reduces contaminant flux
  • Controls post-application geotechnical characteristics of a site

• Has been found to be lower cost alternative
  • Less Excess soil displaced, less mixing/handling
  • Combined remedy in a single application

• Technology synergies:
  1. Shared alkaline sources
  2. Contaminant degradation by ISCO can reduce leachate (SPLP) concentrations
  3. ISCO can oxidize organics interfering with the cementitious process resulting in lower hydraulic conductivities if dosed appropriately
  4. Control over post soil mixing application soil characteristics

Acknowledgements & Ressources

✓ Peroxychem
✓ Journal articles from Vipul Srivastava and Dan Cassidy/Western Michigan University
  • Srivastava et al, (2016) Chemosphere, 154, 590-598
✓ Conference presentations
  • Klemmer et al, (2017) “Combining In Situ Chemical Oxidation and In Situ Solidification for Coal Tar – Synergy or Conflict?” 19th Railroad Environmental Conference, Champaign, IL

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