In Situ Stabilization and Solidification (ISS) + ISCO: Benefits of Adding Sodium Persulfate to S/S binders

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Presentation Outline

• Corporate Introduction

• Technology overview
  • In Situ Chemical Oxidation (ISCO)
  • In Situ Stabilization (ISS)
  • In Situ Soil Mixing process

• Combined Remedy
  • Benefits
  • Synergies

• Summary
following Decades of Experience, we will soon have a New Name.

1988 WR Grace Remediation R&D Program
1994 First Application of Daramend® Reagent
1999 First Application of PermeOx® Plus
2002 Adventus Remediation Technologies was formed via WR Grace Divestiture
2004 Launch of Klozur® Persulfate
2006 Launch of Klozur® CR
2007 Klozur Demand Testing
2011 Klozur 2012 EnviroMetal Technologies Acquired by Adventus
2014 FMC Corporation divested the Peroxygens Group, PeroxyChem was founded
2020 EnviroMetal Technologies Division Formed
In Situ Chemical Oxidation

- Powerful **destructive** remedial technology
- Applied via injection, recirculation, backfill amendment, and soil mixing

Alkaline Activated Persulfate

- Thousands of successful applications, worldwide
- Oxidative and reductive CoC destruction pathways
  - Complex comingled plumes
- Minimized corrosivity on carbon steel equipment
- Little to no heat or gas evolution

Success is **enough oxidant (reducer)** *in contact* with the contaminant for a **long enough period of time** to react effectively

- **Reagent load**
- **Distribution**
- **Reagent persistence**
- **Contaminant Destruction**
In Situ Stabilization

- In Situ Stabilization (ISS)
  - Contaminant *sequestration or mass flux reduction* remedial technology
  - Decreases the hydraulic conductivity of soils
  - Depending on reagents, can control post-application compressive soil strength
  - Applied through soil mixing / blending techniques
    - Using Portland cement & SCMs (Supplementary Cementitious Materials)
      e.g. pozzolans
In Situ Soil Mixing

- Application method using mechanical mixing to break apart soils

- Establishes contact
  - Typically more rapid treatment

- Minimizes impact of site heterogeneity
  - Soil (low vs high permeable soils)
  - Contaminants (averages variability in distribution)

- Several modern tools can apply reagents at depth

- Excavator Bucket
- Specialized Mixing Heads
- Augers
Combined ISCO-ISS Remedy

• ISS and ISCO reagents can be blended together using in situ soil mixing
  • Establishes contact
  • Homogenizes contaminant and soils

• Economical: ISCO-ISS = ca. 50% the cost of “dig and dump”
  • Will be site and country-specific

• Highly contaminated sites

Contaminant destruction and mass flux reduction remedial technologies in a single application.

Initial Articles from Dan Cassidy/Western Michigan University’ lab:
• Srivastava et al (2016) Chemosphere, 154, 590-598
Synergy #1: Alkali Reagents

ISS reagents

✓ Portland Cement (~65% CaO)
✓ Calcium hydroxide [Ca(OH)\textsubscript{2}]
✓ Calcium oxide (CaO)
✓ Fly Ash (Class C & F)
✓ Blast furnace slag
✓ Lime kiln dust
✓ Cement kiln dust
✓ Other SCMs / pozzolans
✓ Bentonite

Activated sodium persulfate reagents

✓ Klozur® SP(oxidant)

✓ Alkaline activation: one, or more, of the following:
  • 25% NaOH (typical for injections)
  • Calcium hydroxide [Ca(OH)\textsubscript{2}]
  • Calcium oxide (CaO)

✓ Heat activation
  • CaO upon hydration releases heat
Combining ISCO-ISS


- Highly contaminated site
  - >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 ratio (1:2 w/w)
  - CaO in PC is alkali and heat source (activation)

- ISCO:
  - Under dosed for complete treatment of TPH
  - Used to preferentially treat BTEX (>90%) and Naphthalene (>80%)

- ISS used to:
  - Decrease hydraulic conductivity
  - Increase compressive soil strength:

![Contaminant Reduction](chart)

![Reduced Hydraulic Conductivity](chart)

![Increasing Compressive Soil Strength](chart)

![Six Order of Magnitude Decrease](chart)
Synergy #2: Destruction Reduces Leachability

- Contaminant leachate reduction
  - Contaminant destruction (ISCO) reduces leachate concentrations [synthetic precipitation leaching procedure (SPLP)]

- Destruction by ISCO - preferentially oxidized highly soluble organic contaminants

- Portland cement alone - preferentially reduced leachate concentrations in larger, less soluble compounds

Synergy #3: Enhanced Cementitious Process

- Organic contaminants can interfere with cementitious process
  - Soils covered in oil do not bind well!

- Sufficiently dosed ISCO oxidizes the organics, enhances the cementitious process

**Highly contaminated soils:**
- Hydraulic conductivity and compressive soil strength a function of Portland Cement

**Less contaminated soils:**
- Hydraulic conductivity also a function of Klozur SP content
- Compressive soil strength variable
Balancing Reagents

• Key points when balancing reagents:
  • Remedial Goals:
    • Contaminant destruction (ISCO)
    • Contaminant flux (ISS; ISCO-ISS)
  • Post-Application site characteristics
    • Hydraulic conductivity
    • Compressive soil strength

• Reagents to be balanced:
  I. Oxidant: Klozur SP
  II. Alkali source
    • Portland cement
    • Hydrated lime
    • et al.
  III. ISS reagents
    • Cementitious reagents
    • Bentonite
    • et al.
**ISCO - ISS**

**Primary remedial goal is contaminant immobilization**

- ISS reagents dosed to solidify soil matrix
- Contaminant degradation by ISCO:
  - Reduces leachate (SPLP) concentrations
  - Helps the cementitious process (ISS)

**ISCO - ISS**

**Primary remedial goal is contaminant destruction by ISCO**

- ISCO maximizes contaminant destruction
- ISS is used to:
  - Create workable soil (~30-50 psi / 200-400 kPa)
  - Help decrease hydraulic conductivity (long term mass flux)
Different blends can be used at the same site

Example:

- Highly contaminated center:
  - ISCO dosed to preferentially treated COCs (e.g. not all TPHs)

- Outer ring ("stockade design")
  - Forms best hydraulic barrier around areas of extreme contamination
  - ISCO dosed to treat most TPHs, ISS is balanced with ISCO to create a hydraulic barrier
    - Possible replacement for sheet pile!
Where to Use ISS and ISCO

• Source zone immobilisation
  • Very highly contaminated sites (NAPL)
    • Poly Aromatic hydrocarbons (gasworks)
    • cVOC (chlorinated hydrocarbons)

• To create hydraulic barriers
  • Lower hydraulic conductivities for ISS with ISCO, rather than just ISS alone

• Soil mixing application strategy

• Need a different ratio of reagents to accomplish site-specific goals
  • Balance contaminant destruction, solidification, and post-application site soil characteristics
Summary

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

• Technology synergies:
  1. ISS reagents as an activation source for KLOZUR® SP sodium persulfate
  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
• Former MGP Site in Denmark (COWI Consult)
  • 3% Klozur SP
  • 8% Portland Cement/Slag

• ISS Goals:
  • UCS: 100% > 20 psi (150 kPa) after 80 days

• Permeability:
  • Avg: 2.1 x 10^{-7} cm/sec
  • 100% of 26 samples ≤ 1 x 10^{-6} cm/sec

<table>
<thead>
<tr>
<th>Compound</th>
<th>Baseline Concentration(^1) (mg/Kg)</th>
<th>Post Application Concentration (mg/Kg)</th>
<th>Reduction due to Treatment (%)</th>
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<tbody>
<tr>
<td>Benzene</td>
<td>13 to 27</td>
<td>ND</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>100 to 160</td>
<td>23</td>
<td>80-85</td>
</tr>
<tr>
<td>Phenols</td>
<td>3</td>
<td>0.04</td>
<td>99</td>
</tr>
<tr>
<td>TOC</td>
<td>500 to 800</td>
<td>23</td>
<td>85-90</td>
</tr>
</tbody>
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1. Based on conversion of contaminant mass estimates

• Contaminant reduction

• Eliminate free product

• Stable (compressive strength)

• Minimize waste generation

BAUER BG24H soil mixing machine
Case Study: Bolzano, Italy

- Treatment volume:
  - 3,500 m³ (~4,600 yd³)

- Depth:
  - 3 to 8 m bgs (9.8 to 26 ft bgs)

- 556 columns

- Reagents
  - 0.7 to 1% Klozur SP
  - 4 to 8 percent Portland cement

- Treatment speed:
  - 37 MT/hr

Courtesy of Ladurner
1. ISS (with ISCO)
   - Remedial Goal:
     - Immobilize contaminants
     - Post application soil characteristics
   - Add Klozur SP:
     - Reduce soil displaced
     - Better influence over:
       - Hydraulic conductivity
       - Compressive soil strength
     - Lower leachate concentrations

2. ISCO (with ISS)
   - Remedial Goal:
     - Contaminant Mass Reduction
   - Add ISS reagents:
     - Target post application site geotechnical characteristics
     - Compressive soils strength
     - Soil mixing applications (if needed)

3. ISCO-ISS
   - Remedial Goals:
     - Single application
     - Contaminant Mass Reduction
     - Immobilize residual contamination
     - Target post application soil characteristics
   - Adjust reagent blends to target site specific remedial goals

Can be a lower cost alternative to:
- ISS alone, sheet piling or excavation
- Combined remedy in single application
Questions…

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