Combined In Situ Chemical Oxidation and Stabilization/Solidification for Full-Scale Remediation of a Coal Tar Source Area

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Acknowledgments

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Capital Region of Denmark

Kim Jensen - Arkil
Søllerød Gaswærk Site, 1954
Benzene in Groundwater, 2015
Why In Situ Chemical Oxidation (ISCO) + In Situ Stabilization / Solidification (ISS)?

- Treats all waste on-site.
- Rapid implementation.
- In U.S.A., ISS typically is applied alone. ISS is a mature technology used at hundreds of sites.
- At Søllerød, proximity of downgradient municipal supply well prompted need for destructive treatment (ISCO) as well as ISS.
- Published laboratory studies show promise for ISCO + ISS.
ISCO / ISS Bench Test Approach

• **Reagents/Additives:**
  – ISCO using base-activated persulfate (BAP) [2, 3, 4%]
  – ISS using CEM III/B (slag cement) [8 to 10%]
  – CEM I 42,5 N - SR5 (similar to Portland Type V marine cement)

• **Performance Targets:**
  – Oxidation and *reduction in leaching* of dissolved phase coal tar constituents (i.e., BTEX, sVOCs, and phenolic compounds);
  – Acceptable values of slurry density, viscosity, and pH (API RP13B-2);
  – Average *hydraulic conductivity* \((K_h)\) < 1x10^{-6} cm/s with no more than 10% of the samples > 1x10^{-5} cm/s
  – *Unconfined compressive strength* (UCS) > 0.15 MPa at 28-day
Phase 0 - Baseline Geologic Material Homogenization and Sampling

Phase 1A – ISCO Optimization

- E2+E3 (67:33) spiked with neat benzene to target a concentration of 10 mg/kg (dry weight basis)
- 350 g/L persulfate solution
- 2%, 3%, and 4% by dry weight BAP
- Amended with 10 M NaOH to target a pH of 11.5
Bench Test Phase 1B – ISS Optimization

Phase 0 - Baseline Geologic Material Homogenization and Sampling

Phase 1A – ISCO Optimization

Phase 1B – ISS Optimization

- Spike with neat benzene to target a concentration of 10 mg/kg
- ISS Mix Designs
  - 8% CEM III/B (dry weight)
  - 10% CEM III/B (dry weight)
  - 8% CEM I 42,5 N – SR5 (dry weight)
  - 1:1 W:C
- UCS (ASTM D1633)
- Hydraulic Conductivity (ASTM D5084)
- Leach Testing (USEPA LEAF 1315)
Bench Test Phase 2 – ISCO + ISS

Phase 0 - Baseline Geologic Material Homogenization and Sampling

Phase 1A – ISCO Optimization

Phase 1B – ISS Optimization

Phase 2 – ISCO + ISS

- Spike with neat benzene to target a concentration of 10 mg/kg
- Optimal ISS+ISCO Combination:
  - 8% CEM III/B (dry weight)
  - 3% BAP (dry weight)
- **Two-Step** (Sequential ISCO – ISS)
  - NaOH base activation
  - 15-day reaction time
  - Followed by ISS
- **One-Step** (Simultaneous ISCO + ISS)
  - Cement hydration activation
  - ISCO/ISS treatment same day
- UCS, K, Leach Testing
## Bench Test Results Summary

<table>
<thead>
<tr>
<th>Geotechnical test</th>
<th>Unit</th>
<th>ISCO</th>
<th>ISS</th>
<th>ISS+ISCO - One step</th>
<th>ISS + ISCO - Two step</th>
<th>Target value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unconfined compressive strength (UCS)</strong></td>
<td>MPa</td>
<td>NA</td>
<td>3.8</td>
<td>0.59</td>
<td>2.92</td>
<td>0.15 Mpa (&gt; 24 psi)</td>
</tr>
<tr>
<td><strong>Average hydraulic conductivity</strong></td>
<td>cm/s</td>
<td>NA</td>
<td>$1.9 \times 10^{-5}$</td>
<td>$2.7 \times 10^{-7}$</td>
<td>$1.8 \times 10^{-6}$</td>
<td>$&lt; 1 \times 10^{-6}$ cm/s with no more than 10% of the samples &gt; $1 \times 10^{-5}$ cm/s with the least amount of additional reagents</td>
</tr>
<tr>
<td><strong>Swell of geologic materials</strong></td>
<td>%</td>
<td>NA</td>
<td>14-22</td>
<td>23-31</td>
<td>24-33</td>
<td>Not defined</td>
</tr>
</tbody>
</table>

### Mass destruction

<table>
<thead>
<tr>
<th></th>
<th>%</th>
<th>ISCO</th>
<th>ISS</th>
<th>ISS+ISCO - One step</th>
<th>ISS + ISCO - Two step</th>
<th>Target value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>99</td>
<td>NA</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>Not defined</td>
</tr>
<tr>
<td>Phenol</td>
<td>100</td>
<td>NA</td>
<td>83</td>
<td>83</td>
<td>83</td>
<td>Not defined</td>
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<tr>
<td>TPH</td>
<td>26</td>
<td>NA</td>
<td>39</td>
<td>37</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>-19</td>
<td>NA</td>
<td>58</td>
<td>77</td>
<td></td>
<td></td>
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</tbody>
</table>

### Leach reduction

<table>
<thead>
<tr>
<th></th>
<th>%</th>
<th>ISCO</th>
<th>ISS</th>
<th>ISS+ISCO - One step</th>
<th>ISS + ISCO - Two step</th>
<th>Target value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td></td>
<td>NA</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Phenol</td>
<td></td>
<td>NA</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;98</td>
</tr>
<tr>
<td>TPH</td>
<td></td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Naphthalene</td>
<td></td>
<td>NA</td>
<td>93</td>
<td>80-98</td>
<td>80-84</td>
<td></td>
</tr>
</tbody>
</table>
Target Treatment Zones – Cross Section

Residual Tar in All Zones (~ 3 tonnes)

- **Område E.1 (0-2/5 m u.t.):**
  - TOC: ca. 1.000 kg
  - Benzen: 5-10 kg

- **Område E.2 (2/5-10 m u.t.):**
  - TOC: 500-1000 kg
  - Benzen: ca. 25-50 kg

- **Område E.3 (10-12/15 m u.t.):**
  - TOC: 500-1000 kg
  - Benzen: ca. 25-50 kg
Transition From Bench to Pilot Scale

- **Pilot Test Challenges**
  - First-time use in Denmark (learning)
  - Process scale up from bench to field
  - Residential neighborhood, spatial constraints above ground, proximity to houses
  - Challenging Geology: 3m to 5m peat – stability concerns, highly plastic clay, confined aquifer, tight site logistics
  - Verification of treatment performance
  - Handling and mixing of potentially corrosive materials
Conceptual Full-Scale Layout of ISS Columns

<table>
<thead>
<tr>
<th>Design</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag Cement (CEM II/B)</td>
<td>8 % dw</td>
</tr>
<tr>
<td>Persulfate</td>
<td>3 % dw</td>
</tr>
<tr>
<td>Auger diameter</td>
<td>2 m</td>
</tr>
<tr>
<td>Auger Mixing area</td>
<td>3.14 m²</td>
</tr>
<tr>
<td>Total target treatment area</td>
<td>188 m²</td>
</tr>
<tr>
<td>Number of columns</td>
<td>75</td>
</tr>
<tr>
<td>Area of all columns</td>
<td>235.5 m²</td>
</tr>
<tr>
<td>Column overlap</td>
<td>35 m²</td>
</tr>
<tr>
<td>Overlap %</td>
<td>17.5</td>
</tr>
</tbody>
</table>
Pilot Test ISCO / ISS Columns

Objectives
- Test auger mixing approach
- Test persulfate and cement mixing
- Collection of QA / QC samples
- Attainment of UCS, $K_h$ performance criteria

- 5 test columns in target treatment area
- 1 outside treatment area

<table>
<thead>
<tr>
<th>Column ID</th>
<th>Area</th>
<th>Mix Design</th>
<th>Top El. (m EL)</th>
<th>Start Treatment Depth (m EL)</th>
<th>Bottom El. (m EL)</th>
<th>Design Depth (mbs)</th>
<th>Treatment Thickness (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friday 2</td>
<td></td>
<td>1</td>
<td>22.8</td>
<td>19.8</td>
<td>14.8</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>Friday 3</td>
<td></td>
<td>1</td>
<td>22.8</td>
<td>19.8</td>
<td>14.8</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>D6</td>
<td>E2+E3, Shallow Bench</td>
<td>1</td>
<td>22.3</td>
<td>19.3</td>
<td>9.3</td>
<td>13</td>
<td>10</td>
</tr>
<tr>
<td>D7</td>
<td>E2+E3, Shallow Bench</td>
<td>1</td>
<td>22.3</td>
<td>19.3</td>
<td>9.3</td>
<td>13</td>
<td>10</td>
</tr>
<tr>
<td>G8</td>
<td>E2+E3, Deep Bench</td>
<td>1</td>
<td>22.3</td>
<td>17.3</td>
<td>7.3</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>G9</td>
<td>E2+E3, Deep Bench</td>
<td>1</td>
<td>22.3</td>
<td>17.3</td>
<td>9.3</td>
<td>13</td>
<td>8</td>
</tr>
<tr>
<td>G7</td>
<td>E2+E3, Deep Bench</td>
<td>TBD</td>
<td>22.4</td>
<td>17.4</td>
<td>7.4</td>
<td>15</td>
<td>10</td>
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<td>E7</td>
<td>E2+E3, Shallow Bench</td>
<td>TBD</td>
<td>22.3</td>
<td>15.3</td>
<td>10.3</td>
<td>12</td>
<td>9</td>
</tr>
<tr>
<td>E8</td>
<td>E2+E3, Shallow Bench</td>
<td>TBD</td>
<td>22.3</td>
<td>15.3</td>
<td>10.3</td>
<td>12</td>
<td>9</td>
</tr>
</tbody>
</table>
2-m Diameter Mixing Auger, Column Casing

- Geology/Stability Solution:
  - Excavated peat in 2m DIA steel casing to 3 to 5 mbs
  - ISS through each casing
  - 3 mixing passes – established optimum blade rotation number to mix plastic clay
  - Cleaned augers after first mixing pass to remove accumulated clay
“Trap Door” Sampler for Wet Grab Samples

Pocket Penetrometer for Field measurement of UCS

Tools Supporting Quality Control Assessment
Construction Quality Assurance Sample Processing

- Verification of homogenous mixing
- Field measurement parameters: moisture content, pH, temperature
- Field Observations: unmixed clods, color/consistency, free phase NAPL
- Screening and molding CQA samples
- Curing samples
Pilot Test Findings & Lessons for Full-Scale

• $K_h$. All QA/QC samples met criterion of $\leq 1 \times 10^{-6}$ cm/sec.

• **UCS.** 8 of 13 samples exceeded 0.35 MPa and 10 of 13 samples exceeded minimum criteria of 0.15 Mpa. (3 samples failed initially but cured later in time)

• UCS improved by optimizing blade rotation / mixing energy, sealing leaks, reducing slurry water content

• **Contaminant destruction** – reduction in benzene concentrations ranged from 6x to 133x.
Full-scale Implementation
Full-Scale Design By the Numbers

- Treatment Area – 188 m²
- 75 columns, 17% overlap
- Rate - 100 m³/day (10 m³/hr)
- Cement – 15 tons/day
- Water – 32 m³/day
- Persulfate – 6.5 tons / day
- Mixing cycles – 3 cycles; 300 m³/day
Some Lessons Learned

- 2.0 diameter auger successful with 100 ton rig
- Best day – 36 m³/hr (113 m³)
- Many days – 0 m³
- Corrosivity of persulfate stock solution requires special handling
- High water content of clay matrix slowed rate of cement curing, but
- UCS achieved in field was faster than in lab QA/QC samples (field temp in August > lab)
Søllerød Post-Remediation
Further Information
1(866) 251-1747 or (519) 515-0839

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