Biodegradation of Sulfolane in Soil Using Aerobic Biopile Technology

Successfull Collaboration Between Academia and Industry – Breaking Open Sulfolane Remediation strategies

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Outline

- Sulfolane Key Properties
- Environmental Standards
- Previous Sulfolane Presentations
- Development of Sulfolane Treatment Technology
- Aerobic Biodegradation of Sulfolane in Soil
- Lab Degradation of Sulfolane
- Pilot Demonstration-Biopiles
- Full Remediation on Sulfolane Contaminated soil
Sulfolane Key Properties

- Gas Sweetening
- Aromatics Extraction
- Textiles
- Production 18,000-36,000 tones [1]
- Soil and Groundwater contamination
- Ongoing Toxicity Studies (NTP)

- Chemically stable
- Thermally stable
- Boiling Point: 287.3 °C [2]
- Vapor Pressure @ 20°C: 1.33 pa [3]
- Water Solubility @ 20°C: 1266 g/L [3]
- Soil Adsorption:
  - $K_{oc} = 0.07$ [3]
  - $K_d$ (montmorillonite) = 0.94 L/kg [4]
  - $K_d$ (kaolinite) = 0.08 L/kg [4]
Environmental Standards

- Alberta
- BC
- Alaska
- Texas
- Louisiana
- California
- Michigan

Health Canada interim drinking water guideline: 0.04 mg/L.

Soil: 0.18 mg/kg
Groundwater: 0.09 mg/L

CCME: 0.8 mg/kg
0.09 mg/L

AB: 0.18 mg/kg
0.09 mg/L

Texas: 0.61 mg/kg
0.32 mg/L
Previous Sulfolane Presentations

- **EBA 2005 – Lab Scale**
  - Soil: Bio-treatability
  - Groundwater: Bio-treatability; Chemical Oxidation
- **Biogenie 2006 – Full Scale**
  - Soil: Bio-treatability
- **WorleyParsons Komex 2008 – Pilot and Full Scale**
  - Groundwater: Bio-treatability
- **Waterline 2016 – Pilot Scale**
  - Soil: Bio-treatability; Chemical Oxidation
- **Trium 2016 – Lab Scale**
  - Groundwater: Chemical Oxidation
- **Maxxam 2017 – Lab Scale**
  - Laboratory Methods
- **WorleyParsons 2017**
  - Groundwater Remedial Options Review
## Development of Sulfolane Treatment Technologies

<table>
<thead>
<tr>
<th>Groundwater</th>
<th>Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advanced Oxidation – Lab and Field Pilot</td>
<td><strong>Bioremediation</strong> – Lab Scale, Field Pilot, Full Scale</td>
</tr>
<tr>
<td>Bioremediation – Lab and Field Pilot</td>
<td>Soil Flushing &amp; Washing – Lab Scale and Field Pilot</td>
</tr>
<tr>
<td>Carbon Adsorption – Lab and Field Pilot</td>
<td>In-Situ Chemical Oxidation (ISCO) – Lab Scale</td>
</tr>
<tr>
<td>Reverse Osmosis – Lab Scale</td>
<td>Oxygen Releasing Compounds (ORC) – Lab Scale and Field Pilot</td>
</tr>
<tr>
<td>Isotope Fractionation – Lab Scale</td>
<td></td>
</tr>
<tr>
<td>Integrated Technology-Lab scale</td>
<td></td>
</tr>
</tbody>
</table>
Aerobic Biodegradation of Sulfolane in Soil

- N, P & micronutrients
- Proper pH
- Proper temperature

\[ \text{Sulfolane} + 6.5O_2 \rightarrow 4CO_2 + 3H_2O + H_2SO_4 \]

**Lab Investigation:**
- Treatability study
- Optimization

**Pilot Demonstration:**
- Evaluation
- Modification

**Full Remediation:**
- Modification
Lab Study: Experimental Setup

Soil Texture

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Sand percentage</td>
<td>8.3</td>
</tr>
<tr>
<td>Silt percentage</td>
<td>43.0</td>
</tr>
<tr>
<td>Clay percentage</td>
<td>48.6</td>
</tr>
<tr>
<td>Texture</td>
<td>Silty Clay</td>
</tr>
</tbody>
</table>

300 g of soil was loosely packed in a beaker (ø= 15 cm)

- Moisture: 18%
- Oxygen: exposed to atmosphere
- Temperature: 22 °C
- Nutrients: different conditions
- Sulfolane metabolized microorganisms were present in the contaminated soil.
- N-P amendment samples yield the best degradation results.
Pilot Study: Setup of Soil Bio-Piles

Tarp

Perforated PVC pipe

bp1 bp2 bp3 bp4 bp5 bp6

Bio-Piles
## Details of Soil Piles

<table>
<thead>
<tr>
<th>Soil pile</th>
<th>Size of pile (m$^3$)</th>
<th>Covered with Tarps</th>
<th>Nutrient Amendment</th>
<th>Aeration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Nitrogen nutrient</td>
<td>Phosphate nutrient</td>
</tr>
<tr>
<td>bp 1</td>
<td>25</td>
<td>Yes</td>
<td>Yes</td>
<td>NO</td>
</tr>
<tr>
<td>bp 2</td>
<td>25</td>
<td>Yes</td>
<td>Yes*</td>
<td>Yes</td>
</tr>
<tr>
<td>bp 3</td>
<td>25</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>bp 4</td>
<td>25</td>
<td>Yes</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>bp 5</td>
<td>50</td>
<td>Yes</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>bp 6</td>
<td>500</td>
<td>No</td>
<td>NO</td>
<td>NO</td>
</tr>
</tbody>
</table>

* The amount of nitrogen added in bp 2 was only 1/10 of that in bp 1
Six random samples were collected from each soil pile.

- CO₂, O₂ and water moisture content were monitored.

- Temperature data was obtained from Alberta Climate Information service.
Oxygen

1 – Air, N

2 – Air, N*&P

3 – Air, N&P

4 – Air, Alfalfa

5 – Air

6 – Control
Treatment Comparison

1 – Air, N
2 – Air, N*&P
3 – Air, N&P
4 – Air, Alfalfa
5 – Air
6 – Control
## Summary of Degradation Kinetics

<table>
<thead>
<tr>
<th>Soil Piles</th>
<th>BP1</th>
<th>BP2</th>
<th>BP3</th>
<th>BP4</th>
<th>BP5</th>
<th>BP6</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Order</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kinetics</td>
<td>K (Day⁻¹)</td>
<td>0.09</td>
<td>0.09</td>
<td><strong>0.17</strong></td>
<td>0.03</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Half life (Day)</td>
<td>5.3</td>
<td>5.4</td>
<td><strong>3.0</strong></td>
<td>17.9</td>
<td>NA</td>
</tr>
<tr>
<td>Zero Order</td>
<td>Rate (mg/kg/Day)</td>
<td>24</td>
<td>26</td>
<td><strong>42</strong></td>
<td>17</td>
<td>NA</td>
</tr>
<tr>
<td>Kinetics</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The highest zero order degradation rate observed in lab was **220 mg/kg/day**.
Remediation Program - Contaminated Site

- 8,000 m³
- 26,000 m³
- 20,000 m³
- **Former Flare Pit**
  - Sulfolane, DIPA, PHCs
  - Soil Texture
    - 23% Sand
    - 40% Silt
    - 37% Clay
  - Sulfolane [0.42 - 8170 mg/kg]
    - Average 364 mg/kg
  - Impacts 2 – 9 mbgs
Full Scale Remediation – Year 1

- Former Flare Pit
  - Excavated June & July 2016
Full Scale Remediation – Year 1

- ~8000 m$^3$ soil placed in windrows
  - volume assessed with drone
- Per m$^3$ of soil: 0.1 kg MAP and 0.29 kg urea
  - based on TOC and 100:5:1 - C:N:P
- Oxygen
  - blower aeration
  - mechanical aeration
Blower Aeration – Year 1
Mechanical aeration
  – July and August

Blower aeration
  – 24/7

Based on half-life from pilot: ~35 days to clean soil with 346 mg/kg of sulfolane.

81 days between excavation and confirmatory samples

2 of 44 windrows exceeded sulfolane guideline
Ongoing Remediation

26,000 m³

~8000 m³

~8000 m³

12,000 m³
- Aerobic biodegradation of sulfolane was observed both in the lab and in the field.
- The addition of nutrients and forcing aeration enhanced sulfolane degradation (Pilot).
- Supplemented with both “N” and “P” nutrient resulted the best sulfolane degradation rate, the half-life is 3 days (optimal pilot conditions)
- Mechanical and forced aeration were both successful in full scale


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Thank you!

Questions?