Field Remediation Trials for Sulfolane Impacted Soil and Groundwater: Aeration, Nutrient Amendments and/or Peroxide?

RemTech 2016

Brent Lennox, M.Sc., P.Geol., Senior Hydrogeologist
Eric Pringle, M.A.Sc., P.Eng., Principal Hydrogeological Engineer
Waterline Resources Inc.
Sulfolane

- Used in Sulfinol for sour gas sweetening since 1960s
- Human health related guidelines
- Poorly adsorbed to soil
- High solubility in water
- Microbial degradation slow in typical groundwater conditions
- Clear, colourless, no field indicators (visual or olefactory)
Sulfolane

- Microbial degradation rapid in aerobic environments and surface water (CCME, 2006)
  - \( \text{C}_4\text{H}_8\text{O}_2\text{S} + 6.5\text{O}_2 \rightarrow 4\text{CO}_2 + 3\text{H}_2\text{O} + 2\text{H}^+ + \text{SO}_4^{2-} \)

- Nutrients improve degradation times
- Low pH conditions inhibit degradation
- Typical degradation times: 2 to 4 days at 28°C and 8 to 12 days at 8°C (Green et al., 1998), average air temperatures during trials ranged from 6.9 to 14.1°C
Sulfolane: Previous Remediation Approaches

Groundwater and Soil
- Oxygen and nutrients (soil tilling, blowers) (Biogenie, 2006)

Groundwater
- Activated Sludge Treatment System (WorleyParsons Komex, 2008)
- Oxidants (e.g., hydrogen peroxide) and/or UV light
  - Mixed success (Barr Engineering, 2013; Gallegos et al., 2013; EBA, 2015)
  - Peroxide and iron catalyst shown to be more effective than peroxide (Gallegos, 2013)
  - No sulphate as by-product
Site Description

- Site is an operating gas plant located in southern Alberta
- Constructed in 1960s
- Sulfolane investigation and monitoring since 1994
Landfill Area: History

- No active facilities
- Downgradient of active facilities
- Majority of plant waste stored here before the 1980s
- Potential materials disposed: alumina catalyst, filters (compressor, sulfinol, salt water, glycol, solvent receiver), zeolite, etc.
- Cells (but likely not soil) excavated in 1993
Predominately sulfolane and EC (sulphate) issues
Currently >10,000 tonnes of sulfolane impacted soil
Impacts extend into groundwater and bedrock around former landfills

<table>
<thead>
<tr>
<th>Soil Impacts</th>
<th>Water Impacts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfolane</td>
<td>Sulfolane</td>
</tr>
<tr>
<td>Electrical Conductivity (EC) (predominately sulphate)</td>
<td>Sulphate</td>
</tr>
<tr>
<td>Minor DIPA, hydrocarbon, elemental sulphur impacts</td>
<td>DIPA</td>
</tr>
</tbody>
</table>
Site Setting

Ground

Average Groundwater Elevation

Sulfolane Impacted Soil

Average Depth to the Overburden/Bedrock Contact

Silt

Siltstone
Soil Remediation: Trials

- Control
- Aeration
- Aeration and Nutrient Amendment
- Hydrogen Peroxide
- Treated ~10 m$^3$ impacted soil/test cell
- Excavated and stockpiled treated soil for 11 days
- Lined and backfilled test cells after 11 days
- Sets of 5 soil samples collected ~3 to 45 days after remediation activities
Soil Remediation: Control

- Heterogeneous sulfolane concentrations
- Potential outliers

Legend:
- Sulfolane in Soil (mg/kg)
  - Maximum
  - 75th Percentile
  - Median
  - 25th Percentile
  - Mean (% remediated)
  - Minimum

Tier 1 Sulfolane Guideline (Ag./Ind.) (Fine Grained)

Pre-treatment: t=0 (Excavate and Stockpile)
- t = 4 days
- t = 11 days
- t = 46 days
- t=11 days (Backfilled Test Cell)
Soil Remediation: Soil Oxidative Blender

- Two hammer mills and rotating augers to homogenize soil
- Timeline: Hours to complete, issues with wet silt during trials not typically encountered with clay
- Trials included:
  - Aeration
  - Aeration/nutrient amendment
  - Hydrogen peroxide/UV
Soil Remediation: Soil Oxidative Blender Aeration

Legend
- Sulfolane in Soil (mg/kg)
  - Maximum
  - 75th Percentile
  - Median
  - 25th Percentile
  - Mean (% remediated)
  - Minimum

Sulfolane Concentration (mg/kg)

- Tier 1 Sulfolane Guideline (Ag./Ind.) (Fine Grained)

Pre-treatment
- t = 0 (Aeration)
- t = 3 days
- t = 10 days
- t = 45 days
- t = 10 days (Backfilled Test Cell)
Soil Remediation: Soil Oxidative Blender Aeration and Nutrient Amendment

- N:P:K ratio 28:14:14, 200 mg/kg dose
- Identical results to aeration only indicate that the fertilizer application did not have a measurable influence
Soil Remediation: Soil Oxidative Blender Aeration, Hydrogen Peroxide and Natural UV Exposure

- 11% hydrogen peroxide with citric acid stabilizer, 1,000 L applied to ~10 m³ soil
- Hydrogen peroxide is a disinfectant in other applications, possibly reduced naturally occurring microbe population
Soil Remediation: ALLU Bucket/Nutrient Amendment

- Aerated twice with Allu bucket
- N:P:K ratio 28:14:14, 200 mg/kg dose
- 20 minutes to complete remediation
Soil Remediation: ALLU Bucket/Nutrient Amendment

![Graph showing Sulfolane Concentration over time withlegend and data points.

Legend:
- Maximum
- 75th Percentile
- Median
- 25th Percentile
- Mean (% remediated)
- Minimum

Tier 1 Sulfolane Guideline (Ag./Ind.) (Fine Grained)

Pre-treatment
- t = 3 days
- t = 3 days
- t = 10 days
- t = 45 days

- t=0 (Aeration)
- t=0 (Aeration and Nutrients)
- t=10 days (Backfilled Test Cell)
Soil Remediation: Summary

- 97 to 98% reduction in sulfolane concentrations using aeration and/or nutrient application
- ALLU Bucket trial concentrations after treatment < Tier 1 guidelines
- Peroxide application: No apparent remedial benefit
Groundwater Remediation

- Groundwater trials completed opportunistically
- Test cells excavated into shallow bedrock
- Test cells left open for ~1 week while completing soil trials
- <24 hour duration groundwater trials

Approaches:
- No treatment (Control)
- Aeration with trash pump
- Sparging
- Hydrogen peroxide

- Pumping test completed and test pit went dry after storage within test pit was pumped off
Groundwater Remediation: No Treatment

**Legend**
- Pre-treatment Sample
- Post-treatment Sample
- Post-treatment 2nd Sample

**Date and time of sample collection**
- 22-Sep-15 11:20

**(-/-)% remediated**
- 22%

**Tier 1 Sulfonate Guideline (Ag./Ind.)**
- No Treatment
Groundwater Remediation: Aeration with Trash Pump

- Re-circulated pit water ~9 times
- Nitrate in groundwater present before and after trial (8 to 9 mg/L)
Regenerative blower with slotted pipe, 6 hours
Non-detectable nitrate in groundwater not favourable for microbial degradation of sulfolane?
Trial too short or the entire water column not aerated?
11% hydrogen peroxide with citric acid stabilizer, 1,000 L hydrogen peroxide added to 1,000 L of groundwater

Groundwater diluted by half initially, excluding dilution=minor remedial benefit
Groundwater Remediation

Legend
- Pre-treatment Sample
- Post-treatment Sample
- Post-treatment 2nd Sample

22-Sep-15 11:20 Date and time of sample collection
22% (+/-)% remediated

Sulfolane Concentration (mg/L)

Tier 1 Sulfolane Guideline (Ag./Ind.)
Peroxide/exposure to natural UV light generally not as effective as aeration/nutrient amendment approaches. Simple, practical, and cost effective approaches can be taken to remediate sulfolane in soil and groundwater.

- Soil: aeration/nutrient amendment
- Groundwater: water re-circulation/aeration

Due to the site setting and potential for groundwater re-contamination, a groundwater remediation approach should be applied.
Questions?

Thank You

Brent Lennox
Eric Pringle
Waterline Resources Inc.

http://www.waterlineresources.com
Barr Engineering, July 31, 2013. Revised point-of-entry treatment system feasibility study and design report.

Biogenie, 2006. Large Scale Sulfolane-Impacted Soil Remediation at a Gas Plant. Remediation Technologies Symposium Presentation, Banff, AB.


