Bioremediation Coupled with Chemical Oxidation for Treatment of Oil-Based Drill Cuttings

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Remediation of Hydrocarbon in Soils

• Typical bioremediation process for hydrocarbons:
  - Fertilizer
    • Provide N and P for hydrocarbon degraders
  - Bulking agent
    • Increase $O_2$ and water infiltration
  - Tilling
    • Mixing
    • Aeration
  - Moisture
Bioavailability of petroleum hydrocarbons

• Most important mechanism
  - Direct contact of microorganisms with a bulk liquid hydrocarbon phase (interfacial contact)
Droplets of mineral oil in a culture of hydrocarbon-degrading bacteria
Recommended practice for landfarms
Getting the microbes together with the hydrocarbon

• Increasing surface area for contact between soil water and hydrocarbon is very important to increasing rates of biodegradation

• If the initial TPH concentration is too high for optimum treatment, you can dilute the contaminated soil with uncontaminated soil to increase rates of bioremediation:
  - Utilize full 6-8 inch depth
  - Utilize surrounding soil as a diluent
  - Rule of thumb: dilute until the soil no longer glistens
What about treatment of drill cuttings?

- Adding topsoil
  - Provides an inoculum
  - Improves moisture holding capacity
  - Improves nutrient retention
  - Improves permeability and aeration
  - Creates more surface area for contact between hydrocarbon and soil moisture
  - Decreases hydrophobicity and improves wettability
  - Increases final volume of treated material which can generate disposal issues
Two drill cuttings samples each blend with topsoil in same ratio and treated in the same way to encourage bioremediation of diesel hydrocarbons:

- Nutrients
- Moisture
- Aeration

Clearly sample A is degrading very slowly compared to Sample B. It’s not a salinity issue!
The Cool-Ox® process

(Producing hydrogen peroxide in situ)

\[ \text{CaO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{H}_2\text{O}_2 \]

(Chelates activate intrinsic catalysts)

\[ \text{H}_2\text{O}_2 + \text{Fe}^{+2} \rightarrow (\text{OH})^- + [\text{OH}]\cdot + \text{Fe}^{+3} \]
\[ \text{H}_2\text{O}_2 + \text{Fe}^{+3} \rightarrow (\text{OH})^- + [\text{OOH}]\cdot + \text{Fe}^{+2} \]

(Radicals react with contaminants)

\[ [\text{OH}]\cdot & [\text{OOH}]\cdot + C_x \rightarrow C_x(\text{OH})_y \]
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Highly biodegradable and hydrophilic
Wettability of Cool-Ox treated hydrophobic cuttings/soil blend: left, control; right, Cool-Ox treated

Timeframe: 1 min
After > 100 days of bio treatment Sample A was split and half treated with Cool-Ox.
Preliminary conclusions

- Cool-Ox treatment greatly accelerated degradation of diesel hydrocarbons in a cuttings/soil blend that was hydrophobic and biodegrading very slowly.
- Was the effect purely oxidation, improved wettability, or both?
ISCO/Bio/ISCO Treatment of Oil-Based Drill Cuttings

- Samples of neutralized drill cuttings (avg. 9 wt% TPH) were pretreated with Cool-Ox: objective was reduction in hydrophobicity.

Pre-bio Cool-Ox treatment of Ohio stabilized cuttings, application rate 10 gal/yd³ (10 day incubation)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>% $\text{H}_2\text{O}_2$</th>
<th>% Cool-Ox Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ohio D</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Ohio E</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Ohio F</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
TPH concentrations in stabilized and neutralized cuttings pre- and post-initial treatment with Cool-Ox
## Biotreatment

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cool-Ox pretreatment</th>
<th>Soil inoculum (2 wt%)</th>
</tr>
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<tbody>
<tr>
<td>OD</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>OD-S</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>OE</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
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<td>yes</td>
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<tr>
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<td>no</td>
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+ nutrients
Bioremediation of Cool-Ox Treated Cuttings

Significantly hydrophobicity all samples at the bioremediation endpoint

TPH (mg/kg)

Incubation Time (days)
## Post-bio Cool-Ox treatment

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Results of post-bio Cool-Ox treatment

- Little or no hydrophobicity after post-bio Cool-Ox treatment

Graph showing TPH (mg/kg) with Pre-Treatment and Post-Treatment data for OD, OD-S, OE, OE-S, OF, and OF-S. The percentage reductions are highlighted as follows:

- OD: 94% reduction
- OD-S: 92% reduction
- OE: 86% reduction
- OE-S: 83% reduction
- OF: 55% reduction
- OF-S: 79% reduction
Results of post-bio Cool-Ox treatment

- No pre-bio Cool-Ox

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Conclusions

- Pre-bio Cool-Ox treatment of stabilized drill cuttings had no detectable effect on TPH concentration but may have positively affected final results of a ISCO/bio/ISCO treatment chain
- Biotreatment alone did not achieve treatment goals likely due to hydrophobicity
- Biotreatment followed by ISCO achieved treatment goals and rendered cuttings non-hydrophobic
  - Reductions in hydrophobicity makes soil washing to remove salts feasible