Water Treatment and Reuse in Oil Sands Development

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Work In-Progress

Presented today:
• Treatment of Produced Water
• Extraction of Bitumen from Oil Sands – New Technology

Additional task in progress:
• Removal of naphthenic contaminants
Technologies & Rights

- Heightened Ozonation Treatment (HOT) – U-3996; PCT filed
- Heightened Oil Sand Extraction (HOSE) – U-4313; PCT filed

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Heightened Ozonation Treatment (HOT) with Compression and Decompression Cycles

1. O3/air mixture is compressed into the reactor to an elevated pressure (100-120 psi)
2. Pressure is released to normal pressure to generate in-situ micro bubbles
3. Micro bubble flotation and coagulation effects remove dispersed oil droplets
4. More cycles will be conducted to remove the remaining oil droplets

Accumulation of organics and high free radical concentration in the air-water interfacial layer

Air Phase
Interfacial Reactive Zone
Water Phase
Hydrophobic Part
Hydrophilic Part
Products
Heightened Ozonation Treatment (HOT) -- Microbubbles of O₃ in Oil/Sheen Removal

Combine flotation with O₃ treatment
Remove dispersed oil by flotation
Chemically convert dispersed oil for removal via emulsification, coagulation, coarse filtration
Chemically convert dissolved, trace oil into acids, preventing sheen formation
Rapid, cost-effective, wide operating conditions
Other Related Technologies for Produced Water Treatment

- **Microbubble floatation - dispersed oil removal**
  - Achievements: > 95% removal of oil; remove oil droplet > 3 microns
  - Drawbacks: microbubbles are mechanically generated (injection and turbulence), cannot totally prevent oil sheen

- **Micro ozone/air bubble treatment – dissolved oil treatment (Oak Ridge National Laboratory)**
  - Achievement: accelerates degradation of hydrocarbons in the aqueous phase
  - Drawbacks: fouling of the electrostatic sprayer; not effective for high-salinity water
Synthetic Produced Water (SPW) and Real Produced Water (RPW)

SPW -- prepared by mechanically mixing Rangely crude oil with water.

RPW -- from Conoco Phillips, Inc.
TOC = 370 mg/L,
SOC = 155 mg/L.

Size distribution (as #/L) of oil droplets according to size in SPW.
GC/MS Analyses of Hexane-Extractable Hydrocarbons Dissolved in SPW and RPW

Hexane-extractable hydrocarbons in SPW

Hexane-extractable hydrocarbons in RPW
<table>
<thead>
<tr>
<th><strong>Purpose</strong></th>
<th><strong>Sample COD (mg/L)</strong></th>
<th><strong>Treatment method</strong></th>
<th><strong>Solid floated (COD mg/L)</strong></th>
<th><strong>Solid filtered (COD mg/L)</strong></th>
<th><strong>COD after vacuum filtration, (mg/L)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro bubble floatation effects on different size oil droplets</td>
<td>78</td>
<td>No treatment</td>
<td>0</td>
<td>35</td>
<td>36</td>
</tr>
<tr>
<td>10 cycles CDC ozonation effects on different COD water</td>
<td>97</td>
<td>CDC air, (10 cycles)</td>
<td>45</td>
<td>10</td>
<td>31</td>
</tr>
<tr>
<td>10 cycles CDC ozonation effects on different COD water</td>
<td>97</td>
<td>Ordinary air, (10 minutes)</td>
<td>0</td>
<td>58</td>
<td>37</td>
</tr>
<tr>
<td>10 minutes ordinary ozonation effects on different COD water</td>
<td>91</td>
<td>CDC ozone</td>
<td>0</td>
<td>40</td>
<td>52</td>
</tr>
<tr>
<td>10 minutes ordinary ozonation effects on different COD water</td>
<td>320</td>
<td>CDC ozone</td>
<td>195</td>
<td>75</td>
<td>42</td>
</tr>
<tr>
<td>50 CDC cycles ozonation effects on different COD water</td>
<td>97</td>
<td>CDC ozone</td>
<td>0</td>
<td>32</td>
<td>64</td>
</tr>
<tr>
<td>50 CDC cycles ozonation effects on different COD water</td>
<td>320</td>
<td>CDC ozone</td>
<td>210</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>50 minutes ordinary ozonation effects on different COD water</td>
<td>282</td>
<td>Ordinary ozone</td>
<td>163</td>
<td>70</td>
<td>43</td>
</tr>
<tr>
<td>Ozonation with H₂O₂</td>
<td>293</td>
<td>CDC ozone/ H₂O₂, (10 cycles)</td>
<td>148</td>
<td>85</td>
<td>56</td>
</tr>
<tr>
<td>Ozonation under basic condition</td>
<td>329</td>
<td>CDC ozone/pH=11, (10 cycles)</td>
<td>20</td>
<td>236</td>
<td>70</td>
</tr>
</tbody>
</table>

a. CDC (compression/decompression); b. 1 cycle takes 1 minute.
Hydrophilic Products from SPW & Effects of Salinity

- Pressure-assisted ozonation of SPW generates hydrophilic organics
- Hydrophilic organics increase with increasing ozonation cycles while COD decreases.
- High salt content (high ionic strength) enhanced coagulation/deposition, improving oil removal
**Ozonation Results For RPW**

<table>
<thead>
<tr>
<th>Method</th>
<th>COD after treatment (mg/L)</th>
<th>COD after filtration (mg/l)</th>
<th>COD after additional treatment (mg/l)</th>
<th>COD after filtration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without treatment</td>
<td>1035</td>
<td>789</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 CDC aeration + vacuum filtration</td>
<td>880</td>
<td>610</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sand Filtration</td>
<td>1043</td>
<td>730</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 CDC ozone + vacuum filtration</td>
<td>700</td>
<td>546</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 CDC ozone + vacuum filtration</td>
<td>594</td>
<td>512</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 CDC ozone + sand filtration + 30 CDC ozonation + sand filtration</td>
<td>708</td>
<td>598</td>
<td>428</td>
<td>420</td>
</tr>
<tr>
<td>40 CDC ozone + sand filtration</td>
<td>588</td>
<td>535</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Solvent-Extractable Products in Treated SPW and RPW

Mass chromatogram of partially degraded hydrocarbons in SPW.

Mass chromatogram after more cycles of CDC ozonation.
GC/MS Analyses of the Hydrophilic Products in SPW and RPW

Some identified organics: 1,3-Dioxolane-4-methanol, 2,2-dimethyl-[s]-; Hexadecanoic acid, methyl ester; Propanoic, 2-methyl-butyl ester; Methyl 2-tetradecyclohexanecarboxylate; 2-Acetylbenzoic acid; 2-Propenoic, 3-[4-hydroxyphenyl], methyl ester; 2-Naphthalenamine, 5,6,7,8-tetrahydro-, 1-[2,3,4,5-Tetramethylphenyl]ethanone; 2-Hydroxy-2,4,4-trimethyl-3-[3-methylbuta-1,3-dien], Naphtho[2,3-b]thiophene; Dienzothiophene, 4-methyl-, 9H-Fluoren-ol, 9-butyl-; Dibenzothiophene, 4-methyl; [1,1’-Biphenyl]-2,2’-dicarboxaldehyde; 2,8-Dimethylethyldibenzo[b,d]thiophene; Fluorenone oxime; Dibenzothiophene sulphone.

40 cycles SPW, hydrophilic compounds originated from dispersed hydrocarbons.

Some identified compounds are: 3.622 min, Thiazole, tetrahydro-; 5.720 min, Cyclopentylcarboxylic acid; 6.926 min, Cyclopentaneacetic acid; 7.114 min, Cyclohexanecarboxylic acid; 8.132 min, Cyclohexanecarboxylic acid, 4-methyl-; 9.606 min, 2-Butyl-3,4,5,6-tetrahydropyridine; 9.812 min, Cyclohexane, 1-methyl-2-pentyl.
**Prevention of Oil Sheen**

**Observations:**
- Ordinary bubbling ozonation or aeration (even with compression-compression cycles does not prevent oil sheen formation.
- Once ozone contact the oil droplets, it changes surface properties and viscosity, resulting in coalescing of droplets and spreading of oil.
- Ozonation products as dissolved hydrophilic acids does not form sheen.

**Evaluation by Visual Inspection** -- The thickness of oil sheen can be estimated based on the following table. The removal of oil sheen is evaluated by visual inspection.

<table>
<thead>
<tr>
<th>Oil type</th>
<th>Appearance</th>
<th>Approximate Thickness</th>
<th>Approximate Volume (m³/km²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil sheen</td>
<td>Silver</td>
<td>&gt;0.0001 mm</td>
<td>0.1</td>
</tr>
<tr>
<td>Oil sheen</td>
<td>Iridescent (rainbow)</td>
<td>&gt;0.0003 mm</td>
<td>0.3</td>
</tr>
<tr>
<td>Crude and Fuel Oil</td>
<td>Brown to Black</td>
<td>&gt;0.1 mm</td>
<td>100</td>
</tr>
<tr>
<td>Water-in-oil Emulsions</td>
<td>Brown/Orange</td>
<td>&gt; 1 mm</td>
<td>1000</td>
</tr>
</tbody>
</table>
Design of HOT Process for Produced Water

1. Brief ozonation cycles to promote coagulation of dispersed oil and removal via flotation
2. Coarse filtration to remove coagulated oil
3. More ozonation cycles to convert dissolved oil into organic acids and biodegradable products, preventing sheen formation
Summary

- Ozonation with pressure cycles coagulate dispersed oil and remove oil by flotation

- Ozone converts dissolved oil into highly soluble organic acids that are more biodegradable, eliminating the potential to form sheen

- Pressure cycles provide abundant gas-liquid interface as reactive zone for ozone and hydrophobic compounds to react
Conventional Hot Water Extraction of Bitumen form Oil Sands

Hot water process consists of two steps: separation and recovery of bitumen.

Disadvantages:
• < 75% bitumen are recovered from oil sands
• Caustic reagents and other additives are needed
• Generation of tailings

Recently efforts have been on reducing process costs by reducing the slurry temperature, with increased uses of additives and co-solvents.
**Heightened Oil Sands Extraction (HOSE) with Pressure Cycles (U-4313)**

- **1) Higher product yield** – penetration of dissolved air into small spaces of deposit particles during compression; subsequent decompression results in gaseous micro bubbles expanding within the mineral particle, prying open the sands to expose the bitumen deposited within thus enhancing recovery.
- **2) Easier product separation** – decompression results in countless micro bubbles that provide a huge area at the gas-liquid interface that attracts and gathers hydrophobic bitumen, effectively separating and lifting the bitumen globs to the water surface for collection (i.e., the flotation effect).
- **3) Energy saving** – due to enhanced bitumen exposure, lower water temperature can be used for higher yield, which results in energy saving that more than compensates the minimal energy expended in compression with air.
- **4) Shorter process time** – the new process with rapid pressure cycles cuts down contact time of tar sands by hot water. Our preliminary results show > 90% yield of bitumen within 20 min, in comparison to extraction without the pressure cycles that requires 3 hours of contact with hot water and under intense agitation.
- **5) Less materials and energy** – the new process requires no agitation or addition of caustics that are often used with conventional extraction [and potentially little agitation].
- **6) Higher throughput** – the extracted sands show excellent settling characteristics requiring no elaborate, time-consuming separation equipment and process.
- **7) Application for indigenous tar sands** – the new process has been preliminarily tested and found to be equally suited for Utah’s tar sands that are oil wet; unlike Canadian’s water wet oil sands, the oil wet property is an impediment to effective recovery by conventional hot water extraction method. Thus, this is a new tool central to developing Utah’s unique, rich tar sands resources.
Bitumen Extraction with Pressure Cycles

Asphalt Ridge oil sands, Utah, containing $12 \pm 1.7\%$ bitumen by wt.

Depleted and settled oil sands (left)
Extracted, separated bitumen (right)

Conditions:
- $T = 85 \, ^\circ\text{C}$;
- $P = 100 \, \text{psi}$; 20 cycles
- Total extraction time: 10 min
Extraction with Pressure Cycle of Air
(solid/water ratio varied)
Extraction with Pressure Cycle of Air
(P = 150 psi)

Solid to Water Ratio = 0.5:1 (v/v)
Extraction with Pressure Cycle of Air

Solid to Water Ratio = 0.5:1 (v/v)
THANK YOU FOR YOUR ATTENTION!

QUESTIONS?