Pressurized Ozone Treatment (POT) and Pressurized Hot Water Extraction (PHWE)

- **Similarities:**
  - Treatment process - cyclic compression/decompression (CDC)
  - Purpose - removal of hydrocarbons
  - Mechanism – gas floatation
  - Fast separation and Low cost

- **Differences:**
  - Condition – POT’s ozone vs. PHWE’s hot water
  - Concept – POT’s synergistic flotation and ozonation vs. PHWE’s degassing effects
Some Produced Water Treatment Technologies Related to POT

- Micro bubble floatation - dispersed oil removal
  - Achievements: > 95% removal of oil; remove oil droplet > 3 microns
  - Drawbacks: micro bubbles 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
Pressurized Ozone Treatment Process at the University of Utah

Combined micro bubble floatation and ozonation together to enhance dispersed oil removal and prevent oil sheen formation with benefits:

- A pressurized ozonation cycle consists of alternating compression and decompression stages that create micro bubbles rich in ozone
- Micro bubble formation resulting in dispersed oil removal via flotation
- Chemically convert trace dispersed oil to enhance removal via emulsification, coagulation, and filtration concertedly
- Chemically convert dissolved oil to prevent oil sheen formation
- Synergistic effects that are more effective than Micro-Bubble Flotation and Ozonation alone or combined
- Meet regulatory requirements
- Works with a wide range of parameters: salinity, temperature, solids, etc.
- Low cost

Micro bubbles generate after decompression
Synthetic Produced Water (SPW) and Real Produced Water (RPW)

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

Size distribution (as #/L) of oil droplets according to size in SPW.

RPW was from ConocoPhillips Alaska, Inc. Total organic carbon concentration = 370 mg/L, Soluble organic carbon concentration = 155 mg/L.
GC/MS Analyses of Hexane-Extractable Hydrocarbons Dissolved in SPW and RPW

Hexane-extractable hydrocarbons in SPW

Hexane-extractable hydrocarbons in RPW
## Ozonation Results for SPW

<table>
<thead>
<tr>
<th>Purpose</th>
<th>Sample COD (mg/L)</th>
<th>Treatment method</th>
<th>Solid floated (COD mg/L)</th>
<th>Solid filtered (COD mg/L)</th>
<th>COD after vacuum filtration, (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CDC (compression/decompression)</td>
<td>0</td>
<td>35</td>
<td>36</td>
</tr>
<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></td>
<td>97</td>
<td>CDC air, (10 cycles)</td>
<td>45</td>
<td>10</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>228</td>
<td>CDC air, (5 cycles)</td>
<td>150</td>
<td>52</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>Ordinary air, (10 minutes)</td>
<td>0</td>
<td>58</td>
<td>37</td>
</tr>
<tr>
<td>10 cycles CDC 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></td>
<td>320</td>
<td>CDC ozone</td>
<td>195</td>
<td>75</td>
<td>42</td>
</tr>
<tr>
<td>10 minutes ordinary ozonation effects on different COD water</td>
<td>95</td>
<td>Ordinary ozone</td>
<td>22</td>
<td>30</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>245</td>
<td>Ordinary ozone</td>
<td>130</td>
<td>60</td>
<td>39</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></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>Emulsification effect of the ozonated oil</td>
<td>660</td>
<td>Ordinary ozone, (50 minutes, neutralized after ozonation)</td>
<td>110</td>
<td>280</td>
<td>257</td>
</tr>
<tr>
<td>Ozonation with H$_2$O$_2$</td>
<td>293</td>
<td>CDC ozone/ H$_2$O$_2$, (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 Ozonation Products in SPW and Influence of Salinity on Ozonation

Pressure-assisted ozonation generated hydrophilic organics from oil droplets. Concentration of hydrophilic organics increased with increasing ozonation cycles while the total COD decreased.

High salt concentration enhanced removal. This is likely due to enhanced coagulation/deposition by increased ionic strength, as well as by accelerated floatation of oil droplets.
## 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.

intermediates
Some identified organics: 1,3-Dioxolane-4-methanol, 2,2-dimetnyl-[s]-; Hexadecanoic acid, methyl ester; Propanoic, 2-methyl-, butyl ester; Methyl 2-tetrade cycloiranecarboxylate; 2-Acetylbenzoic acid; 2-Propenoic, 3-[4-hydroxyphenyl], methyl ester; 2-Naphthalenamine, 5,6,7,8-tetrahydro-, 1-[2,3,4,5-Tetramethylphenyl] heptanone; 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-; Dibenzo thiophene, 4-methyl; [1,1′-Biphenyl]-2,2′-dicarboxaldehyde; 2,8-Dimethylethyl dibenzo[b,d] thiophene; Fluorenone oxime; Dibenzo thiophene sulfone.

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-tetrahydro pyridine; 9.812 min, Cyclohexane, 1-methyl-2-pentyl.
Prevention of Oil Sheen Formation - Evaluation by Visual Inspection

Ordinary bubbling and CDC aeration did not prevent oil sheen formation (room temperature).
Once ozone contacted oil droplets, the surface properties and viscosity of the oil droplets were greatly changed. These changes resulted in oil droplets coalescing together that prevented spreading of the oil. More hydrophilic dissolve hydrocarbons can prevent further oil sheen formation.

The thickness of oil sheen can be estimated using 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>
Based on relatively fast removal of oil droplets and slow degradation rate of dissolved organics, a two-stage ozonation process is recommended:

One small CDC ozonation reactor is employed to quickly remove most dispersed oil droplets. Another larger CDC reactor is employed to degrade dissolved hydrocarbons. This will increase efficiency of ozone.
Conclusions

- Ozone degrades/converts dissolved hydrocarbons in aqueous phase, resulting in organic acids that do not form sheen subsequently. These highly dissolved organic acids are expected to be more biologically accessible and treatable.

- Pressure cycles are used advantageously for the conversion and removal of dispersed hydrocarbons in aqueous phase.

- Pressurized ozonation treatment accelerates the degradation dissolved hydrocarbons in aqueous phase by increasing reactive interfacial zone, that attract hydrophobic chemicals and concentrate them to region near the ozone-rich gas phase.
Advantages of POT Process

- High treatment rate — can be treated in a short period (e.g., 30 min or shorter by adjusting headspace/liquid volume ratio)
- High capacity — ozonation reactor can be scaled up and the capacity is determined by the ozone generator
- Total removal of dispersed hydrocarbons
- Total transformation of dissolved hydrocarbons into compounds that do not form sheen
- Ease in operation (mild pressure)
- Low cost
Hot Water Extraction Process (HWEP) of Oil Sands

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

Disadvantages:
1. Averagely less than 75% bitumen can be recovered from oil sands;
2. Caustic reagents and other additives are used;

Recently much attention has been paid to the possibility of reducing commercial process costs by reducing the slurry temperature, but more additives and (or) co-solvent are needed.
Why Pressurized Hot Water Extraction (PHWE)

Advantages:

- Accelerate processing time – separation and recovery simultaneously;
- Increase recovery efficiency – more than 95% bitumen can be recovered, even for low grade oil sands;
- Avoid usage of caustic reagents – caustic reagents and other additives are not necessary;
- Recycle hot water – no tailings, hot water can easily recycled.
Mechanism

PHWE process takes advantage of ablation, mixing, mass and heat transfer, and chemical reactions during degassing procedure to displace and disengage bitumen from sands.

Asphalt Ridge oil sands contain 12±1.7% by weight bitumen. Separation of bitumen from Utah oil sands requires more intensive shearing force and caustic wetting agent such as sodium hydroxide for HWEP.
If water temperature is higher than its boiling point under normal pressure (100-105 °C), degassing procedure can separate and recover bitumen more effectively since releasing of the accumulated potential heat during degassing procedure generates more bubbles.
150 Psi

Recovered bitumen (%) vs Cycle

- Overheated
- 95 degree
- 85 degree
- 75 degree
- 65 degree
Extracted bitumen (%) over cycles under 50 Psi.

- Overheated
- 95 degree
- 85 degree
Recovery Efficiency at Different pH

The graph shows the recovery efficiency of bitumen at different pH levels. As the pH increases from 7 to 11, the recovery efficiency decreases. The values are given in weight percent (wt %). The images below the graph depict the experimental setup for different pH values: pH = 8.5, pH = 9.5, pH = 10.5, and pH = 11.5.
THANK YOU!

QUESTIONS PLEASE?

- For license agreement, please contact Mr. Zachary Miles, TCO at the University of Utah, email: zach@tco.utah.edu