Fate, Behavior & Modeling of Spilled Oil Sands Products (Freshwater & Marine Environments)

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Oil Sands Products Training
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Introduction

Understanding Fate, Behaviour & Modelling

Behaviour Factors:
• Evaporation (and dissolution)
• Photo-oxidation
• Water Uptake and Emulsions
• Sediment Interactions and dispersion in water
• Temperature

Chemical changes to oil
• Evaporation
• Biodegradation

Open Questions
Oil Fate, Behaviour and Models

Model:
Quantitative or semi-quantitative prediction of oil movement in environment (trajectory), and transformation by environmental factors (weathering)

Oil Behaviour:
A physical/chemical transformation of the oil, a “weathering” process

Oil Fate:
The eventual end-point state an oil may reach
Weathering

• In the environment crude oil and refined products are modified by natural physical, chemical, and biological processes that change their composition and fate.
• These processes are collectively referred to as weathering.
• Primary processes include: evaporation, formation of emulsions, dissolution, photochemical and biological oxidation.
• The oil properties and how they change in the environment are one of the major drivers of oil behaviour (what it does), fate (where it goes), persistence (how long it lasts) and effects (who gets hurt).
Behaviour and Fate
# Selected Physical Properties

<table>
<thead>
<tr>
<th>Commercial Type</th>
<th>Heavy Sour Synbit</th>
<th>Sweet Synthetic Crude</th>
<th>Condensate</th>
<th>Heavy Sour Dilsynbit</th>
<th>Heavy Sour Dilbit</th>
<th>Light Sweet Crude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>MacKay River Bitumen Diluted with Light Synthetic Crude Oil</td>
<td>Syncrude Synthetic Light Crude Oil</td>
<td>CRW Condensate</td>
<td>Albion Heavy Synthetic</td>
<td>Wabasca Heavy</td>
<td>West Texas Intermediate</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Property</th>
<th>0 °C</th>
<th>15 °C</th>
<th>0 °C</th>
<th>15 °C</th>
<th>0 °C</th>
<th>15 °C</th>
<th>°C</th>
<th>°C</th>
<th>°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/mL)</td>
<td></td>
<td>0.9463</td>
<td>1.0109</td>
<td>0.8594</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity (mPa·s)</td>
<td>465</td>
<td>241.9</td>
<td>6</td>
<td>0.6</td>
<td>156</td>
<td>128100</td>
<td>19.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flash Point</td>
<td>10</td>
<td>&lt;-5</td>
<td>&lt;-5</td>
<td>&lt;-5</td>
<td>-23</td>
<td>151</td>
<td>-10</td>
<td>-6</td>
<td>-22</td>
</tr>
<tr>
<td>Pour Point</td>
<td>&lt;-24</td>
<td>&lt;-24</td>
<td>&lt;-25</td>
<td>&lt;-30</td>
<td>-6</td>
<td>-22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur (%)</td>
<td>2.3</td>
<td>4.7</td>
<td>0.90%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Bruce Hollebone, PhD (December 2012)
Effects of Weathering on Models

- Weathering affects oil characteristics, density, viscosity, surface/interfacial tensions
- Physical and chemical changes cause differences in trajectory behaviours and oil fate

<table>
<thead>
<tr>
<th>Oil Type</th>
<th>Wind Drift or Leeway (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>3--4</td>
</tr>
<tr>
<td>Diesel</td>
<td>3--4</td>
</tr>
<tr>
<td>Fresh IFO</td>
<td>3</td>
</tr>
<tr>
<td>Fresh Crude</td>
<td>3--4</td>
</tr>
<tr>
<td>Weathered IFO</td>
<td>2--3</td>
</tr>
<tr>
<td>Emulsified Oil</td>
<td>1--2</td>
</tr>
<tr>
<td>Scattered Tarballs</td>
<td>0.5--2</td>
</tr>
</tbody>
</table>
Factors: Evaporation

- Best understood weathering process.
- Evaporation is influential behavioural component.
- A light crude can lose as much as 75% in two days and a medium crude as much as 40%.
- A physical/thermodynamic process, molecules are removed from the oil, but not changed chemically.
- One of the best studied types of weathering, many major types of models for oil -> air evaporation.
Evaporation of Oil Sands Products

- Light, Sweet Crude (Alberta)
- Synthetic (Upgraded) Crude --- "Syncrude"
- Bitumen diluted with Syncrude --- "dilsynbit"
- Bitumen
Dissolution and Solubility

- Not a major effect on oil behaviour, but can have large effects on organisms and habitats
- Affected by oil concentration, mixing energy, temperature and time
- Can be limited by diffusion rates through oil
- Physical models well developed
Factors: Photo-oxidation

- Observed to cause increase in density in real-world spills
- "Skin" formation
- Appears to increase oxidized components of oil
  - Enhances water uptake and emulsion formation
- No models for behaviour
Factors: Water Uptake

- Formation of finely dispersed water droplets in an oil phase --- Emulsions and other dispersions
- Oil densities increase, viscosities greatly increase
- Changes state of oil, but not chemistry.
- Changes transport: oil is lower in water, has higher stickiness and much higher viscosity
- “Entrained water”– simple viscosity-bound water in oil – may persist for significant amounts of time
- Models for water uptake and retention are not well developed --- all data is empirical/experimental
Evaporation and Photo-oxidation Effects on Water Content of Oil
Factors: Sediment Interaction

• Observed sedimentation of sunken oil at several spills
  – Quantitative data from spills of opportunity is sparse.

• Quantitative models just now starting to be developed

• Several modes of uptake
  – Suspended particulates (OMA/OFI/OSA/SPM, etc...)
  – Surf-zone interactions
Percent Material Added

Resulting Density g/mL

0.96 0.98 1.00 1.02 1.04 1.06 1.08

Light material - grass, etc.
Mixed material
Mixed heavier material
Sand

Sinks
floats

Sand
Mixed heavy
Mixed
Light

Percent Material Added
Dispersion and Sediment Interaction

- Dispersion of oil into small droplets occurs in high-energy environments: breaking waves, storms, floods, surf zones.
- Dispersion can promote rapid weathering because of proportionately large surface areas to volume of oil
  - Dissolution
  - Emulsification
  - Sediment uptake
  - Water uptake
- Sinking and “tarball formation”
- Models are under active development

Khelifa et al, 2008
Water Surface
Immediately After Agitation
A Few Minutes Later
Factors: Temperature

• Oil density increases with decreasing temperature

• Cyclic - daily and seasonal variations, with additional weather factors

• Temperature affects many oil properties (viscosity, interfacial tensions)
  – Potential for non-linear interactions

• Empirically well understood, practical models exist
Sediment Uptake vs Temperature

![Bar chart showing sediment concentration (mg/mL) vs average density (g/mL) at different temperatures (15C and 5C). The graph displays three concentrations: 0, 1, and 10 mg/mL, with bars indicating the average density at each concentration and temperature.](chart.png)
Chemical Weathering

- Chemical distribution of oil changes in the environment.

  Removal:
  - Evaporation
  - Dissolution and dispersal

  Transformational:
  - Chemical degradation/oxidation (e.g., photo-enhanced)
  - Biological degradation
Weathering changes to oil

- Largest changes occur rapidly after spill, with slow degradation later
- Rapid removal of light ends <C25 (F1 + F2)
- The fate of the oil strongly affects degradation
- Densities uniformly increased with exposure
- Oil does not weather evenly; highly degraded skins can contain less weathered oil.
- Models are mostly empirical
Chemistries---Fresh oils

Saturate n-Alkanes

Polycyclic Aromatic Hydrocarbons (PAH)
Effects of Evaporation

Saturate n-Alkanes

Polycyclic Aromatic Hydrocarbons (PAH)
Biodegradation

- Long-term action of microbes on oil
- Almost reverse of photo-oxidation: smaller molecules affected first, straight-chain alkanes preferred, followed by unalkylated aromatics.
- Can last for months to years.
- Aerobic can be much faster than anaerobic.
- Availability of fertilizers and electron acceptors
Biodegradation of Heavy Oil
Bio-oxidation in natural samples

Hollebone et al, 2011
Open Questions

• Changes to dilbit chemistry by evaporation of diluent components (rate of change)
• Dispersion of oil in water (droplet size, rise time, coalescence)
• Resuspension and remobilization potential
• Dissolution in water & bioavailability
• Toxicity, chemical and physical
• Persistence
• Interactions of factors to affect behaviours
Questions? Comments?

END