Acid Generation and Metal Release in Oil Sands Froth Treatment Tailings

Matthew Lindsay, Ph.D.
Associate Professor
NSERC/Syncrude IRC in Mine Closure Geochemistry
Department of Geological Sciences
University of Saskatchewan
matt.lindsay@usask.ca
www.mbjlindsay.ca
Oil Sands Deposits

- Oil sands deposits contain 168B barrels of proven bitumen reserves
- Hosted in sands and sandstones of the Cretaceous McMurray formation
- Ore comprised of:
  - Bitumen (8–15% w/w)
  - Water (2–5% w/w)
  - Solids (80–90% w/w)
- Approximately 3.4% (4800 km²) of deposit area accessible by surface mining
  - Active mining footprint > 950 km² (2017)

Figure: https://www.aer.ca/providing-information/by-topic/oil-sands
Data: http://osip.alberta.ca/library/Dataset/Details/27
Oil Sands Ore

- contains bitumen characterized by:
  - high viscosity and density
  - high molecular weight carbon
  - low hydrogen-to-carbon ratio
  - elevated sulfur and nitrogen
- extraction and upgrading required to produce synthetic crude oil
  - diluted bitumen also exported
Surface Mining

• open pit mining used where ore is within ~100 m of surface
  • truck and shovel method
  • high recovery rates (cutoff grade ~8% w/w)
  • open pits can exceed 10 km²
  • large water and energy requirements
  • accounts for ~50% of bitumen production

Image Credit: “Truck and shovel” by Syncrude Canada Ltd.
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Source: https://www.flickr.com/photos/syncrudecanada/16939468045/
**Bitumen Extraction**

1. **Hydrotransport**
2. **Primary Separation**
3. **Secondary Separation**

**Data:**
- 2018: 245M m$^3$ of non-saline water
  - 2.9 m$^3$/1.0 m$^3$ oil
- 2018: 745M m$^3$ recycle water
  - 8.7 m$^3$/1.0 m$^3$ oil

**Figure after:** Mikula (2012) *In: Restoration and Reclamation of Boreal Ecosystems. Ch. 6, pp. 103-122.*
Froth Treatment Tailings (FTT)

- produced during bitumen froth treatment
  - diluent hydrocarbons added to aerated bitumen froth lowers viscosity and liberates entrained solids
  - solids comprised of (phyllo)silicates, oxides, carbonates, and sulfides
- sub-aerial or sub-aqueous deposition within engineering tailings facilities
  - diluent recovered before hydrotransport
FTT Geochemistry

• sulfides concentrated in FTT relative to other tailings streams
  • principally pyrite and marcasite
• potential environmental concerns include:
  • acid generation
  • metal(loid) release
  • biogenic gas production
• geochemical evolution variable among mines and within deposits
  • sub-aerial versus sub-aqueous deposition
  • naphthanic versus parrafinic solvent
  • differences in ore mineralogy and processing
Plant 6 FTT Deposit

- partially water-saturated beach deposit
- located in Mildred Lake Settling Basin (MLSB)

approximate sub-aerial extent in 08/2018

Image Credit: Google Earth © 2019 DigitalGlobe
Field Study: 2013

• purpose:
  • preliminary examination of FTT geochemistry and mineralogy

• methods:
  • auger: 0.0 – 0.3 m b.g.s. (frozen upper layer)
  • sonic coring: 1.3 – 3.3 and 3.3 – 5.3 m BGS

• analyses:
  • particle-size distribution: laser diffraction
  • mineralogy: optical, SEM, XRD
  • geochemistry: digestions, EPMA, PCA
  • ABA: modified Sobek with siderite correction
Mineralogy

- silicates + phyllosilicates dominate
  - marcasite also observed
  - complex sulfide textures
- carbonate content similar to sulfide content
  - siderite dominates
- weathered FTT can have large amorphous component

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal formula</th>
<th>mean ± 1σ (wt. %)</th>
<th>median (wt. %)</th>
<th>minimum (wt. %)</th>
<th>maximum (wt. %)</th>
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<td><strong>Silicates</strong></td>
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<tr>
<td>Almandine</td>
<td>Fe₃Al₂(SiO₄)₃</td>
<td>0.76 ± 0.35</td>
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<td>Dravite</td>
<td>NaMg₃Al₆(BO₃)₂Si₆O₁₈(OH)₄</td>
<td>4.4 ± 1.5</td>
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<td>Quartz</td>
<td>SiO₂</td>
<td>57 ± 13</td>
<td>61</td>
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<td>Zircon</td>
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<td>3.3 ± 1.0</td>
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<td><strong>Phyllosilicates</strong></td>
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<tr>
<td>Kaolinite</td>
<td>Al₂Si₂O₅(OH)₄</td>
<td>5.7 ± 9.0</td>
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<td>Illite</td>
<td>K₀.₆₅Al₂₀(Al₆₈Si₃₃O₁₉)(OH)₂</td>
<td>2.6 ± 0.72</td>
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<td>6.7 ± 4.5</td>
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<td>Anatase</td>
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<td>Ilmenite</td>
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<td>Rutile</td>
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<td>Ankerite</td>
<td>Ca(Fe,Mg,Mn)(CO₃)₂</td>
<td>0.82 ± 0.19</td>
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<td>Calcite</td>
<td>CaCO₃</td>
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<td>Dolomite</td>
<td>CaMg(CO₃)₂</td>
<td>2.5 ± 1.8</td>
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<td>Siderite</td>
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<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>6.5 ± 2.7</td>
<td>7.0</td>
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<td>FeS₂</td>
<td>1.0 ± 0.47</td>
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<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>0.71 ± 0.40</td>
<td>0.56</td>
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<tr>
<td>Jarosite</td>
<td>KFe₅(SO₄)₂(OH)₆</td>
<td>0.22 ± 0.07</td>
<td>0.25</td>
<td>0.11</td>
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</table>


Mineralogy

a–c. FTT sample in (a) transmitted ppl, (b) transmitted xpl, and (c) reflected ppl;

d. leucoxene textured ilmentite (Ilm) in reflected ppl with rutile (Rt) or anatase (Ant), pyrite (Py), magnetite (Mag), dravite (Drv) and quartz (Qtz);

e. siderite (Sd) in transmitted ppl (e);

f. acicular Py and marcasite (Mrc) and elongate subhedral Py with Sd and Qtz;

g–h. clustered Py frambooids with discrete Mag, Sd, Rt and Qtz grains; and

i. Mrc rim on weathered Py frambooid with Sd.

Polished 30 µm thin sections.

ppl: plane polarized light
xpl: cross-polarized light

Mineralogy

a. euhedral pyrite with discrete framboids at arrows;
b. clustered and intergrown pyrite framboids;
c. pyrite (Py) intergrowth with quartz (Qtz);
d. pyrite overgrowth on remnant framboids;
e. pyrite permineralization of organic matter; and
f. acicular radiating pyrite with marcasite.

Geochemistry

- major element composition generally reflect mineral assemblage
- pyrite contains As, Cu, Co, Fe, Mn, Ni (plus trace Se and V)
- Fe, Mn, Ni, Pb, Sr and Zn associated with carbonates
- REEs, Th and U likely associated with zircon, monazite, and xenotime
- Cr and V likely associated with multiple phases

Acid-Base Accounting

- consistent negative net neutralization potential (NNP)
- low or negative neutralization potential (NP)
  - negative values attributed to partial dissolution of Fe(II)-bearing phases during acid addition
- potential for acid generation during oxidative weathering
  - findings consistent with mineralogical analysis

Field Study: 2015

• purpose:
  • preliminary examination of FTT pore-water chemistry

• methods:
  • direct-push coring to refusal (< 1 to ~3 m bgs)
  • hardpan encountered at L04, L05, L06

• analyses:
  • pore-water: squeezing, chemistry
  • mineralogy: optical, SEM, XRD
  • geochemistry: digestions, XRF/XAS
  • ABA: modified Sobek with siderite correction
  • microbiology: 16S rRNA gene sequencing
Pore-Water Chemistry

- Locations 01a–03:
  - circumneutral pH, relatively low dissolved metal concentrations
- Locations 04–05:
  - extensive hard pan (limited sample)
- Location 06:
  - acidic pH, no alkalinity, high EC and dissolved metal concentrations
- Location 07:
  - evidence of weathering front
  - Mg and alkalinity low in upper 0.5 m
  - acidic conditions likely to develop with time
Pore-Water Chemistry

• large increase in dissolved metal(loid)s at pH < 5
  • increased solubility of metal (hydr)oxides and carbonates with decreasing pH
  • limited capacity for metal(loid) sorption
Arsenic Mobility

- As released during pyrite oxidation
- As(V) accumulation in vadose zone
  - associated with Fe(III) (oxyhydr)oxides
- Long-term mobility likely controlled by:
  - pH-dependent precipitation-dissolution and sorption reactions
  - As and Fe redox cycling

Left: synchrotron μXRF maps of As speciation.
Middle: reflected light microscope photograph.
Right: synchrotron μXANES spectra.
Mineralogy

- wider range of sulfide and carbonate contents than observed in 2013 study
  - sulfides: 1.3 to 27 wt. % (median 7.2 wt. %)
  - carbonates: < 1 to 15 wt. % (median 5.4 wt. %)
  - siderite accounted for 61 to 100% of carbonates
- varied degree of weathering
  - sulfides and carbonates depleted in highly weathered samples
  - jarosite and gypsum accumulation apparent
- large amorphous component in weathered tailings
  - ongoing research to identify these phases and assess their influence on metal(loid) mobility
Laboratory Study: 2016–present

• purpose:
  • assess acid generation and metal leaching over time in varied samples

• methods:
  • 1 kg (eq. dry wt.) of FTT (no solvent wash) placed in each column
  • glass wool and perforated support
  • ambient lab conditions (PO₂, T, RH)
  • flushed with 1 L of DI every 7th day

• analyses:
  • chemical analysis of leachate
  • mineralogy at beginning and end
Column Drainage

- drainage pH ranges from ~2 to 9
  - weathered FTT samples generated acid for extended time
  - evidence of ongoing oxidation in fresh/non-weathered FTT samples
- ongoing S release indicative of sulfide-mineral oxidation
  - apparent in fresh FTT samples and
    - P6-16-F1, P6-16-F2a, P6-16-F2b
  - S release declining with time for P6-15-06
Column Drainage

- metal(loid)s present in leachate
  - concentrations not representative of potential field conditions
- concentrations generally low in pH 7–9 leachate
  - likely due to sorption or co-precipitation reactions with Fe(III) (oxyhydr)oxides
- highest concentrations observed in FTT sample P6-15-06
  - exhibits pH < 3 and evidence of active oxidation (i.e., S release)
Column Solids

- ABA results indicate that all FTT samples are likely acid generating
- only initially weathered samples generated drainage with pH < 3
- evidence of ongoing sulfide-mineral oxidation in initially non-weathered samples
  - sustained S, Ca and Mg release
- carbonate assemblage comprised of 60 to 100% siderite
  - lower siderite content in initially non-weathered samples
Lessons Learned

- acid generation and metal leaching
  - acid rock drainage type waters can be generated
  - sulfide content and water-saturation are key variables
- acidic waters (pH < 5) characterized by:
  - high dissolved sulfate and iron concentrations
  - high dissolved metal(loid) concentrations
    (i.e., As, Se, V, Ni, Zn, Cu, Co)
- time to acid generation likely fairly long
  - organics may limit initial oxidation rates
  - metal(loid) source terms change over time
- acid generation and metal transport may be mitigated
  - sub-aqueous disposal, soil covers, etc.
  - sulfidogenesis, passive treatment, etc.
Ongoing/Future Research

• develop models of the geochemical evolution of FTT deposits
• assess efficacy of current oil sands mine reclamation strategies
• evaluate new approaches for mitigating acid generation and metal release
Funding:

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