Saline Inflows, Biodegradation and Gas Generation in the Basal Water Sand Aquifer, Athabasca Oil Sands Region, Alberta

Hugh Abercrombie and Ken Baxter
Outline

- Introduction
- Geology
- Hydrogeology
- Geochemistry
- Industrial Significance
  - Biodegradation
  - Gas Generation
  - Saline Inflows
- Summary

Archives, Government of Canada
Key Messages – Basal Water Sand (BWS)

Geology
- Deposited on a highly dissected erosion surface cut into a limestone karst terrain; distribution influenced by both pre- and post-depositional structure

Hydrogeology
- Regional recharge of the BWS east and west of the Athabasca River
- Regional discharge along the Athabasca River where the BWS experiences upward flow of basinal Devonian brines

Geochemistry
- The BWS occurs within the interface between:
  - A hypersaline, oxidized Paleozoic geochemical network, and
  - A fresh to brackish, reducing Mesozoic geochemical network
- In the discharge region, secondary minerals record vertical movement and progressive reduction of oxidized saline brines
Significance to Industry

Oil sands mining
- Saline inflows
- BWS depressuring
- On-site water storage / transfer

In situ
- Brackish groundwater resource
- Potential thief zone

Geochemical Processes
- A locus for water-rock-microbial interactions:
  - Reduced bitumen saturations
  - Biodegradation in discharge (upflow) areas
  - $H_2S$ generation associated with biodegradation
Basal Water Sand

Oil Sand

Basal Water Sand
Basal Water Sand (BWS) aquifer located in the surface mineable oil sands area

The BWS may or may not be present in the Athabasca south region and other areas
Lower Mannville Isopach

- LMnv deposition controlled by salt dissolution (east) and flexural subsidence (west)
- LMnv in NE Alberta includes Basal Water Sands deposited in N prograding delta
- LMnv sediments predominantly supermature quartz derived from the Precambrian Shield

After Cant and Abrahamson (1996)
Stratigraphic Column, Northeast Alberta

<table>
<thead>
<tr>
<th>AGE</th>
<th>Northeastern Alberta Athabasca West</th>
<th>Athabasca East</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOWER CRETACEOUS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALBIAN</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>La Biche Fm.</td>
<td>La Biche Fm.</td>
</tr>
<tr>
<td></td>
<td>Pelican Fm.</td>
<td>Pelican Fm.</td>
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<tr>
<td></td>
<td>Joli Fou Fm.</td>
<td>Joli Fou Fm.</td>
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<tr>
<td></td>
<td>Grand Rapids Fm.</td>
<td>Grand Rapids Fm.</td>
</tr>
<tr>
<td></td>
<td>Clearwater Fm.</td>
<td>Clearwater Fm.</td>
</tr>
<tr>
<td></td>
<td>Wabiskaw Mb.</td>
<td>Wabiskaw Mb.</td>
</tr>
<tr>
<td></td>
<td>McMurray Fm.</td>
<td>McMurray Fm.</td>
</tr>
<tr>
<td>APTIAN AND OLDER</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SUB-CRETACEOUS</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Waterman Fm.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Waberton Fm.</td>
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</tr>
<tr>
<td></td>
<td>Waterfowl Fm.</td>
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</tr>
<tr>
<td></td>
<td>Woodbend Group</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Beaverhill Lake Group</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Precambrian</td>
<td></td>
</tr>
</tbody>
</table>

Oil sand: dark green
Barren sand: light blue
Mudstone: light green

After EUB/AGS Earth Sciences Report 2001-06
Simplified geological cross section north of Fort McMurray

- BWS aquifer sits unconformably on structured Devonian limestone
- Cretaceous McMurray Formation of the Mannville Group exposed along the bank of the Athabasca River
- The McMurray Formation sits unconformably above Devonian limestone of the Waterways Formation, Beaverhill Lake Group
Regional Structural Elements

- Abundant evidence for structural control of BWS distribution
- Salt solution collapse
- Potential basement involvement

Aeromag 2nd VD

Birch Mountain Resources (1997)

After EUB/AGS Earth Sciences Report 2001-06
Clearwater Formation isopach appears to template thickest BWS at Fort Hills

Clearwater Formation is preserved as an inlier

Structural down-dropping of Clearwater may have led to thicker BWS development
Two major flow systems discharge to the Athabasca River
- Deep basin flow system (Devonian)
- Shallow surface flow system (Cretaceous to Quaternary)
- Westward flow of meteoric and glacial/interglacial recharge waters
- Eastward flow of low TDS water in upper section; eastward flow of high TDS basinal brines in lower section
Brine Discharge at La Saline Springs
Simplified Redox Stratigraphy

- Oxidized Elk Point brines (red) and surface waters
- Reduced conditions (green) in rocks in contact with bitumen and deep in basement
Redox-Driven Mineral Alteration

- Vertical flow of oxidizing Na-Ca-Cl-SO$_4$ brines:
  - Oxidation of primary pyrite,
  - In the presence of bitumen, bacterial sulphate reduction produces H$_2$S and CO$_2$
  - H$_2$S reacts forming secondary pyrite and pyrrhotite,
  - CO$_2$ reacts to form H$^+$ and HCO$_3^-$, causing decalcification and siderite precipitation

SECONDARY MINERALS
1. Native S, Keg River Formation.
2. Pyrrhotite, Waterways Formation.
3. Siderite nodules, Lower McMurray Formation.
BWS Conceptual Geochemical Model

Structurally controlled deposition

$T_0$

Oil arrives

$T_1$

Brine incursion

$T_2$

Oil Sands

Decalcification

Redox: $2^\circ$ MC, PY, PO

Sour water

Bacterial sulphate reduction

$SO_4 + Oil = H_2S + CO_2$

Decalcification

Redox:

$1^\circ$ PY oxidation

$S_0$ on fractures

Na-Ca-Cl-SO$_4$

Redox: $1^\circ$ HFO dissolution,

$2^\circ$ Siderite nodules
Industrial Impact of BWS

Oil sands mining
- Saline inflows
- BWS depressurizing
- On-site water storage / transfer

In situ
- Brackish groundwater resource
- Potential thief zone

Geochemical Processes
- A locus for water-rock-microbial interactions:
  - Reduced bitumen saturations
  - Biodegradation in discharge (upflow) areas
  - H$_2$S generation associated with biodegradation
Hydrochemistry of BWS Aquifer

PROCESS VECTORS
- Decalcification
- Dedolomitization
- Halite dissolution
- Gypsum dissolution
- Bacterial sulphate reduction

BWS EVOLUTION
- Rainwater
- Calcite/dolomite
- Ion exchange
- SO$_4$ incursion
- Saline brine incursion

Piper diagram - mass units
Biodegradation and Water Chemistry

- BWS water compositions record multiple processes
- Site specific processes
- Potential importance of redox over chlorinity as an indication of Devonian incursion

BWS EVOLUTION

- Rainwater
- Calcite/dolomite
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- SO₄ incursion
- Saline brine incursion

Piper diagram - mass units
Modeling Bacterial Gas Generation

- PHREEQC used to model gas bubble generation via reaction with bitumen
- Henry’s Law $K_H$ values used for CH$_4$, CO$_2$, H$_2$O, H$_2$S and N$_2$
- Incremental addition of bitumen to reach supersaturation with the least soluble gas (CH$_4$)
- Track total mass and volume of gaseous species in the gas phase
- Decrease containing pressure to simulate depressuring

<table>
<thead>
<tr>
<th>Relative moles</th>
<th>Reactant</th>
<th>30 millimoles of…</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C)2(H)2.93(H)0.01(S)0.04(C)0.02</td>
<td>1.00000</td>
<td>…model bitumen…</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Relative moles</th>
<th>Element</th>
<th>…titrated into 1 Kg of BWS water…</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 2.00000</td>
<td>H 2.93000</td>
<td></td>
</tr>
<tr>
<td>N 0.01000</td>
<td>O 0.02000</td>
<td></td>
</tr>
<tr>
<td>S 0.04000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Gas phase
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Total pressure: 15.0000 atmospheres …at 15 bar pressure…
Gas volume: 2.54e-002 liters
…results in initial bubble formation…

<table>
<thead>
<tr>
<th>Component</th>
<th>log P</th>
<th>P</th>
<th>Initial</th>
<th>Final</th>
<th>Delta</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$(g)</td>
<td>1.13</td>
<td>1.364e+001</td>
<td>0.000e+000</td>
<td>1.469e-002</td>
<td>1.459e-002</td>
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<tr>
<td>CO$_2$(g)</td>
<td>0.12</td>
<td>1.352e+000</td>
<td>0.000e+000</td>
<td>1.459e-003</td>
<td>1.459e-003</td>
</tr>
<tr>
<td>H$_2$O(g)</td>
<td>-1.92</td>
<td>1.159e-002</td>
<td>0.000e+000</td>
<td>1.293e-005</td>
<td>1.293e-005</td>
</tr>
<tr>
<td>H$_2$S(g)</td>
<td>-1.69</td>
<td>2.062e-002</td>
<td>0.000e+000</td>
<td>2.251e-005</td>
<td>2.251e-005</td>
</tr>
<tr>
<td>N$_2$(g)</td>
<td>-5.05</td>
<td>2.916e-006</td>
<td>0.000e+000</td>
<td>9.768e-009</td>
<td>9.768e-009</td>
</tr>
</tbody>
</table>
Depressuring Model Results

- Gas volume at saturation calculated for ~90 m depth (10 atm)
- Gas volume tracked as pressure is reduced; i.e., drawdown
- At ~60 m drawdown gas volume is ~10% of total volume
- This analysis does not consider the salting-out effect which further decreases gas solubilities
Implications for Depressuring

- Biodegradation of small quantities of bitumen may provide sufficient gas to saturate BWS at depth.
- Schematically, a pumping drawdown of 60 m on a gas-saturated BWS water at 90 m depth can result a loss of 60% relative permeability to water.
- Analysis is qualitative, but illustrates the importance of understanding BWS, including biodegradation, gas generation and salinity.

Saline Inflows – The Devonian Connection

- Operators in the Mineable Oil Sands area have, from time to time, encountered inflows of saline water inferred to originate in Devonian aquifers.
- BWS provides part of the pathway linking Pz and Mz formations.
- Present-day salinity distribution suggest little connection between Devonian and McMurray Formations.
- Mineralogy, bitumen chemistry and structure imply in the past there may have been connection.
- Prior structural / hydrogeological fairways may be reactivated during mining – multiple layered datasets are needed to locate these fairways.
BWS Summary

- Regionally, the BWS is subjected to numerous physical, chemical and biological processes:
  - Meteoric recharge to the east and in elevated areas to the west
  - Interglacial to early post-glacial recharge
  - Upflow of Devonian brines, themselves influenced by
    - Decalcification and dedolomitization
    - Gypsum and/or halite dissolution
  - Bacterial sulphate reduction is expected where upflowing waters carrying sulphate encounter bitumen, leading to:
    - Production of $\text{H}_2\text{S}$ and $\text{CO}_2$
    - Reductive dissolution of hydrous ferric oxide minerals
    - Precipitation of sulphide minerals
- Site-specific knowledge of Devonian and BWS waters is required to address key issues of concern to oil sands industry, regulators
Questions…

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