An Investigation of Natural Attenuation and Plume Geochemistry at an Oil Sands Mining Facility

Prepared for Remtech 2006

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Acknowledgements

- Analytical Support: Marianne vanderGriendt (University of Waterloo) & Shirley Chatten (UW)

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- Syncrude Canada Ltd: Barry Esford, Grey Kampala, Mike MacKinnon, Lori Cyprien, Karen Chovan, Steve Carroll

- Field and Lab Assistance: Mike Gunsinger (UW), Rich Amos (UBC), Ed Cey (UW), Bill Marsh (University of Alberta), Naoki Yasuda (UW), Lindsay Oiffer, Wayne Noble (UW), Matt Lindsay (UW), Jeff Bain (UW)

- Funding from: The Canadian Foundation for Innovation, The Canada Water Network, NSERC and Syncrude
Outline

1. Objectives
2. Plume Dynamics
3. Sampling Network
4. General Plume Composition
5. Naphthenic Acid Attenuation Mechanisms
6. Trace Metals Release Mechanisms
Objectives

1. Identify the groundwater fate and transport properties of constituents of concern of seepage waters (Primary Effects)

2. Determine the potential for trace metal release from the solid phase (Secondary Effects)
Plume Dynamics

Objectives

Sampling Network

General Plume Composition

NAs Introduction

NAs Attenuation

NAs Biodegradation

NAs Sorption

NAs Conclusions

TMs Introduction

TMs Dissolved Concentrations

TMs Release Mechanisms

TMs Controls for Release

TMs Solid Phase Content

TMs Reductive Capacity of Plume

TMs Conclusions
General Plume Composition

- Maximum Concentrations Near Source (Adjacent to Tailings Dyke)

* below detection limit
Naphthenic Acids - Introduction

Naphthenic Acids - Attenuation

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[Graph showing chloride, sodium, and naphthenic acid concentrations along a flow path]
Naphthenic Acids - Attenuation

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R² = 0.94
Naphthenic Acids - Attenuation

Objectives
- Plume Dynamics
- Sampling Network

General Plume Composition
- NAs Introduction
- NAs Attenuation
- NAs Biodegradation
- NAs Sorption
- NAs Conclusions

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R² = 0.55

Naphthenic Acid (mg/L) vs. Chloride (mg L⁻¹)
Naphthenic Acids - Biodegradation

Increasing Distance Along Flow Path

Relative Proportion of Mixture (%)
Naphthenic Acids - Sorption

Units: mg/L

Source: Schramm et al. 2000
Naphthenic Acids - Sorption

- Sand from sand aquifer in Fort McMurray Area
- Naphthenic Acids from tailings water
- Solution TDS of approximately 1,700 mg/L
- pH varied between 7 and 8
- Fraction of Organic Carbon (foc): 1%
- Velocity relative to groundwater: 56 – 67%

\[ C_{\text{NA.S}} = 5 \times 10^{-8} C_{\text{NA.w}}^{1.2456} \]

\[ R^2 = 0.9964 \]

Stock NA concentration
Average of stock NA concentration
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NAs Sorption

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TMAs Introduction
TMAs Dissolved Concentrations
TMAs Release Mechanisms
TMAs Controls for Release
TMAs Solid Phase Content
TMAs Reductive Capacity of Plume
TMAs Conclusions

Naphthenic Acids - Sorption

56 – 67%?
Naphthenic Acids - Conclusions

- Overall retardation of Naphthenic Acids is low.
- Significant Biodegradation of Naphthenic Acids is not interpreted.
- Weak sorption could explain Naphthenic Acid retardation.
- Difficult to account for initial conditions → Constant Source?
### Trace Metals - Introduction

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidizing Conditions</th>
<th>Reducing Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>Pb(OH)^+ &amp; Pb^{2+}</td>
<td>Pb(OH)^+ &amp; Pb^{2+}</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu^{2+} &amp; Cu^+</td>
<td>Cu_{(s)} &amp; Cu^+</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni^{2+}</td>
<td>Ni^{2+}</td>
</tr>
<tr>
<td>Cd</td>
<td>Cd^{2+}</td>
<td>Cd^{2+}</td>
</tr>
<tr>
<td>Co</td>
<td>Co^{2+}</td>
<td>Co^{2+}</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn^{2+}</td>
<td>Zn^{2+}</td>
</tr>
<tr>
<td>Cr</td>
<td>CrO_4^{2-}</td>
<td>Cr_{2}O_{3(s)} &amp; CrOH^{2+} &amp; CrO^{+}</td>
</tr>
<tr>
<td>As</td>
<td>H_2AsO_4^- &amp; HAsO_4^{2-}</td>
<td>H_3AsO_3^-</td>
</tr>
<tr>
<td>Se</td>
<td>SeO_4^{2-}</td>
<td>SeO_3^{2-}</td>
</tr>
</tbody>
</table>
Trace Metals - Dissolved Concentrations

- Dissolved Arsenic Associated with Plume (mg/L)

![Graph showing dissolved arsenic concentrations along the flow path.]

- As < 0.4
- 0.4 < As < 5.0
- 5.0 < As < 10.0
Trace Metals – Release Mechanisms

4FeOOH\(_{(s)}\) + CH\(_2\)O + 6H\(^+\) → CO\(_3\) + 4Fe\(^{2+}\) + 6H\(_2\)O

Some Possible Fe Mineral Phases in Oxidizing Settings:
- Fe(OH)\(_3\)
- FeOOH
- Fe\(_3\)O\(_4\)
- Fe\(_2\)O\(_3\)

Fe\(^{2+}\) & As
Trace Metals – Controls for Release

- Two Controlling Influences in Trace Metal Release:
  - Trace Metal Content of Aquifer Material
  - Reductive Capacity of the Seepage Waters
As content in solid phase determined using solid phase extractions:

<table>
<thead>
<tr>
<th>Compounds</th>
<th>0.5M HCl</th>
<th>5.0M HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous FeS, Greigite, Mackinawite &amp; Pyrrhotite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite &amp; Elemental Sulphur</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amorphous Oxyhydroxides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poorly crystalline metal oxides, hydroxides, monosulfides, adsorbed metals &amp; ion exchangeable metals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystalline Metal Oxides/Oxyhydroxides &amp; Metals bound in Clays</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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Trace Metals – Solid Phase Content

![Graph showing As (mg/kg) concentrations]

- *Extracted using 0.5M HCl for 24 hours*
- **Extracted using 5.0M HCl for 24 hours**
Trace Metals – Controls for Release

- Two Controlling Influences in Trace Metal Release:
  - Trace Metal Content of Aquifer Material
  - Reductive Capacity of the Seepage Waters
Trace Metals - Reductive Capacity of Plume

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Some uncertainty regarding contribution of Fe, Mn, NH$_4$ and CH$_4$(aq) (COD) to biological oxygen demand results

- Contribution of Naphthenic Acids?
Trace Metals - Conclusions

Possible causes for low dissolved As concentrations:

1. Plume is assumed weakly reducing
2. Low As content in solid phase
3. Phase association of As


Questions?
Extra Slides
Advective Front

![Diagram showing concentration vs. distance with $C_{\text{max}}$ and $0.5C_{\text{max}}$.]
Ammonium
Coring

Step 1
With pointed plug in place, core barrel is pushed into subsurface to top of sampling interval.

Step 2
Pointed plug is loosened and slides up interior of liner as core barrel is advanced through sampling interval.

Step 3
Core barrel is pulled to surface; the plastic liner within core barrel is removed. Sample is contained within liner and prevented from falling out bottom with "core catcher" device.