Sulphide Oxidation in Tailings Storage Facilities:
An Influence to Long Term Dam Stability

Jennifer Durocher, Lindsay Robertson, and
Brent Usher
Sulphide Oxidation in TSF’s: An Influence to Long Term Dam Stability

Outline

• Sulphide oxidation
  • ARD/ML
  • Secondary products in tailings and dam embankments
  • Alter the physical and hydrological properties of materials \(\rightarrow\) design intent

• Implications of secondary products on dam hydrogeochemistry, and the materials physical properties (grain size, shape and pore space)

• Screening and geochemical testing \(\rightarrow\) Planning stages

• Monitoring and evaluation \(\rightarrow\) Existing dams
Sulphide Oxidation in TSF’s: An Influence to Long Term Dam Stability

Sulphide Oxidation

Common Secondary Fe Minerals precipitating from ARD

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>pH range</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Soluble iron sulfate salts</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melanterite</td>
<td>Fe$^{III}$SO$_4$·7H$_2$O</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Rozenite</td>
<td>Fe$^{III}$SO$_4$·4H$_2$O</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Szomolnokite</td>
<td>Fe$^{III}$SO$_4$·H$_2$O</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Copiapite</td>
<td>Fe$^{II}$Fe$^{III}$ (SO$_4$)$_2$(OH)$_2$·20H$_2$O</td>
<td>2–3</td>
</tr>
<tr>
<td>Coquimbite</td>
<td>Fe$^{II}$Fe$^{III}$ (SO$_4$)$_2$·9H$_2$O</td>
<td>2–3</td>
</tr>
<tr>
<td>Rhombochlace</td>
<td>(H$_2$O)Fe$^{II}$Fe$^{III}$ (SO$_4$)$_2$·3H$_2$O</td>
<td>2–3</td>
</tr>
<tr>
<td>Halotrichite</td>
<td>Fe$^{II}$Al$_2$(SO$_4$)$_2$·22H$_2$O</td>
<td>2–3</td>
</tr>
<tr>
<td><strong>Iron hydroxides/hydroxy sulfates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jarosite</td>
<td>KFe$^{III}$SO$_4$(OH)$_6$</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Natrojarosite</td>
<td>NaFe$^{III}$SO$_4$(OH)$_6$</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Hydronium jarosite</td>
<td>(H$_2$O)Fe$^{III}$SO$_4$(OH)$_6$</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Schwertmannite</td>
<td>Fe$^{III}$SO$_4$(OH)$_6$</td>
<td>2–4</td>
</tr>
<tr>
<td>Goethite</td>
<td>α-Fe$^{III}$O(OH)</td>
<td>2.5–7</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>Fe$_3$$^{III}$HO$_8$·4H$_2$O</td>
<td>5–8</td>
</tr>
</tbody>
</table>

Primary sulfides reacting: po + py, py > po, py

Secondary minerals:
- Native S
- Marcasite
- Fe-oxyhydroxides
- Fe$^{III}$-Fe$^{II}$-sulfates
- Jarosite
- Goethite
- Fe$^{III}$-sulfates
- Jarosite
- Jarosite
Sulphide Oxidation in TSF’s: An Influence to Long Term Dam Stability

Sulphide Tailings Hydrogeochemistry

Fe$^{2+}$ (aq) $>>$ Fe$^{3+}$ (aq)

Oxidized Tailings

Fe$^{2+}$ (1ry) $>$ Fe$^{2+}$ (2ry) $>>$ Fe$^{3+}$ (2ry) Mins

Decreasing Fe$^{2+}$ Sulphide Oxidation, Increasing Neutralization Reactions

Decreasing Eh, Increasing pH

Acidic Pore Water

Seepage Water

Oxidation Front

Pore Water

Fe$^{2+}$ (s & aq) $\rightarrow$ Fe$^{3+}$ (aq) $\rightarrow$ Fe$^{3+}$ (2ry) (Fhy, Goe)

Increasing pH

 Decreasing Eh

Increasing Mobility/Migration of Fe$^{2+}$

Decreasing Mobility/Migration of Fe$^{3+}$
Sulphide Oxidation in TSF’s: An Influence to Long Term Dam Stability
Sulphide Tailings Hydrogeochemistry

Silicate and Sulphide Tailings Grains
- Less Weathered
- Angular grains
- Large sulphides
- Empty pore spaces
- Weathered
- Grain size/shape changes
- Very small sulphides
- Secondary mineral precipitates filling pore spaces

Secondary Fe-Coatings: Seepage-Rock Surface

Silicates
Jarosite
Ferrihydrite

100µm
### Physical Properties of Common Primary and Secondary Minerals

<table>
<thead>
<tr>
<th>Primary Mineral</th>
<th>Sym</th>
<th>Chemical Formula</th>
<th>Molecular Weight (g/mol)</th>
<th>Specific Gravity</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrrhotite</td>
<td>Po</td>
<td>Fe((1-x))S</td>
<td>85.12</td>
<td>4.61 (avg)</td>
<td>3.5-4.5</td>
</tr>
<tr>
<td>Pyrite</td>
<td>Py</td>
<td>FeS₂</td>
<td>119.98</td>
<td>5.01</td>
<td>6.5</td>
</tr>
<tr>
<td>Galena</td>
<td>Gl</td>
<td>PbS</td>
<td>239.27</td>
<td>7.4</td>
<td>2.5</td>
</tr>
<tr>
<td>Chalcoprytite</td>
<td>Cpy</td>
<td>CuFeS₂</td>
<td>183.53</td>
<td>4.1-4.3</td>
<td>3.5-4.5</td>
</tr>
<tr>
<td>Alkali Feldspar</td>
<td>Fp</td>
<td>(K,Na)[Al(3)O(8)]</td>
<td>278.33</td>
<td>2.55-2.63</td>
<td>6</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>Pg</td>
<td>Na[Al(2)Si(3)]-Ca[Al(2)Si(2)]</td>
<td>270.77</td>
<td>2.62-2.76</td>
<td>6-6.5</td>
</tr>
<tr>
<td>Muscovite</td>
<td>Mv</td>
<td>K(<em>{2})Al(</em>{5})<a href="OH,F">Si(<em>{6})Al(</em>{2})O(_{20})</a>(_{4})</td>
<td>398.71</td>
<td>2.77-2.88</td>
<td>2-2.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Secondary Mineral</th>
<th>Sym</th>
<th>Chemical Formula</th>
<th>Molecular Weight (g/mol)</th>
<th>Specific Gravity</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jarosite</td>
<td>Jar</td>
<td>KFe(<em>{3})SO(</em>{4})(<em>{2})(OH)(</em>{6})</td>
<td>500.81</td>
<td>2.9-3.3</td>
<td>2.5-3.5</td>
</tr>
<tr>
<td>Schwertmannite</td>
<td>Sch</td>
<td>Fe(<em>{10})O(</em>{26})(OH)(<em>{22})(SO(</em>{4})(_{2}))</td>
<td>1545.76</td>
<td>3.77-3.99</td>
<td>2.5-3.5</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>Fhy</td>
<td>Fe(<em>{3})O(</em>{3})•0.5(H(_{2})O)</td>
<td>168.70</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Melaterite</td>
<td>Mel</td>
<td>Fe(^{2+})(SO(<em>{4}))•7(H(</em>{2})O)</td>
<td>278.02</td>
<td>1.89-1.9</td>
<td>2</td>
</tr>
<tr>
<td>Rozenite</td>
<td>Roz</td>
<td>Fe(^{2+})(SO(<em>{4}))•4(H(</em>{2})O)</td>
<td>223.97</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Copiapite</td>
<td>Cop</td>
<td>Fe(^{2+})Fe(^{3+})(<em>{4})(SO(</em>{4}))(<em>{6})(OH)(</em>{2})•20(H(_{2})O)</td>
<td>1249.94</td>
<td>2.1</td>
<td>2.5</td>
</tr>
<tr>
<td>Halotrichite</td>
<td>Hal</td>
<td>Fe(^{2+})Al(<em>{2})(SO(</em>{4}))(<em>{4})•22(H(</em>{2})O)</td>
<td>890.40</td>
<td>1.78-1.9</td>
<td>1.5-2</td>
</tr>
<tr>
<td>Goethite</td>
<td>Gt</td>
<td>FeOOH</td>
<td>88.85</td>
<td>4.3</td>
<td>5-5.5</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>Ah</td>
<td>CaSO(_{4})</td>
<td>136.1</td>
<td>2.97</td>
<td>3.5</td>
</tr>
<tr>
<td>Gypsum</td>
<td>Gp</td>
<td>Ca(SO(<em>{4}))(</em>{2})2H(_{2})O</td>
<td>172.2</td>
<td>2.3</td>
<td>2</td>
</tr>
<tr>
<td>Cerrusite</td>
<td>Cer</td>
<td>PbSO(_{4})</td>
<td>267.21</td>
<td>6.58</td>
<td>3-3.5</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Kln</td>
<td>Al(<em>{4})<a href="OH">Si(<em>{6}]O(</em>{20})</a>(</em>{8})</td>
<td>258.16</td>
<td>2.61-2.68</td>
<td>2-2.5</td>
</tr>
<tr>
<td>Smectite</td>
<td>Smc</td>
<td>(1/2Ca,Na)(<em>{0})•(Al,Mg,Fe)(</em>{4})(<a href="OH">(Si,Al)(<em>{6})O(</em>{20})</a>(<em>{4}).nH(</em>{2})O</td>
<td>2-2.7</td>
<td>1.5-2</td>
<td></td>
</tr>
<tr>
<td>Illite</td>
<td>Il</td>
<td>K(<em>{1.5-1.0})Al(</em>{4})<a href="OH">Si(<em>{6.5-7.0})Al(</em>{1.5-1.0})O(_{20})</a>(_{4})</td>
<td>389.34</td>
<td>2.6-2.9</td>
<td>1-2</td>
</tr>
</tbody>
</table>
Sulphide Oxidation in TSF’s: An Influence to Long Term Dam Stability
Secondary Precipitates and Implications for Drainage

Early Stage Development

- Partially reacted tailings (unoxidized → partially)
- Seepage is characteristic of early ARD development
  - Mildly to moderately acidic pH (6-4)
  - Elevated acidity, sulfate, metal(loid)s
- Precipitates include Fe-oxyhydroxides and gypsum
- Less influence to drainage

Late Stage Development

- Reacted tailings (oxidized)
  - Developed oxidation profiles throughout dam section
  - Tailings mostly altered to secondary phases at the toe
- Seepage is characteristic of ARD
  - Acidic pH (1-4)
  - High concentrations of acidity, sulfate, metal(oid)s
- Precipitates include Fe-(oxy)sulphates > oxyhydrohides
- Drainage can be impeded or slowed
  - Can lead to a saturated toe and a rise in the phreatic surface
Sulphide Oxidation in TSF’s: An Influence to Long Term Dam Stability
Secondary Precipitates and Implications for Drainage

Rock Fill Embankments, Dykes and Buttresses

- Sulphidic tailings characterized by early to late stage ARD development
- Rock fill adds to the system, design and material consideration
- Pore and seepage water physiochemical conditions change
- Precipitates vary with seepage pH and Eh
  - Precipitates form coatings on rockfill filling pore space
  - Over time precipitates crystalize and cement
- Drainage can be impeded or slowed
  - Migrating seepage emergence point up slope
  - Plugged drainage pipes
Sulphide Oxidation in TSF’s: An Influence to Long Term Dam Stability

Dam Planning: Geochemical Review and Testing

- **Screening**
  - Geochemical characterization of construction materials
  - Understand potential geochemical reactions between dam materials and seepage or porewater that may influence the downstream environment (ARD/ML) and the influence to the physical nature of the materials

- **Physical**
  - Solid construction material characterization (rock, tailings, soils and sediments)
  - Chemical composition
  - Specialized solids testing
  - Mineralogical identification

- **Chemical**
  - Seepage and porewater (± process water)
  - Water quality
  - Geochemical testing of solids + seepage or porewater
  - Hydrological and hydrogeological modelling and prediction
  - Geochemical modelling and prediction

- **Specialized**
  - Customized testing
  - Laboratory testing
  - Field trials
Sulphide Oxidation in TSF’s: An Influence to Long Term Dam Stability

Active Dams: Monitoring

Planning
- Anticipate potential geochemical reactions with seepage or porewater
- Perform a geochemical characterization study
- Develop and implement a long term monitoring plan

Monitoring
- Regular seepage monitoring (e.g. seep emergence location, flow rate, physiochemical parameters, water quality, presence of secondary minerals)
- Periodic subsurface investigations (e.g. core extraction, strength testing)
- Installation and monitoring of strategically placed monitoring wells built up with subsequent dam raises (water levels, physiochemical parameters, water quality)

Instruments
- Instrumentation in monitoring wells, drains, and seeps
  - Eh and pH probes and data loggers
  - Vibrating wire piezometers and data loggers

Specialized
- Regular geochemical, hydrogeological and geotechnical dam reviews
Sulphide Oxidation in TSF’s: An Influence to Long Term Dam Stability

Existing Dams: Investigating a Possible problem?

- Problem:
  - Observed changes in geochemistry or hydrogeology (e.g. phreatic surface, seepage emergence, porosity and permeability, pore or seepage water quality)
  - Observed physical changes in tailings and dam materials

  **Perform: Geochemical, hydrogeological and geotechnical review**

- Physical
  - Subsurface investigations (test pitting, drilling, core extraction, geotechnical testing)
  - Solid material characterization (rock, tailings)
  - Chemical and mineralogical composition

- Chemical
  - Seepage and porewater quality
  - Geochemical testing of solids + seepage or porewater
  - Hydrological and hydrogeological modelling and prediction
  - Geochemical modelling and prediction

- Specialized
  - Customized laboratory testing and field trials
  - Risk reduction and remediation
Weathering primary sulphide minerals and the formation of secondary minerals is common in ARD tailings storage facilities;

- Mineral alteration is a geochemical process that occurs at the mineral-fluid interface
- Reactions are controlled by the surrounding physiochemical conditions and depend on the composition of the solids and liquids in the system
- Results in physical and chemical changes to the materials

Geochemistry’s influence on the physical stability of dams is not well known and not an aspect evaluated in today’s state of practice.
Changes to the physical and chemical nature of dam materials and seepage waters are important factors that should be considered in dam design and TSF management:

- Regular physical monitoring will help identify problems associated with mineral weathering and precipitate formation.
- Specialized field monitoring and laboratory testing is needed to evaluate geochemical processes.
- Understanding reaction pathways can help predict outcomes and even mitigate issues early/less costly.

The importance of geochemical processes and understanding these complex systems will likely become increasingly important as greater scrutiny is placed on TSF’s now and in the future.

Silicate primary minerals and secondary Fe products filling pore spaces.
Sulphide Oxidation in TSF’s: An Influence to Long Term Dam Stability Questions?

Thank You

Jennifer Durocher
jdurocher@klohn.com