Passive treatment of highly contaminated iron-rich acid mine drainage

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Task Force-ASMR-ARRI Joint Symposium 2017, April 13, WV, USA
Outline

○ Context: Fe-rich AMD
  – Occurrence
  – Passive treatment

○ Case studies
  I) Lorraine mine site: lab vs field testing
  II) East Sullivan mine site: 14 y water quality evolution

○ Concluding remarks
Mine sites rehabilitation

• Step 1: **Control** AMD generation
  - Limit the availability of one (or more) of the three main contributing factors (sulfides, oxygen & water), or control tailings temperature

  - Example of developed methods
    - **Oxygen barriers** (case study I and II)
    - Water infiltration barriers
    - Desulphurization
    - Thermal barriers

(Bussière and Aubertin, 2016)
Mine sites rehabilitation

• Step 2: **Passive treatment** of generated AMD
  - **Limestone/dolomite drains (DOL)**
    - pH and alkalinity increase, metals (and sulfate) precipitation
  - **Passive biochemical reactors (PBRs)**
    - Metals and sulfate removal
  - **Wetlands [(an)aerobic]**
    - Polishing of residual contaminants

- **NEWER → Dispersed alkaline substrate (DAS) reactors**: mixtures of highly porous (wood chips) and alkaline (calcite, MgO) materials
  - Pre-treatment of high contamination loads

(Ayora et al., 2013; Genty, 2012)
Pilot-scale DAS reactors (T1-T3)

- T1 & T2: calcite-DAS
- T3: MgO-DAS

(Ayora et al., 2013)
Examples of Fe-rich AMD

Comparison of some of the most acidic waters and highest concentrations of metals derived from tailings pore water, surface water, and underground mine workings (Moncur et al., 2005)

<table>
<thead>
<tr>
<th>Parameter (g/L) (except pH)</th>
<th>pH</th>
<th>Cu</th>
<th>Zn</th>
<th>Cd</th>
<th>As</th>
<th>Fe_\text{t}</th>
<th>SO_4^{2-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sheridan tailings (pore water), MB, Canada</td>
<td>0.67</td>
<td>1.6</td>
<td>55</td>
<td>0.1</td>
<td>0.05</td>
<td>129</td>
<td>280</td>
</tr>
<tr>
<td>Heath Steele (tailings pore water), NB, Canada</td>
<td>0.80</td>
<td>0.6</td>
<td>6</td>
<td>n/a</td>
<td>n/a</td>
<td>48</td>
<td>85</td>
</tr>
<tr>
<td>Genna Luas (surface water), Sardinia, Italy</td>
<td>0.60</td>
<td>0.22</td>
<td>10.8</td>
<td>0.06</td>
<td>0.07</td>
<td>77</td>
<td>203</td>
</tr>
<tr>
<td>Iron Mountain (mine shafts/drifts), CA, USA</td>
<td>-3.6</td>
<td>4.76</td>
<td>23.5</td>
<td>0.21</td>
<td>0.34</td>
<td>141</td>
<td>760</td>
</tr>
<tr>
<td>Other sites (mine shafts/drifts/pore water)</td>
<td>0.67</td>
<td>468</td>
<td>50</td>
<td>0.04</td>
<td>22</td>
<td>57</td>
<td>209</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter (g/L) (except pH)</th>
<th>pH</th>
<th>Cu</th>
<th>Zn</th>
<th>Cd</th>
<th>As</th>
<th>Fe_\text{t}</th>
<th>SO_4^{2-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lorraine mine site, QC, Canada (Potvin, 2009)</td>
<td>3.6</td>
<td>n/a</td>
<td>0.8</td>
<td>0.4</td>
<td>n/a</td>
<td>6.9</td>
<td>15</td>
</tr>
<tr>
<td>East Sullivan mine site, QC, Canada (Germain et al., 1994)</td>
<td>2</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>7</td>
<td>17</td>
</tr>
<tr>
<td>*Carnoulès, France (Giloteaux et al., 2013)</td>
<td>1.2</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>12</td>
<td>20</td>
<td>29.6</td>
</tr>
<tr>
<td>Iberian Belt Pyrite, Spain (Macias et al., 2012)</td>
<td>3</td>
<td>0.005</td>
<td>0.44</td>
<td>n/a</td>
<td>n/a</td>
<td>0.3</td>
<td>3.6</td>
</tr>
</tbody>
</table>
Case study I: Lorraine mine site
- Historic, Progressive Rehabilitation
Lorraine mine site: historic

1964-1968: Cu, Au, Ag, Ni
acid-generating tailings: 15.5 ha (up to 6 m)

(Nastev & Aubertin, 2000)
Lorraine mine site: rehabilitation

- **Control AMD generation**
  - Multilayer cover

- **Passive treatment of Fe-rich AMD**
  - Phase I: dolomite and calcite drains (1999) - chemical
  - Phase II: 3-unit system (2011) - biochemical
  - Phase III: DAS reactors (?) - biochemical

- **Passive treatment of Fe-rich AMD: challenges**
  - Limited space, topography, high water table
  - Abundant precipitation, harsh winter (7-8 months)
  - Lab testing required prior to construction of a field system
Lorraine mine site: rehabilitation

- **1999**: CCBE (cover with capillary barrier effect = O$_2$ barrier): control AMD generation

- **1999**: 3 Dolomite drains (Dol-1 to Dol-3) and 1 calcite drain (Cal-1): passive treatment of Fe-rich AMD (Phase I)
  - pH 3.6, 7 g/L Fe, 15 g/L sulfate

(Potvin, 2009)
Dolomite drains: design

Trenches filled with dolomite (70%) (20-60mm)

- HRT (Dol-1 & Dol-2): 10 to 20 h

(Fontaine, 1999; Maqsoud et al., 2007)
Cal-1, Dol-1, and Dol-3


(Bernier et al., 2002)
# Dolomite/calcite drains: 1999-2001

Tableau 3: Influent and effluent average pH, alkalinity and acidity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1999 (n=7)</th>
<th></th>
<th>2000 (n=6)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>Alkalinity</td>
<td>Acidity</td>
<td>pH</td>
</tr>
<tr>
<td>PO-6</td>
<td>3.17 (0.47)</td>
<td>0</td>
<td>5239 (341)</td>
<td>3.78 (0.36)</td>
</tr>
<tr>
<td>Cal-1 out</td>
<td>6.72 (0.08)</td>
<td>470 (63)</td>
<td>0</td>
<td>6.82 (0.09)</td>
</tr>
<tr>
<td>Dol-1 out</td>
<td>6.09 (0.14)</td>
<td>145 (192)</td>
<td>116 (307)</td>
<td>6.19 (0.06)</td>
</tr>
<tr>
<td>Dol-2 out</td>
<td>5.37 (0.17)</td>
<td>8 (11)</td>
<td>2000 (1920)</td>
<td>5.57 (0.14)</td>
</tr>
<tr>
<td>Dol-3 out</td>
<td>4.44 (0.28)</td>
<td>0</td>
<td>2407 (1114)</td>
<td>4.70 (0.07)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>2001 (n=6)</th>
<th></th>
<th>2002 (n=4)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>Alkalinity</td>
<td>Acidity</td>
<td>pH</td>
</tr>
<tr>
<td>PO-6</td>
<td>3.81 (0.57)</td>
<td>0</td>
<td>6293 (1125)</td>
<td>4.16</td>
</tr>
<tr>
<td>Cal-1 out</td>
<td>6.77 (0.06)</td>
<td>456 (47)</td>
<td>0</td>
<td>6.83 (0.08)</td>
</tr>
<tr>
<td>Dol-1 out</td>
<td>6.14 (0.08)</td>
<td>58 (31)</td>
<td>0</td>
<td>6.18 (0.1)</td>
</tr>
<tr>
<td>Dol-2 out</td>
<td>5.64 (0.08)</td>
<td>4 (6)</td>
<td>3160 (1614)</td>
<td>5.49 (0.07)</td>
</tr>
<tr>
<td>Dol-3 out</td>
<td>4.74 (0.16)</td>
<td>0</td>
<td>3432 (986)</td>
<td>4.4 (0.08)</td>
</tr>
</tbody>
</table>

Alkalinity and acidity are in mg CaCO₃/L

(Bernier et al., 2002)
Dol-3 (2009): clogged
Phase II: lab testing (6.7L to 2m³)

3-unit train lab system

- Input Fe: 2-4 g/L
- Output Fe: < 1 mg/L

(Genty, 2012)
Field pilot construction: design

Components (% dw)

<table>
<thead>
<tr>
<th>Component</th>
<th>PBR1</th>
<th>PBR2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood chips</td>
<td>36</td>
<td>18</td>
</tr>
<tr>
<td>Manure</td>
<td>17</td>
<td>10</td>
</tr>
<tr>
<td>Compost</td>
<td>24</td>
<td>12</td>
</tr>
<tr>
<td>Sand</td>
<td>21</td>
<td>10</td>
</tr>
<tr>
<td>Calcite</td>
<td>2</td>
<td>50</td>
</tr>
</tbody>
</table>

(Genty, 2012)
Field pilot construction: within 5 days

Before Dol-3 excavation

Dol-3 excavation

Material mixing

AMD drain collection

(Genty, 2012)
Field pilot construction: within 5 days

1. Inferior HDPE membrane placement
2. Material placement
3. Superior HDPE membrane
4. Covering system with soil

(Genty, 2012)
Results: pH
Results: S

Souffre (mg/L)

AMD
PBR₁
WA
PBR₂
Exit

2010, Nov 18
2011, July 26
2012, Apr 1
2012, Dec 7
2013, Aug 14
2014, Apr 21
2014, Dec 27
2015, Sep 3
2016, May 10
2017, Jan 15

RIME
Research Institute of Mines and Environment
Monitoring data (2011-2016)

• Metals / metalloids removal
  – Compliance with regulation, except for Fe (and Mn)

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>pH</th>
<th>As</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMD</td>
<td>4.3 – 6.9</td>
<td>&lt;0.06</td>
<td>&lt;0.003</td>
<td>1 800</td>
<td>0.62</td>
<td>0.19</td>
<td>0.26</td>
</tr>
<tr>
<td>Treated effluent</td>
<td>5.8 – 7</td>
<td>&lt;0.01</td>
<td>&lt;0.003</td>
<td>411</td>
<td>0.06</td>
<td>0.03</td>
<td>0.07</td>
</tr>
<tr>
<td>Best quality (August 2015)</td>
<td>6</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>389</td>
<td>&lt;0.004</td>
<td>&lt;0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>Quebec discharge regulation</td>
<td>6-9</td>
<td>0.2</td>
<td>0.3</td>
<td>3</td>
<td>0.5</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Compliance with regulation</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
</tr>
</tbody>
</table>

(Genty et al., 2016)
Cascade aeration downstream (2016) (Rakotonimaro, 2017)
Natural wetland downstream (2016)
Dolomite drains: 2016

Dol-1

Dol-2

(Rakotonimaro, 2017)
Phase III: lab testing (2 years)

**Step 1 – Batch testing (1 L)**
Selection the most efficient DAS

**Step 2 – Column testing (1.7 L)**
Select optimal HRT (1–5 d);
Evaluate $k_{sat}$ and $n$

**Step 3 – Multi-step (10.7 L)**
Performance evolution

Synthetic AMD: pH 4, 2.5 g/L Fe, 5.4 g/L $\text{SO}_4^{2-}$

**Monitored parameters:** physicochemical, hydraulic, microbiological, mineralogical

HRT: Hydraulic Retention Time; $k_{sat}$: permeability; $n$: porosity
Results: batch testing

DAS reactors and PBRs

- **Most efficient mixture: DAS-wood ash**
  - High pH (6.25 - 7.14) and alkalinity
  - 4 h of contact time enough, if Fe < 1.5 g/L
  - 6–11h required, if Fe initial > 1.5 mg/L
  - WA50 (50% wood ash, 50 % wood chips): optimal

- DAS- calcite and DAS-dolomite: comparable efficiency
  - **DAS- calcite** : more efficient than DAS-dolomite, only temporarily
  - **C20** (20% calcite, 80% wood chips): used as post-treatment

- Low $\text{SO}_4^{2-}$ removal in all reactors

(Rakotonimaro et al., 2016)
## Results: column testing

<table>
<thead>
<tr>
<th>Parameters</th>
<th>DAS reactors</th>
<th>PBRs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WA50</td>
<td>C20</td>
</tr>
<tr>
<td>pH</td>
<td>5.3–6.3</td>
<td>6–7</td>
</tr>
<tr>
<td>Alkalinity (mg CaCO$_3$/L)</td>
<td>130–350</td>
<td>16–50</td>
</tr>
<tr>
<td>Acid neutralisation (%)</td>
<td>62</td>
<td>18–47</td>
</tr>
<tr>
<td>Fe removal (%)</td>
<td>up to &gt;96</td>
<td>47–73</td>
</tr>
<tr>
<td>SO$_4^{2-}$ removal (%)</td>
<td>&lt;35</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

- **WA50, R5**: maximal efficiency at 5d of HRT
- **C20**: maximal efficiency at 2d of HRT, temporarily
- **Low SO$_4^{2-}$ removal in PBRs**

(Rakotonimaro, 2017)
Comparative performance: lab vs. field

- **Multi-step** – Laboratory vs field (Fe and $\text{SO}_4^{2-}$ removal)

- Lab: best efficiency with scenario 3
- Field: 91 % Fe (first 2 years), then 53 %
  68 % $\text{SO}_4^{2-}$ (first 2 years), then 43 %

(Rakotonimaro, 2017)
Comparative results: lab vs. field

- **Multi-step** – Laboratory vs field (hydraulic evolution)

  - $k_{\text{sat labo}} = 1\text{–}2$ order of magnitude higher than $k_{\text{sat terrain}}$
  - $Q$ variable in field ($\text{HRT} = \text{variable}$) $\neq Q$ lab controlled ($\text{HRT} = ct$)

(Rakotonimaro, 2017)
## Comparative results: literature

<table>
<thead>
<tr>
<th>System type</th>
<th>Design factors</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Biochemical</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anaerobic wetland (AnW)</td>
<td>3,5 g acidity/m²/d ; 10 g Fe/m²/d</td>
<td>Hedin et al (1994); Skousen and Ziemkiewicz (2005)</td>
</tr>
<tr>
<td>Vertical flow wetland (VFW)</td>
<td>35 g acidity/m²/d</td>
<td>Kepler and McCleary (1997)</td>
</tr>
<tr>
<td>PBR (mussel shell)</td>
<td>29 g SO₄²⁻/m³ substrate/d (94%)</td>
<td>McCauley et al (2009)</td>
</tr>
<tr>
<td><strong>PBR (calcite)</strong></td>
<td>4–73 g Fe/m³/d, 2–117 g SO₄²⁻/m³/d (∼99 %)</td>
<td>Rakotonimaro (2017)</td>
</tr>
<tr>
<td>(Following two DAS; initial Fe = 35 mg/L; SO₄²⁻ = 1000 mg/L)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Geochemical</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anoxic limestone drain (ALD)</td>
<td>15 h residence time; 50 g acidity/t/d</td>
<td>Watzlaf (2004); Skousen and Ziemkiewicz (2005)</td>
</tr>
<tr>
<td>Limestone leach bed (LLB)</td>
<td>2 h residence time ; 10 g acidity/t/d</td>
<td>Skousen and Ziemkiewicz (2005)</td>
</tr>
<tr>
<td>DAS (C20)</td>
<td>HRT (1 d), 42 % Fe</td>
<td>Rötting et al (2008a)</td>
</tr>
<tr>
<td>(initial Fe = 250 mg/L)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>DAS (C20)</strong></td>
<td>Fe (73%, HRT = 2 d)</td>
<td></td>
</tr>
<tr>
<td>(initial Fe = 2000 mg/L)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>DAS (C50)- pretreatment</strong></td>
<td>Fe (67%, HRT = 3 d)</td>
<td>Rakotonimaro (2017)</td>
</tr>
<tr>
<td>(initial Fe = 1800 mg/L)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>DAS (WA50)</strong></td>
<td>Fe (&gt; 89% , HRT = 3 d)</td>
<td></td>
</tr>
<tr>
<td>(initial Fe = 2000 mg/L)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Skousen et al., 2017; Rakotonimaro, 2017)
Summary

- DAS-wood ash: most efficient for Fe pre-treatment
- 2 units of pre-treatment: more efficient than one
- DAS-calcite and DAS-dolomite: comparable efficiency
- No clogging issues in lab testing
- Treatment performance (lab / field) depends on $Q$, $Fe$, $SO_4^{2-}$

Future work

- Excavation of the 3 units and replacement by 2-3 DAS systems
- Mineralogical and microbiological characterization of solids
Case study II: East Sullivan mine site
- Historic, Rehabilitation
6 km E of the Val-d’Or town, SW QC, Canada
East Sullivan mine site: historic

1942-1979: Cu, Zn, Au, Ag, Cd

- 15 Mt (200 ha) of tailings, 200kt of acid generating material; 228 ha impacted
- 3.6% S, thickness of 7.3 m in average

http://sebastienlavoie.com/maitrise/photos.html

http://www.mrn.gouv.qc.ca/mines/restauration/restauration-sites-east-sullivan.jsp
East Sullivan mine site

- Pore-water quality in 1990
  - pH ≈ 2
  - Fe (Fe$^{2+}$): up to 17 g/L
  - SO$_4^{2-}$: up to 37 g/L
  - Cu, Pb, Zn: 0.1-1 g/L
East Sullivan: rehabilitation

- **1984**: Wood waste cover (prevention and treatment)
- **1990**: Seepage collection system
- **1992-1996**: Confining dike (6 km)
- **1998-2005**: “Active” treatment of collected AMD in wetlands
- **[2014]**: Wood cover of the eastern sector, not completed

⇒ Some effluents are still acidic

Figure 1. Map of the East Sullivan tailings impoundment in 1994

(Tassé and Germain, 2004)
East Sullivan: monitoring (2000-2014)

- 12 sampling points
  - 7 points: dam and settling ponds
  - 5 points: tailings edges

- Parameters
  - pH, alkalinity, TDS, Fe, Al, Mn, Cu, Zn, Pb, SO$_4^{2-}$

- Compliance, except for the uncovered tailings area

(Rakotonimaro et al., 2015)
Summary

- Efficiency of wood-waste cover for over 14 years
- Significant improvement of water quality
- Site presently turning into birds’ refugee (southern and eastern ponds, more than 190 species listed)

Future work

- Completion of the eastern part of tailings by wood-waste and sludge (< 10% of total)
- Mineralogical / microbiological characterization of solids
- Further risk assessment
East Sullivan: 2015

Eastern pond

Eastern tailings

Wood waste and sludge

Eastern tailings not covered

(Rakotonimaro et al., 2015)
Concluding remarks

• Use of residual materials (dolomite, wood ash, compost, manure): low cost
• Relatively easy to install and operate
• Maintenance (more or less) required

BUT

• Limited performance at high contamination level: multi-step systems (?)
• Unpredictable long-term efficiency
• Solutions not available for sludge management

However, sometimes is the only available option


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