Weathering of Mine Wastes and Tailings in Water-limited (Arid) Settings: Implications for Geochemical and Environmental Control

Protection of groundwater and surface-water, and other environmental values

Dr GD Campbell
Graeme Campbell & Associates Pty Ltd
Bridgetown, Western Australia

Asmara Mining Conference 2014
1-5 October 2014, Palace Hotel, Asmara, Eritrea
Generics

A. Terminology

- Acid-Rock Drainage (ARD) or Acid Mine Drainage (AMD)
- Neutral Mine Drainage (NMD) or Metalliferous Drainage

B. Commodity Context

- hard-rock mines, coal mines, minerals sands mines, etc.

C. Rock-water-air (geochemical) interactions

- control local pH regime and solute chemistry
- pH is Master-Variable = f (acid-base balance)
ARD Formation: Thermodynamics / Reaction Mechanism

A. Thermodynamics at earth-surface-P/T

- stable versus unstable minerals

B. Gibbs free-energy change ($\Delta G$) as governed by enthalpic ($\Delta H$) and entropic ($\Delta S$) terms, e.g.

$$\text{FeS}_2 \text{ (pyrite)} + O_2 + H_2O = H_2SO_4 + \text{Fe(OH)}_3 \quad \text{(unbalanced equation)}$$

C. Mechanistically, fundamental to understand that:

- pyrite oxidation is an electrochemical reaction \(\text{(Rimstidt and Vaughan 2003)}\)

- 'freely-available' \(H_2O\) is required for oxidation of reduced-S forms

Control oxidation at arid sites by preserving residual moistures of ex-pit reactive rock – the latter invariably 'dry-n-dusty'!
ARD Formation: Kinetics

A. Rates of surface-chemical reactions:
   - specific-surface area
   - unsaturated, moist conditions for peak oxidation rates

B. Relative saturations less than 80-85% for O_2 supply to be non-limiting

C. Water content above residual, so H_2O is 'freely-available' for reaction
   - porefluid flow also needed for removal of solutes for peak oxidation rates

Oxidation at arid sites is restricted by infrequent and limited wetting-front penetration
Laboratory Testwork Approaches (1)

- Prescriptive (?) Compendia for Geochemical Testing
  - MEND (2009)
  - GARD Guide, AMIRA (2002), and others
  - originators may not intend these to be prescriptive, but can easily be perceived as prescriptive by regulators, consultants, etc.

But, in undertaking a characterisation programme:

- 'horses for courses'
- personal preferences of individual practitioners
- professional judgement as governed by 'drivers' from experience
- R&D / creativity leads to advancement (cf. 'dumbing down')
Laboratory Testwork Approaches (2)

A. **Static Testing** ('whole-rock' analyses and tests)
   - S Forms (Sulphide-S, Cr(II)-Reducible-S, SO₄-S)
   - Acid-Neutralisation Capacity (chiefly carbonates)
   - Net-Acid Generation
   - mineralogy

B. **Kinetic Testing** (real-time behaviour with varying moisture / aeration regimes)
   - humidity cells and weathering columns
   - oxygen-consumption cells

Static and kinetic testing approaches equally applicable for both *water-limited* and *well-watered* sites.
Kinetic-testing (1): Humidity Cells [e.g. ASTM 2013]
Kinetic-testing (2): Weathering Columns (e.g. AMIRA 2002)
Kinetic-testing (3): Oxygen-consumption Cells

use weathering-columns to measure Oxygen-Consumption Rate (OCR) directly
Kinetic-testing (4): Hybrid Approach

use flood-lamps to dewater 'sludge' immediately after flushing to a 'middling-moisture', then keep in an incubator
Sulphide Oxidation and Moisture Status:

Least-Limiting-Water Range (LLWR)

- Long-held concept in soil science and agronomy

Moisture limits on plant growth:

- 'wet-end': \( \theta_v > 80-90\% \text{ of } \phi \) \( \Rightarrow \) impeded, \( \text{O}_2\text{-limited} \)
- 'middling': \( \Rightarrow \text{optimal} \)
- 'dry-end': \( \Psi_t > \text{c. 10-20 bars} \) \( \Rightarrow \) impeded, \( \text{H}_2\text{O}\text{-limited} \)

Moisture limits on sulphide oxidation:

- 'wet-end': \( \theta_v > 80-90\% \text{ of } \phi \) \( \Rightarrow \text{impeded, } \text{O}_2\text{-limited} \)
- 'middling': \( \Rightarrow \text{optimal} \)
- 'dry-end': \( \Psi_t > \text{c. 10-20+ bars} \) \( \Rightarrow \text{impeded, } \text{H}_2\text{O}\text{-limited} \)

Value of looking beyond geology and engineering, and cross-correlating with concepts from other earth-science disciplines.
Pulsed & Zonal Weathering in Arid Lands

A. **Pulsed Dynamics** in Arid Lands shared by:

- **biotic responses** – from microbial soil surface crusts to growth stimuli and fruiting by under and upper storey plant species; commencement of next predator-prey cycle, etc.

- **rock-water-air interactions**

B. *'Weathering-windows'* for oxidation are:

- restricted to sizeable wet-spells (e.g. 10+ mm)

- transient / short-lived as rapid drying immediately kicks-in

C. **Locus of weathering** confined to reach of irregular, 'fingered' wetting-front

**Seasonality of oxidation 'spikes'** at arid sites allows preparation ahead of major storm arrivals (e.g. **rate-of-rise of reactive profile** during waste-dump construction linked to timing of episodic wet-spells).
Sulphide Oxidation and Moisture Status: Demo 1

Grey-Tails $\Rightarrow$

Rapid Drying
(hours-to-days)

Brown-Tails $\Rightarrow$

Delayed Drying
(weeks+)

Slurry of near-monomineralic pyrite left to free-drain with $E_p$ (at tailings-bed surface) approx. 10 mm/day; pH = 2-4
Sulphide Oxidation and Moisture Status: Demo 2

Localised moisture gradients, due to segregation of fines

- **Dark Grey** saturation-zones ⇒ *unoxidised*
- **Light-brown** and “just damp” distal from saturation-zones ⇒ *least oxidised*
- **Orange** and moist proximal to saturation-zones ⇒ *most oxidised*

Reactive tailings wetted from below via wicking; reaction over weeks

After rapid drying (days)
**Wetting/Weathering-Front Coincidence**

**After 1st Wetting-Cycle**
- **lag-phase** (i.e. circum-neutral) weathering of PAF-tailings with/without 'store-release-cover'
- Fe-pigmentation = **locus of sulphide-oxidation**
- 23 mm pulse of water + 1 day of redistribution
  + 6 days of $E_p$ of c. 10-15 mm/day via heating-lamps with side-wall insulation $\Rightarrow$ strong diurnal-T gradients

**After 1st Drying-Cycle**
- 'Grey-Tailings' ($\Rightarrow$ largely unoxidised) in top cm, due to instant evaporative-drying, and thus stifled sulphide-oxidation
Field Example: Hardpan Formation in an 'Old' (30-40 yrs) Massive-Sulphide-TSF in NSW Arid-Zone

Alternative Interpretation: Wetting-front versus O$_2$-diffusion-front control

Agnew and Taylor (2000), 5th ICARD (Denver)
Key Management Outcome: **Climate Dependence** of Oxidation

A. Pyrite Oxidation in **Well-Watered Settings**

\[ \text{FeS}_2 + \frac{15}{4} \text{O}_2 + \frac{7}{2} \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{Fe(OH)}_3 \]

⇒ **Control of O}_2\)-supply** is 1\(^{st}\)-order control strategy

B. Pyrite Oxidation in **Water-Limited Settings**

\[ \text{FeS}_2 + \frac{15}{4} \text{O}_2 + \frac{7}{2} \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{Fe(OH)}_3 \]

⇒ **Control of H}_2\text{O}\)-supply** is 1\(^{st}\)-order control strategy

Locate pyrite beneath reach of shallow seasonal wetting-front

⇒ optimise 'unsaturated freeboard' in terms of **Water Holding Capacity (WHC)**
Engineering & Cost Implications

A. Basal-blanket of benign soil / regolith materials (cf. HDPE liners, etc.)
   - not compacted, but paddock dumped and dozed
   - WHC likely 300+ mm (site-specific specification)

B. End-tipping versus bottom-up construction during waste-dump operation
   - WHC of reactive profile being built; rate-of-rise of reactive profile
   - role of traffic layer at top of lifts: enhanced WHC

C. Free-draining cover profile for infiltration control at closure (cf. multi-layered, heavily engineered covers at well-watered sites)
   - not purpose compacted
   - WHC likely 300+ mm (site-specific specification)
   - erosion stability
   - 'patched' distribution of vegetation – natural analogue in arid lands

Arid sites generally offer more 'degrees of freedom' for geochemical control
Quantifying Water-Holding Capacity (1)

- **Suction-plates** and **pressure-chambers**
- Only suited to small moulds, due to equilibration-time constraints
Quantifying Water-Holding Capacity (2)

- **Column-Infiltration Technique**
  - can be applied to estimate WHC of reactive lithotypes being isolated
    
    e.g. pyritic carbonaceous shales with WHC c. 100 mm/m
Cover Ripline Infiltration Capacity (1)
Cover Ripline Infiltration Capacity (2)

- 60 mm Total Storm-Depth
CONCLUSIONS

A. **Geochemical Instability** (e.g. pyritic units) does **NOT** depend on site climate – it is, what it is, where ever it is!

However, expression of this instability in terms of **Reactivity** **DOES** depend on climate – reactivity suppressed in strongly arid settings.

B. Testing approaches relevant to both arid and well-watered sites.

C. **Pulsed oxidation dynamics** at arid sites from episodic rainfall

Locate pyritic units beneath reach of shallow seasonal wetting-front

D. Arid sites generally offer more 'degrees of freedom', and longer 'response times', for geochemical control

- 'unsaturated freeboard' and water holding capacity
Acknowledgements

- Eamonn Dare, Bisha Mining Share Company
- Asmara Mining Conference Committee (Seife Berhe)
- Serge Smolonogov (formerly at Bisha)
- Lots of clients since the late-1980s
- Ann Evers / John Flynn, Genalysis Laboratory Services
- Roger and Daniel Townend, Townend Mineralogical Laboratory