Controlling Sulfidic Tailings Oxidation with Surface Application of Crude Glycerol – Column Experiments

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Ore Knob Mine
• Former copper/zinc mine
• Mining began in 1850s
• Abandoned in 1962
• Some remediation work in 1980s
• Listed on EPA NPL in 2009

Ore Knob Branch
• pH = 2.9-3.4
• Acidity = 420 – 2100 mg/L
• Fe = 200 – 900 mg/L
• SO4 = 700 – 3300 mg/L
• Al = 3 – 31 mg/L
• Cu = 0.1 – 0.8 mg/L
• Zn = 0.7 – 3.3 mg/L

Treatment Approach
• Approach
  – Surface apply ~ 2.5 cm crude glycerol
  – Allow to infiltrate with rainfall
• Treatment Concept
  – Glycerol consumes oxygen
  – Ferments to H2 and fatty acids
  \[
  C_3H_5(OH)_3 + 3H_2O \rightarrow 3CO_2 + 7H_2
  \]
  \[
  4H^+ + 2H_2^+ + SO_4^{2-} \rightarrow H_2S + 4H_2O
  \]
• Crude Glycerol
  – Byproduct of biodiesel production (0.1 Kg / Kg biodiesel)
  – Worldwide glut in 2007-2008
  – Chemical Oxygen Demand = 1.1 g/g
  – Contains some residual caustic (0.1 g/g)
  – Soluble, easy to infiltrate

Glycerol Pilot Test
• Four experimental columns
  • 140 cm x 30 cm diameter
  • Packed with fine grained, reduced tailings
  \( pH = 4.3, D_{50}=40 \mu m \)
  • Buried in pile
  • Redox electrodes & porous cup samplers at 25 cm intervals
  • Bottom drain
  • Glycerol added 6 months after construction
  • Two columns as untreated controls

Results
• Untreated
  – pH = 4.3 – 5.0
  – Acidity = 1000 – 1200 mg/L
• Treated
  – pH = 6.6-6.7
  – Acidity = 30 - 70 mg/L

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12-15 Months after Glycerol Addition

- TOC = 2200 mg/L
- Fe = -96%
- Acidity = -96%
- SO₄ = -55%

12-15 Months after Glycerol Addition

- Al = -99%
- Cu = -78%
- Mn = -97%
- Zn = -7%
- H₂S ~ 3 mg/L

Conclusions

- Waste glycerol easy to apply and infiltrate
- Glycerol addition resulted in large, statistically significant improvement in:
  - pH, Acidity, Fe, SO₄
  - Al, Cu, Mn
  - Maximum H₂S production at 15 months
  - Large amount of TOC in soil at 16 months
- Future work - geochemical modeling