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

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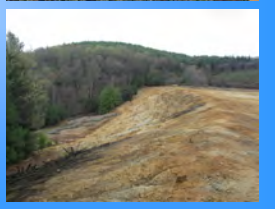
Ore Knob Mine

- 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
  - SO_4 = 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 H_2 and fatty acids
    $C_3H_5(OH)_3 + 3H_2O \rightarrow 3CO_2 + 7H_2$
    $4H_2 + 2H^+ + SO_4^{2-} \rightarrow H_2S + 4H_2O$
- 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

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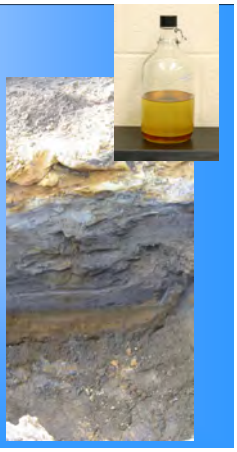
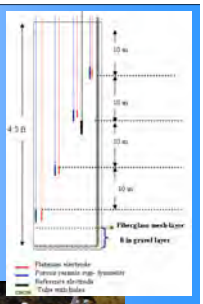


Glycerol Pilot Test

- Four experimental columns
  - 140 cm x 30 cm diameter
  - Packed with fine grained, reduced tailings pH = 4.3, D_{50}= 40 µm)
  - 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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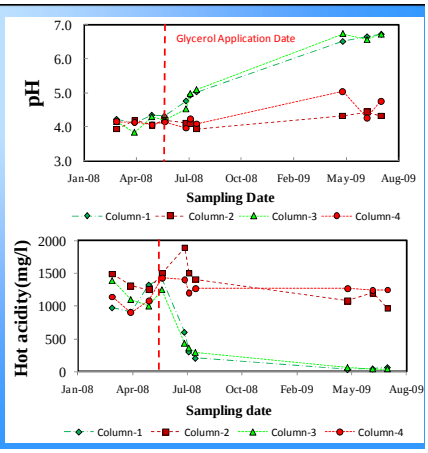

Results

- Untreated
  - SO_4^{2-} = 3200 – 3700 mg/L
  - Fe = 520 – 590 mg/L
- Treated
  - SO_4^{2-} = 1000 – 2200 mg/L
  - Fe = 18 – 32 mg/L

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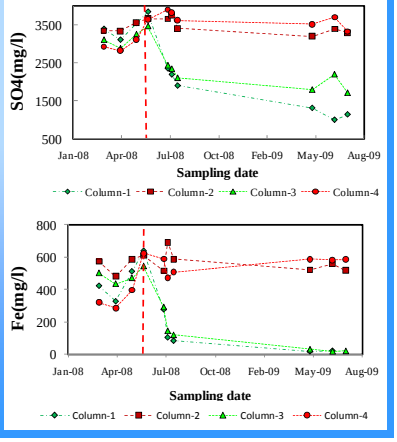
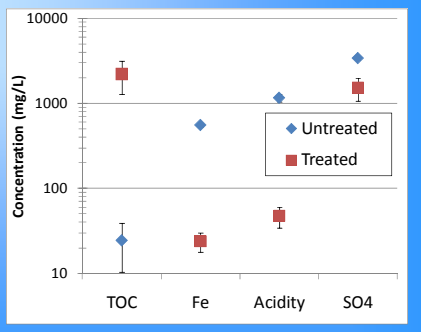


12- 15 Months after Glycerol Addition

- TOC = 2200 mg/L
- Fe = -96%
- Acidity = - 96%
- SO_4 = - 55%



Error Bars = ±1 standard deviations

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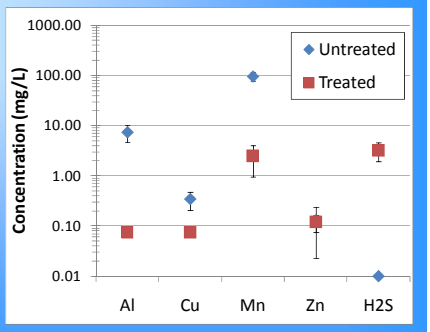
12- 15 Months after Glycerol Addition

- Al = - 99%
- Cu = - 78%
- Mn = - 97%
- Zn = - 7%
- H_2S ~ 3 mg/L



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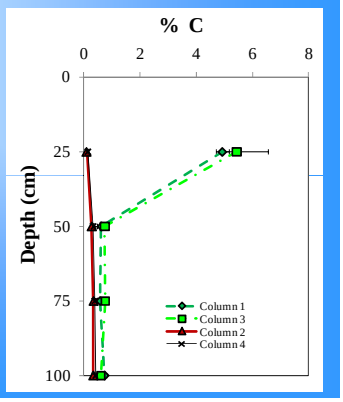
16 Months after Glycerol Addition

- Large TOC increase near surface
- Some TOC increase throughout column



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Conclusions

- Waste glycerol easy to apply and infiltrate
- Glycerol addition resulted in large, statistically significant improvement in:
  - pH, Acidity, Fe, SO_4
  - Al, Cu, Mn
  - Maximum H_2S production at 15 months
  - Large amount of TOC in soil at 16 months
- Future work - geochemical modeling

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