In-Situ Bioremediation Demonstration of Coal-Based Acid Mine Drainage

#### Tide Mine Site Indiana County, Pennsylvania

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## AMD Chemistry

#### Initiation Reaction: $\operatorname{FeS}_{2(s)} + \operatorname{H}_2O + 3.5 \operatorname{O}_2 \rightarrow \operatorname{Fe}^{2+} + 2 \operatorname{SO}_4^{2-} + 2 \operatorname{H}^+$

Propagation Reactions:  $Fe^{2+} + 0.25 O_2 + H^+ \rightarrow 0.5 H_2O + Fe^{3+}$ ↓ 14  $Fe^{3+} + FeS_{2(s)} + 8 H_2O \rightarrow 15 Fe^{2+} + 2 SO_4^{2-} + 16 H^+$ (Singer & Stumm, 1970)

In-situ treatment can eliminate the causative agents of AMD



# Breaking the AMD Triangle

- Provide an alternative sink for oxygen and ferric iron (e.g., a carbon source)
- Oxidation of the carbon source generates carbon dioxide/alkalinity
- Eliminating/minimizing water flushing - not required





# Tide Mine Schematic





## **Demonstration Project Plan**

3 months of recirculation system operation with caustic and molasses injection to affect net change in biogeochemistry
Bromide tracer study to characterize mine pool hydraulics
Carbon dioxide gas injection to alter mine atmosphere
Additional 3 months of passive methanol injection to demonstrate sustainability of in-situ treatment





#### Bromide Tracer Test to Evaluate Mine Pool Hydraulics





#### Elevated TOC Results in Sulfate Reducing Conditions





#### Metals Performance Monitoring Data



Aluminum concentrations decreased greater than 50% during treatment – function of pH



### Continuing Sources of Iron in Mine Workings

- Reductive dissolution of solid-phase ferric hydroxide in the saturated portion of the mine workings
  - Controlled through FeS precipitation and maintaining sulfate reduction in the mine pool
  - Saturated portion accounts for approximately 6% of mine workings

AMD-impacted water from the unsaturated portions of the mine workings

- Gas phase oxygen provides continuous source of AMD causative agents (i.e., dissolved oxygen and ferric iron)
- Requires gas phase treatment for AMD prevention or continuous liquid phase treatment for control
- Unsaturated portion accounts for approximately 94% of mine workings



#### Carbonate Alkalinity Is Now Dominant In Previously Acidic Mine Pool





## **Re-Oxidation of Observed FeS?**

In-Situ Treatment:  $FeS + 2O_2 \rightarrow FeSO_4 + no acidity$ 

Natural Aerobic State:  $FeS_2 + 3.5O_2 + H_2O \rightarrow FeSO_4 + H_2SO_4$ 

At the same operating re-dox state, oxidation of ferrous sulfides will not generate acidity in contrast with pyritic sulfides. Consistent with this expectation, alkalinity is observed from Tide Mine during the treatment period after washout of the NaOH neutralization effect







#### Carbon Dioxide Injection -Why Control the Gas Phase? Oxygen Molar Balance

- Pyrite oxidation stoichiometry indicates  $O_2:SO_4$  is 2:1
- Oxygen-saturated water holds 8 ppm or  $0.25 \text{ mM O}_2$
- Assuming full conversion, 0.25 mM of O<sub>2</sub> creates 0.125 mM SO<sub>4</sub>
- Tide mine water has  $\approx 8$  mM sulfate
- Therefore, at a maximum, 1.5% of the sulfate produced by the mine is generated by aqueous phase oxygen
- 98.5% of the sulfate (and acidity) is being generated by gas phase molecular oxygen
- With O<sub>2</sub> consumed by AMD reactions, resulting gas is buoyant maintaining 5% CO<sub>2</sub> through direct injection or biological activity generates a dense anaerobic blanket



# CO<sub>2</sub> addition to the mine atmosphere broke the Oxygen "supply lines"





## Results

- Tide Mine project demonstrated the efficacy of insitu treatment – proof of concept
- No dissolved oxygen in the mine pool or ferric iron in the mine pool
- Sustained increased pH in the mine pool, continued alkalinity detection
- Decreasing overall iron concentrations, reduced aluminum concentration
- Gas exchange occurs over large footprint of unsaturated mine workings; therefore, sustained CO<sub>2</sub> injection required for gas phase control at Tide Mine



# How Does In-Situ Treatment Fit with the "Big Picture"?

- Economics of prevention vs. collection and treatment
- System-wide application of in-situ technology to stop or reduce AMD, minimize risk with blowout or mine failure
- Low cost O&M system implemented insitu
  - Sludge settling occurs in mine workings
  - Use of local agricultural products and waste streams
  - Compatible with passive polishing systems

