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

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**Abstract** Oxidative dissolution of sulfidic tailings in Ore Knob tailings pile, Ash County, NC, releases acidic, high sulfate, and heavy metal laden AMD to Ore Knob Branch and Peak Creek in the New River basin of North Carolina. This paper describes application of crude glycerol in controlling AMD production. Four experimental columns were installed in the field. After four months, crude glycerol was added to surface of two columns. There were large declines in Fe (560 to 97 mg/L), $SO_4$ (3560 to 1870 mg/L), and hot acidity (1310 to 205 mg/L).

**Key Words** Crude glycerol, Acid mine drainage, Treatment, Ore Knob

## Introduction

Acid mine drainage is produced when mining activities expose sulfidic minerals to a moist oxidative environment releasing sulfuric acid and a variety of heavy metals present in the sulfide mineral structure (Singer and Stumm 1970). A variety of readily available carbon sources have been used to support iron and sulfate reduction during passive treatment of AMD. Different organic electron donors have been tested to treat AMD including hay, straw, leaf compost, manure and compost, sewage sludge, waste activated sludge, molasses, rubber waste effluent, and cheese whey (Chang et al. 2000; Coetser et al. 2006; Kaufman et al. 1996; Obarsky et al. 1984; Oleskiewicz et al. 1986; Pipes 1960; Rabenhorst et al. 1992).

Worldwide biodiesel production has grown rapidly over the past several years resulting in the production of large amounts of crude glycerol containing some residual NaOH or KOH. Without further refining, crude glycerol is a low value material that could potentially be used for AMD treatment through two complementary processes. In the first process, residual base in the glycerol neutralizes sulfuric acid in the AMD. In the second process, glycerol ($C_3H_5(OH)_3$) is used as an electron donor by a consortium of naturally occurring fermentive and $SO_4$ reducing bacteria (SRB) to reduce $SO_4$ to hydrogen sulfide ($H_2S$) as shown in the following simplified reaction:

$$H_2SO_4 + C_3H_5(OH)_3 \rightarrow H_2S + 4\ H_2O + 3CO_2$$

Sulfide produced in this reaction will react with a variety of metals mobilized during AMD production (e.g. Fe, Ni, Zn, Cd, Pb, Cu, Hg), forming insoluble metal sulfides. The crude glycerol could be used in a bioreactor or passive treatment system to treat AMD, or could be applied directly to the surface of the tailings, reducing AMD production by consuming available oxygen and treating AMD within the tailings pile. A major advantage of direct addition to the tailings pile is that it eliminates the need for construction of large treatment units and no waste products (e.g. sludge) are produced requiring transport and eventual disposal.

In this study, we evaluate the direct application of crude glycerol to the surface of unweathered sulfidic tailings to reduce AMD production and treat AMD that has already been produced within the tailings pile. Four experimental columns were constructed and monitored for 15 months. Crude glycerol was applied to two experimental columns on June 2008 to evaluate its effect on AMD. The study was conducted at the Ore Knob tailing pile in Ash County, North Carolina. The site is a former copper/zinc mine that has severely polluted 1.5 km of Ore Knob Branch and 4.7 km of Peak Creek feeding the New River. The US Environmental Protection Agency (EPA) has recently placed the Ore Knob site on the National Priorities List (NPL) of hazardous waste sites requiring remediation.

## Experimental Methods

Four 137 cm long × 30 cm diameter PVC columns were packed with 122 cm of homogenized, fine-grained, reduced sediment excavated from the tailings pile. The columns were left exposed to the atmosphere at the surface and buried within the existing tailings pile to simulate naturally occurring variations in temperature and rainfall within the pile. A slotted PVC pipe covered with 20 cm of gravel and a fiberglass mesh was installed at the bottom of each column to sample water draining out the column bottom. Platinum redox electrodes and porous cup lysimeters were installed at 25 cm intervals vertically to monitor redox and geochemical conditions within the unsaturated tailings. Water samples were collected periodically throughout the experimental period and monitored for dissolved oxygen (DO), $H_2S$, and pH using field test kits (CHEMetrics) and meters. Redox potential was measured as the voltage generated from the platinum electrode and compared to a reference electrode buried at the soil surface (Vepraskas, Cox 2002). Major cations and metals (Al, Cu, Ca, Mg, Mn, Na, Pb, Co, Ni, Cr, K, Si, and Zn) were analyzed by inductively coupled plasma spectroscopy (ICP). Pb, Ni, Co, and Ni were always below detection limits. Anions ($SO_4$, $NO_3$, $NO_2$, $PO_4$, Cl, and Br) were analyzed by ion chromatography (IC). $NO_3$, $NO_2$, $PO_4$, Cl, and Br were below detection in all samples. Field samples were collected and preserved as described by Eaton et al. (1989).A total of 2.2 Kg of glycerol were applied to the surface of columns 1 and 3 in June 2008 while columns 2 and 4 were left as untreated controls. The amount of glycerol applied was designed to consume oxygen entering the column surface over a 12 month period assuming an oxygen diffusion depth of 5 cm and an air filled porosity of 14%. The glycerol was applied by removing the top 15 cm of tailing, blending with 2.2 kg of glycerol, and then adding the mixed glycerol-tailings back to the surface of the column. This would be equivalent to spray application and tilling 3 cm of crude glycerol into the tailings surface.

## Results and Discussion

Sulfate is produced during AMD formation from oxidation of iron sulfides. It is hypothesized that glycerol addition would generate anaerobic conditions, stimulating the growth of sulfate reducing bacteria and reduction of sulfate ($SO_4$) to hydrogen sulfide ($H_2S$). The $H_2S$ would then precipitate dissolved iron and other metals from the system. Figure 2 shows the variation in the effluent pH, sulfate, dissolved iron (Fe) and hot acidity in all four columns over time. Prior to glycerol addition, the pH of all columns varied between 4.0 and 4.5 and sulfate varied between 2800 and 3600 mg/L. Following glycerol addition, there was a gradual increase in the pH to 6.5 and decrease in sulfate to 990 mg/L in the treated columns (1 and 3). Before glycerol addition, hot acidity varied between 1000 and 1500 mg/L and iron varied between 285 and 586 mg/L. Following glycerol addition, there was a gradual decrease in hot acidity to 40 mg/L and iron to 20 mg/L in the treated columns (1 and 3). In the untreated columns (2 and 4), $SO_4$, Fe, and hot acidity gradually increased over the monitoring period due to continued oxidation of iron sulfides in the columns. $H_2S$ also increased dramatically in the glycerol treated columns indicating onset of anaerobic conditions. These re-

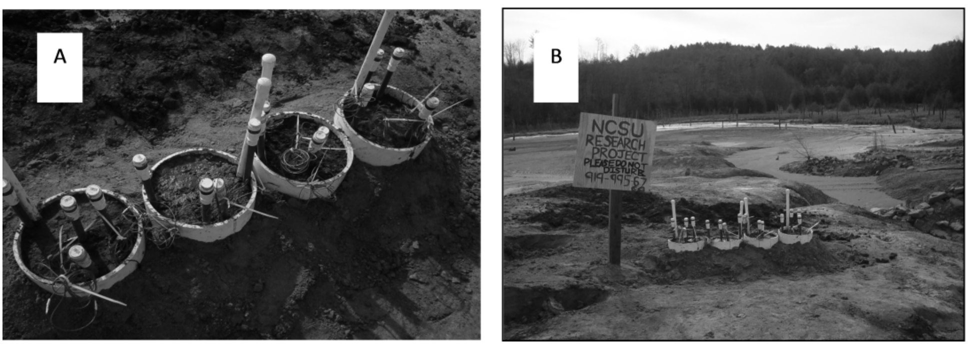


***Figure 1*** *Experimental columns installed in Ore Knob tailing pile to evaluate crude glycerol performance on AMD.*

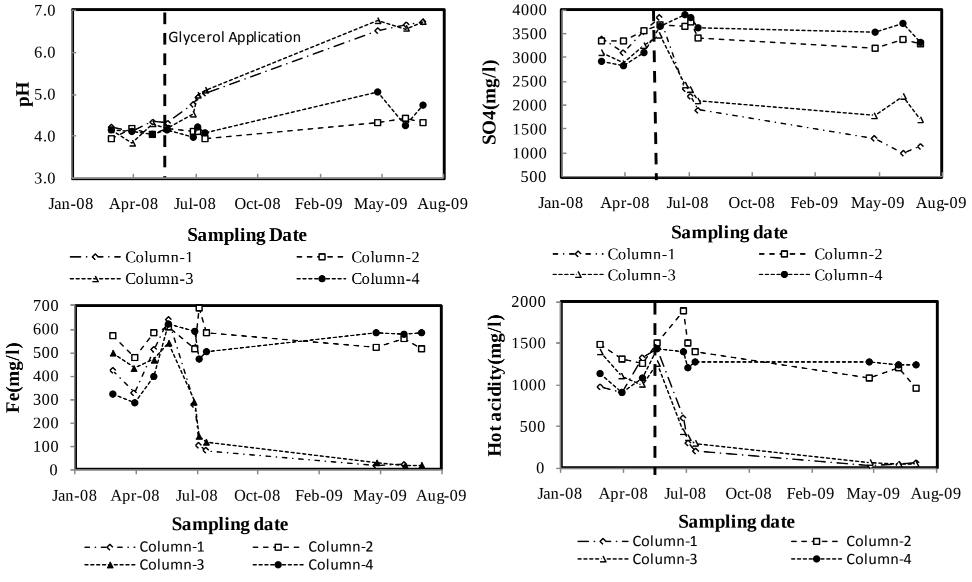


*Figure 2* pH, sulfate, iron and Hot acidity versus time in experimental column effluent. Column 1, 3 are treated columns.

sults demonstrate that glycerol addition: (a) dramatically reduced AMD production; and (b) generated conditions appropriate to actually treat AMD within the tailings pile.

Table 1 shows a comparison of contaminant concentrations in the effluents of the glycerol treated columns (1 and 3) and untreated control columns (2 and 4) before and after glycerol addition in June 2008.

Concentrations of all major parameters decreased following glycerol addition. In comparison, concentrations of most parameters actually increased in the untreated controls. A statistical analysis showed that after June 2008, concentrations of Fe, $SO_4$, acidity, Al, Ca, Cu, Mg, Mn, and K were all lower in the treated columns than the untreated control columns at the 95% level. Average Zn concentrations in the treated columns were much lower than the untreated columns. However, the change in Zn and Na were not significant at the 95% level due to the high variability in the monitoring data.

*Table 1* Comparison contaminant concentrations before and after glycerol addition in June 2008 in treated and untreated control columns. Bold and underline values are statistically significant at the 95% level (N=number of data used in analysis).

| **Pooled data analysis** | | | | | | **mg/L** | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | N | Fe | SO4 | Al | Ca | Cu | K | Mg | Mn | Na | Zn |
| Ave. Conc. (mg/L) before glycerol addition | 16 | 483 | 3316 | 8.9 | 524 | 0.2 | 132 | 259 | 87 | 11 | 0.8 |
| Ave. Conc. (mg/L) after glycerol addition. in treated columns | 12 | 97 | 1869 | 0.3 | 372 | 0.1 | 123 | 182 | 15 | 8 | 0.2 |
| Ave. Conc. (mg/L) after glycerol addition. in control columns | 12 | 559 | 3551 | 8.0 | 552 | 0.3 | 142 | 264 | 95 | 10 | 0.6 |
| % Decrease from before to after glycerol add. in treated columns | | 80 | 44 | 97 | 29 | 54.8 | 7 | 30 | 82 | 23 | 78.5 |

## Conclusion

A pilot test was conducted at the Ore Knob tailings pile to evaluate the use of crude glycerol for treating acid mine drainage (AMD). Glycerol addition resulted in large and statistically significant decreases in all important parameters. There were large changes in Fe (declined from 560 to 97 mg/L), $SO_4$ (declined from 3560 to 1870 mg/L), and hot acidity (declined from 1310 to 205 mg/L). Changes in Na and K were more limited (K declined from 142 to 123 mg/L and Na declined from 10.2 to 8.5 mg/L). Glycerol addition appears to both reduce the rate of AMD production and treat AMD after it is formed through hydrogen sulfide production (sulfide increased from 0 to 5 mg/L). The sampling results of experimental columns will be used with a geochemical model to characterize AMD production in the vadose zone of the tailing pile.

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