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TECHNICAL ARTICLE

Waste Glycerol Addition to Reduce AMD Production in Unsaturated Mine Tailings

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Abstract A 20 month long column study was conducted to evaluate the surface application of waste glycerol (WG) to reduce release of acid mine drainage constituents from mine tailings. Beneficial characteristics of the WG include high aqueous solubility, high organic content, and high alkalinity. Four columns were packed with fine-grained sulfide rich tailings and incubated in the field under ambient temperature and precipitation conditions. In the two replicate untreated control columns, diffusion of oxygen into the tailings resulted in large increases in dissolved iron, sulfate, manganese, magnesium, aluminum, zinc, and hot acidity with an associated drop in pH. In the two replicate treated columns, WG was blended into the top 0.18 m of tailings 7 months after the columns were established, resulting in large reductions in iron, sulfate, hot acidity, aluminum, copper, and manganese. Observed pollutant reductions resulted from a combination of processes including: (a) neutralization of acidity by the KOH present in the WG (b) reduction of SO_4 to H_2S with subsequent precipitation of dissolved metals, and potentially (c) consumption of oxygen, slowing oxidation of the tailings.

Keywords Acid mine drainage · Tailings · Waste glycerol · Organic amendments

Introduction

Mining can produce enormous quantities of waste rock and mill tailings that may contain reactive sulfide minerals (Moncur et al. 2005). These wastes are often deposited in impoundments or piles where they are exposed to atmospheric oxygen (O_2) and infiltrating rainwater, leading to the formation of acid mine drainage (AMD). The adverse effects of AMD can continue for centuries after mining has ended (Blowes et al. 1992; Nordstrom and Alpers 1999; Pyatt and Grattan 2001).

AMD can be treated by a variety of methods. While both chemical and biological AMD treatment methods can be effective, they often require ongoing maintenance, substantial land area, and produce metal-containing sludge that must be managed (Coetser et al. 2006). Instead of treating AMD after it is produced, tailings piles can be managed to prevent AMD production by reducing contact between the tailings and oxygen. Common approaches for reducing oxygen contact include installation of clay or synthetic caps and flooding the pile with water. Organic covers have also been proposed as an oxygen-consuming barrier to prevent AMD production (Germain et al. 2003). In theory, a wide variety of electron donors can be used including wood chips, sawdust, composted municipal sewage sludge, poultry manure, and leaf compost (Waybrant et al. 2002; Zagury et al. 2006). In test cells packed with mine tailings, Hulshof et al. (2006) observed a 80–99.5 % reduction in iron concentrations when woodchips and pulp waste were blended into the upper 1 m compared to untreated controls.

In this study, we report on the use of waste glycerol (WG), a by-product of biodiesel production, to reduce release of metals, sulfate, and acidity from unsaturated tailings at the Ore Knob Mine, a former copper-zinc mine located in Western North Carolina. From 1957 to 1962,

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Appalachian Sulphides, Inc. operated a mine and processing facility at the site. Most waste tailings were pumped to an impoundment located on Ore Knob Branch, eventually forming a 9 ha tailings pile with a maximum tailings depth of 21 m at the center of the embankment face. The hydrological and geochemical characteristics of the pile have been described by Behrooz and Borden (2012). Oxidation of pyrrhotite and related sulfide minerals in the vadose zone of the Ore Knob Mine tailings pile produces AMD, which is rapidly transported through the pile by infiltrating surface water. Annual pollutant loads (kg/yr) released by the pile are estimated to be 220,000 acidity, 100,000 Fe, 370,000 SO_4, 900 Mn, 2,400 Al, and 280 Zn.

Rapid growth in biodiesel production has increased the availability of WG, which typically contains large amounts of soluble organic material (glycerol, methanol, and other soluble constituents) and significant amounts of alkalinity from residual base added as a catalyst in the transesterification process (Colucci et al. 2005). The WG could be tilled into the surface of tailings piles to treat and/or prevent AMD production. As the dissolved WG is transported deeper into the tailings with infiltrating rainfall, the residual base would neutralize acidity while the soluble organic components could consume oxygen as it diffuses into the tailing and serve as electron donor for SRBs to reduce sulfate to sulfide precipitating dissolved metals. The effectiveness of WG in reducing AMD production was examined in situ in a 20 month column study.

Materials and Methods

Four experimental columns were installed in December 2007 at Ore Knob tailings pile (Behrooz and Borden 2012) and were loaded with reduced tailings believed to have limited prior exposure to oxygen. The experimental columns were allowed to equilibrate for 3 months before sampling began in March 2008. Each column was 1.37 m long by 0.3 m diameter PVC pipe with approximately 0.17 m of pipe projecting above the ground surface to contain precipitation that fell on the column. Figure 1 shows the structure of the experimental columns.

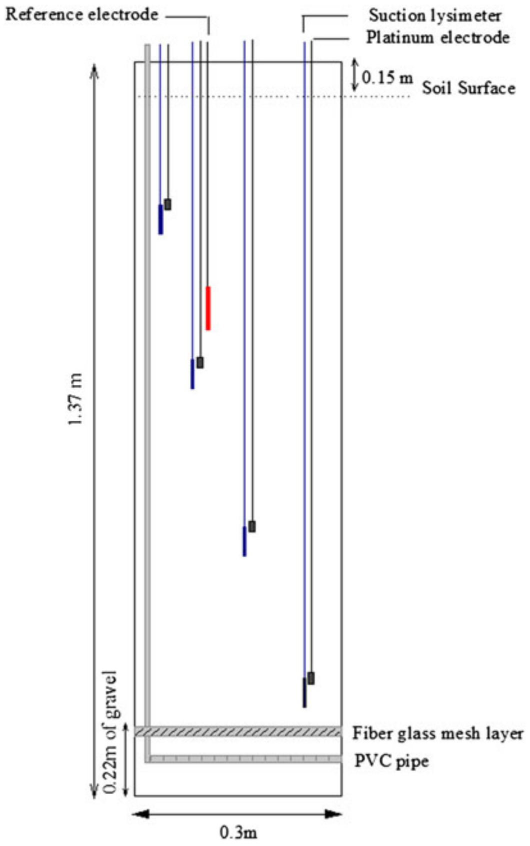

Fig. 1 Schematic of experimental columns

The columns were buried in the tailings pile in an attempt to replicate in situ temperature variations. Platinum electrodes were installed at 0.25, 0.50, 0.75 and 1 m below the tailings surface to monitor changes in Eh, following methods developed by Fiedler et al. (2007). Suction lysimeters were installed at the same four depths to monitor changes in pore water chemistry. A slotted PVC pipe covered with 0.2 m of gravel and a fiberglass mesh was installed at the bottom of each column to collect any accumulated liquid. The suction lysimeters were sampled with a vacuum pump following methods described by Chaimberg et al. (1992). Water samples from the bottom of the columns were collected with a peristaltic pump and passed through a 0.45 μm Whatman filter to remove particulate material. All samples were placed on ice immediately after collection and transported to the laboratory within 24 h for analysis.

Experimental columns were monitored periodically over the 20 month experimental period. Dissolved oxygen (DO), H_2S, pH, and redox potential (Eh) were measured in the field. DO and H_2S were measured using visual Chemetrics kits. The Eh was measured using a voltmeter, a platinum electrode, and a gel-filled Calomel reference electrode (Fiedler et al. 2007). The pH was measured using a handheld meter with an ACCUMET combination electrode, which was calibrated prior to each use at pH = 4, 7, and 10. The total organic carbon (TOC) was measured using a Shimadzu TOC analyzer (ASI-L TOC Autosampler). Alkalinity of WG was measured following Standard Methods 2320-B4D (APWA 1989). The chemical oxygen demand (COD) of the WG was measured following method 8000-USEPA (U.S. EPA 1980). Cations and metals (Al, Cu, Ca, Mg, Mn, Na, Pb, Co, Ni, Cr, K, Si, and Zn) were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Perkins Elmer Plasma II Ion Coupled Plasma Argon Emission Spectrometer (ICP-AES) following methods equivalent to U.S. EPA method SW-846 6010C. Pb, Ni, Co, and Ni were always below detection limits (less than 0.05 mg/L) and will not be discussed further. Dissolved anions (SO_4^{-2}, NO_3^-, NO_2^-, PO_4^{-3}, Cl^-, and Br^-) were analyzed using ion chromatography (Dionex IC) following methods equivalent to U.S. EPA method SW-846 9056. NO_3^-, NO_2^-, PO_4^{-3}, Cl^{-1}, and Br^{-1} were below detection limits (less than 2.5 mg/L) in all samples. Carbon content of the tailings was measured using a Perkin Elmer 2400 CHN Elemental Analyzer. Hot acidity was measured by boiling the sample in the presence of hydrogen peroxide and sulfuric acid and then titrating to pH = 8.2 with sodium hydroxide to measure acidity associated with dissolved metals (Clesceri 1989).

Physical properties of tailings, including porosity, air-filled porosity, and hydraulic conductivity were measured by Behrooz and Borden (2012) on fresh, unoxidized tailings collected from 0.5 m below the ground surface immediately adjoining the test columns. The tailings were characterized by X-ray diffraction (XRD), scanning electron microscope with energy dispersive X-ray spectroscopy (SEM/EDS), and extraction of the sediment with HCl/HNO_3 and H_2O_2 following U.S. EPA method 3050 B, followed by ICP-AES analysis.

After 6 months of operation to establish baseline conditions, 2.5 kg of WG were applied to the surface of two replicate columns; two columns remained as replicate controls. The amount of WG applied was estimated to consume any oxygen entering the surface of the column over a 12 month period, assuming an oxygen diffusion depth of 0.25 m and an air filled porosity of 10 %. The WG was applied by removing the top 0.18 m of tailings, blending it with 2.5 kg of WG, and then adding the mixed WG tailings back to the surface of the column. The experimental columns were installed in December 2007 and then monitored in March, April, May, and June 2008 to establish baseline conditions. The WG was applied in June 2008 and then monitored in July 2008, August 2008, June 2009, and August 2009. The columns were frozen from December 2008 to February 2009 and could not be sampled.

Experimental Results

Column Installation and Material Properties

The columns were packed with reduced tailings, believed to have limited prior exposure to oxygen. These tailings have a $D_{50} = 40$ µm, $D_{10} = 4$ µm, particle density of 3.03, bulk density of 1.69, porosity of 0.44, saturated hydraulic conductivity (K_{SAT}) of 4.6×10^{-6} m/d (Behrooz and Borden 2012). However, these properties could have been altered over the experimental period by oxidation or WG addition. The tailings used to pack the columns had a pH of 4.3 (Sobek et al. 1978), an acid neutralization potential of −2 kg H_2SO_4/t and a potential acidity of 900 kg H_2SO_4/t (Sobek et al. 1978). X-ray diffraction measurements indicate the tailings are principally albite, quartz, and chlorite with smaller amounts of pyrrhotite and pyrite. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) analysis of these sediments was performed to quantify bulk chemical composition. Based on SEM/EDS analysis, the atomic fractions of the tailings were 52 % Si, 14 % Al, 10 % S, 10 % Fe, 5 % Na, 4 % Mg, 3 % K, 2 % Ca, and 0.1 % Mn. Extraction of the sediment with HCl/HNO_3 and H_2O_2 following U.S. EPA method 3050 B and analysis by ICP-AES indicates the tailings also contain 4.1×10^3 mg/kg of Zn and 1.1×10^3 mg/kg of Cu.

The WG used to treat the columns had a chemical oxygen demand (COD) of 1.1×10^6 mg/kg, and a total organic carbon content (TOC) of 3.5×10^5 mg/kg. The WG contained 1×10^5 mg/kg of alkalinity as $CaCO_3$ and 2.9×10^4 mg/kg of K, presumably from the KOH used in the biodiesel production. Al, Ca, Cu, Fe, Mg, Mn, Na, NO_3^-, PO_4^{-3}, SO_4^{-2}, S, Si, Cl^-, and Br^- were all below detection (<0.05 mg/g).

Major Anions and Cations in the Column Effluent

Variations in parameter concentration versus time are shown for 0.5 m below the tailings surface (Fig. 2) and for the column effluent (Fig. 3). Figure 4 shows profiles of contaminant concentrations versus depth in the four columns 1 year after WG addition. Complete pore water and leachate monitoring results are provided in the supplementary material (Tables S-1 to S-4; these tables can be downloaded for free with the electronic version of the paper by all subscribers to this journal). On some dates, there was not enough liquid sample to analyze for all of the parameters, so the number of samples analyzed for each column varies. There was also an extended period between 61 and 274 days when the columns were frozen and could not be sampled.

TOC values were near the analytical detection limit (10 mg/L) over the monitoring period. In the treated columns, TOC increased to roughly 5,000 mg/L immediately after WG addition in the 0.5 m samples (Fig. 2a) and column effluent (Fig. 3a), indicating that some portion of the WG rapidly penetrated the full length of the columns (Fig. 4a). At 1 year after WG addition (Fig. 4a), high TOC concentrations remained throughout the treated columns. If the WG was uniformly distributed throughout the column, the TOC concentration would have increased to approximately 22,000 mg/L, suggesting that most of the organic

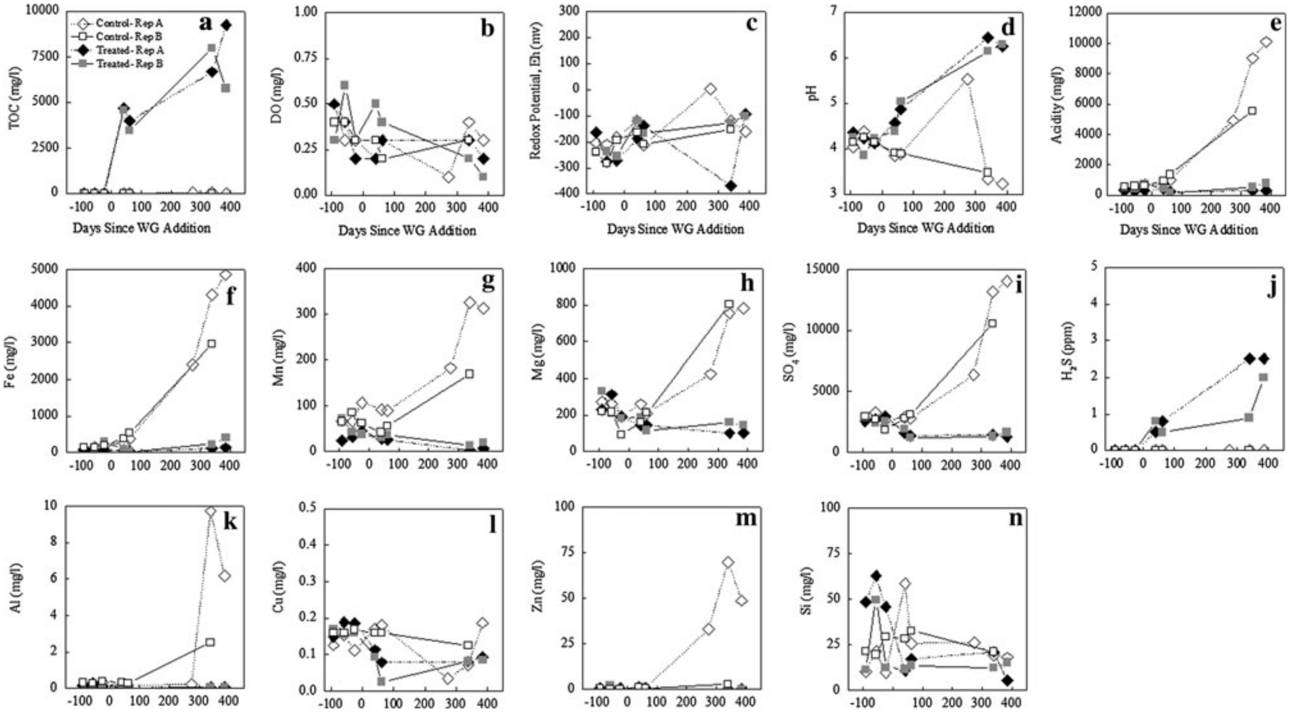

Fig. 2 Variation in **a** total organic carbon (TOC), **b** dissolved oxygen (DO), **c** redox potential (Eh), **d** pH, **e** acidity, **f** iron (Fe), **g** manganese (Mn), **h** magnesium (Mg), **i** sulfate (SO_4), **j** hydrogen sulfide (H_2S), **k** aluminum (Al), **l** copper (Cu), **m** zinc (Zn), and **n** silica (Si) at 0.5 m below surface in experimental columns over time

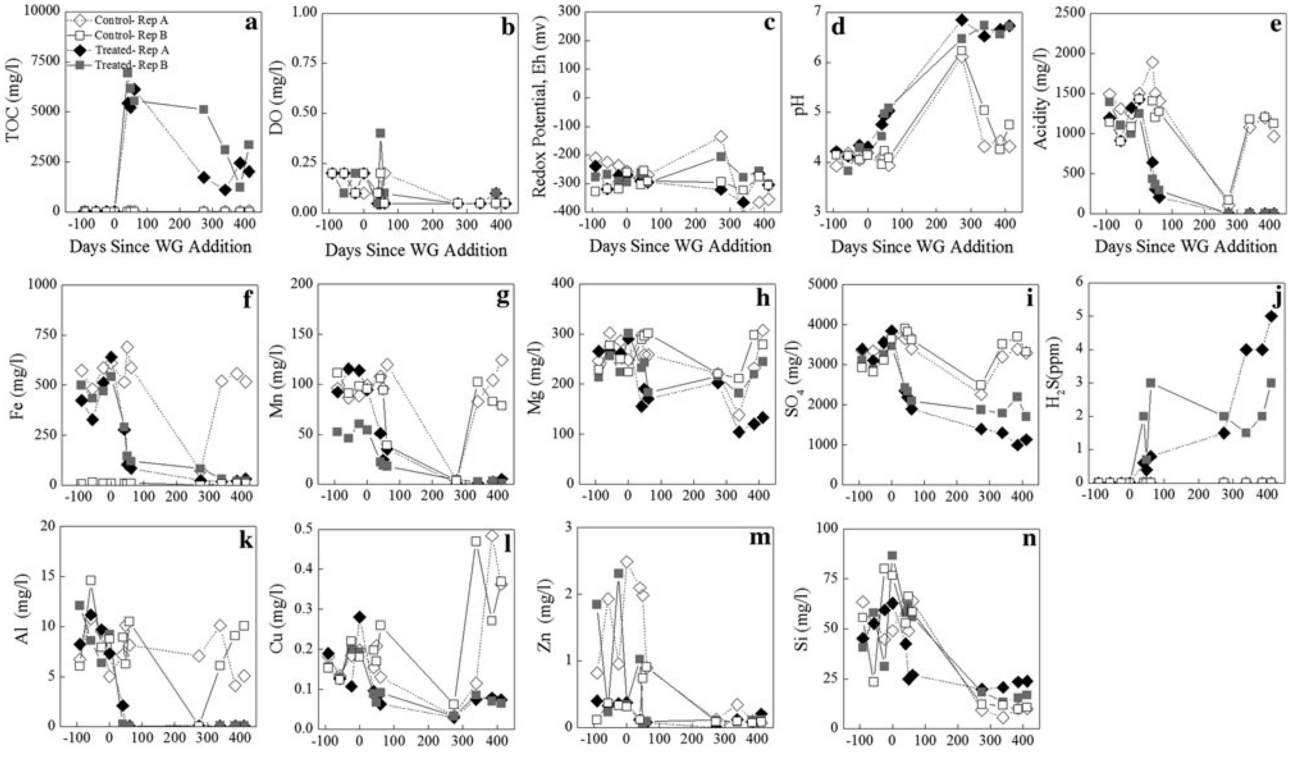

Fig. 3 Variation in **a** total organic carbon (TOC), **b** dissolved oxygen (DO), **c** redox potential (Eh), **d** pH, **e** acidity, **f** iron (Fe), **g** manganese (Mn), **h** magnesium (Mg), **i** sulfate (SO_4), **j** hydrogen sulfide (H_2S), **k** aluminum (Al), **l** copper (Cu), **m** zinc (Zn), and **n** silica (Si) in column effluent (1.2 m depth) in experimental columns over time

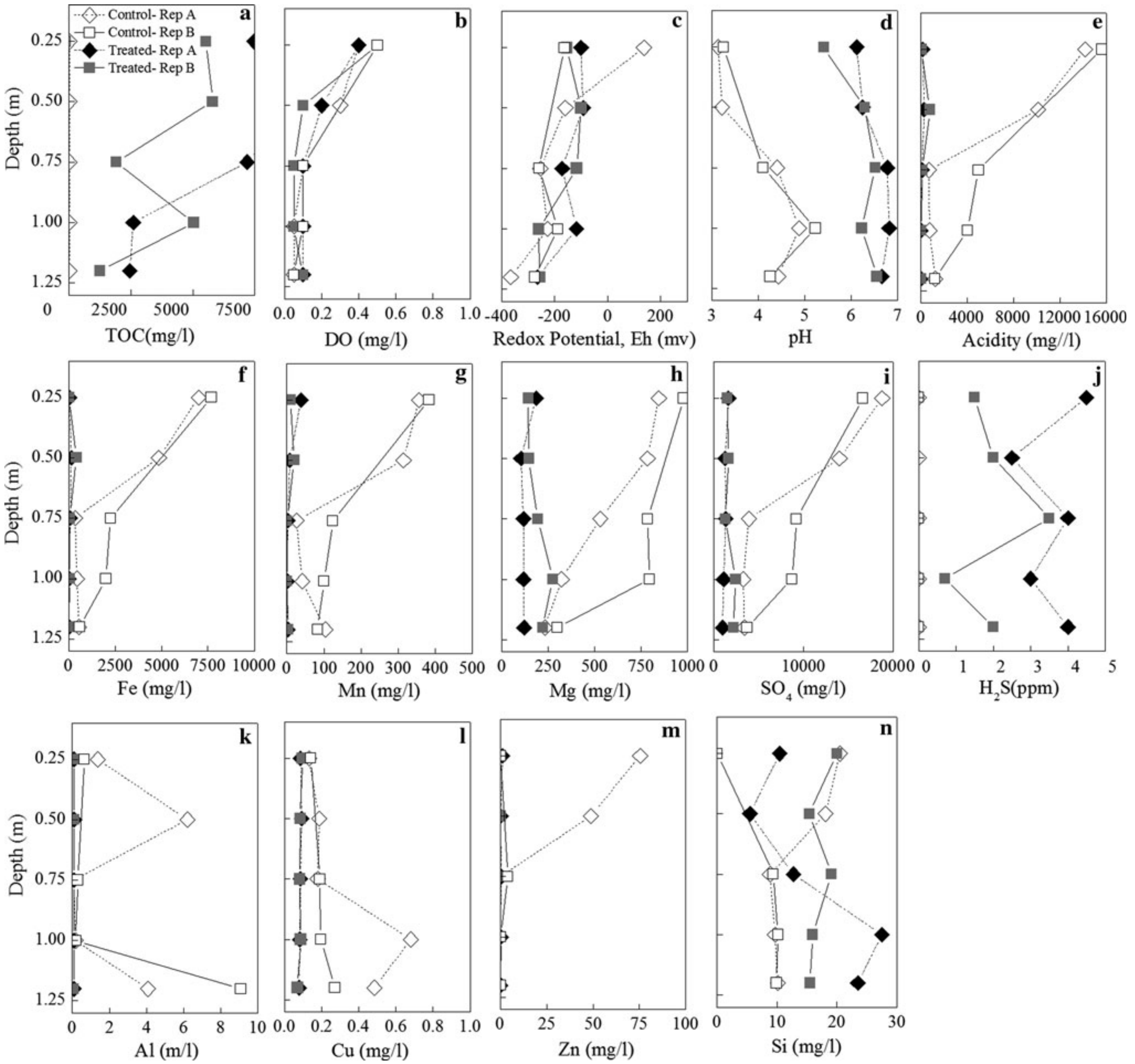

Fig. 4 Profiles of **a** total organic carbon (TOC), **b** dissolved oxygen (DO), **c** redox potential (Eh), **d** pH, **e** acidity, **f** iron (Fe), **g** manganese (Mn), **h** magnesium (Mg), **i** sulfate (SO_4), **j** hydrogen sulfide (H_2S), **k** aluminum (Al), **l** copper (Cu), **m** zinc (Zn), and **n** silica (Si) versus depth at 1 year after WG addition

material was not present in solution. The rapid penetration of relatively high TOC concentrations throughout the column was somewhat surprising since the average hydraulic residence time (HRT) in the columns was more than a year. The rapid WG penetration could be due to: (a) heterogeneities in the columns; (b) the high density of WG (1.3 grams/mL); or (c) the intermittent nature of groundwater recharge where pulses of water migrate through the vadose zone following rainfall events.

Figure 5 shows the total carbon distribution in the column sediment at the end of the experiment. It was not possible with analytical method employed to distinguish between organic and inorganic carbon. However, all water samples were undersaturated with respect to $FeCO_3$, $CaCO_3$, and $MgCO_3$, suggesting that most of the carbon in the sediment was organic. The carbon content of the treated 0.5, 0.75, and 1.0 m samples were elevated compared to the control columns, consistent with some penetration of carbon throughout the column. However, the carbon content of the 0.25 m treated samples were much higher, indicating that most carbon was retained in the upper portion of the columns.

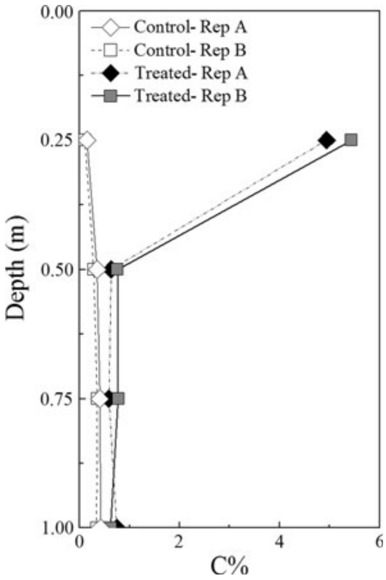

Fig. 5 Carbon content of the tailings in control and treated columns at the end of the study

As part of the data analysis, we attempted to perform a mass balance on the carbon added to the column in the form of WG and recovered in the column effluent and solid tailings. The total TOC discharged in the treated columns effluent was 70 g or 8.5 % of the carbon added in the WG, consistent with retention of most TOC within the columns. The highest carbon concentrations in the tailings were measured in sediment samples collected from 0.25 m below the surface. If these samples are assumed to be representative of all material from 0 to 0.25 m in the column, the carbon content of this zone was increased by approximately 1.56 kg or roughly twice the carbon added in the WG (0.82 kg organic carbon). Clearly, the addition of 0.82 kg of carbon should not increase the tailings carbon content by 1.56 kg. This apparent error is likely due to assuming the carbon is uniformly distributed throughout the upper 0.25 m of the column. If the carbon content of the sediment was much lower near the surface, this would explain the apparent mass balance error. Overall, the carbon analysis results indicate that only a small amount of organic carbon was released in the column effluent and a large amount of carbon was still present near the tailings surface, 15 months after WG application.

Dissolved oxygen (DO) and redox potential (Eh) followed the same general pattern in both treated and control columns. There was a small decline in DO with time in both the 0.5 m and effluent samples (Figs. 2b and 3b), presumably due to oxygen consumption by oxidation of sulfide minerals. The Eh remained essentially constant (≈ -300 mv) in the effluent samples, but slowly increased in the 0.5 m samples, due to the gradual oxidation of the surficial tailings. The similarity in DO and redox measurements across the control and treated columns suggests that WG addition did not measurably reduce oxygen penetration into the columns. However, it is difficult to reliably measure oxygen concentrations less than 0.5 mg/L, so WG may have somewhat reduced oxygen availability.

While oxygen penetration in the treated and control columns may have been similar, acidity production and the resulting pH were dramatically different. Prior to WG addition, the pH of the columns varied between 4.0 and 4.5 and acidity varied between 1,000 and 1,500 mg/L. In the control columns, acidity increased dramatically with time in the 0.5 m samples with an associated decline in pH (Fig. 2d, e). In the control column effluents (Fig. 3d, e), acidity was relatively constant with a small increase in pH. In the treated columns, acidity remained constant or increased slightly with time at 0.5 m below the surface and declined to <1 mg/L in the column effluent (Figs. 2e and 3e). The pH followed a similar trend, increasing to between 6 and 7 from 0.5 m to the column effluent 1 year after WG addition (Fig. 4d). The increase in pH immediately after WG addition is likely associated with the KOH present in the WG. The larger pH increase and acidity decline in the second year may be associated with oxygen and/or SO_4 consumption by the added organic material. An exception to these overall trends was monitoring data collected in March immediately after the spring snow melt (274 days after WG addition). When first sampled after snowmelt, all the columns appeared to be saturated with cold water. In the control columns, saturation with cold water resulted in a large increase in pH and decline in acidity. However, by the following June (day 232), acidity and pH had returned to the levels observed the previous summer.

In the control columns, the large increase in acidity in the shallow 0.5 m samples corresponds with a similar increase in dissolved iron (Fe) and sulfate (SO_4), presumably due to oxidation of pyrrhotite and pyrite. There were also substantial increases in manganese (Mn), magnesium (Mg), aluminum (Al), and zinc (Zn) in these samples, released from the tailings by oxidation and/or low pH. In control column effluents, Fe, Mn, Mg, SO_4, and Al remained relatively constant with time due to the long HRT and slow flushing of dissolved salts through the column. Similar to pH and acidity, there were large apparent drops in Fe, Mn, SO_4, and Al immediately after spring snowmelt.

In the treated columns, results were dramatically different. In the shallow 0.5 m samples, dissolved Fe, Mn, Mg, Al, and Zn remained relatively constant. SO_4 declined from 2,500 to 3,000 mg/L to below 1,500 mg/L. These declines were likely associated with reduced production of SO_4 and/or reduction of SO_4 to H_2S by SRBs (Fig. 2j). The highest H_2S levels were observed in the second summer, presumably due to growth of SRBs over time and increased reduction of SO_4 to H_2S at higher temperatures.

In the treated column effluents, there were large declines in Fe, Mn, SO_4, and Zn coincident with hydrogen sulfide (H_2S) production. There were smaller decreases in sodium (Na), potassium (K), and calcium (Ca) with time in the control or treated columns effluents (supplementary material, Tables S-1 to S-4). Given the long HRT of the columns, the observed declines in Fe, Mn, and Zn were probably not due to reduced oxidation of the surficial tailings, but due to reduction of SO_4 to H_2S and precipitation as metal sulfides. Na, K, and Ca do not commonly precipitate as sulfides, so these cations were not as effectively removed.

The beneficial effects of organic substrate addition are most apparent in chemical profiles at 1 year after WG addition (Fig. 4). TOC remains high throughout the treated column profile. While the DO profiles are similar, redox potential is somewhat higher in the shallowest control samples. This results in very high acidity, Fe, Mn, and SO_4 in the shallowest control samples with corresponding low pH due to intense oxidation at the tailings surface. The high acidity and low pH results in high levels of Mg and Zn. In the shallow treated column samples, acidity, Fe, Mn, Mg, SO_4, Al, Cu, and Zn remain low, indicating much more limited oxidation of the tailings. Deeper in the treated columns, Fe, Mn Al, and Zn declined.

Figure 6 shows the total mass discharged from the control and treated columns after WG addition. The large increase in TOC in the treated column effluents corresponds to large reductions in acidity, Fe, Mn, Al, and Cu. In the 12 months following WG addition, 6–10 % of the applied TOC was recovered in the treated column effluents. The WG applied to the treated columns provided 250 g of alkalinity as $CaCO_3$, which exceeds the acidity discharged in the untreated control columns, indicating that the residual base (KOH) was a major component of the treatment process.

Figure 7 shows average parameter concentrations for the five sampling dates after WG addition for the treated columns (A and B) and control columns (A and B). With the exception of TOC, concentrations of all major parameters decreased following WG addition. In comparison, concentrations of most parameters increased in the untreated controls. Same day contaminant concentrations in the treated column effluents were reduced by the following amounts compared to the untreated controls (± one standard deviation): 86 ± 12 % for acidity, 83 ± 18 % for Fe, 48 ± 9 % for SO_4, 97 ± 6 % for Al, 84 ± 16 % for Mn, 67 ± 13 % for Cu, 29 ± 74 % for Zn, 33 ± 11 % for Ca, 30 ± 8 % for Mg, 11 ± 24 % for Na, and 13 ± 10 % for K. Removal efficiencies for most major parameters increased with time, reaching a maximum in the second summer after WG addition (Fig. 8).

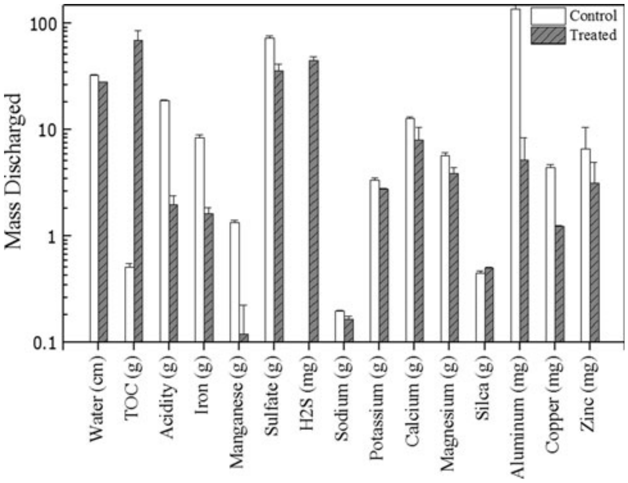

Fig. 6 Average mass discharged from control and treated in 14 months following substrate addition. *Error bar*s are maximum value observed

Mineral Precipitation

The PHREEQC geochemical modeling program with an internal PHREEQC database (Parkhurst and Appelo 1999) was used to calculate the saturation index (SI) for potential mineral precipitates. SI is defined as the base ten log of the ion activity product (IAP) divided by the mineral solubility product (Ksp) (SI = log (IAP/Ksp), so a SI value of 1 indicates the dissolved mineral concentration is a factor of ten above saturation. The anomalous data collected immediately after spring snowmelt was not included in this analysis since it was likely associated with a short-term event and may not be representative of longer term trends. A charge balance was computed for each sample as a quality control check. With the exception of a few samples collected from the treated columns during active H_2S production, average charge balance errors were 4–5 %. In the few cases where the charge balance error exceeded 10 %, these samples were excluded from the analysis.

Figure 9 shows the average and range of SI for different minerals at 1.0 m below the ground surface in the treated and control columns. The control columns were somewhat supersaturated with quartz (SI = 0.2–1.1) throughout the profile. The shallow sampling ports in the control columns were also slightly supersaturated with gypsum (SI = 0–0.14), while the deeper ports were consistently supersaturated with alunite. Gypsum saturation is consistent with the very high sulfate concentrations observed in the 0.5 m samples. By the second summer, the deeper pore waters were also saturated with gibbsite, potassium (K) mica, and kaolinite.

In the two summer months immediately after WG addition, the treated columns were undersaturated with respect to most minerals (except quartz). However during

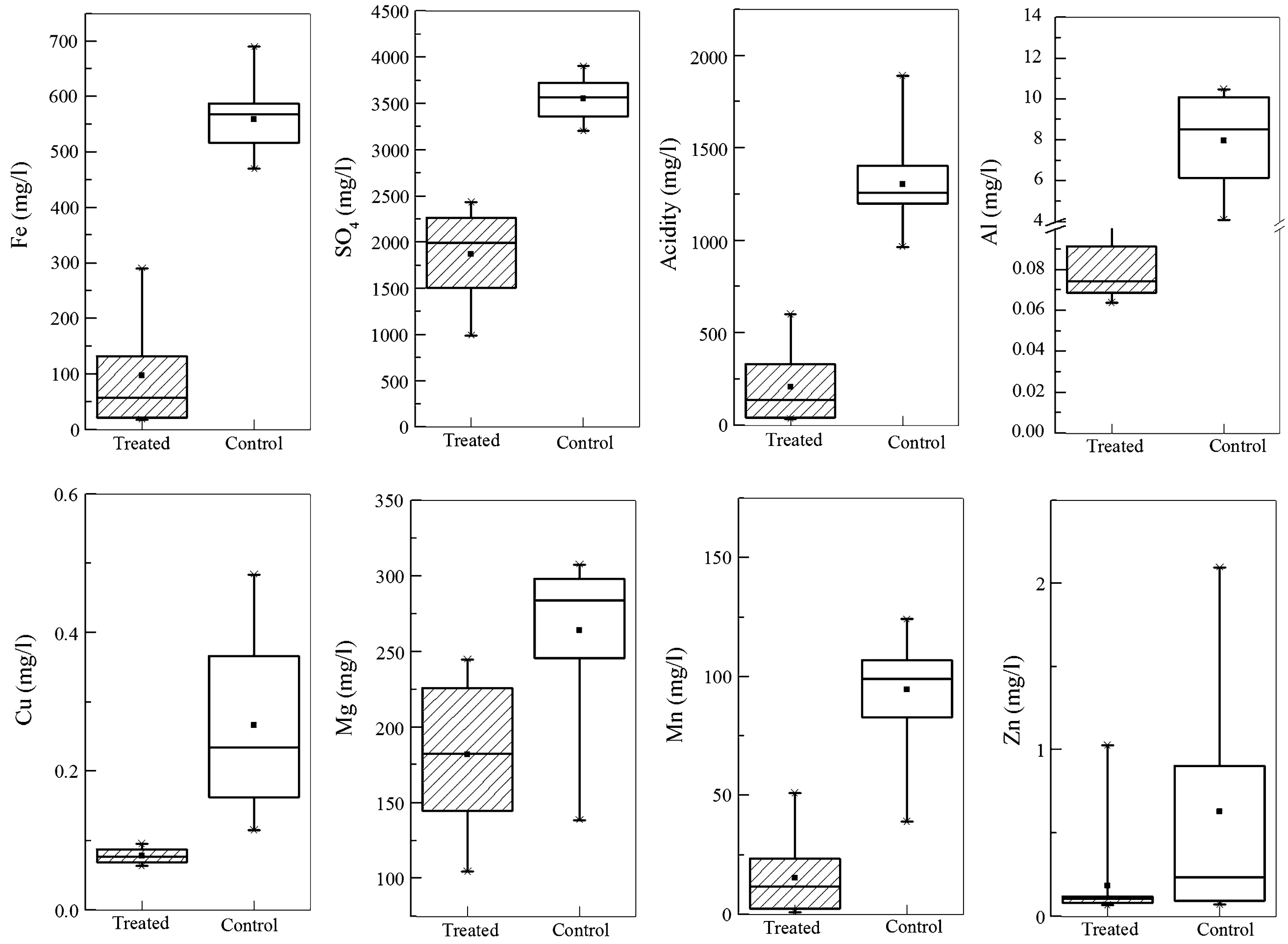

Fig. 7 Comparison of contaminant concentrations in the treated columns and control columns during the treatment period (June 2008 to August 2009). Graphs include minimum, maximum, upper quartile, lower quartile and average of each data set

the following summer, the increase in H_2S caused the bottom sampling ports in the treated column to be strongly supersaturated with a variety of sulfide minerals (amorphous FeS, mackinawite, pyrite, and sphalerite), while the increase in pH caused the bottom sampling ports to be supersaturated with aluminum minerals (alunite, gibbsite, calcium montmorillonite, illite, potassium feldspar, potassium mica, and kaolinite). Precipitation of some aluminum minerals may be slow, and solutions may remain supersaturated with some alumino-silicates for extended periods (Nagy et al. 1991). However, sulfide precipitation is expected to be relatively rapid, removing dissolved Fe and Zn (Rickard 1995).

Potential Field Application

Waste glycerol (WG) could potentially be used to reduce AMD production from mine tailings by spraying the material onto the tailings surface, and then tilling it into the tailings using a disc harrow or similar implement. WG and associated fermentation products that migrate deeper into the tailings could then reduce concentrations of AMD constituents that have already been produced. In humid areas, natural rainfall infiltration would carry the WG deeper into the tailings. However in arid areas, surface irrigation may be required.

As reported above, 2.5 kg of WG was blended into the surface of 0.3 m diameter columns containing mine tailings (application rate = 35 kg/m^2) and was effective in reducing concentrations of major AMD constituents in the column effluents. Acidity was reduced by an average of 86 %, Fe by 83 %, Al by 97 %, Mn by 84 %, and Cu by 67 %, when compared with same day concentrations in the untreated controls. Observed removal efficiencies for acidity, iron, and aluminum were similar to those achieved in well operated, passive treatment systems employing alkalinity addition, aeration, and sedimentation (PIRAMID Consortium 2003). Anaerobic bioreactors using solid organic substrates can achieve similar removal efficiencies. Zagury et al. (2006) reported removal efficiency of up to

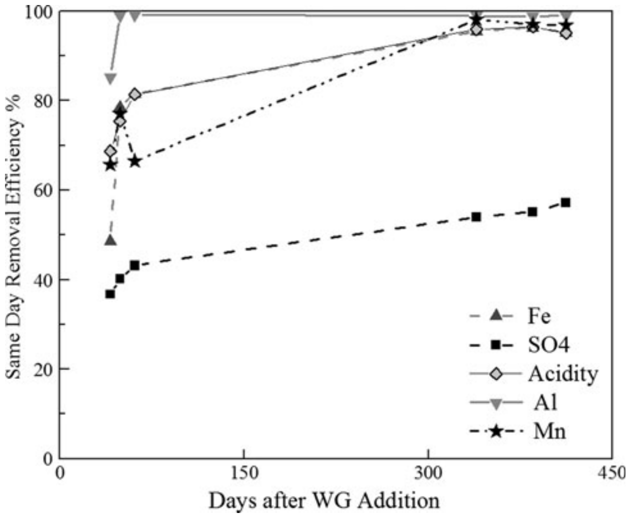

Fig. 8 Variation in treatment efficiency over time following WG addition

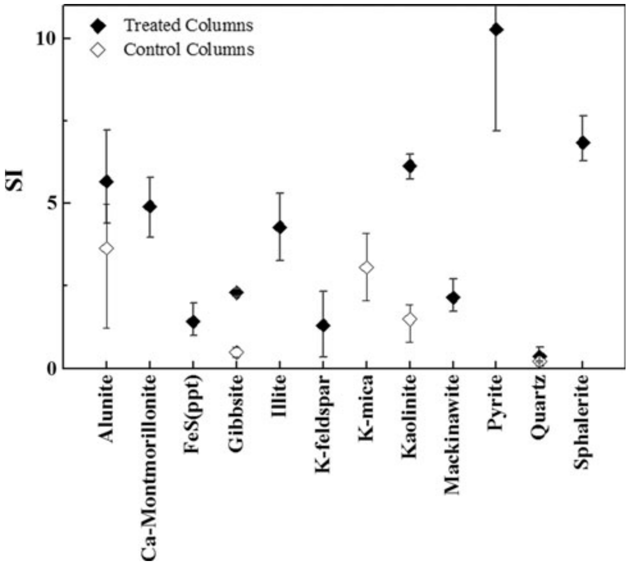

Fig. 9 Average saturation index of potential mineral precipitates in control and treated columns in the second summer after WG addition at 1.0 m below ground surface. *Error bars* are average of minimum and maximum saturation indices

100 % for Fe, 99 % for Mn, 99 % for Cd, 99 % for Ni, and 94 % for Zn in batch experiments using a variety of organic substrates. In pilot scale bioreactors filled with spent mushroom compost conditioned with gypsum and limestone, Dvorak et al. (1992) observed over 95 % reductions in Al, Cd, Fe, Mn, Ni, Zn, and acidity. However, bioreactors require significant land area for construction and must be regularly replenished with fresh organic substrate to maintain treatment performance.

Acidity is released from tailings piles when oxygen (O_2) reacts with pyrite (FeS_2) releasing Fe^{+2}, SO_4, and acidity. Once released from the pile, the AMD will react with additional oxygen causing the Fe^{+2} to precipitate as $Fe(OH)_3$ with the following overall reaction.

$$3FeS_2 + 11.25O_2 + 10.5H_2O \rightarrow 6H_2SO_4 + 3Fe(OH)_3 \quad (1)$$

WG can treat and/or reduce acidity through two major processes. Large amounts of residual alkalinity (0.1 kg of $CaCO_3$/kg WG used in this project) are present in the some WG products associated with the KOH or NaOH used in biodiesel production and will neutralize H_2SO_4 that has already been produced. Glycerol, methanol, and other dissolved organic material in the WG provide 1.1 kg of COD per kg of WG, which can reduce oxygen before it reacts with FeS_2 or reduce the SO_4 back to sulfide, causing Fe^{+2} to precipitate. Based on the stoichiometry of Eq. 1, the overall effect of these two processes would be to reduce acidity generation by approximately 2 kg of acidity as $CaCO_3$ per kg of WG. As of August 2011, WG cost \$0.11–0.18/kg in bulk quantities (http://www.icispricing.com/, downloaded March 1, 2012). If only the residual base in the WG is considered, the alkalinity in WG would cost \$1.1–1.8 \$/kg $CaCO_3$, which is much higher than other common alkalis. However, if the beneficial effects of the soluble organic carbon in reducing AMD production are considered, WG will reduce acidity production by 0.055–0.09 \$/kg of acidity, a much lower cost than other materials.

Using the same application rate as in the column experiments and a conservative cost of \$0.18/kg WG, treatment of the 9 ha Ore Knob tailings pile would cost \$550,000 (\$62,000 per ha) plus costs for transportation to the site, spray application, and tilling into the tailings surface. This cost is substantial, but much lower than the \$11,000,000 that will be expended by U.S. EPA for short-term management of the site (U.S. EPA 2010). Costs could possibly be reduced further by using a smaller amount of WG. In the column experiment, most of the organic carbon added to the tailings was still present at the end of 1 year, indicating that the amount of material added was much greater than that required for short-term treatment. Behrooz and Borden (2012) reported that the Ore Knob Tailings pile was currently releasing approximately 220,000 kg/yr of acidity. Treating this acidity would require ≈110 t of WG per year at a cost of \$20,000 per year plus transportation and surface application.

The analyses presented above show that WG can be a cost effective alternative to common commercial alkalis. However, the primary benefits of this process would be the ease of application. In the process described above, treatment occurs within the pile, so there is essentially no land required, no permanent treatment facilities (tanks, basins, aeration equipment, etc.), no power required for aerators, pumps or mixers, and no waste sludge or other residuals produced. The process is effective at reducing a variety of contaminants, not effectively removed by alkali addition.

While the process described above can be cost-effective, it is not a permanent solution. Additional WG would need to be periodically reapplied to maintain performance. A potentially more efficient approach would be to apply WG prior to installation of a permanent cap. The WG would treat/neutralize acidity already produced in the pile and provide a reservoir of reducing power to control future AMD production.

Conclusions and Applications

Monitoring data collected during the course of this project demonstrated that surface application of WG effectively reduced pollutant concentrations and total loads for over 15 months, with most carbon still present in the tailings at the end of the monitoring period. WG addition reduced effluent acidity by an average of 86 %, Fe by 83 %, Al by 97 %, Mn by 84 %, and Cu by 67 %, compared to same day concentrations in the treated and untreated controls. Treatment likely occurs through a combination of processes including: (a) neutralization of acidity by the KOH present in the WG; (b) reduction of SO_4 to H_2S with subsequent precipitation of dissolved metals, and potentially (c) consumption of oxygen, slowing oxidation of the tailings. Geochemical modeling indicates the effluents of the treated columns were supersaturated with amorphous FeS, mackinawite, pyrite, and sphalerite, which could result in relatively rapid removal of iron and zinc. The column effluents were also supersaturated with alunite, gibbsite, calcium montmorillonite, illite, potassium feldspar, potassium mica, and kaolinite due to the increased pH. However, the slower kinetics of alumino-silicate precipitation could reduce treatment efficiency.

Surface application of WG could potentially be very cost-effect for temporary treatment of mine tailings. WG is easy to apply and material costs are comparable to other common alkalis. Major advantages of this approach include no permanent infrastructure or land required, no sludge production, minimal maintenance, and high removal efficiencies for a broad range of contaminants.

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