ABSTRACT

The stabilization of rock waste from Ljusnarsbergs mine in Kopperberg, Sweden was investigated in two column experiments with partially unsaturated mine waste for 700 days. The first column was filled with untreated rock waste and the second was filled with rock waste stabilized with biosludge and alkaline paper mill sludge. The results of the column experiments indicate that the stabilization of the rock waste with the reactive amendments succeeded in maintaining a pH between 6.2 and 6.8 in the leachate with an alkalinity of 300 – 500 mg/L HCO$_3^-$ for at least 700 days, compared to a pH of 3.0 – 3.5 in the leachate from untreated rock waste. In the leachate from the treated waste, Cu and Zn were detected at concentrations less than 0.1 and 1 mg/L, respectively, suggesting that adsorption to prevalent iron oxides at near – neutral pH controls the concentrations of these metals. There is no indication that the addition of biosludge as a reactive amendment has a significant effect on metal discharge from the stabilized rock waste, although the dissolution of ferric iron minerals under saturated conditions was observed.

Additional key words: organic carbon, DOC, PHREEQC

INTRODUCTION

The two most successful and commonly used techniques for the prevention of sulfide oxidation in sulfidic mine wastes involve the installation of soil cover or a water cover over the mine waste deposit (Höglund et al., 2004). By reducing the rate of oxygen diffusion into the deposits, these covers generally decrease the rate of heavy metal release compared to untreated deposits. In cases when it is not possible to immediately apply one of these remediation methods after tailings deposition (e.g. in the absence of appropriate cover material or in arid climates), thereby increasing the risk for oxygen penetration into the deposits, it may be beneficial to stabilize the wastes. Mine waste stabilization implies adding a chemically reactive component to the waste system so as to minimize acid production and element mobilization from the solid phase. Stabilization can have a variety of functions, but the overall goal is to improve the quality of mine leachate discharging from the deposit.

Various stabilization amendments have been tested in laboratory and field studies. In general, amendments are either alkaline materials for acid consumption, or compounds that react with the wastes and thereby restrict sulfide oxidation or bind metals in the reaction product. Examples of alkaline materials are limestone, slaked lime (calcium hydroxide), incinerator fly ash, paper sludge ash, and alkaline paper mill waste (e.g. Bellaloui et al., 1999; Chtaini et al., 2001; Herbert et al., 2007), while examples of reactive compounds for the inhibition of sulfide oxidation and the prevention of metal release are phosphate, silicate, and sewage sludge (e.g. Evangelou and Zhang, 1995; Alakangas and Öhlander, 2006; Höckert, 2007).

In this study, the stabilization of rock waste from Ljusnarsbergs mine in Kopperberg, Sweden was investigated in column experiments with partially unsaturated mine waste. In order to inhibit the generation of acidic leachate and the release of metals from the rock waste, biosludge (activated

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sewage sludge) and alkaline paper mill sludge were mixed with the sulfidic mine waste. Biosludge was added as a potential metal-binding agent, and paper mill sludge was added for acid neutralization. The purpose of this investigation was to determine if the introduction of these reactive amendments into an acid–producing waste rock would lead to an improvement of leachate quality in terms of a higher pH and lower concentrations of potentially hazardous metals in the waste leachate.

MATERIALS AND METHODS

The stabilization of waste rock was studied as a column experiment, with one column containing untreated waste rock and the other containing stabilized waste rock. Waste rock was acquired from rock dumps near the Ljusnarsberg mine in Kopparberg, Sweden; the material is highly weathered. The waste rock collected for these experiments is classified as a gravel-rich sand, with >80% of the material in the grain-size range of 0.2 mm – 20 mm. The major minerals in the waste, identified by X-ray diffractometry, are quartz, amphibole (tentatively identified as manganan cummingtonite), and biotite. Jarosite, goethite and gypsum are abundant secondary precipitates in the waste. The waste rock used for the experiments has a very limited acid-neutralization capacity and an average reduced sulfur concentration of 1.9 wt%, which occurs primarily in pyrite, but also in pyrrhotite, chalcopyrite, sphalerite and galena (see below).

The fine–grained fraction from the Ljusnarsberg waste rock was analyzed in thin–section by optical microscopy and using an electron microprobe coupled to a wave–dispersive X–ray spectrometer. These analytical methods were used to identify the opaque minerals occurring in the waste rock; the presence of magnetite, pyrrhotite, pyrite, chalcopyrite, sphalerite and galena was confirmed by point analyses using wave–dispersive X–ray spectroscopy.

The column experiments were conducted using two PVC columns, 60 cm high and with an inner diameter of 15 cm. The tops of the columns were open to the atmosphere, and the bottoms were sealed with a PVC lid that was fitted with a small bore nipple in the center of the lid. Prior to filling with waste rock, the base of the column was covered with a fine mesh net and covered with a thin layer of quartz sand, in order to prevent fine particulates from clogging the column outlet. Both columns were filled with 9.5 liters of material, which filled the columns to a depth of about 50 cm. The first column was only filled with air-dried waste rock (15 kg untreated waste rock; bulk density 1560 kg/m$^3$). For the second column, 15 kg waste rock was stabilized by thoroughly mixing with 1 kg alkaline paper mill sludge and 0.5 kg moist biosludge (activated sewage sludge). The alkaline paper mill sludge consists primarily of calcium carbonate and is produced during the causticization of a green liquor (Na$_2$CO$_3$ – Na$_2$S solution) from a paper mill using the Kraft pulp (sulfate) process.

Over the course of the experiment, distilled water was sprinkled over the upper surface of the waste rock at a rate of about 155 mL/day, which is equivalent to an infiltration of 3200 mm/year. This infiltration rate is about ten times the expected infiltration rate for central Sweden. In order to ensure a uniform distribution of infiltrating water, a sintered glass plate (12 cm diameter) was placed on the upper surface of the waste. In order to prevent oxygen entering the column from below, an artificial groundwater table was created in the columns at a depth of ca. 30 cm below the surface of the material. Below this level, the material was completely water-saturated; above this level, the material was only partially water-saturated, and oxygen diffusion through air-filled pores was hence possible.

Water samples discharging from the base of both columns were collected intermittently; at the beginning of the experimental period, water samples were collected approximately 1 – 2 times per week over the course of 51 days. The results from this period are also reported in Höckert (2007) and Herbert et al. (2007). After this initial period and to the end of the experimental period (700 days), water samples were collected every 30 – 100 days. After sampling, samples were filtered through 0.2 μm membrane filters, preserved with concentrated HNO$_3$, and stored at 4°C until analysis for metals, sulfur, and dissolved organic carbon (DOC). Untreated samples were analyzed for pH, redox potential, and alkalinity. Metal and sulfur concentrations were determined by
inductively – coupled plasma – optical emission spectroscopy, and DOC was determined on a Shimadzu TOC-5000 analyzer after filtration through 0.2 μm membrane filters. Alkalinity was determined by titration with 0.01 N H₂SO₄ to a pH 5 end-point. The redox potential is presented in pe – units, calculated from the measured redox potential relative to the potential of the standard hydrogen electrode.

RESULTS

Metal and sulfate concentrations
Changes in the leachate composition during the 700 day experimental period are shown in Figures 1 – 6. The results indicate that the untreated waste rock is acid – producing, with a leachate pH between 2 and 3 (Fig. 1). The effluent concentrations for a number of constituents, including sulfate (Fig. 2), Zn and Cu (Fig. 3), are initially quite high for the first ca. 30 days, after which concentrations for these constituents start to decrease. Contrary to the behavior of these oxidation products, the Fe concentration in the leachate from the untreated material reaches a maximum at ca. 50 days (Fig. 4). Calcium concentrations decrease initially but then increase and stabilize at a relatively constant level for the remainder of the experiment (Fig. 5).

The analyses from the stabilized mine waste indicate that amendment with biosludge and paper mill sludge buffers the column effluent at a much higher pH than in the untreated case, with an effluent pH in the range 6 – 7 (Fig. 1). The stabilized material was consistently acid – consuming, with an alkalinity ranging from 1340 – 1560 mg/L HCO₃⁻ at the beginning of the experimental period (Fig. 5), but decreasing to ca. 300 mg/L HCO₃⁻ after 300 days. Sulfate and Fe concentrations (Figs. 2 and 4, respectively) are significantly lower in the stabilized material during most of the experiment period but, by 700 days, the sulfate and Fe concentrations are similar in both columns. Heavy metals such as Cu and Zn (Fig. 3) readily adsorb to the abundant Fe oxide surfaces at near neutral pH in the stabilized material; the effluent concentrations of these elements are thus low (<0.1 mg/L Zn and <0.01 mg/L Cu at end of period). Calcium concentrations (Fig. 5) are higher in the stabilized column because of the addition of calcium carbonate (i.e. paper mill sludge).

Visual inspection of the stabilized mine waste in the semi-transparent PVC column revealed a change in the color of the waste rock material below the artificial water table; this change was readily apparent after ca. 100 days. The color of the material changed from yellow – brown to dark brown, suggesting that ferric iron minerals (e.g. goethite, jarosite) had at least partially dissolved below the artificial water table in this column; this was not observed in the untreated materials.

Figure 1: pH and pe in leachate from untreated and stabilized mine waste.

Figure 2: Sulfate in leachate from untreated and stabilized mine waste.
Dissolved organic carbon

Since sewage sludge has been added as an amendment to the stabilized waste rock, it might be expected that the concentrations of DOC in the column effluent would be much greater than in the effluent from the untreated material. The waste rock in both columns, however, contained significant amounts of organic material (wood fragments, bark) that were incorporated into the material when the waste rock was moved from one location to another over the course of years. Therefore, although DOC concentrations were somewhat higher (10 – 15 mg/L) in the effluent from the stabilized column at the beginning of the experiment, the DOC concentration was very similar after 250 days (5 – 10 mg/L). There is, however, no data on the nature of the DOC from each respective column, and whether the DOC has the same binding capacity and metal complexation properties.

Geochemical equilibrium calculations

The secondary minerals gypsum, goethite and jarosite have been identified in the waste rock by XRD. Thermodynamic calculations using PHREEQC (Parkhurst and Appelo, 1999) indicate that gypsum is in equilibrium or slightly oversaturated in the column effluent from both the untreated and stabilized materials (Fig. 7). Goethite is greatly oversaturated in the effluents from both columns, while jarosite saturation indices fluctuate within ±1 of saturation, but do not stabilize for any extended period of time. A more poorly – crystalline Fe oxyhydroxide, ferrihydrite, is undersaturated in the effluents from the untreated material yet displays relatively stable undersaturation for most of the experimental period. In contrast, ferrihydrite is oversaturated in the effluents from the stabilized material and the degree of oversaturation increases with time. Calcite, which has been added to the stabilized material, is slightly oversaturated in the effluent from the
stabilized column. Amorphous Al hydroxide, which can potentially precipitate in the pH range presented in the stabilized column, is generally undersaturated in the effluents.

Figure 7: Variations in saturation indices for mineral phases that are known to be present in the waste rock material, or that are close to saturation in the column effluents.

Geochemical speciation calculations with PHREEQC were used to determine charge balance errors for the analytical results from both columns; in the first case, the effect of DOC on speciation was excluded; in the second case, DOC was included. The calculations indicate a relatively large positive charge balance error for analyses of the effluent from the untreated column during the first 50 days (Fig. 8), where an “acceptable” charge balance error is less than ±5% (Appelo and Postma, 2005). After this period, the charge balance error is less than 5%. The charge balance error for analyses from the stabilized column is less than 5%, except for a period at the start of the experiment when the error was < -10%. For the untreated column, the positive charge balance error is probably due to error in the analysis of cations (especially Cu and Zn) that were detected at high concentrations in the column effluent.

The effect of DOC on metal speciation and charge balance was introduced into the PHREEQC model by including a new anionic species “DOC” with a -2.8 charge and a binding site density of 7.18 meq/g (Christensen et al., 1999). Complexation with Cu$^{2+}$, Zn$^{2+}$ and H$^+$ was included in the model using conditional stability constants from Christensen et al. (1999) and Christensen and Christensen (2000). The results of these speciation calculations for the untreated material indicate that 30 – 60% of the total Cu concentration and 2 – 6% of the total Zn concentration consist of organic complexes with DOC. In the stabilized material, where the pH was higher and competition with H$^+$ was therefore less, 70 – 90% of the total Cu concentration and 10 – 30% of the total Zn concentration consist of organic complexes. However, it should be noted that the charge balance error did not improve with the inclusion of DOC in the geochemical calculations (Fig. 8). The addition of metal – DOC complexes results in a less positive error as Cu and Zn speciation is shifted from divalent cation species to anionic organic complexes.
Figure 8: Percent error in charge balance based on geochemical speciation calculations with PHREEQC. Results shown for calculations with and without the inclusion of Cu$^{2+}$, Zn$^{2+}$ and H$^+$ complexation by DOC. Note that the high charge balance error at 101 and 144 days for the stabilized column is due to the absence of alkalinity data (cf. Fig. 5).

DISCUSSION AND CONCLUSIONS

Major physical and geochemical processes controlling leachate quality

The relatively large variations in metal and sulfate concentrations in the effluent from the untreated and stabilized columns indicate that a number of physical and geochemical processes are controlling the aqueous composition. These processes include sulfide oxidation, silicate and carbonate weathering, secondary mineral precipitation and dissolution, ion exchange, and metal sorption. In both columns, the initially high concentrations of sulfate, copper, zinc, DOC and magnesium (not shown) that eventually decrease to relatively low, stable concentrations suggest that these compounds are being flushed from the column. Considering the abundance of soluble secondary minerals (e.g. gypsum) in the waste rock, these minerals are most likely dissolving at a constant rate at the start of the experiment, yielding a constant concentration in the column effluent. Effluents concentrations decrease as these mineral phases dissolve and are consumed, at least in regions where active flow occurs. X-ray diffractometry has not indicated the presence of any other soluble secondary minerals than gypsum, but it is likely the hydrated ferrous sulfates are initially present in the waste rock. Minerals such as melanterite (FeSO$_4$$\cdot$7H$_2$O) and rozenite (FeSO$_4$$\cdot$5H$_2$O) are readily soluble and can incorporate relatively large amounts of various trace elements (e.g. Cu, Zn; Nordstrom and Alpers, 1999). Dissolved inorganic carbon is, of course, not derived from mineral dissolution but from labile organic matter that is mobilized during the establishment of a steady – state flow field in the column.

After the initial flushing period, sulfate and Ca concentrations stabilize in both columns. Gypsum equilibrium is probably regulating the sulfate and Ca concentrations, as indicated by gypsum saturation indices (Fig. 7). In addition, however, sulfate concentrations are also partially controlled by the sulfide oxidation rate above the artificial water table. Furthermore, calcite dissolution in the stabilized column provides an additional source of Ca. Calcite is somewhat oversaturated in the column effluent, which may be the result of excess Ca being supplied by gypsum dissolution.

Sulfate is often used as a tracer for sulfide oxidation in laboratory experiments, and the sulfate release rate can often be recalculated to a sulfide oxidation rate (e.g. Gleisner et al., 2006; Malmström et al., 2006). This method assumes that sulfate behaves conservatively. In this study, such an assumption cannot be made since additional equilibrium processes (i.e. gypsum and calcite equilibrium) complicate the accurate determination of sulfide oxidation rates in the material. Reactive transport modeling is required to extract oxidation rates from the analytical data.
Iron is primarily derived from the oxidation of pyrite and pyrrhotite in the waste rock, and also from the dissolution of soluble ferrous sulfates at the start of the experiment (see above). In the stabilized column, iron is apparently also released during the reductive dissolution of Fe oxyhydroxides and jarosite below the artificial water table; the absence of dissolved oxygen and the presence of organic carbon as an electron donor would promote this process. In the oxic conditions that exist above the water table in both columns, Fe concentrations are also controlled by the precipitation of Fe oxyhydroxides.

In contrast to the behavior of sulfate, Cu and Zn in the column effluent, iron reaches maximum concentrations after 40 – 50 days from the start of the experiment. Lower Fe concentrations at the start of the experiment may be explained by a limited availability of molecular oxygen; O₂ may have been consumed by the oxidation of ferrous iron that was released during the dissolution of hydrate ferrous sulfates (see above). Furthermore, this period may correspond to the lag phase of bacterial growth in the column, during which the activity of acidophilic iron-oxidizing bacteria was relatively low.

As a final note, it is necessary to mention that the water residence time in the columns is an important factor that effects the final effluent concentrations. For kinetically controlled processes (e.g. sulfide oxidation), the infiltration rate will generally inversely affect effluent concentrations (i.e. high flow, low effluent concentrations). However, flow rates do not effect concentrations controlled by equilibrium processes (e.g. gypsum dissolution).

**Dissolved organic carbon**

In both columns, a relatively large amount of dissolved organic carbon (DOC) is initially released from the waste rock. Even with the addition of biosludge to the stabilized column, this only resulted in somewhat greater DOC levels (20 – 30 mg/L) in the effluent. In both cases, the effluent DOC concentrations rapidly decrease over the course of the experiment as the result of column flushing. Most of the DOC flushed from the columns is therefore derived from organic matter that is originally present in the waste rock (see Results).

There is often a concern that the interaction of organic material with oxidized mine waste may eventually lead to an increased metal mobilization due to metal – DOC complexation. This concern is commonly voiced with the establishment of sealing layers consisting of sewage sludge on mine tailings, and is also relevant in this study where biosludge is mixed with waste rock. The apparent dissolution of secondary ferric oxides below the artificial water table, in the stabilized column, supports the concern for increased mobilization. Indeed, the speciation calculations indicate that Cu is primary present as an anionic Cu – DOC complex. Nevertheless, the near – neutral pH of the stabilized system prevents significant mobilization as metals adsorb to the abundant Fe oxyhydroxide surfaces directly, form metal – DOC ternary surface complexes, or precipitate as metal carbonates. Since a control experiment was not performed with waste rock stabilized with only paper mill sludge, it is not possible to determine if metal mobility would have been less under these conditions, compared to the current case with a mixture of biosludge and paper mill sludge.

**Effect of stabilization on leachate quality**

The results of this study indicate that the stabilization of sulfidic waste rock with biosludge and paper mill sludge results in near – neutral pH leachate, where concentrations of Cu and Zn are reduced to low levels, compared to untreated waste rock. Based on these results, it appears that the Ca carbonate addition (as paper mill sludge) has a positive effect on effluent quality. The most significant effect of the biosludge addition may be the reductive dissolution of secondary ferric oxides and sulfates (e.g. goethite, jarosite) under oxygen – limited conditions. Although the specific effect of reductive dissolution on leachate quality, in this study, is difficult to separate from other processes controlling leachate composition, it can be assumed that resulting metal releases are not
desirable. Thus, the use of biosludge as a stabilization agent for oxidized mine waste should be avoided below the water table.

REFERENCES


