Sulphate Removal from Acid Mine Drainage: Evaluation of Granular BaCO₃ with Column Experiments

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INTRODUCTION

Acid Mine Drainage (AMD) is the most common pollution related to mining. It consists of an aqueous solution containing high metals and sulphate concentration. Once the mining activity is over, polluting discharges can persist for decades or even centuries with no specific responsible entity. In-situ passive remediation technologies are especially suitable for these orphan sites. The concept is to insert a reactive porous material in the natural flow path of contaminated surface and ground waters, and it is implemented through infiltration ponds and reactive barriers, respectively. Calcium carbonate pea-size gravel is the common alkalinity supplier to neutralize acidity and precipitate metals.

These remediation systems have been traditionally implemented in coal mines. However, the acid drainages from massive pyrite deposits contain metal concentrations one to two orders of magnitude higherthan those from coal mines, and require special designs to avoid quick clogging or passivation (coating) of the grains of reactive material. To overcome these problems, a Dispersed Alkaline Substrate (DAS) mixed from fine-grained limestone sand and a coarse inert matrix (e.g. wood shavings) was developed (Rötting et al., 2008). The small grains provide a large reactive surface and dissolve almost completely before the growing layerof precipitates passivates the substrate. The high porosity and the dispersion of nuclei for precipitation on the inert surfaces retard clogging. However, limestone dissolution only raises pH to values around 6.5, which is sufficient to precipitate the hydroxides of trivalent metals (Al, Fe), but it is not alkaline enough to remove divalent metals. Magnesium oxide, which hydrates to Mg hydroxide upon contact with water, buffers the solution pH between 8.5 and 10. A DAS system replacing limestone with caustic magnesia efficiently remove divalent metals from drainage previously treated with limestone.

The main problem of DAS, however, is the lack of sulphate removal. Only a minor fraction of AMD sulphate is removed by chemical reactions occurring in DAS (schwertmannite, basaluminite and gypsum precipitation). Reducing and Alkalinity Producing Systems (RAPS) have been described to scavenge sulfate from AMD. Essentially, a RAPS is a calcite gravel overlain by a bed of organic matter (compost, manure, etc.), which consumes the dissolved O₂ and reduces Fe(III) to Fe(II). Although it was not originally assumed in the RAPS design, an additional source of alkalinity can be produced from bacterial mediated sulphate reduction in the organic layer. The generation of H₂S and subsequent precipitation of insoluble metal sulphides is also possible within the organic layer, although this process is highly dependent on the water residence time in the system.

The long residence time needed to generate metal sulphides is commonly outside the design of conventional RAPS and DAS. Therefore, alternative methods of sulphate removal have to be tested. We describe here the first column experiments to test the efficiency of a DAS with witherite (BaCO₃) instead calcite to remove sulphate as barite precipitate.

MATERIALS AND METHODS

Two columns were fabricated from transparent polymethyl methacrylate (9.6 cm inner diameter, height 35 cm) and equipped with lateral ports for taking 0.1 µm filtered water samples. One column was filled with a mixture of 430 g calcite sand and 430 g wood chips. The other column was similar, but filled with commercial "Solvay Barium Carbonate Granular- D" (230 g) sand supplied by J. Castillo (Free State University, South Africa). Column porosity was around 0.45 (Fig. 1).

The columns were operated with AMD from Poderosa Mine (SW Spain) as input water, at a mean flow rate of 0.30 L/day or 0.041 m³/m²·day (residence time of 2 days) until the end of reaction (outflow chemistry equal to inflow). The columns had 25 cm of substrate and 5 cm of supernatant, and ports for pore water sampling at 4 cm intervals. Water samples were collected every week at the outflow of the columns, and each two weeks at the sampling ports throughout the column. Substrate and precipitates of the columns were excavated after the end of the experiments from the top and kept dried for observation. After measuring pH, Eh, dissolved O₂ and Electrical Conductivity (EC), the samples were filtered at 0.2 µm, their alkalinity was measured and were acidulated for storage at 4° C. Major and trace elements were measured by ICP-AES and ICP-MS, respectively.
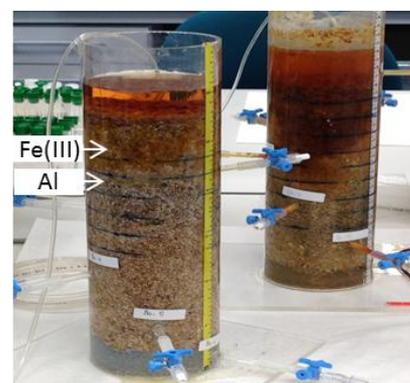
fig 1. DAS-witherite (front) and DAS calcite columns showing the Fe(III) and Al precipitation fronts .

RESULTS AND DISCUSSION

Both columns developed a double reaction front as AMD was neutralized by the dissolution of carbonate filling. Firstly, when pH reached to 3.5, Fe(III) precipitated as schwertmannite. Then, when pH rose up to 5, basaluminite (and amorphous $Al(OH)_3$ in DAS-witherite due to the SO_4 scarcity) formed (Fig. 1). This behavior has been extensively documented for DAS-calcite treatments at column and field scales (Rötting et al., 2008; Macias et al., 2012), and will not be reproduced here.

SO4

Al

pH

Cu

Zn
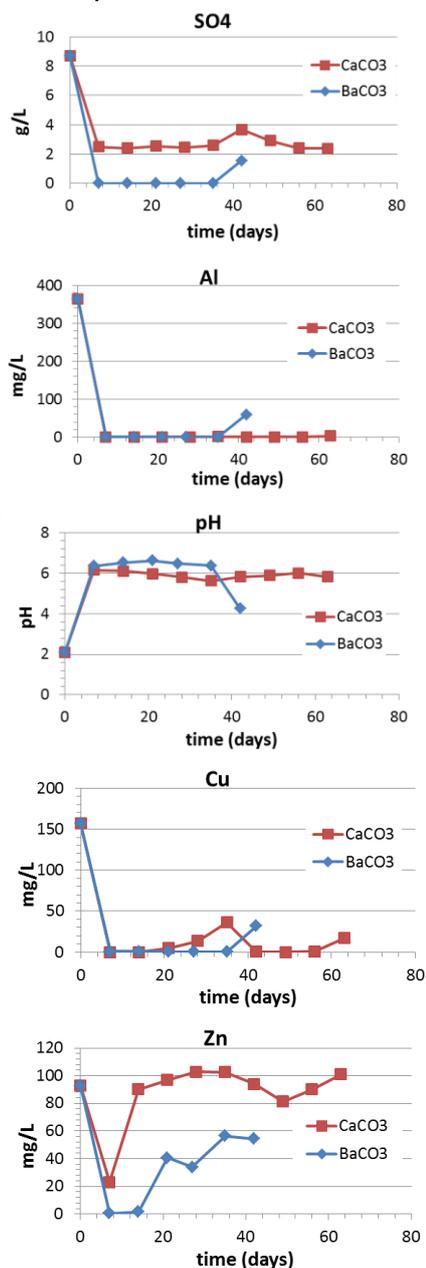
fig 2.Evolution of main parameters in the output solution of the two columns of DAS-calcite and DAS-witherite.

The comparison between the conventional DAS-calcite column and the new DAS-witherite column is in Fig. 2. Removal of Al and Fe(III) was complete in both columns (Fig. 1). Both columns also abated the EC of the water due to the precipitation of schwertmannite and basaluminite. However, the decrease of DAS-whiterite was higher due to the depletion of SO_4 as barite according to the reaction:

$$BaCO_3 + SO_4^{2-} + H^+ = BaSO_4 + HCO_3^-$$
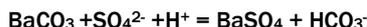
Removal of Cu and REE (do not represented) were also efficient in both cases (Figure 2). Although deeper research is needed, the removal of these elements seems associated to the precipitation of basaluminite. Nevertheless, micron-size plate spots of high Cu concentration have been detected inside basaluminite aggregates under Field Emission-Scanning Electron Microscope. Removal of the rest of divalent metals (Zn, Co, Ni, Cd, Mn) was more efficient in the case of witherite, probably due to the more efficient sorption in basaluminite for the slightly higher pH reached.

DAS-calcite column worked for more than two months, and was expected to be active for months, according to previous experiences (Caraballo et al., 2011). However, DAS-witherite became unreactive after 40 days of functioning as shown by the pH decrease to 4, and increase in metal content (Fig. 2). The post-mortem inspection of the solid residue revealed a dense coating of barite around the witherite grains, that cause their early passivation (Fig. 3).

Taking into account the flow rate, sulphate concentration of the input water and the length of the experiment, only 200 mg of the initial 700 g of witherite have dissolved.

CONCLUSION

DAS-witherite was much more efficient than calcite in removing SO_4 and divalent metals from solution. However, coating of the granular witherite grains with barite caused the early passivation of the reagent when a very minor fraction of the reactive was consumed. This fact, together with the high price of commercial granular witherite makes it uncompetitive with respect to calcite in AMD passive remediation systems.
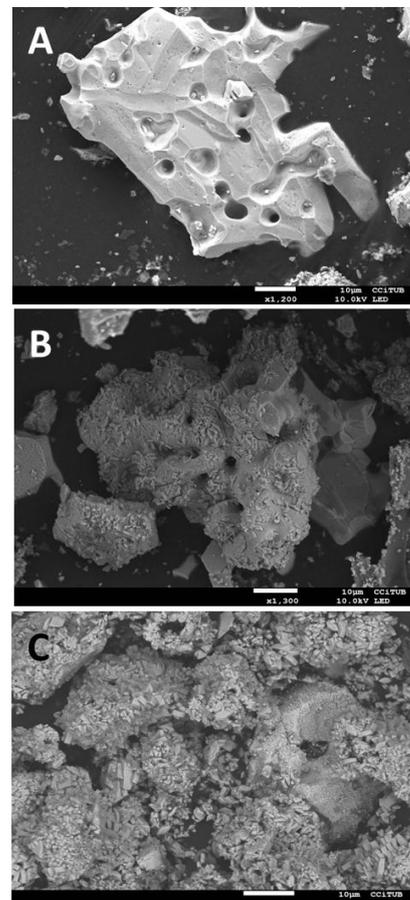
fig 3. Progressive coating and passivation of witherite grains (A) with barite (B,C). Images of Field Emission Electron Microscope.

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