

CHEMICAL AND HYDRAULIC PERFORMANCE OF “DISPERSED ALKALINE SUBSTRATE” (DAS) FOR PASSIVE TREATMENT OF ACID MINE DRAINAGE WITH HIGH METAL CONCENTRATIONS

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Abstract

Passive treatment systems are being employed increasingly to treat acid mine drainage. Nevertheless, conventional calcite- or organic matter-based systems are prone to clogging and passivation (loss of permeability or reactivity) when treating high metal concentrations, and do not remove satisfactorily divalent metals such as Zn, Mn, Cu, Pb, etc. In the present study, a novel “Dispersed Alkaline Substrate” (DAS) consisting of a fine-grained alkaline reagent (calcite or MgO) mixed with a coarse inert matrix (wood chips) was used to treat waters with high metal concentrations. The coarse inert matrix of DAS ensures a high permeability of the bulk substrate, while the small alkaline grains can react almost completely before the growing layer of precipitates impedes further dissolution. Calcite sand was used in calcite-DAS to remove Al, Fe(III), Cu and Pb almost completely from AMD with $\text{pH} \approx 3$ and mean net acidity of 1500 mg/L as CaCO_3 . Caustic magnesia (MgO) dust was used in MgO-DAS to deplete 300 mg/L Zn and 30 mg/L Mn to below ICP-AES detection limit. Depth profiles of chemical parameters and hydraulic conductivity were regularly measured in laboratory column studies during over one year. The experiments show that DAS combines high reactivity, good hydraulic performance and maximum durability of the alkaline reagents.

Introduction

Conventional passive treatment systems based on the dissolution of calcite gravel are widely used to remediate acid mine drainage. Nevertheless, they only tolerate low metal concentrations or acidity loads, because they are prone to clogging and passivation (loss of permeability or reactivity; e.g. Younger et al., 2002; Watzlaf et al., 2004). Also, calcite- or organic matter-based systems do not remove satisfactorily divalent metals such as Zn, Mn, Cu, Pb, Ni, Cd, Co etc. (Cortina et al., 2003). Therefore, new passive treatment designs are necessary to treat waters with high metal concentrations.

In order to overcome these problems, a novel Dispersed Alkaline Substrate (DAS) made up of calcite sand and wood chips was developed. It consists of an inert, coarse high-surface media mixed with a fine-grained alkaline material, so that the surfaces of the inert material are covered with the reactive material. The small grain size of the alkaline material provides a greater reactive surface than the same amount of coarse material, which should increase reactivity. Also, a larger fraction of each grain should dissolve before the crust of precipitates becomes too thick and impedes further dissolution. This should reduce passivation. The coarse particles of the inert material provide large pores and high permeability and separate individual limestone grains, so that precipitates do not fill the entire pore space between grains. This should reduce clogging problems.

Calcite dissolution usually produces a pH between 6 and 7, at which trivalent metals such as Fe(III) and Al have low solubilities. Nevertheless, this pH is insufficient to precipitate divalent metals. Caustic magnesia (MgO), which hydrates to brucite ($\text{Mg}(\text{OH})_2$) upon contact with water, buffers solution pH between 8.5 and 10 where solubilities of many divalent metals are low (Cortina et al., 2003). It is therefore an attractive material for the passive treatment of water with high divalent metal concentrations. However, columns with coarse-grained MgO had lost reactivity or permeability due to the accumulation of precipitates when only a small portion of the reagent had been spent (Cortina et al., 2003). We postulate that the application of MgO in Dispersed Alkaline Substrate should overcome these problems.

This study presents laboratory column tests which investigate the chemical and hydraulic effectiveness of calcite-DAS and MgO-DAS to treat waters with high metal concentrations.

Materials and Methods

Two columns were fabricated from transparent acrylic glass (9.6 cm inner diameter, height 35 cm). Sampling ports for 0.1 μm filtered water samples (Eijkkelkamp Macro Rhizon[®]) and pressure ports for measurement of hydraulic conductivity were placed at depth intervals of 2.5 - 5 cm. Both columns contained a perforated drain pipe (outlet) and a 2.5 cm layer of quartz gravel at the bottom. One column was filled with 18 cm of calcite-DAS made up of 25 vol % limestone sand ($d_{10}=0.3$ mm, $d_{50}=1.2$ mm, $d_{100}=5$ mm) and 75 vol % wood chips, and was used to treat Al- Fe- and Zn-rich real AMD with $\text{pH} \approx 3$ and mean net acidity 1500 mg/L as CaCO_3 (100 mg/L Al, 250 mg/L Fe, 370 mg/L Zn, 22 mg/L Mn, 3 mg/L Cu, 0.7 to 0.15 mg/L Co, Ni, Cd, Pb) from a metal mine in

Southern Spain. The second column was filled with 13 cm of MgO-DAS which contained only 12.5 vol % of caustic magnesia ($d_{10}=0.06$ mm, $d_{50}=0.1$ mm, $d_{100}=1$ mm) and 87.5 vol % wood chips, and was used to treat synthetic solutions with 300 mg/L Zn and 30 mg/L Mn and pH 6. The input solutions were fed to the supernatant of the columns with a Gilson[®] Minipuls 3 peristaltic pump at flow rates ranging from 0.16 to 0.76 L/day (0.023 to 0.11 m³/m²-day).

pH was measured using a Crison[®] glass electrode, redox potential was measured using a ThermoOrion SureFlow[®] Pt combination electrode. Total (gross) alkalinity was measured using CHEMetrics[®] "Titrets" test kits. Major cations (Ca, Mg, Zn, Fe, Al, Mn, Si) and total S were measured by ICP-AES (Perkin-Elmer[®] Optima 3200 RL) and trace metals (Cu, Ni, Cd, Co, Pb) by ICP-MS (Perkin-Elmer[®] Sciex Elan 6000). Ferrous and total Fe were measured by spectrophotometer (Stookey, 1970), Fe(III) was calculated as difference.

Net acidity (mg/L as CaCO₃ equivalents, denoted "mg/L" in the following) was calculated according to Kirby and Cravotta (2005) as:

$$\text{Net acidity} = 50045 * (3 * c_{Al} + 2 * c_{Fe} + 2 * c_{Mn} + 2 * c_{Zn} + 10^{-pH}) - \text{alk}$$

where c_X are molar concentrations (mol/L) and *alk* is measured gross alkalinity (mg/L as CaCO₃ equivalents). The factor 50045 converts moles of charge into mg of CaCO₃ equivalents.

Relative metal removal *r* (%) at the drain pipe was calculated as

$$r = \frac{(c_{sup} - c_{out})}{c_{sup}} \cdot 100$$

where c_{sup} is supernatant concentration (mg/L) and c_{out} is drain pipe concentration (mg/L).

Hydraulic conductivity profiles of the substrates were calculated using Darcy's Law by measuring head-loss between the different pressure ports at high flow rates. Porosity of the calcite-DAS column was determined close to the beginning and end of the experiment by injecting distilled water with a known concentration of Br⁻ tracer. Both saturation and desaturation curves were measured at the column outflow using a ThermoOrion ionplus[®] Br⁻-electrode. Initial porosity of the MgO-DAS column was measured gravimetrically while saturating the column with water. No tracer tests were performed on this column.

After the end of the experiments, the substrate and precipitates of the columns were excavated from the top in a glove box under N₂ atmosphere. Powder diffractograms of ground samples were obtained using a Bruker[®] D5005 X-Ray Diffractometer (XRD) with Cu K α radiation. Total inorganic carbon (TIC, essentially the amount of carbonates) was determined by measuring the volume of CO₂ gas produced after addition of 16% HCl to a known mass of ground solid sample. Chemical compositions of the solid samples were determined by dissolution in HNO₃ 7.5 M and analysis by ICP-AES.

Results and Discussion

1. Calcite-DAS column

pH of the calcite-DAS column (Fig. 1) rose from values between 2.5 and 3 in the input and supernatant to 6.0 - 6.4 at the drain pipe and further to 6 - 7 in the output container due to CO₂ degassing. The high values of pH 4 in the supernatant and 8.4 in the output container (weeks 14 to 20) were due to injection of distilled water during the first tracer test. Net acidity and metal concentrations of the input water varied due to natural variations of the AMD which was collected periodically in the field. During weeks 6 to 13 and 34 to 38, 200 mg/L of Fe(II) as FeSO₄·7H₂O were added to the input AMD to study the effect of higher Fe(II) concentration on the column. Net acidity elimination fluctuated between 900 and almost 1600 mg/L (mean 1150 mg/L). Aluminium removal ranged from 90 % to > 99 %. Total Fe varied considerably in the input container due to oxidation of Fe(II) and precipitation of Fe(III) phases. Dissolved Fe in the supernatant was mostly Fe(III) (2%-55% Fe (II)). 90 % to > 99 % of Fe(III) were eliminated within the substrate. Iron inside the substrate and in the drain pipe was mostly Fe(II) (73-98%). Concentration of Fe(II) decreased by up to 70 mg/L from the supernatant to the drain pipe due to oxidation and subsequent precipitation. On average, 99 % of Pb and 94 % of Cu were removed (not shown). Zinc, Mn, Cd, Ni and Co were not significantly removed in the calcite-DAS column, but some Zn, Ni and Cd was precipitated in the output container (not shown).

Hydraulic conductivity of the high-flow column was measured for the first time after two weeks (Fig. 2A). By then, it had already accumulated important brownish precipitates in the first 3 cm of the substrate, but hydraulic conductivity was still very high in depth. With time hydraulic conductivity decreased throughout the substrate and especially in its upper part, but the calcite-DAS column did not clog at any time. The first series of tracer tests was conducted after 15 weeks of operation and yielded a mean calculated porosity of 73%. After 63 weeks

of operation, a second series was conducted. Mean calculated porosity was 82%. This indicates that porosity of the substrate increased, and that calcite dissolution created at least as much pore space as was consumed by formation of precipitates. The porosity values are higher than those obtained in granular substrates (maximum usually about 40% for well-sorted spheres), because the curved flakes of wood in DAS form a matrix with larger pore space than round particles of the same size.

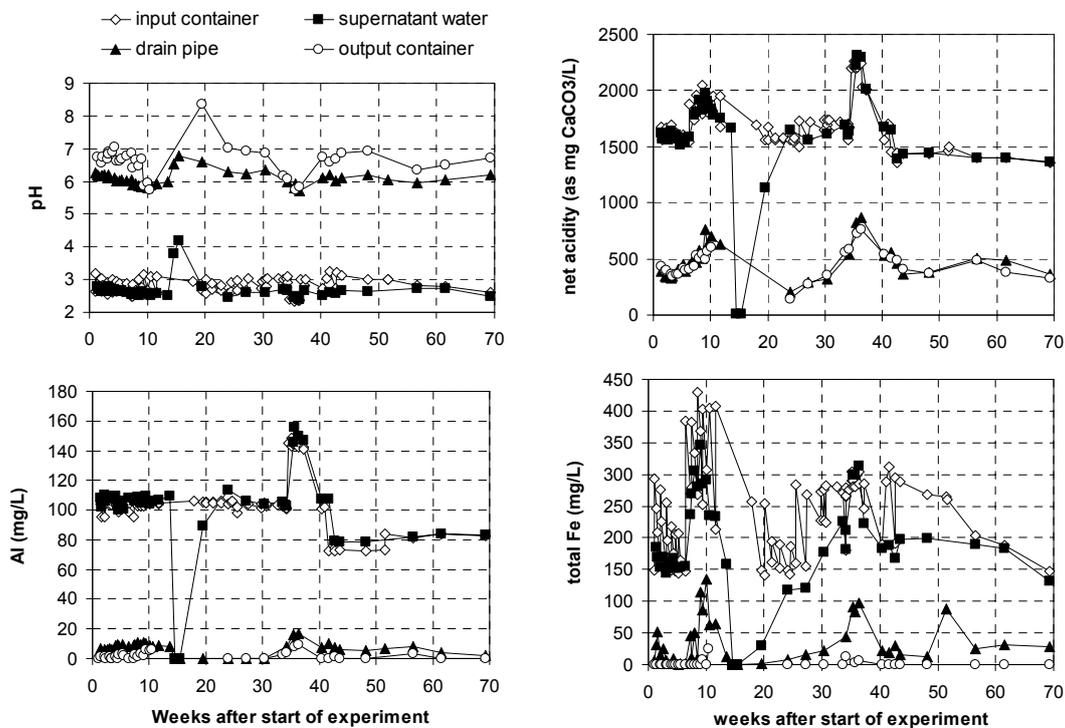


Figure 1. pH, net acidity, Al and total Fe at different sampling points of the calcite-DAS column.

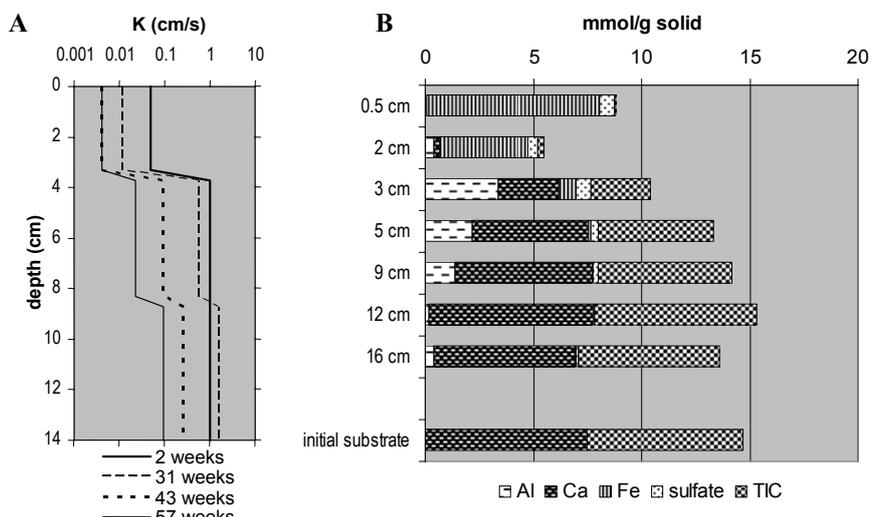


Figure 2. (A) Hydraulic conductivity profiles and (B) composition of solid samples from the calcite-DAS column.

The uppermost 3 cm of excavated substrate of the calcite-DAS column consisted of moderately cemented wood chips covered with dark brown Fe-rich precipitates (Fig. 2B). Calcite had dissolved almost completely, which shows that Fe precipitates do not passivate DAS. XRD showed the characteristic peaks of goethite, but molar Fe:S ratios in these samples ranged from 8 to 11, suggesting that a mixture of goethite and schwertmannite was present. From 3 to 10 cm depth, a hard, yellowish-white precipitate covered the wood chips and calcite grains.

This layer contained high Al concentrations, especially in the upper part. XRD revealed peaks of calcite and gypsum, but no peaks could be attributed to any Al-bearing compound. Molar Al:S ratios of the bulk samples (after correction for S associated with gypsum) ranged from 5.8 to 9.7. This indicates that amorphous Al-hydroxysulphates and Al-hydroxides precipitated inside the DAS columns. From 10 cm depth to the bottom, the column contained loose wood chips and calcite grains with few white precipitates. XRD showed only the peaks of calcite and gypsum.

2. MgO-DAS column

Drain pipe pH of the MgO-DAS column was near 10 throughout the study; drain pipe Mg concentration rose to 120 mg/L within 10 weeks and remained close to this value (Fig. 3). Zinc and Mn were always below detection limit at the drain pipe. pH in the output container was near 8 at all times (maximum 8.65). The decrease with respect to the drain pipe value is probably due to CO₂ uptake from the atmosphere. This is an advantageous property, because very alkaline waters usually have to be neutralized with additional chemicals before discharge to comply with regulations. While this is often necessary after treatment with lime, caustic soda etc. which produce pH > 11, it is unnecessary for treatment with caustic magnesia.

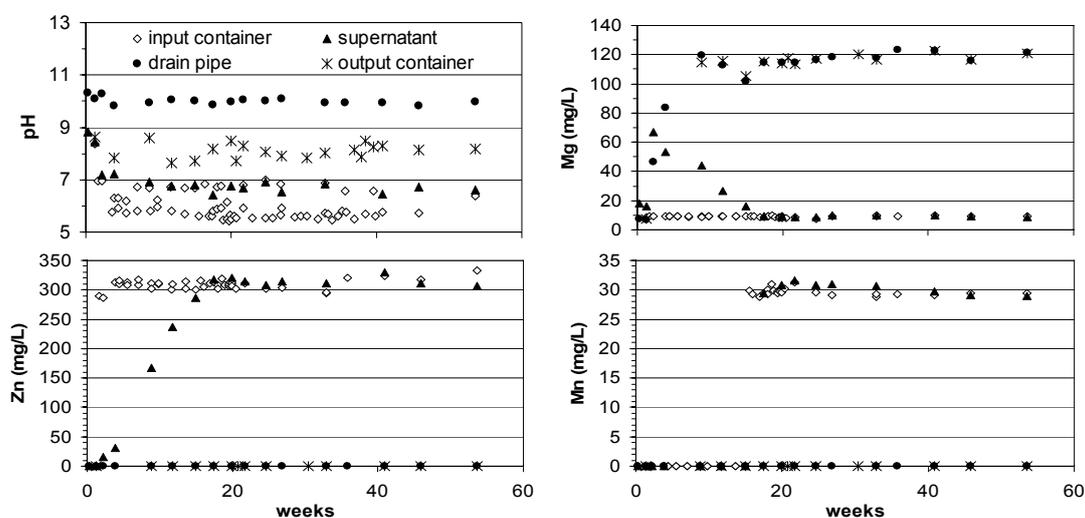


Figure 3. pH, Mg, Zn and Mn at different sampling points of the MgO-DAS column.

Initial gravimetric porosity of the MgO-DAS column yielded 71%. Hydraulic conductivity was high throughout the substrate during the first two measurements, except for the depth interval 1-3.5 cm where it decreased with time (Fig. 4A). In the last measurement, it had also decreased considerably in the interval 3.5-8.5 cm. This suggests that precipitates were accumulating in an increasing volume of substrate over time. Despite the substantial decrease of hydraulic conductivity, the MgO-DAS column did not clog at any time.

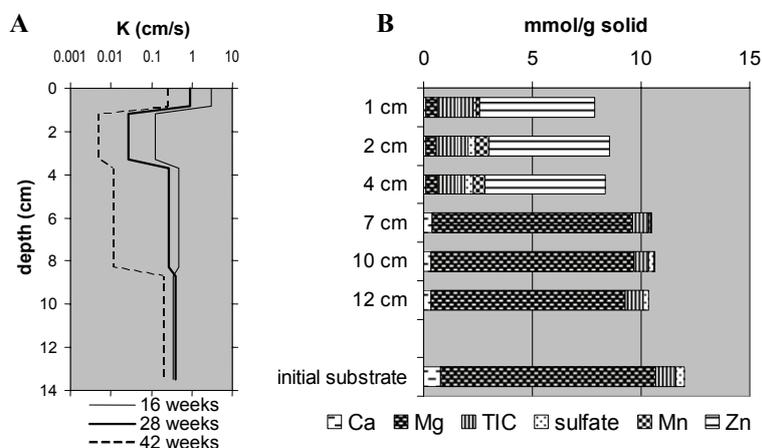


Figure 4. (A) Hydraulic conductivity profiles and (B) composition of solid samples from the MgO-DAS column.

Up to 6 cm depth the column contained cemented wood chips covered by dark grey precipitates and white spots with high Zn concentrations and some sulfate and Mn (Fig. 4B). Residual Mg was only about 5% of the initial concentration, demonstrating that the MgO-DAS uses the alkaline reagent very efficiently. XRD revealed peaks of brianyoungite ($Zn_{12}(CO_3)_3SO_4(OH)_{16}$), $Zn(OH)_2$, hydrozincite ($Zn_5(CO_3)_2(OH)_6$) and $Zn_4CO_3(OH)_6 \cdot H_2O$. No Mn-bearing phase could be identified by XRD. This had to be expected, because Mn concentrations in the input solution and in the solid samples were about ten times lower than those of Zn. From 6 cm depth to the bottom, the column contained loose wood chips covered with brownish dust, apparently unreacted MgO. These samples contained about 10% less Mg than the initial substrate. This confirms that metal elimination was essentially complete above 7 cm depth in the MgO-DAS column.

Conclusions

- The calcite-DAS column removed 900-1600 mg/L net acidity as $CaCO_3$, 3 to 4.5 times more than conventional passive treatment systems.
- The oxic supernatant is an essential part of the treatment system when high Fe(II) concentrations are present in the input water. In this study, the column supernatant was capable of oxidizing up to 70 mg/L of Fe(II).
- Al, Fe(III), Pb and Cu were almost completely removed within the calcite-DAS column. Some Zn, Ni and Cd were removed at low flow rates.
- Removal of divalent metals (e.g. Zn, Mn, Ni, Cd, Co) was poor in calcite-DAS, because these metals hydrolyze at a higher pH than that achieved by calcite dissolution.
- 300 mg/L Zn and 30 mg/L Mn were successfully removed using MgO-DAS. Other divalent metals (Cu, Pb, Cd, Ni, Co) can also be removed using MgO (Cortina et al., 2003; Rötting et al., 2006).
- The detailed hydraulic conductivity profiles indicate that metal precipitates reduce DAS permeability over time. Nevertheless, both DAS columns were operated during over one year without clogging. Despite precipitation of Al, Fe and other metals, the pore volume of the calcite-DAS column increased.
- DAS reactivity is greater than that of limestone gravel based conventional passive treatment systems, because in DAS fine-grained alkaline materials can be used which provide a higher reactive surface. This minimizes passivation of DAS.
- The high acidity removal is possible because Al, Fe(III) and other metals accumulate intentionally in DAS. Metal hydrolysis and precipitation release protons which enhance calcite dissolution.
- The large pores of the inert DAS matrix and the dispersion (separation) of the alkaline grains minimize clogging problems in DAS.

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