Passive treatment of Acid Mine Drainage with high metal concentrations: Results from experimental treatment tanks in the Iberian Pyrite Belt (SW Spain)

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ABSTRACT

Passive treatment of acid mine drainage (AMD) have been applied successfully at many sites where metal concentrations are relatively low, but experience is scarce for waters with higher metal loads. In this study, we tested the suitability of caustic magnesia (MgO) as an alkaline reagent at field scale, with and without a prior calcite dissolution step. Three pilot systems where tested at the “Monte Romero” mine (Southwest Spain). One treatment tank was filled with a mix of MgO and silica gravel only, while a second one contained two layers of calcite followed by one of MgO. The third tank was similar to a reducing and alkalinity producing system (RAPS). It contained layers of calcite mixed with sheep manure followed by MgO mixed with silica gravel. The RAPS received water with an very high acidity of up to 29000 mg/L as $CaCO_3$ equivalents, while inflow acidity of the other two tanks was around 2380 mg/L as $CaCO_3$.

The tank which contained only MgO had severe clogging problems from the beginning, and showed a poor chemical performance. The tank containing calcite and MgO and the RAPS removed high portions of Al and Cu, but only small to insignificant portions of Fe and Zn. Aeration and decantation improved the removal of Fe. Calcite eliminated acidity more effectively than MgO. Nevertheless, the calcite and magnesia tank clogged after seven months of operation due to precipitation of Al-phases.

Comparison with published data revealed that even though percentage removals were below our expectations, performance in absolute values was good compared to other systems. The high acidity removal rates are due to the elevated Al concentrations which are easily removed.

INTRODUCTION

During the last two decades, passive systems have become a widely used option for the treatment acid mine drainage (AMD) in northern America and increasingly in Europe (e.g. Younger *et al.,* 2002, Ziemkiewicz *et al.,* 2003). Nevertheless, these systems have mainly been applied at coal mines and other sites with relatively low metal concentrations, while experience is scarce for waters with higher metal loads. The abandoned mines of Iberian Pyrite Belt (SW Spain) discharge acid waters with high heavy metal concentrations to the Rio Tinto and Rio Odiel river basins (e.g. Olias *et al.*, 2004). Passive treatment systems which once built only require naturally available energy sources and infrequent maintenance may be an economical option to improve water quality in this region.

Passive treatment system are usually based on calcite dissolution which achieves an outflow pH up to about 8 (Younger *et al.,* 2002, Cortina *et al.,* 2003). Nevertheless, this pH may be insufficient to precipitate divalent metals (Cortina *et al.,* 2003) such as Zn, Mn, Cu, Pb, Ni, Co, and Cd which are often found in AMD (Younger *et al.,* 2002). Caustic magnesia (MgO) has the attractive property of raising solution pH up to 9-10, where divalent metals precipitate readily as hydroxides. In laboratory column studies (Cortina *et al.,* 2003), it was found that MgO can reduce concentrations of 75 mg/L of Zn, Cu, Pb and Mn in the inflowing water to values below 0.04 mg/L. Nevertheless, MgO has not yet been applied in passive treatment systems at field scale.

In this study, we tested the suitability of caustic magnesia (MgO) as an alkaline reagent at field scale in three pilot systems, with and without a prior calcite dissolution step.

MATERIALS AND METHODS

The present study was carried out at the “Monte Romero” abandoned mine in South-western Spain (Huelva province, Fig. 1). This was a massive pyrite deposit with minor amounts of Zn, Pb and Cu sulphides. The enclosing rocks are siliclastic schists with no carbonate beds present. The AMD emerging from the adit has a mean pH of 3.3, an acidity of over 2300 mg/L as $CaCO_3$ equivalents and contains 400 mg/L Zn, 350 mg/L Fe (83% Fe(II)), 260 mg/L Mg, 210 mg/L Ca, 130 mg/l Al, 18 mg/L Mn, 11 mg/L Cu and 1200 mg/L sulphate. Flow rate is usually around 2 L/s.

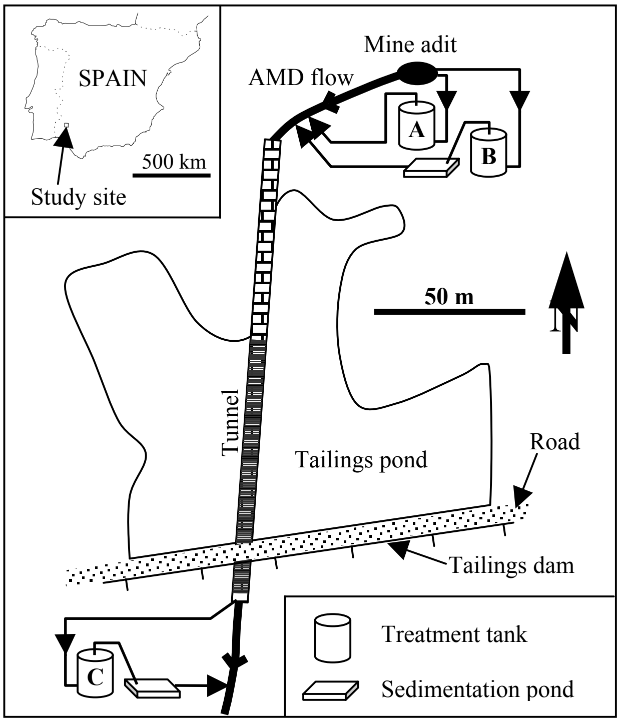

Figure 1: Schematic map of Monte Romero field site and location of experimental treatment tanks

Filling materials

- Caustic magnesia (MgO) was provided by Magnesitas de Navarra S.A. In this study, a residue from the magnesite calcination process was used. It contains 60-70% of MgO, together with minor amounts of silicates and carbonates. It is economic, but it has a wide range of particle sizes from powder to pebble size (0-2 cm)
- Calcite gravel (99% $CaCO_3$, particle size 0.6-1.2 cm) was purchased at a quarry near Morón de la Frontera.
- Silica gravel (0.5-2 cm) was purchased at a local quarry.
- Sheep manure was obtained from a local farm.

Description of treatment tanks

220 L plastic barrels were used as upflow reactors. Two treatment tanks (“A” and “B”) were installed close to the adit where AMD emerges from Monte Romero Mine (Fig. 1). The input water is taken directly from the adit and feeds the tanks by gravity flow. Tank “C” was installed at the exit of the tunnel that passes underneath the tailings pond. The input water is taken from a V-notch weir located inside the tunnel and feeds the tank by gravity flow. In all tanks AMD enters at the bottom where a layer of quartz gravel distributes flow evenly, flows upwards through the reactive material and exits the barrel though an elbow pipe in the lid. Flow rate was controlled by a compression valve at the inlet. All tanks were equipped with piezometric tubes connected to the in- and outlet and to the intermediate sampling points in order to measure hydraulic conductivity. The tanks were set up from September 17th to 19th of 2003 and operated until July of 2004.

Tank A (Fig. 2) contains a mixture of 15 vol. % of MgO and 85 vol. % of quartz gravel. It was designed to act in a similar manner as an anoxic limestone drain. Design flow rate was calculated as 220 mL/min (residence time 6 hours with a supposed porosity of 40%). In laboratory trials (Cortina *et al.*, 2003), this residence time had proven sufficient for equilibrium between caustic magnesia and the input solution.

Tank B contains (from bottom to top) 25 cm of 50 vol. % calcite gravel and 50 vol. % quartz gravel, 32 cm of pure calcite gravel, and 25 cm of 50 vol. % MgO and 50 vol. % quartz gravel. A sampling port is located at the contact between the upper calcite and the caustic magnesia layer. The calcite layer was introduced to provide a first rise of pH, MgO was meant to boost pH up to higher values (ph 9-10) than those achievable by calcite dissolution (pH 8). Design flow rate was calculated as 55 mL/min as to provide a residence time of 16 hours within the calcite layers and 6 hours within the MgO layer.

Tank C contains (from bottom to top), 25 cm of 35 vol. % sheep manure and 65 vol. % quartz gravel, 38 cm of 25 vol. % sheep manure and 75 vol. % calcite gravel, and 16 cm of 50 vol. % caustic magnesia and 50 vol. % quartz gravel. These three reactive zones are separated from each other by layers of 6 cm of quartz gravel equipped with sampling ports (Fig. 2). Tank C was designed to act in a similar manner as a reducing and alkalinity producing system (RAPS), again with MgO as a final pH booster. Design flow rate was calculated as 30 mL/min (residence time of 24 hours within the manure layers and 6 hours within the MgO layer).

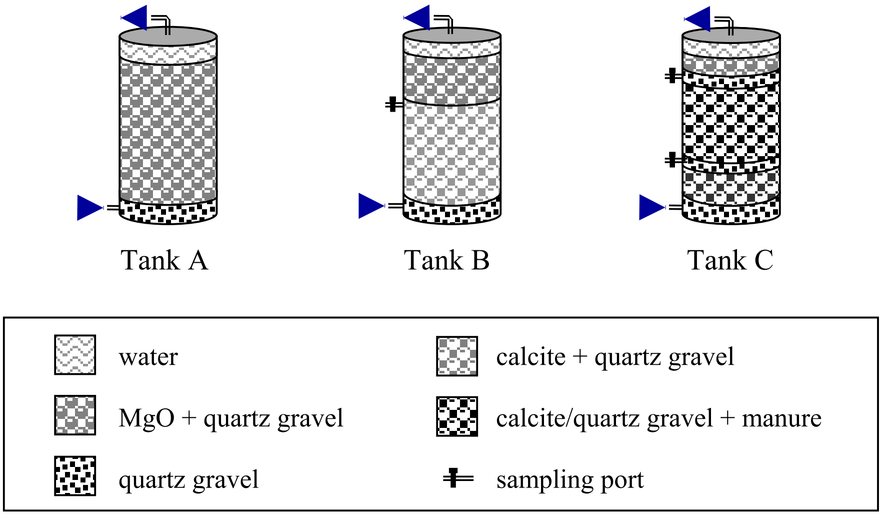

Figure 2: Filling materials of the treatment tanks

Field monitoring and sampling

Periodically (intervals from 1 to 2 months), water samples were taken at the in- and outlet of the tanks and at the intermediate sampling ports. Field pH, temperature and redox measurements were made using Crison electrodes. For analysis of mayor elements, samples were filtered through 0.45 µm and acidified with HNO_3 to pH lower than 1. For iron speciation, samples were filtered through 0.1 µm and acidified with HCl to pH lower than 1 and stored in the dark. Mayor elements were analysed with ICP-AES, total iron (Fe_{tot}) and Fe(II) were determined spectrophotometrically (ferrozine method modified after To *et al.,* 1999). The concentration of Fe(III) was calculated as the difference between Fe_{tot} and Fe(II).

Acidity (mg/L as $CaCO_3$ equivalents) was calculated as

$$Aci = 50045 * (3*c_{Al} + 2*c_{Cu} + 3*c_{Fe} + 2*c_{Mn} + 2*c_{Zn} + 10^{-pH}) \qquad (1)$$

where c_X are molar concentrations (mol/L).

After seven months of operation, the reactive material of tanks A and B was dug out and solid samples were taken in order to investigate the newly formed precipitates. The samples were observed under a JEOL 3400® Scanning Electron Microscopy with Energy Dispersive System (SEM-EDS). The mineral phases were identified with a BRUKER D5005® X-Ray Diffractometer (XRD), with Cu Lα radiation. Moreover, portions of each sample were dissolved in 1M HCl for analysis of mayor cations and sulphur in order to obtain more detailed information about its chemical composition.

Evaluation of treatment performance

Overall treatment performance was evaluated in terms of :

- Absolute metal (mg/L) or acidity (mg/L as $CaCO_3$) removal R_{abs}

$$R_{abs} = c_{in} – c_{out} \qquad (2)$$

where c_{in} and c_{out} are in- and outlet metal concentration or acidity, respectively.

- Relative metal or acidity removal R_{rel} (%)

$$R_{rel} = 100 * (c_{in} – c_{out})/c_{in} \qquad (3)$$

In tanks B and C which contained calcite and MgO, the relative contributions of both reagents in the generation of alkalinity were estimated from the rise in Ca and Mg concentrations between the in- and outlet of each tank.

Comparison with published data

The performance of the treatment tanks was also compared with a study by Ziemkiewicz *et al.* (2003) where 83 passive treatment systems were evaluated. For each published system and each tank of this study, the following statistics were computed:

- Inflow acidity,
- Absolute acidity removal
- Relative acidity removal
- Acid load reduction normalized by system area R_A (g/(m^2*day))

$$R_A = Q * (Aci_{in} – Aci_{out})/A \qquad (4)$$

where Q is flow rate (m^3/day) and A is horizontal area of the treatment system (m^2).

- Acid load reduction normalized by substrate mass R_m (g/(t*day))

$$R_m = Q * (Aci_{in} - Aci_{out})/m \quad (5)$$

where m is the mass of reactive substrate used in the treatment system (t).

RESULTS AND DISCUSSION

It proved to be very difficult to maintain the rather low flow rates. The valves clogged frequently due to formation of precipitates. In each sampling campaign, flow was always much lower than the value that had been established at the end of the last campaign, and on several occasions flow had stopped completely. Due to these fluctuations of flow rate, the chemical performance also varied considerably between campaigns. In the following, results will be presented as median values over all the samples taken at each sampling point in order to put less weight on extreme values.

Tank A

Tank A clogged immediately after construction. The pores of the reactive material became obstructed by a fine-grained paste which revealed to consist of brucite with some calcite and a minor fraction of gypsum. This effect was also observed to a lesser extent in the MgO layers of tanks B and C. The MgO layers of the tanks were excavated and washed in order to eliminate the fine-grained material.

During the following months, median flow rate was 120 mL/min, about half of the intended value. Despite this low flow rate, chemical performance was poor (Fig. 3). PH rose slightly above 4, and only 17% of Al, 11% of Cu, 10% of Zn, 7% of Fe and 7% of Mn were eliminated (all median values). Only on one occasion (not shown), removals between 26% and 35% for Al, Cu and Fe and of 17% for Zn were measured at a very low flow rate of 26 mL/min and an outflow pH of 4.3.

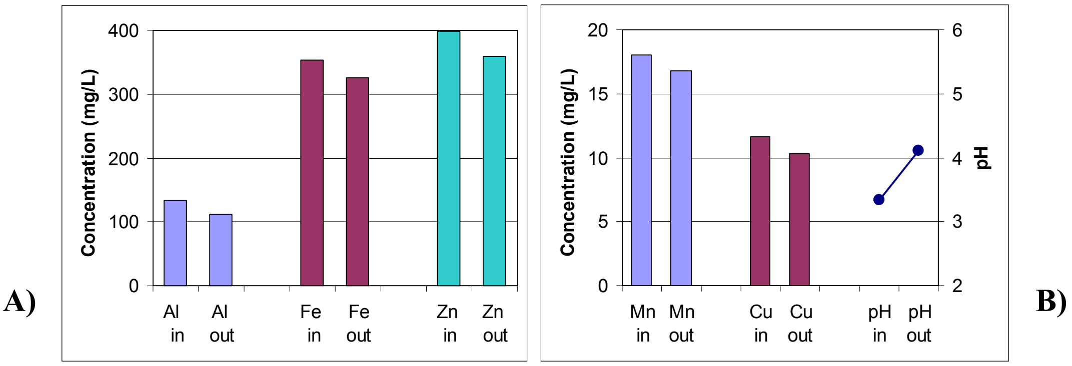

Figure 3: A) Medians of Al, Fe and Zn concentrations, B) medians of Mn and Cu concentrations (columns) and pH (filled circles) at the in- and outlet of Tank A

After seven months, the filling material was sampled. Near the outlet, precipitates with high amounts of Fe (identified as Schwertmannite) and minor fractions of Al and/or Zn were found. The pores of the reactive material were found to be filled again by a fine-grained paste that contained brucite and some gypsum. Even though the reactive material had been washed, a thorough examination revealed that some of the coarser grains of the caustic magnesia were conglomerates of fine-grained material which probably broke down gradually during operation. Therefore, it is possible that flow only passed through a small fraction of the whole volume of tank A, diminishing the contact between the water and the reactive material and lowering the real residence time.

The hydraulic conductivity of the reactive material decreased steadily from 1500 m/day immediately after washing the material to only 50 m/day after seven months.

Tank B

The flow rate varied between 7 and 182 mL/min, with a median value of 114 mL/min, about twice the design flow. Despite this high flow rate, chemical performance (Fig. 4) was better than in tank A. PH increased to values between 4.4 and 6.2, and median removal rates of 67% for Al, 52% for Cu, 16% for Zn, 10% for Fe and 5% for Mn were achieved. After four months of operation, a tracer test was performed in order to measure the porosity of the reactive material. The porosity of the calcite layer was determined to be 41%, that of the MgO layer 34%.

After seven months of operation, the different layers of reactive material were excavated and sampled. Just the day before solids sampling, the flow in tank B had ceased completely. Excavation revealed that a hardpan had formed at the contact between the 50% calcite/50% quartz layer and the pure calcite layer. The cement of the hardpan contained a high amount of Al and minor concentrations of Fe, Ca and sulphate. XRD detected only gypsum, but the high content of Al suggests that the cement was mainly made up of amorphous Al-hydroxide or -hydroxysulphates. Similar precipitates have been found in other calcite bases passive treatment systems receiving Al-rich AMD (e.g. Robbins *et al.*, 1996; Watzlaf *et al.*, 2000). Also the precipitates found near the outlet of the tank contained high concentrations of Al and sulphate, and minor amounts of Fe, Zn, Ca and Si.

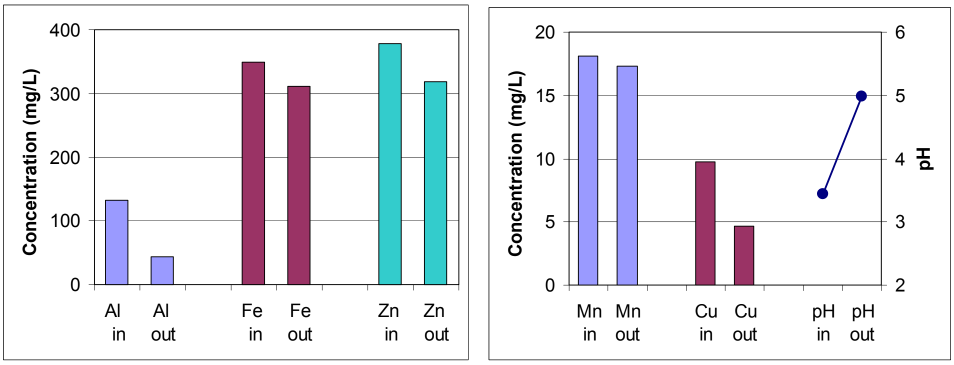

Figure 4: A) Medians of Al, Fe and Zn concentrations, B) medians of Mn and Cu concentrations (columns) and pH (filled circles) at the in- and outlet of Tank B

Precipitates scraped from the surface of MgO fragments in the MgO layer had very high concentrations of Zn. Even though XRD did not identify any crystalline Zn-bearing phase, this suggests that Zn precipitates directly at the surface of caustic magnesia fragments.

The low removal rate of Fe at the outlet of tank B is due to the high fraction of Fe(II) (about 83%) in the AMD. After the sampling of the reactive material, tank B was filled again and AMD flow was reconnected. An aeration cascade and a small sedimentation pond (area 1 m^2, volume 55 L) were installed at the outlet of the tank, and operation of the system continued for two months. The excavation of the reactive material reactivated the chemical performance of the system (Fig. 5), probably by exposing new alkaline surfaces. PH at the outlet of the tank rose to over 6, and 18% of the inflow concentration of Fe were eliminated. The removal rates of Al, Cu and Zn were also higher than the median values of the entire sampling period (not shown). The sedimentation pond increased the removal of Fe to 47%, while pH lowered less than 0.8 units. Median flow rate during this period was 73 mL/min, leading to a residence time of about 12h in the sedimentation pond. Probably a larger pond with a longer residence time or an additional step of aeration and sedimentation could even have increased Fe removal, because pH at the outflow of the pond was still well above the inlet value. The precipitates collected in the pond contain high concentrations of Al, Fe and sulphate, and minor amounts of Zn, Ca and Si. XRD detects gypsum and Bianchite (zinc sulphate hydrate).

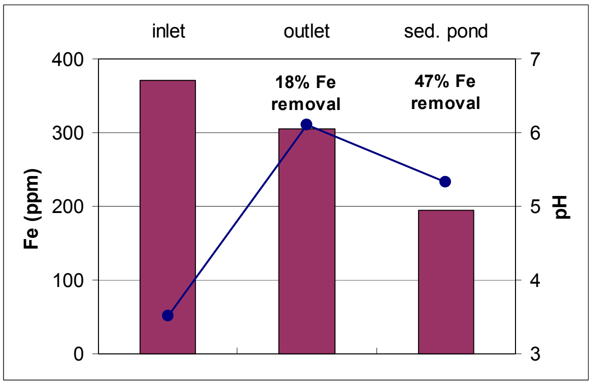

Figure 5: Effect of the aeration and sedimentation system on Fe elimination: Mean Fe concentrations (columns) and pH (filled circles) at the in- and outlet of Tank B and at the outlet of the sedimentation pond, and Fe removal relative to the inlet concentration

The hydraulic conductivity of the reactive material diminished steadily from an initial value of about 700 m/day to only 10 m/day after seven months. After the solids sampling, the hydraulic conductivity rose again to 400 m/day and stayed constant during the last two months of the experiment.

Tank C

It was expected that the water collected in the V-notch weir at the exit of the tunnel would be slightly more oxidized AMD from the Monte Romero mine adit. However, during this study it became evident that also seepings from the tailings pond accumulated at the bottom of the tunnel behind the weir. First, metal concentrations in the input water of tank C rose only slightly, but in mid December 2003 heavy rains accumulated a large amount of sediments behind the weir, burying the input collection pipe of tank C. The seepings filled the pore space within the sediment, leading to a high rise of the metal concentrations. At the end of May 2004 the sediments were excavated from behind the weir, so that in a sample taken in July 2004 metal concentrations were low again. In the following, we will only consider the period of very high metal loads from March to May 2004 (three sampling campaigns). During this period, the input water of tank C had a pH of 3.2, an acidity of almost 29000 mg/L as $CaCO_3$ equivalents, and contained 8580 mg/L Fe, 2400 mg/L Zn, 810 mg/L Mg, 355 mg/l Al, 350 mg/L Ca, 76 mg/L Mn, 3.5 mg/L Cu and 24500 mg/L sulphate (all median values).

The flow rate varied between 10 and 132 mL/min, with a median value of 18 mL/min, about half the design flow (estimated residence time of almost 48 hours within the manure layers and 12 hours within the MgO layer). Despite this low flow rate, no signs of sulphate reduction were found in the outflow (not shown), probably due to the extremely high metal concentrations which probably were toxic to microorganisms. During the three months considered here, pH rose to values around 4.7 (Fig. 6). Al decreased by 71% or 253 mg/L, Cu by 86%. Fe diminished by 3% or 285 mg/L. Zn and Mn did not change significantly.

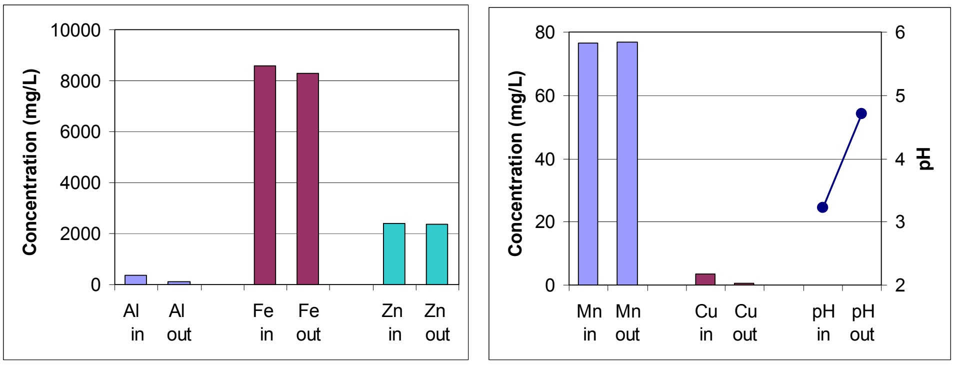

Figure 6: A) Medians of Al, Fe and Zn concentrations, B) medians of Mn and Cu concentrations (columns) and pH (filled circles) at the in- and outlet of Tank C

Since March 2004, an aeration cascade and a small sedimentation pond had also been installed at the outlet of the tank C, but due to the low flow rate and strong evaporation all solute concentrations increased in the pond (not shown). Solid samples of sediments taken from the sedimentation pond contained high concentrations of Fe and sulphate and minor amounts of Ca and Zn. XRD identified gypsum, schwertmannite, quartz and clay minerals.

Efficiency of alkalinity generation from calcite and MgO

As can be seen from the outflow pH which were far below the theoretical values, neither calcite nor MgO dissolution reached equilibrium in the tanks. The MgO seems to have become passivated rapidly. Al, Fe and Zn precipitation may play a significant role in this process.

In tank B and C, the rises in Mg and Ca concentrations suggest that about two thirds of the alkalinity was generated by calcite dissolution, and one third by MgO dissolution. Nevertheless, these calcite dissolution may be subestimated, because geochemical calculations showed that gypsum may precipitate inside the calcite layer. It may therefore also partly be responsible for the passivation of the MgO layer.

Comparison with published data

Ziemkiewicz *et al.* (2003) presented data for five types of passive treatment systems: anaerobic wetlands (AnW), vertical flow wetlands (VFW), anoxic limestone drains (ALD), open limestone channels (OLC), and limestone leachbeds (LSB). For each type, minimum, first quartile, median, third quartile and maximum over all systems of one type were computed. For tanks A-C, the same statistics were computed over the different sampling campaigns.

First of all, it should be noted that the tanks A-C received AMD with much higher acidities than any but one of the systems published by Ziemkiewicz *et al.* (2003). In that study, the median inflow acidity of all 83 systems is 146 mg/L as $CaCO_3$ equivalents, the maximum is 2398 mg/L as $CaCO_3$. In contrast, inflow acidity of tanks A and B had a median of 2379 mg/L and a maximum of 2448 mg/L as $CaCO_3$ equivalents, while tank C received AMD with a median and maximum inflow acidity of around 29000 mg/L as $CaCO_3$ equivalents during the period considered here.

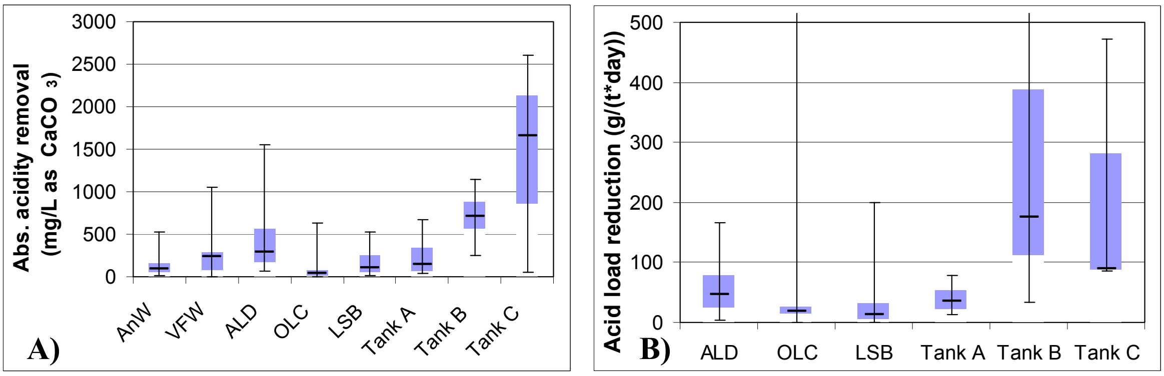

Figure 7: Box-and-whisker plots of A) absolute acidity removal and B) acid load reduction normalized by system area for the different passive treatment system types (acronyms: see text) published by Ziemkiewicz *et al.* (2003) and for tanks A-C

Absolute acidity removal (Fig. 7A) in tank A was comparable to that of the majority of the published systems, while absolute removal of tanks B and C exceeded the performance of most of the published systems. In terms of relative acidity removal, however, tanks A-C perform poorer than most of the systems published by Ziemkiewicz *et al.* (2003). Tank B only achieved a median relative acidity removal of 31%, and tanks A and C a median of only 6% in each tank. In contrast, median relative removal was 52%-53% for AnW and OLC, 74% for LSB, and over 100% for ALD and VFW. Note that a relative removal rates greater than 100% means that a treatment system converts net acidic AMD into net alkaline water.

For ALD, OLC and LSB, Ziemkiewicz *et al.* (2003) calculated acid load reduction normalized by substrate mass (Fig. 8B), while for AnW and VFW they published it in terms of system area (not shown). For tanks A-C both values were computed, and results of the comparison were similar for both statistics (only shown in terms of substrate mass, Fig. 7B): Tank A performs comparably to the majority of the published systems, while tanks B and C exceed the acid load reduction of most of the published systems.

CONCLUSIONS

- For the reactive materials used in this study, calcite was more efficient in generating alkalinity than MgO. At least two thirds of the alkalinity was generated by calcite dissolution, and at most one third by MgO dissolution. The powder fraction contained in the caustic magnesia generated severe clogging problems in all the tanks. Maybe a product without the fine-grained fraction would obtain better results.
- Compared to the systems published by Ziemkiewicz *et al.* (2003), the treatment tanks performed favourably in terms of acid load reduction and absolute acidity removal, but poorly in terms of relative acidity removal. The good absolute numbers were mainly due to the high Al loads of the waters treated at Monte Romero mine. Al is easily eliminated in calcite based systems, but can also clog the reactive material rapidly.
- In tank B Al clogging occurred in a layer of pure calcite gravel. Mixing of calcite with an inert matrix seems to retard this process by generating additional pore space.
- A bigger sedimentation pond and additional aeration (and sedimentation) steps may have increased Fe(II) elimination of tank B, because pH at the outflow of the pond was still higher than that of the input AMD.

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