The Use of Caustic Magnesia to Remove Cadmium from Water

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ABSTRACT

Conventional passive treatment systems are based on calcite dissolution. This increases the pH to values between 6 and 7, which are insufficiently high to precipitate divalent metals. Alternative treatments are based on sulphate reduction with organic matter in order to precipitate metal sulphides. However, redox reactions are usually too slow to treat large groundwater flows as currently found in gravel aquifers (>50 m/a). In the present study caustic magnesia obtained from calcination of magnesium carbonate was tested as an alternative material to devising passive remediation systems. Caustic magnesia reacts with water to form magnesium hydroxide (brucite), which dissolves increasing the pH to values higher than 8.5. At this pH values, cadmium is precipitated as a carbonate (otavite) and to a minor amount as a hydroxide. Thus, metal concentrations as high as 75 mg/L in the inflowing water are depleted to values below 0.5 μg/L. Magnesia dissolution is sufficiently fast to treat flows as high as 100 m/a. Nevertheless, the new precipitates may lead to a permeability drop in the porous treatment system.

INTRODUCTION

Metal pollution from acid mine drainage (AMD) and industrial activities poses a major threat to ecosystems. The conventional solution to the problem consists of treatment plants where chemicals are added to the water in controlled doses. In the case of groundwater, prior pumping is necessary. This is expensive and requires continuous maintenance. An alternative is passive treatment whereby filters are constructed in the path of acidic drainage, for example in the form of reducing and alkalinity producing systems (RAPS) (Hedin *et al.*, 1994) and permeable reactive barriers (PRB) (Blowes *et al.*, 2000). These filters are simple biogeochemically-based systems to improve water quality by means of reactions such as calcite dissolution, sulphate reduction, etc. These methods make use of natural energy sources (gravitational gradients) and require very low maintenance. The materials needed for such systems should be: 1) reactive so as to form an insoluble solid to retain metals; 2) permeable in order to allow the water to percolate, 3) durable, and 4) available and inexpensive so as to be competitive.

In passive systems to treat AMD, such as RAPS and PRB, organic matter with calcite is used as filling material (Younger *et al.*, 2002, Benner *et al.*, 1997). Due to two main reasons they only remove part of the metal load from groundwater. First, sulphate reduction is a slow process and the water needs a long residence time (several days or weeks) within the barrier for the reduction to take place (Benner at al., 2002). This would require uneconomically thick barriers for fluxes higher than 50 m/a commonly found in alluvial aquifers. Second, the pH values reached by calcite dissolution and sulphate reduction range between 6 and 7. As shown in Fig. 1, this pH is not high enough for divalent metal hydroxides and particularly Cd to precipitate. High pH values can also be achieved with lime (CaO) or portlandite (Ca(OH)$_2$) dissolution. Nevertheless, the solubility of metal hydroxides increases again for very high pH values, and the addition of these compounds in excess, such as occurs in passive treatments, raises pH up to 12. Magnesium oxide dissolution, in contrast, can buffer solutions between pH 8 and 10.

Caustic magnesia produced from the calcination of magnesium carbonate is an inexpensive product where magnesium oxide is the main component. As an active treatment reagent, although it is more expensive than lime, caustic magnesia raw material produces less waste, is less hazardous, and is therefore cheaper to handle (Younger *et al.*, 2002). An earlier paper showed the suitability of caustic magnesia to retain Zn, Cu, Pb and Mn in permeable reactive barriers (Cortina *et al.*, 2003). The present paper investigates the removal of Cd, an active carcinogenic agent with an allowed concentration limit as low as 5 μg/L (USEPA, 2001). Caustic magnesia should be suitable to remove Cd down to very low concentrations from the fluxes of water expected in aquifers and ponds, should also be sufficiently permeable and should function for reasonable time spans (a number of years).
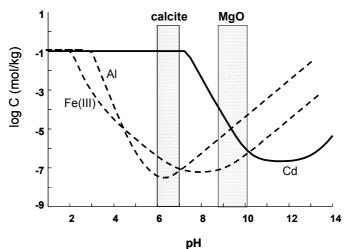
Figure 1: Solubilities of Al, Fe(III) and Cd as a function of pH, and ranges of pH values typically achieved by dissolution of calcite and MgO

MATERIALS AND METHODS

The commercial product Magna L manufactured by Magnesitas Navarras S.A., Spain, was selected in accordance with grain size and permeability criteria. It is mainly made up of periclase (MgO), with minor amounts of lime (CaO), quartz (SiO_2), magnesite ($MgCO_3$), and calcite ($CaCO_3$). A basic characterization is shown in Table 1. For the experiments, caustic magnesia was sieved to grain sizes ranging from 4 to 2 mm.

Table 1: Chemical composition and grain size distribution of caustic magnesia

Chemical composition (weight %)[1]						Particle Size (weight %)		
MgO	CaO	SiO_2	Fe_2O_3	Al_2O_3	Fire loss[2]	<0.5 mm	4 to 0.5 mm	>4mm
76±2	11±2	5±1	3.5±1	0.6±0.1	1.5±0.4	4%	86%	10%

[1] Ranges in composition usually observed in the production plant for the "Magna L" comercial product.
[2] Loss of mass of $CO_2(g)$ after heating the sample to 1500 °C.

Column experiments were designed to measure the reactivity of caustic magnesia under flow conditions similar to those expected in transmissive aquifers. Solutions were administered continually through Teflon tubing connected to a multichannel variable-speed Gilson Minipuls® peristaltic pump. The inlet fluxes employed are shown in Table 2. They were selected to match the higher range of flux conditions expected in alluvial aquifers. Tracer tests were conducted to verify uniform flow conditions in the columns and to determine effective transport porosity. A known concentration of acetone was added to the inflow solution, and the outflowing water was introduced into a Hewlet-Packard HP53® spectrophotometer by using a flow-through cuvette for continuous monitoring of acetone. Measured pore volumes for the different columns are given in Table 2. Inflowing solutions are described in Table 3, and were prepared by dissolving the metal sulphates in deionized milli-Q water. In order to obtain solid amount sufficient for mineralogical determination after a reasonable time span (months), the Ca concentrations of the inlet solution ranged between 15 and 75 mg/L, depending on the experiment, more than one order of magnitude of those reported for AMD (Eary, 1999; Aslibekian *et al.*, 1999; Tarras-Wahlberg *et al.*, 2001; Ludwig *et al.*, 2002).
All pH measurements were made routinely in a sealed flow-through cell placed at the exit of the column using a Crison glass electrode. The measured values were accurate within ±0.01.

Table 2: Summary of the physical characteristics of the different column experiments

Experiment				1	2
Column	Length	mm		60	200
	Section	mm²		314	700
	Solid	g		20	88
	Magnesia	wt.%		100	100
	Pore vol.	mL		6.1	43
	Porosity			0.32	0.31
	Flow	mL/min		0.06	0.2
	Darcy flux	m/a		100	150
	Residence	min		100	215

Column effluent samples were filtered through 0.45 μm and acidified with HNO_3 to pH lower than 1. Flow rates were determined gravimetrically. Most of elements were analysed with ICP-AES equipped with an Ultrasonic Nebulizer (USN). Analytical detection limits were in (mg/L): 0.25 for Mg; 0.20 for Ca, 0.03 for Fe, 0.02 for Al. Analyses of Cd were performed with ICP-MS, and the detection limit was 0.5 μg/L. In all cases, analytical errors were lower than 5 % in accordance with the reproducibility of the standard.

After the conclusion of the experiments, the substrate of the columns was observed under a JEOL 3400® Scanning Electron Microscopy with Energy Dispersive System (SEM-EDS). Moreover, the mineral phases present in the column fillings were identified with a BRUKER D5005® X-Ray Diffractometer (XRD), with Cu Lα radiation.

Table 3: Chemical characteristics of the inflow water for the different column experiments

Experiment			1	2
Inlet	pH		2	3
	Cd	mg/L	75	15
	Al	mg/L	-	10
	Fe	mg/L	-	20
	Ca	mg/L	-	360
	SO$_4$	mg/L	960	960

RESULTS

Metal retention from a monocomponent acid solution

A solution containing 75 mg/l of Cd at pH 2 was used as inflow solution for a column filled with caustic magnesia (Tables 2 and 3, experiment 1). The experiment lasted for 11 months.

The evolution of Cd concentration and pH of the outflowing solution are represented in Fig. 2. The initial pH values around 12 correlated with high Ca concentrations and were attributed to the dissolution of a minor amount of lime present in the caustic magnesia sample. After lime exhaustion, the Ca concentration dropped to the inflowing limit, the Mg concentration reached values between 20 and 25 mg/L, and the pH remained between 9 and 10. This is attributed to the dissolution of brucite, which coats the magnesia grains (Cortina et al., 2003). The concentration of Mg stabilized around 25 mg/L, indicating that equilibrium with brucite, $Mg(OH)_2$, was achieved during the residence time of the water in the column (Cortina et al., 2003).

After 2000 pore volumes, the pH decreased to values lower than 8. Mass balance considerations show that only 6 wt.% of the magnesia was consumed at that point. The fall in the pH could be due to the armouring of the periclase-brucite surface with precipitates or to the switch from pervasive pore flow to preferential flow paths caused by precipitates. The pH decrease below 8 is accompanied by a significant increase in the Cd content in the outflowing solution. The Cd concentration in some samples exceeds the inflowing value (75 mg/L) due to the dissolution of the previously formed solids.

The extrapolation of the experiment (2000 pore volumes) to a field scale treatment suggests that a 1 m thick system could be operative during several years for a water flux as high as 1 m/day.
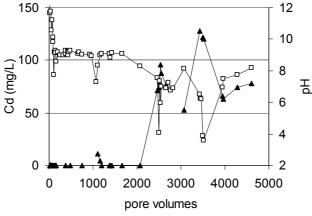

Figure 2: Concentration of Cd (solid triangles), and pH (open squares) during the column experiment 1.

At the end of experiment 1, several XRD diagrams of the solids collected from the pore material clearly confirmed the presence of otavite ($CdCO_3$) as a major phase. In one case, several peaks of the $Cd(OH)_2$ solid phase were also identified. SEM-EDS observations of precipitates from the column showed the ubiquitous presence of Cd-bearing rhombohedra, which were interpreted as otavite (Fig. 3). Oavite has been found to control the Cd concentration in aquifers and mine pit lakes (Zhan & Seiler, 1992; Eary, 1999; Woo & Choi, 2001). It has also been observed to precipitate in columns of apatite to remediate heavy metal polluted waters (Chen et al., 1997).
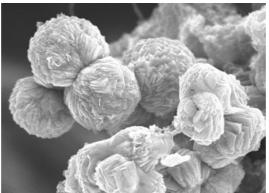
Figure 3: SEM image of otavite crystals in a sample from column experiment 1

Cadmium retention from a Fe-Al-bearing acid solution

Since acid waters usually contain aluminium and iron in variable concentrations, the behaviour of Cd in a Ca-SO$_4$ rich solution of pH 3 containing Al (10mg/L), Fe (20 mg/L) and Cd (15 mg/L) was used as an inflow water. The rest of the experimental conditions are detailed in Table 2, experiment 2. The experiment lasted for 60 days, and the evolution of the Cd concentration and of the pH in the outflowing solution are represented in Fig. 4. The pH started with values close to 12 due to lime dissolution, and then decreased to values close to 9, indicating the exhaustion of lime and brucite control. Brucite dissolved sufficiently fast to reach equilibrium during most of the experiment run (residence time of 215 min.), and was able to maintain the pH stable.

After 160 pore volumes, the flow was increased from 0.2 to 2 ml/min. The residence time dropped to 21 min. and the magnesia present in the column was not able to attain equilibrium, and the pH dropped to 6.0. This demonstrates that a thickness of magnesia exceeding 0.2 m is necessary to neutralize very high fluxes of acid water (>4 m/day). When the initial flow of 0.2 ml/min was restored the pH rose again to values between 9 and 10. At 400 pore volumes, the flow dropped below 0.1 mL/min, and the Mg concentration and pH decreased. This is attributed to the partial clogging of the column and the formation of preferential flow paths due to the precipitation of new solid phases.
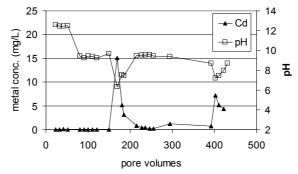

Figure 4: Cd concentration and pH during the multicomponent column study

Cd concentration in the outlet is closely correlated with pH (Fig. 4). For pH exceeding 8.5 the outflowing solution had a Cd concentration below the detection limit, whereas for pH between 8.0 and 6.0 it increased significantly. It should be noted that Fe and Al concentrations were below the detection limit throughout the experiment regardless of the pH.

After the experiment, the column was dismantled and half of the solid was digested and analyzed. The mass of cadmium in the outflowing solution plus that in the digested samples resembled that in the inflowing solution with errors below 10%. SEM-EDS observations showed a crust, not crystalline in appearance, covering the brucite surface and mainly formed by Al, Fe and O. Cd was always found as traces in the non-crystalline crust. No crystalline phases other than periclase and brucite were recognized by XRD.

As expected from hydroxide solubilities (cf. Fig 1), three valent metal ions such as iron and aluminium show low concentrations for any pH value exceeding 6. As suggested by the scattered presence of Cd under SEM-EDS observations, Cd sorption on Al-Fe oxyhydroxides or co-precipitation with these phases are possible mechanisms for Cd fixation in the column. Cadmium sorption on amorphous Fe(OH)$_3$ and Al(OH)$_3$ is strongly dependent on pH, being practically sorbed for pH higher than 6 to 7 (Dzombak & Morel 1990). Therefore, the dependence of the outlet Cd concentration on pH (Fig. 4) suggests that sorption on Al-Fe-hydroxide surface is a step previous to its final fixation in this phase (co-precipitation).

This column experiment demonstrates that caustic magnesia can reduce the Cd concentration down to regulatory levels for fluxes of polluted water that are characteristic of permeable aquifers. However, the system clogs when only a small fraction of magnesia (<1%) is consumed, indicating that mixing with an inert matrix is required to increase the available pore volume and to extend the duration of permeability.

CONCLUSIONS

- The reactivity of caustic magnesia is high enough for the fluxes expected in aquifers.
- Durability in the laboratory indicates that the system could be operative for several years at high flow rates (>0.5 m/day).
- However, the treatment capacity fails before the magnesia is exhausted, either by clogging (if Al and Fe are present) or by coating. Mixing of caustic magnesia with an inert matrix may improve system longevity and reagent efficiency.
- Tests at field scale are required to confirm applicability of caustic magnesia as a reagent for passive treatment systems.
- After exhaustion, Cd concentration in some samples exceeds the inflowing value (75 mg/L) due to the dissolution of the previously formed solids. Therefore, the remediation system must be removed once the first symptoms of exhaustion appear.

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