Processes affecting the efficiency of limestone in passive treatments for AMD: Column experiments

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Abstract

Experiments using columns packed with calcite grains (size 1-2 mm) were carried out to study the behavior of passive treatment systems designed to remediate contaminated water from acid mine drainage (AMD). Two types of synthetic acidic solutions (H_2SO_4) were injected in the columns: (1) iron-rich with Fe(III) at pH 2, and (2) aluminum-rich at pH 2 and 3. Fluid flow was constant during the experiments with Darcy velocities ranging from 6×10^{-4} to $1 \times 10^{-3} \text{ L m}^{-2} \text{ s}^{-1}$.

The columns worked efficiently removing aqueous iron and aluminum as long as calcite dissolved and buffered the solution pH (increasing pH and promoting the precipitation of Fe(III)- or Al-oxyhydroxides). However, Ca released from dissolving calcite, along with the sulfate in solution, led to formation of gypsum coatings on the calcite grain surfaces which eventually prevented calcite dissolution. This passivation process limited the efficiency of the columns. Larger input sulfate concentrations or higher pH led to shorter passivation times.

Characterization of the pore structure and composition by X-ray microtomography (mCT) and X-ray microdiffraction (mXRD) showed the precipitation of gypsum coatings on the calcite grains and secondary oxyhydroxides between the grains. This secondary mineral precipitation favored the formation of preferential flow paths, isolating regions of non-reacted limestone. An improved experimental design (mixing limestone grains and glass beads) minimized the formation of these preferential flow paths.

Experimental results have been modeled with the CrunchFlow reactive transport code. Fitting of the results required a decrease in the reactive surface area of calcite, which is consistent with the passivation process.

Keywords: Acid Mine Drainage, passive treatment, passivation, clogging, X-ray microtomography

1. Introduction

Acid Mine Drainage (AMD) is defined as the outflow of acidic water from metal or coal mines both in activity or abandoned. It poses an additional risk to the environment by the fact that it frequently contains elevated concentrations of metals (iron, aluminum, manganese, and possibly other heavy metals) and metalloids (of which arsenic is generally of greatest concern) [1,2]. These contaminants can persist in environment during several centuries after interruption of mining activity [3]. The main AMD-generating mineral is pyrite (FeS_2) [4-8], according to the following reactions [9]

SO_4^{2-} , Fe(II) and protons are released to solution. Fe(II) is oxidized to Fe(III) according to Eq. (2). Fe(III) may precipitate as schwertmannite [10]

78 releasing more protons, or as a Fe(III)-hydroxide (ferrihydrite), also releasing protons.

79 But, at pH lower than 3.5, Fe(III) remains mainly in solution and acts as another

80 oxidizing agent for pyrite according to

81

83

84 Since AMD can be highly acidic, it has the capacity to dissolve rocks that are

85 commonly formed by clays and other aluminosilicates. This process releases major rock

86 constituents (e.g. silica, aluminum, iron, sodium, potassium, magnesium, calcium),

87 together with heavy metals, into the environment [1].

88

89 The main purposes of AMD treatments are retention of metals (precipitation of the
90 contaminant metals) and neutralization of acidity. One of the possible and most

91 common passive treatment systems is the Anoxic Limestone Drain (ALD), or systems

92 derived from it (e.g. Reducing and Alkalinity Producing Systems), characterized by low

93 maintenance needs and low cost [11-17]. ALD uses ditches of buried limestone gravel.

94 Acid water flows through the gravel and limestone dissolves, raising pH and alkalinity,

95 yielding metal retention as Me-oxyhydroxide precipitates. The efficiency of the ALD

96 systems is however limited because secondary mineral precipitation causes the

97 passivation (armoring) of the limestone grains and clogging of the pores, reducing

98 limestone reactivity and acid neutralization [18-24]. In addition, the presence of

99 aqueous sulfate leads to gypsum precipitation [25-27], which essentially contributes to

100 passivation and affects greatly the efficiency of the treatment systems.

101

102 Soler et al. [27] reproduced at the laboratory scale the behavior of ALD systems using
103 column reactors filled with limestone grains. Injecting acid solutions (pH 2, HCl and
104 H_2SO_4) with initial concentrations of Fe(III) ranging from 9.27×10^{-3} to 3.61×10^{-2} mol
105 L^{-1} , it was observed that (1) gypsum coating was responsible for calcite passivation, (2)
106 passivation time in the column was dependent on the initial aqueous sulfate
107 concentration and (3) change in porosity and permeability was due to precipitation of
108 both gypsum and Me-oxyhydroxides. Moreover, once the columns were passivated, X-
109 ray microtomography was used *a posteriori* to examine the precipitates responsible for
110 the porosity changes.

111

112 To enhance our knowledge on the loss of calcite reactivity due to grain coating or
113 clogging of porosity initially discussed by Soler et al. [27], this study presents three
114 main innovations:

115

116 The first innovation is that the column experiments were performed using calcite sand
117 and synthetic acid solutions not only containing $\text{Fe(III)-SO}_4^{2-}\text{-H}^+$ as in Soler et al., [27],
118 but also containing $\text{Al-SO}_4^{2-}\text{-H}^+$ as major components at pH 2. Moreover, two
119 experiments were performed at pH 3. Concentrations of Fe(III) and Al ranged from 3.49
120 $\times 10^{-3}$ to 2.60×10^{-2} mol L^{-1} and from 3.60×10^{-3} to 3.61×10^{-2} mol L^{-1} , respectively,
121 which fall in the range found in AMD [1,28].

122

123 The second innovation is that in the present study, in order to clarify how the secondary
124 phases precipitate and influence the porosity change, several X-ray microtomography
125 (mCT) measurements were carried out. mCT images were collected at different times
126 during the experiment (before the experiment start and several times till the end of the

experiment) with the goal of (i) allowing an accurate characterization of the passivation mechanism, which consists of calcite dissolution, consequent surface coating by gypsum precipitates and precipitation of metal oxyhydroxides, and (ii) quantifying porosity changes during the experiments, the contribution of metal oxyhydroxides in the decrease in porosity, and the role of gypsum in the calcite passivation mechanism.

The overall process is represented by the following reactions:

or

Reactive transport modeling is a suitable tool for interpreting mathematically the coupled physical and chemical processes occurring in the passive treatment systems. The third innovation is that in this study, the reactive transport code CrunchFlow [29] is used to simulate the processes occurring in the column experiments. As the calcite passivation mechanism (gypsum coating on calcite surface) is not implemented in the code, the following was considered. Assuming that the gypsum coating reduces the calcite reactive surface area, a decrease in calcite area was forced at different times to fit the model results to the experimental data. The resulting simulations allow quantification of the phenomena responsible for the changes in passive treatment efficiency.

2. Materials and methods

2.1 Sample preparation and characterization

Limestone sand was obtained from the Roca Quarry in the Garraf area (Barcelona). This sand was used by Soler et al. [27] and XRD profiles showed only calcite peaks. The grain size used in the experiments was 1-2 mm. To remove calcite microparticles in the column, grains were pre-washed with de-ionized water several times until clear output water was collected. Thereafter grains were dried at 50 °C for 24 h. The specific surface area of the non-reacted sample was $0.447 \text{ m}^2 \text{ g}^{-1}$ measured by the BET method using 5-point N_2 adsorption isotherms on a Micromeritics ASAP 2000 surface area analyzer.

2.2 Column experiments

Cylindrical columns were made from transparent polymethyl methacrylate with inner diameters ranging from 1.2 to 2.6 cm and lengths ranging from 1.1 to 6 cm (Tables 1 and 2). Diameters were sufficiently large so they were about an order of magnitude larger than the limestone grain size. Lengths were sufficiently small so passivation (gypsum coating of the limestone grains) could be achieved in a reasonably short time. All columns included a bed of glass beads (2 mm in diameter) of 3 mm of thickness at the top and bottom to homogenize the influent and effluent solutions (Fig. 1a). Columns were hand filled with the pre-washed calcite grains. In a few columns, calcite grains were mixed with glass beads (33 wt% of grains and 67 wt% of beads) to improve solution circulation (Fig. 1b). Column porosity was calculated from the known calcite mass, volume of the column and calcite density (2.71 g cm^{-3}) and also from the acquired

mCT images of the columns using the gray-scale segmentation method. The initial porosity, based on density calculations and mCT measurements, ranged from 40 to 60 % (Tables 1 and 2). Input solutions were injected from the column bottom upwards by a Gilson peristaltic pump under constant flow rate, yielding fluxes of 6×10^{-4} and 1×10^{-3} L $m^{-2} s^{-1}$. Residence time ranged from 1.6 to 3.4 h. The experiments run for mCT measurements (see below) were temporarily stopped at different times in order to acquire the mCT images before the experiment (d0) and after 4, 8 and 12 days (d4, d8 and d12). After each image acquisition the experiments were restarted again.

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After the experiments, epoxy resin was injected in some columns. Once it hardened, the column was cut into slices for further mineralogical inspection by scanning electron microscopy (SEM) and micro X-ray diffraction (mXRD). Most experiments were replicated three times.

186

2.3 Solutions

188

Input solutions were made from adequate amounts of $Fe_2(SO_4)_3 \cdot 5H_2O$ and $Al_2(SO_4)_3 \cdot 16H_2O$ reagents (pro analysis grade) and Millipore MQ water (18 M Ω cm). The solutions (H_2SO_4) had initial concentrations of Fe(III) ranging from 3.49×10^{-3} to 2.60×10^{-2} mol L^{-1} and of Al ranging from 3.60×10^{-3} to 3.61×10^{-2} mol L^{-1} . Sulfate concentrations ranged from 1.02×10^{-2} to 4.39×10^{-2} mol L^{-1} for iron columns and from 1.04×10^{-2} to 5.92×10^{-2} mol L^{-1} for aluminum columns. In most of the experiments solution pH was 2 and only in two aluminum experiments the pH was 3. pH was adjusted by adding concentrated H_2SO_4 to the iron sulfate or aluminum sulfate solutions (Tables 1 and 2).

198

199 2.4 Analytical methods

200

201 Input and output concentrations of Fe, Al, S, Mg, Ca, Na and Si were measured by
202 Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES), using a
203 Thermo-Jarrel Ash spectrometer equipped with a CID detector. The detection limits for
204 Fe, S, Mg, Ca, Al and Si were 1.8×10^{-7} , 3.5×10^{-6} , 10^{-5} , 5×10^{-6} , 7.5×10^{-7} and 7×10^{-7}
205 mol L⁻¹, respectively. The error associated with ICP-AES measurement was estimated
206 to be around 3%, based on measurement of different standard solutions in the
207 calibration process. The solution pH was measured during the experiments with a
208 Thermo Electron Orion 720 A+ pH meter at room temperature (22 ± 2 °C) with an error
209 of ± 0.02 pH units. The electrode was regularly calibrated with buffer solutions at pH 2
210 and 7. The output solution pH was continuously measured by placing the electrode in a
211 sealed tube in which the output solution circulated (Fig. 1a). The saturation indexes for
212 calcite and gypsum were calculated at 25 °C using the PHREEQC code [30] and
213 MINTEQ database [31].

214

215 Two sets of X-ray microtomography (mCT) images were taken using two different X-
216 ray sources. The reason was time availability for the instruments. The first set was taken
217 at the 8.3.2 beamline of the Advanced Light Source (ALS, Berkeley, California).
218 Images were taken at X-ray energy of 40keV using a superbend magnet source and a
219 multilayer monochromator. The columns were mounted on a rotary stage and images
220 were collected every 0.25° through a full 180° rotation. Transmitted X-ray light was
221 converted to visible light using a CdWO₄ single crystal scintillator, magnified by a
222 Cannon 2X lens, and imaged on a Cooke PCO 4000 CCD camera with a final pixel size

223 of 4.4 μm . Three exposures of 200 ms each were averaged together for a total of 600 ms
224 exposure per image. Nine dark images (with X-ray shutter closed) and 25 open beam
225 images (with sample removed from beam) were taken at the end of the data collection
226 and used for background subtraction and normalization. Raw images were reconstructed
227 using the Octopus commercial software package [32].

228

229 A second set of mCT images was taken at the National Institute for Lasers, Plasma and
230 Radiation Physics (NILPRP, Bucharest-Magurele, Romania). The mCT equipment
231 worked with Cone beam CT rapid scan ($180^\circ + \frac{1}{2}$ fan angle), Oblique View Cone
232 Beam. X-ray energy was 225 kVp and a maximum power of 10/15 W, using a tungsten
233 filament source. The columns were mounted on a rotary stage, and images were
234 collected every 0.5° . The linear detector, using 1,024 scintillator - photo diode
235 assemblies, yielded 16-bit output digital files that were reconstructed using the
236 VGstudio Max 2.0 software package [33]. All mCT images were taken before and
237 during the experiments at regular time intervals. The segmentation method (separation
238 of gray-scale range values) was applied to quantify porosity using the ImageJ software
239 [34]. This method permits separation and measurement of the pore space between
240 calcite grains and precipitates over the whole image pack.

241

242 Quantification of precipitated gypsum and oxyhydroxides was carried out manually
243 using the Amira 5.2 3D visualization software [35]. Since acquirement of mCT images
244 is based on the different density of the materials, and the density of Al-hydroxides is
245 very low, it was impossible to obtain mCT images of the Al-compounds in the
246 aluminum columns. Hence, only the mCT images in some of the iron columns were
247 used to characterize the mineral variation with time at different time intervals. Time to

capture the mCT images was ~ 2 h. In the mCT images each mineral (calcite, Fe-oxyhydroxides, gypsum, glass beads) has a different gray color according to its density and composition (X-ray absorption coefficient). The pore space is black.

In order to identify the mineral phases in the columns, X-ray microdiffraction (mXRD) measurements of several thin sections from the passivated columns were performed at the 12.3.2 beamline, ALS (Berkeley, California). The instrument uses Kirkpatrick-Baez optics to focus the monochromatic X-ray beam delivered by the synchrotron superconducting magnet source down to a size of about $15 \times 2 \mu\text{m}^2$ at the sample position. The sample was mounted on a precision XY stage and illuminated with a 8 keV ($\lambda = 1.55 \text{ \AA}$) monochromatic X-ray radiation at an incidence angle of 10° . Iron X-ray fluorescence signal was also collected using a Si-drift Vortex detector. mXRD patterns were obtained using a MAR133 X-ray CCD detector. The CCD was set to an angle of $2\theta = 40^\circ$ at a distance of 119 mm from the sample. The exposure time per point for the diffraction patterns was 200 s. The signal collection time per point for fluorescence was 0.2 s.

Scanning Electron Microscopy (SEM) images were taken on C-coated samples using a Hitachi H-4100FE instrument under a 15–20 kV potential.

2.5 Reactive transport modeling

One-dimensional simulations of the column experiments were performed using the CrunchFlow reactive transport code [29]. Crunchflow solves numerically the advection-dispersion-reactions equations

$$\frac{\partial(\phi C_i)}{\partial t} = \nabla \cdot (\mathbf{D} \nabla C_i) - \nabla \cdot (\mathbf{q} C_i) + R_i \quad (i = 1, 2, 3, \dots, n) \quad (10)$$

where ϕ is porosity, C_i is the concentration of component i (mol m⁻³), q is the Darcy velocity (m³ m⁻² s⁻¹), R_i is the total reaction rate affecting component i (mol m⁻³ rock s⁻¹) and D is the combined dispersion-diffusion coefficient (m² s⁻¹). The total reaction rate for component i is given by

$$R_i = - \sum_m v_{im} \cdot R_m \quad (11)$$

where R_m is the rate of precipitation ($R_m > 0$) or dissolution ($R_m < 0$) of mineral m per unit volume of rock, and v_{im} is the number of moles of i per mole of mineral m . Since mineral reactions are described using kinetic rate laws, initial mineral surface areas and several reaction rate parameters have to be supplied by the user as input. In the simulations, the reaction rate laws that have been used are of the form [36]

$$R_m = A_m \sum_{terms} k_m a_{H^+}^n (\Omega_m - 1) \quad (12)$$

where A_m is the reactive surface area of the mineral (m² m⁻³), k_m is the rate constant (mol m⁻² s⁻¹) and $a_{H^+}^n$ is a term describing the dependence of the rate on pH. The term in brackets stands for the effect of solution saturation state.

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$$\Omega_m = IAP_m / K_m \quad (13)$$

where IAP_m is the ionic activity product of the solution with respect to the mineral and K_m is the equilibrium constant for the dissolution reaction (ionic activity product at equilibrium). If $\Omega_m < 1$, the solution is undersaturated and the reaction is of dissolution; if $\Omega_m > 1$, the solution is supersaturated and the reaction is of precipitation; at equilibrium $\Omega_m = 1$ and $R_m = 0$.

295

Changes in mineral surface area A_m (m²/m³bulk) due to reaction are calculated according to

297

$$298 \quad A_m = A_m^{initial} \left(\frac{\phi_m}{\phi_m^{initial}} \right)^{2/3} \left(\frac{\phi}{\phi^{initial}} \right)^{2/3} \quad (\text{dissolution}) \quad (14)$$

$$299 \quad A_m = A_m^{initial} \left(\frac{\phi}{\phi^{initial}} \right)^{2/3} \quad (\text{precipitation}) \quad (15)$$

300

301 where ϕ_m is mineral volume fraction. The inclusion of a 2/3 dependence on porosity is chiefly to
 302 ensure that as the porosity goes to 0, so too does the mineral surface area available for reaction.
 303 This formulation is used primarily for primary minerals (that is, minerals with initial volume
 304 fractions > 0). For secondary minerals which precipitate, the value of the initial bulk surface
 305 area specified is used as long as precipitation occurs—if this phase later dissolves, the above
 306 formulation is used, but with an arbitrary “initial volume fraction” of 0.01.

307

308 **3. Results and Discussion**

309

310 Tables 1 and 2 show the experimental conditions of the aluminum and iron column
 311 experiments, respectively. The experiments lasted from 142 to 4774 h depending on
 312 their geochemical evolution.

313

314 *3.1 Aluminum columns*

315

316 Fig. 2a shows variation of the output concentrations of Ca, SO_4 and Al and output pH in
 317 a representative Al column experiment (experiment 16 in Table 1). Initial pH was 2 and
 318 initial Al and sulfate concentrations were $2.22 \times 10^{-2} \text{ mol L}^{-1}$ and $3.75 \times 10^{-2} \text{ mol L}^{-1}$,
 319 respectively. As the solution reacted with calcite, the output pH increased to pH
 320 between 6 and 7.5 (for ~ 260 h) and dissolved Al was completely depleted. The

concentration of Ca raised to $\sim 1.6 \times 10^{-2} \text{ mol L}^{-1}$ and the output concentration of sulfate decreased to $\sim 1.6 \times 10^{-2} \text{ mol L}^{-1}$. Therefore, at this stage (Fig. 2a) the calcite-filled column was acting as expected, removing Al from solution, decreasing sulfate concentration and neutralizing acidity. PHREEQC calculations showed that the output solution was undersaturated with respect to calcite, but supersaturated with respect to Al-hydroxide (gibbsite ($\text{Al}(\text{OH})_3$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Both gypsum and gibbsite were identified by mXRD, indicating that both phases precipitate under these conditions. After 260 h (stage II), the output pH and the output Ca concentration gradually decreased to approach a nearly constant value of ~ 4 and $\sim 8.0 \times 10^{-3} \text{ mol L}^{-1}$, respectively, until the end of the experiment (Fig. 2a). Output concentration of SO_4 and Al increased up to the input concentrations. Therefore, this behavior suggests that calcite dissolution diminished likely due to gypsum precipitation on the calcite grain surfaces (*armoring* or *coating* effect), limiting, but not totally avoiding, the buffer capacity of calcite. Precipitation of gypsum and Al-oxyhydroxide (gibbsite) was observed (Fig. 3a, c, and e).

3.2 Iron columns

The variation in the Fe concentration in the Fe(III) columns was similar to that of the Al column experiments. Fig. 2b depicts the variation of the output concentration of Ca, Fe, SO_4 and pH. Dissolution of calcite increased the output pH (~ 6) and the Ca release (up to $2.27 \times 10^{-2} \text{ mol L}^{-1}$). Precipitation of gypsum and Fe-oxyhydroxide (goethite) was clearly observed and identified (Fig. 3b, d and f). After 350 h, the output pH sharply dropped to ~ 2 , the concentration of total Fe increased to the initial level, and Ca decreased to $5.4 \times 10^{-3} \text{ mol L}^{-1}$. SO_4 concentration was higher than the initial one. This

variation suggests that calcite was losing reactivity and the precipitated gypsum was dissolving. However, after ca. 750 h, the output pH and Ca increased back up to 6 and $2.1 \times 10^{-2} \text{ mol L}^{-1}$, respectively, the total SO_4 decreased to $\sim 1.6 \times 10^{-2} \text{ mol L}^{-1}$, and iron was depleted. This behavior indicated that calcite dissolution resumed to yield gypsum and goethite precipitation. Finally, after ~ 1550 h a second, perhaps definitive calcite passivation occurred before the end of the experiment.

3.3 Passivation and clogging processes

The dissolution of calcite in the experiments released Ca from the limestone grains, which combined with the SO_4 in solution and caused precipitation of gypsum on the calcite surfaces. Gypsum coating of the grains eventually prevented access of solutes to the grain surfaces and calcite dissolution (passivation). As a result of passivation, output pH dropped to values close to the input value, metal retention stopped and SO_4 concentrations increased to levels close to the input value (or even higher if gypsum dissolved). The time required to reach passivation (passivation time, t_{pass}), depended on the input concentration of SO_4 , which correlated with metal concentration (Fe and Al were added as sulfate salts). It was considered that columns were passivated when pH remained at values near that of the input solution for 5 consecutive days.

Figures 4a and 4c show plots of t_{pass} normalized to residence time τ (column length divided by initial linear velocity) vs. initial SO_4 concentration. The tendency observed in both Fe and Al columns is that t_{pass} increased when decreasing the input sulfate (and metal) concentrations (Fig. 4a, c). This trend was already observed by Soler et al. [27] in Fe column experiments using two different limestone grain sizes (1-2 and 2-5 mm).

371 In the Al column experiments, t_{pass} also tends to be higher in the experiments run at pH
372 3 than in those at pH 2.

373

374 Calcite dissolution also caused an increase in pH from 2 to ~ 6-7 (proton consumption),
375 resulting in supersaturation of the solutions with respect to Fe- or Al-oxyhydroxides.
376 Clogging of the pore space was observed in some experiments (flow stopped due to the
377 decrease in permeability). Time required to clog the columns was larger than
378 passivation times (arrows in Figs. 4a, b), indicating that when efficiency was better (i.e.
379 the columns lasted longer), clogging took place before any passivation could be
380 observed. Clogging was caused by the precipitation of metal-oxyhydroxides between
381 the grains.

382

383 To check reproducibility of results most experiments were repeated at least 3 times.
384 Reproducibility was little, as significant variability in t_{pass}/τ was observed (Tables 1
385 and 2). For example, results from Fe experiments with initial SO_4 concentration of
386 $\sim 1.0 \times 10^{-2} \text{ mol L}^{-1}$ show that time to reach clogging ranged from ~700 to ~2600 t/τ (Fig.
387 4a). Another factor to take into consideration was the occurrence of temporary calcite
388 passivation events and subsequent reactivations. Soler et al. [27] reported them to occur
389 only in columns with Fe(III)-Cl-H^+ solutions and not in $\text{Fe(III)-SO}_4\text{-H}^+$ solutions. The
390 authors argued that in the sulfate solutions the strong attachment of gypsum onto calcite
391 surfaces could prevent the reactivations. However, temporary passivation and
392 reactivation has now been observed in sulfate solutions. Removal of fine grained
393 precipitates from calcite surfaces could be the mechanism causing these reactivations.

394

Figures 4b and 4d show the amount of metal retained (calculated as the product between input metal concentration in mg L^{-1} , flow rate in L h^{-1} and t_{pass} in h), normalized to the initial mass of calcite, vs. sulfate concentration of the input solution. The figures show no clear trend. Results plotting on the left correspond to experiments with small input sulfate concentrations which gave large t_{pass} values. Results plotting on the right correspond to experiments with larger input concentration which gave lower t_{pass} values (Figs. 4a and 4c). This opposite distribution of input concentrations and t_{pass} can explain the lack of a trend in metal retention versus input concentration.

mCT examinations of column experiment H allowed detailed identification of the mineralogical and porosity changes (Fig. 5). mCT examinations were performed at different times (Fig. 6, Table 2): before injection (d0) and after 4, 8 and 12 days. The four mCT images in Fig. 6 show the same section close to the column inlet. Slight variations in the position of the grains with time were due to sample compaction during the experiment. Initially only calcite grains were present (light gray), separated from each other by pore space (dark areas). After ~ 90 h (d4) some of the calcite grains were coated by a thin gypsum layer (dark gray) and a whitish phase (goethite) was filling the pore space. Both gypsum and goethite were identified by mXRD. At d(8) and d(12) the gypsum coatings grew and goethite content increased. After 12 days the column was passivated and the experiment was finished. Other mCT sections along the passivated column showed that in some portions of the column calcite grains did not react with the solution (Fig. 7). At the inlet (bottom) of the column a noticeable presence of goethite filling the pore space and gypsum coatings on grain surfaces is observed. In the lower middle image (LM) approximately 75 % of the grains reacted, leaving some non-reacted grains visible on the left side. In the upper middle section (UM) the fraction of reacted

grains diminished and at the top only ~50% reacted: a clear separation between reacted and non-reacted regions is readily observed. Formation of preferential paths in the columns was observed in most of the experiments and was more evident in the upper parts of the columns (closer to the outlet).

3.4 Porosity variation

The mCT images showed that precipitation of Me-oxyhydroxides and gypsum caused a decrease in porosity. Once the injected solution reacted with the calcite grains, a reaction front advanced upwards. Fig. 8 shows the porosity variation with time along column H. The black and grey lines represent initial and final porosity, respectively. The two lines in between correspond to the porosity along the column at 4 and 8 days. The lines represent the pore-space area per section area (%) with an error of 2% (the sum of calcite, porosity and precipitates areas ranged from 98% to 102 %). It is inferred that the initial porosity fluctuates along the column within a difference of $\pm 5\%$ with respect to the mean porosity value (45%) because grain distribution varies along the column. After 4 days of constant injection, a porosity decrease occurs only in the low middle part of the column. After 8 days, a porosity decrease is more evident in the low middle part, although a slight decrease is already observable in the upper part. Thereafter, until full passivation (12 days; grey line), porosity decreases all along the column, being still more evident in the lower middle part (25 %) than in the upper middle part (10 %). The final average porosity along the column is 31 %.

443 Formation of preferential flow paths, especially in the upper part of the column (Fig. 7),
444 caused isolation of some portions where calcite grains did not react, limiting the barrier
445 efficiency.

446

447 The contribution of gypsum and goethite precipitates to porosity decrease was
448 calculated using the mCT image segmentation method (Fig. 9). After 12 days,
449 precipitation of goethite and gypsum contributed, respectively, ~ 15% and ~ 5% of
450 porosity decrease from the inlet to the middle of the column. In the upper half,
451 contributions of each phase diminished to 5 to 10 % and 1 to 2 %, respectively (Fig. 9).

452 Variation with time of each phase shows that the reaction front progressed upwards,
453 indicating that precipitation of goethite and gypsum was simultaneous (driven by calcite
454 dissolution) and initiated at the inlet where precipitates were more abundant.

455

456 In order to avoid preferential flow paths, two longer columns (6 cm of length and 2.6
457 cm in diameter) packed with a homogeneous mixture of glass beads (2 mm in diameter;
458 67 wt %) and calcite grains (1-2 mm; 33 wt %) were run in an iron-rich solution (Table
459 2). [Use of glass beads improves solution circulation through the column](#). Variation of
460 the output pH and output Fe, SO₄ and Ca concentrations is shown in Fig. 10. It is
461 observed that full column passivation (output pH drop to initial value and iron increase)
462 was achieved after a longer time compared to that in calcite filled columns (e.g. see Fig
463 4).

464

465 The mCT images before reaction show regular distribution of calcite grains and beads
466 along the columns (Fig. 11). In fact, formation of preferential flow paths was
467 significantly prevented (only a little unreacted region was observed; Fig. 11). Duration

of the bead-filled experiments was longer before full passivation was achieved and reproducibility was improved (Table 2 and Figs. 4 a and b). The longer period of activity originated a larger and homogenous porosity decrease along the column (Fig. 12). Overall, using this column design, the performance of the system was improved. This result is in accordance with those reported by Caraballo et al. [37] and Rötting et al. [38], who showed that addition of inert material in the limestone treatment systems enhances the efficiency of the systems.

3.5 Reactive transport modeling of the columns

3.5.1 Model parameters

Model parameters correspond to those of column experiment H. The length of the one-dimensional domain was 1.2 cm (the length of the column). Grid spacing was 0.6 mm. Calcite was the only initial mineral, and the secondary minerals that were taken into account were goethite and gypsum (Table 3). Initial porosity of the column and initial volume fraction of calcite were 0.494 and 0.506, respectively. The initial surface area of calcite ($20 \text{ m}^2 \text{ m}^{-3}$) was adjusted to fit the model to the experimental results. It has to be noted that this area is much smaller than either the geometric surface area of the limestone assuming spherical grains (ca. $2000 \text{ m}^2 \text{ m}^{-3}$) or the area calculated from the BET measurements (ca. $6 \times 10^5 \text{ m}^2 \text{ m}^{-3}$). An explanation for the small value could be given by the transport (diffusion) control of the net dissolution reactions under acidic pH (e.g. [39]). The resulting small net dissolution rates are implemented in the model through a small surface area term (see eq. 12). Goethite and gypsum surface areas were also adjusted to reproduce the observed experimental data (Table 3). The composition

of the injected water (input solution) was the same as the experimental composition of the input solution (1.74×10^{-2} mol L⁻¹ of Fe(III), 3.11×10^{-2} mol L⁻¹ of SO₄ and pH 2). The composition of the initial water in the column was at equilibrium with calcite and atmospheric CO₂ (Table 3). The dispersivity was considered to be equal to grid spacing. Darcy velocity was calculated from the constant flow rate used in the experiments (Table 3).

Three minerals and 23 species in solution were taken into account in the calculations. The equilibrium constants for the three mineral reactions are given in Table 4. All the chemical equilibria in solution are listed in Table 5. All the equilibrium constants at 25 °C were taken from the database included in CrunchFlow, which is based on the EQ3/6 database [40]. The kinetic rate laws used in the present study were obtained from [41]. Rate parameters for the minerals considered in the calculations are shown in Table 6.

3.5.2 Results

As passivation is controlled by gypsum coating on calcite surfaces, calcite reactivity should diminish as a consequence of the loss of calcite reactive surface area. The initial calcite surface area was adjusted to 20 m² mineral m⁻³ rock. The initial surface area for gypsum and goethite were also fitted to the initial experimental results. During the course of the simulation, the calcite surface area was decreased stepwise at two different times. After 230 h, the value was reduced to 10 m²/m³; after 300 h it was reduced to 0.1 m²/m³ (Fig. 13). The reactive surface areas of goethite and gypsum were assumed constant during the experiment. This is a model simplification, since areas should increase with precipitation. But even with this underestimation of gypsum and goethite

reactivity it was necessary to reduce the calcite surface area to match the experimental results (smaller Ca concentrations due to less dissolution of calcite and larger SO₄ and Fe concentrations due to less precipitation of secondary gypsum and goethite). This simple model (stepwise reduction of calcite surface area) shows that the experimental results are consistent with a reduction of calcite reactivity induced by the precipitation of gypsum.

4. Summary and conclusions

Factors affecting the efficiency of limestone in passive treatment systems for AMD were studied using centimetric-scale columns packed with crushed limestone. In these systems, calcite passivation by gypsum coating is an important limitation to the limestone buffer capacity, and the main factors for controlling passivation time were the initial sulfate concentration and pH. A decrease in sulfate concentration and the use of low flow rate enhance the column passivation time. In those experiments run with higher pH passivation time also improved.

Metal retention does not show the same trends as passivation time: there is little sensitivity of metal retained on initial sulfate (and metal) concentration due to the negative correlation between initial concentration and passivation time.

Another limitation for the treatment efficiency is the formation of preferential flow paths and column clogging. These complementary phenomena are caused by the precipitation of iron or aluminum oxyhydroxides which impede homogeneous circulation of the solutions through the columns. To improve the efficiency in the

passive treatment, mixtures of calcite grains and glass beads were used to pack the columns. The addition of an inert substrate clearly improves the efficiency.

mCT images and mXRD measurements were used to determine how gypsum coating and metal-oxyhydroxide precipitation occurred and to quantify porosity variation along the columns. It was observed that porosity decreased progressively with time. Gypsum coating contributed 5 % in porosity reduction, whereas goethite contribution was ~15%. Gypsum and goethite precipitation was simultaneous.

A good match between experimental results and reactive transport simulations was achieved. Fitting of the results required a reduction in the reactive surface area of calcite with time, which is consistent with a passivation mechanism (formation of gypsum coatings on calcite surfaces).

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681

682

Figure captions

Figure 1. (a) Scheme of the experimental setup. (b) Scheme of a mixed long column (diameter 2.6 cm, length 6 cm). In addition to the layers of glass beads at the bottom and top, glass beads were mixed with the calcite grains (67 wt% and 33 wt%, respectively). (c) Photograph of an assembled column (1.2 cm x 1.2 cm).

Figure 2. (a) Variation of output pH and output concentrations of Al, Ca and SO₄ with time in experiment 16 (Table 1). (b) Variation of output pH and output concentrations of Fe, Ca and SO₄ with time in experiment 3 CAL.

Figure 3. (a) SEM image showing gypsum crystals that coat a calcite grain (not visible under the precipitates) in experiment 16 (Table 1). The surrounding material is Al-hydroxide precipitate (gibbsite) which was identified by X-ray microdiffraction (a and e). (b) SEM image that shows a calcite grain on the right, a gypsum coating and Fe-oxyhydroxide (goethite) in a representative passivated column (1 CAL, $8.7 \times 10^{-3} \text{ mol L}^{-1}$ Fe(III), $1.8 \times 10^{-2} \text{ mol L}^{-1} \text{ SO}_4^{2-}$ and pH 2). (c) and (d) Optical micrographs of the samples. (e) and (f) mXRD profiles indicating the presence of gibbsite, goethite and calcite.

Figure 4. Plots of passivation time normalized to residence time (τ) vs. input concentration of SO₄ are shown in (a, column experiments with Fe₂(SO₄)₃ input solutions) and (c, column experiments with Al₂(SO₄)₃ input solution). Plots of metal retention vs. input SO₄ concentration are shown in (b) and (d). The arrows in (a) and (b) indicate columns that underwent clogging. Arrows in (c) and (d) represent experiment

708 runs with input solution at pH 3. Different symbols represent different column sizes
709 (length and diameter). Flow rate in all experiments is $1.0 \times 10^{-3} \text{ L m}^{-2} \text{ s}^{-1}$.

710

711 **Figure 5.** mCT image of Column H after passivation that shows calcite grains (Cal)
712 coated by gypsum (Gp, dark gray layer surrounding calcite surfaces). Precipitation of
713 goethite (Gth, whitish phases) happens between grains and becomes the main
714 responsible for decrease in porosity. Dark areas are pores.

715

716 **Figure 6.** Four mCT images of the same section (see arrow) of Column H (Table 2)
717 during the experiment: d0, before reaction; d4, d8 and d12, after 4, 8 and 12 days
718 (passivation at $\approx 300 \text{ h}$). As the grains were not cemented, relative positions change
719 slightly in the 4 images.

720

721 **Figure 7.** (a) mCT images of four sections from Column H after passivation ($\approx 300 \text{ h}$)
722 that show the distribution of precipitates along the column. The solid line in the top
723 section separates a reacted from a non-reacted zone. Glass beads are visible at the
724 bottom and top sections of the column. (b) Scheme showing the location of the sections
725 along the column.

726

727 **Figure 8.** Porosity variation with time along column H. The arrow indicates the flux
728 direction. d0, d4, d8 and d12 stand for measurements at 0, 4, 8 and 12 days,
729 respectively. Porosity decreases from an initial value of $48 \pm 2 \%$ to $31 \pm 2 \%$.

730

731 **Figure 9.** Contributions of goethite (a) and gypsum (b) to porosity variation in column
732 H. They were calculated by segmentation of the mCT images taken after 4, 8 and 12

days. After passivation, the average gypsum content is about 3% and that of goethite is ca. 14 %. Consistent with the formation of preferential flow paths, the amount of precipitates decreases from the bottom (inlet) to the top (outlet).

Figure 10. Variation of the output concentrations of Ca, SO₄ and Fe and pH with time in experiment LCAL 1mix.

Figure 11. mCT images of four sections from column LCAL1-mix after passivation. The distribution of precipitates is homogeneous with no preferential flow paths. The whitish particles between grains and beads are goethite. The final mean porosity is $16 \pm 3\%$.

Figure 12. Porosity variation along Column LCAL-1. The upper line is the distribution of porosity along the column ($39 \pm 3\%$) before the experiment start. The lower line is the final porosity after passivation ($16 \pm 3\%$, passivation time was ~ 50 days). The arrow indicates the flux direction. The homogenous distribution of porosity along the column suggests that no preferential flow paths were formed, yielding a constant porosity decrease.

Figure 13. Experimental and modeling results (output concentrations vs. time) from column H.

756 **Table heads**

757

758 **Table 1** Experimental conditions of the aluminum column experiments.

759

760 **Table 2** Experimental conditions of the iron column experiments.

761

762 **Table 3** Parameters used in the reactive transport calculations.

763

764 **Table 4** Equilibrium constants for the mineral reactions considered in the calculations

765

766 **Table 5** Equilibria in solution considered in the calculations.

767

768 **Table 6** Kinetic parameters in the mineral dissolution/precipitation rate laws (25°C)

769 (Palandri and Kharaka, 2004).

770

Figure 1

Figure 2

a)

b)

Figure 3

Figure 4

Figure 5

2 mm

Figure 6

Diameter 1.2 cm

Figure 7

a)

B (bottom, inlet)

LM (lower middle)

UM (upper middle)

T (top, outlet)

Diameter 1.2 cm

b)

Figure 8

Figure 9

a)

b)

Figure 10

Figure 11

B (inlet, bottom)

LM (lower middle)

UM (upper middle)

T (output, top)

Figure 12

Figure 13

Table 1

column	weight limestone (g)	Al (M)	SO ₄ (M)	column length (cm)	column diameter (cm)	porosity (%)	t _{pass} /tau	time (h)	mg Al / g calcite
17	19.8	3.61E-02	5.92E-02	2.5	2.6	45	67	210	20
16	18.8	1.80E-02	3.19E-02	2.4	2.6	46	180	547	27
11	19.7	9.27E-03	1.89E-02	2.7	2.6	49	44	162	4
10	18.5	7.20E-03	1.58E-02	2.6	2.6	51	323	1183	24
4	17.0	7.20E-03	1.58E-02	2.6	2.6	55	291	1147	25
2	14.5	3.60E-03	1.04E-02	2.1	2.6	52	623	1893	24
9	19.0	3.60E-03	1.04E-02	2.6	2.6	49	396	1411	14
C	1.8	1.80E-02	3.19E-02	1.1	1.2	46	101	142	15
A	1.6	9.27E-03	1.89E-02	1.2	1.2	57	152	291	18
M	1.6	7.20E-03	1.58E-02	1.1	1.2	51	178	280	13
N	1.8	7.20E-03	1.58E-02	1.2	1.2	50	168	280	12
6 CAL	15.0	1.80E-02	3.19E-02	6	2.6	40	73	501	31
7 CAL	14.0	3.60E-03	1.04E-02	6	2.6	40	460	3330	44
8 CAL	14.1	3.60E-03	1.04E-02	6	2.6	40	418	3018	40
9 CAL	14.0	3.60E-03	1.04E-02	6	2.6	40	444	3211	42

All column experiments run at $1 \times 10^{-3} \text{ L m}^{-2} \text{ s}^{-1}$.

Initial pH is 2 except in 4 and 2 where it is 3.

All column experiments were passivated.

t denote time in hours needed to passivate the column.

τ denotes residence time calculated as V/Q .

t/τ denotes passivation time normalized with respect to residence time.

mg Al/g limestone denotes amount of aluminum retained by limestone.

column	weight limestone (g)	Fe (M)	SO ₄ (M)	column length (cm)	column diameter (cm)	porosity (%)	flow rate (L/m ² /s)	t _{pass} /tau	time (h)	mg Fe / g calcite	passivated
3	16.40	2.60E-02	4.39E-02	2.8	2.6	59	1.0E-03	141	593	101	YES
8	18.47	1.34E-02	2.51E-02	2.5	2.6	47	1.0E-03	117	331	26	YES
7	19.86	6.72E-03	1.51E-02	2.5	2.6	45	1.0E-03	263	743	27	YES
2 CAL	13.23	8.70E-03	1.80E-02	1.6	2.6	43	1.0E-03	301	518	36	YES
3 CAL	14.65	8.70E-03	1.80E-02	1.7	2.6	40	1.0E-03	972	1676	107	YES
4 CAL	14.63	3.49E-03	1.02E-02	1.8	2.6	44	1.0E-03	2241	4438	113	YES
5 CAL	14.21	3.49E-03	1.02E-02	1.7	2.6	42	1.0E-03	2651	4774	125	CLOG.
1A	1.71	3.49E-03	1.02E-02	1.2	1.2	54	1.0E-03	1273	2201	105	CLOG.
2A	1.56	3.49E-03	1.02E-02	1.2	1.2	58	1.0E-03	744	1385	72	YES
7A	1.67	3.49E-03	1.02E-02	1.1	1.2	50	6.0E-04	1827	1185	33	CLOG.
H	1.86	1.74E-02	3.11E-02	1.2	1.2	49	1.0E-03	188	300	66	YES
D	1.76	1.34E-02	2.51E-02	1.2	1.2	52	1.0E-03	239	402	72	YES
E	1.60	1.34E-02	2.51E-02	1.1	1.2	53	1.0E-03	231	359	71	YES
1 CAL	1.46	8.70E-03	1.80E-02	1.2	1.2	60	1.0E-03	1021	1990	278	CLOG.
F	2.21	1.74E-02	3.11E-02	1.3	1.2	45	6.0E-04	132	360	38	YES
B	1.68	1.34E-02	2.51E-02	1.1	1.2	50	6.0E-04	434	1127	121	CLOG.
B bis	1.61	1.34E-02	2.51E-02	1.2	1.2	56	6.0E-04	355	1129	126	YES
LCAL1 mix	15.00	1.74E-02	3.11E-02	6	2.6	42	1.0E-03	199	1269	158	YES
LCAL2 mix	15.00	1.74E-02	3.11E-02	6	2.6	41	1.0E-03	205	1270	158	YES

Initial pH = 2.

t denote time in hours needed to passivate the column.

tau denotes residence time calculated as V/Q .

t/tau denotes passivation time normalized with respect to residence time.

“mix” indicates column filled with calcite and glass beads ($\sim 1/3$ and $\sim 2/3$ in weight respectively).

mg Fe/g limestone denotes amount of iron retained by limestone.

Table 3

minerals	reactive surface area (m2 mineral/m3 rock)	vol. fraction
calcite	20	0.506
gypsum	10	0
goethite	0.1	0
input water	total conc. (mol/kg)	
Ca ²⁺	1.00E-09	
Fe ³⁺	1.79E-02	
HCO ₃ ⁻	1.29E-05	
SO ₄ ²⁻	3.42E-02	
pH	2.00	
initial rock water	total conc. (mol/kg)	
Ca ²⁺	5.32E-04	
Fe ³⁺	1.00E-19	
HCO ₃ ⁻	1.06E-03	
SO ₄ ²⁻	1.00E-09	
pH	8.22	
effective diffusion coefficient		
De (m ² /sec)	5.00E-10	
dispersivity α (m)	1.30E-03	
Darcy velocity m ³ /m ² /sec	1.03E-06	
nodes	20	

Table 4

	logK _{T=25°C}	
Calcite	1.8480	$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$
Gypsum	-4.4820	$CaSO_4 \cdot 2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$
Goethite	0.5345	$FeO \cdot OH + 3H^+ \leftrightarrow Fe^{3+} + 2H_2O$

Table 5

logK _{25°C}	reactions
-6.3447	$CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+$
10.3288	$CO_3^{2-} + H^+ \leftrightarrow HCO_3^-$
7.0017	$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^- + H_2O$
-1.0467	$CaHCO_3^- \leftrightarrow Ca^{2+} + HCO_3^- + H_2O$
12.8500	$CaOH^+ + H^+ \leftrightarrow Ca^{2+} + H_2O$
-2.1110	$CaSO_{4(aq)} \leftrightarrow Ca^{2+} + SO_4^{2-} + H_2O$
5.6700	$Fe(OH)_2^+ + 2H^+ \leftrightarrow Fe^{3+} + 2H_2O$
12.000	$Fe(OH)_{3(aq)} + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$
21.6000	$Fe(OH)_4^-(aq) + 4H^+ \leftrightarrow Fe^{3+} + 4H_2O$
-3.2127	$Fe(SO_4)^{2-} \leftrightarrow Fe^{3+} + 2SO_4^{2-}$
2.9500	$Fe_2(OH)_2^{4+} + 2H^+ \leftrightarrow 2Fe^{3+} + 2H_2O$
6.3000	$Fe_3(OH)_4^{5+} + 4H^+ \leftrightarrow 3Fe^{3+} + 4H_2O$
0.6088	$FeCO_3^+ + H^+ \leftrightarrow Fe^{3+} + HCO_3^-$
9.5000	$FeOH^{2+} + H^+ \leftrightarrow Fe^{3+} + H_2O$
-1.9276	$FeSO_4^+ \leftrightarrow Fe^{3+} + SO_4^{2-}$
1.0209	$H_2SO_{4(aq)} \leftrightarrow SO_4^{2-} + 2H^+$
-1.9791	$HSO_4^- \leftrightarrow SO_4^{2-} + H^+$

Table 6

mineral	$k_{m,25}[\text{mol m}^{-2}\text{s}^{-1}]$	$n(a_{\text{H}^+}^n)$
calcite	5.01E-01	1
	1.55E-06	-
goethite	1.15E-08	-
gypsum	1.62E-03	-