Contents lists available at ScienceDirect



Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

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



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ARTICLE INFO

Article history: Received 8 July 2014 Accepted 18 September 2014 Available online 22 October 2014

Keywords: Acid mine drainage Passive treatment Passivation Clogging X-ray microtomography

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) ironrich 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 $1 \times 10^{-3} Lm^{-2} s^{-1}$. 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.

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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].

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http://dx.doi.org/10.1016/j.jece.2014.10.013 2213-3437/© 2014 Elsevier Ltd. All rights reserved. These contaminants can persist in environment during several centuries after interruption of mining activity [3]. The main AMD-generating mineral is pyrite (FeS₂) [4–8], according to the following reactions [9]

$$FeS_2 + 3.5O_2(aq) + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
(1)

$$Fe^{2+} + 0.25O_2 + H^+ \rightleftharpoons Fe^{3+} + 0.5H_2O$$
 (2)

$$Fe^{2+} + H_2 O \rightleftharpoons Fe(OH) + 3H^+$$
(3)

 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]

$$8Fe^{3+} + SO_4^{2-} + 14H_2O \rightleftharpoons Fe_8O_8(OH)_6(SO_4) + 22H^+$$
(4)

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releasing more protons, or as a Fe(III)-hydroxide (ferrihydrite), also releasing protons. But, at pH lower than 3.5, Fe(III) remains mainly in solution and acts as another oxidizing agent for pyrite according to

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$
(5)

Since AMD can be highly acidic, it has the capacity to dissolve rocks that are commonly formed by clays and other aluminosilicates. This process releases major rock constituents (e.g., silica, aluminum, iron, sodium, potassium, magnesium, calcium), together with heavy metals, into the environment [1].

The main purposes of AMD treatments are retention of metals (precipitation of the contaminant metals) and neutralization of acidity. One of the possible and most common passive treatment systems is the anoxic limestone drain (ALD), or systems derived from it (e.g., reducing and alkalinity producing systems), characterized by low maintenance needs and low cost [11–17]. ALD uses ditches of buried limestone gravel. Acid water flows through the gravel and limestone dissolves, raising pH and alkalinity, yielding metal retention as Me-oxyhydroxide precipitates. The efficiency of the ALD systems is however limited because secondary mineral precipitation causes the passivation (armoring) of the limestone grains and clogging of the pores, reducing limestone reactivity and acid neutralization [18–24]. In addition, the presence of aqueous sulfate leads to gypsum precipitation [25–27], which essentially contributes to passivation and affects greatly the efficiency of the treatment systems.

Soler et al. [27] reproduced at the laboratory scale the behavior of ALD systems using column reactors filled with limestone grains. Injecting acid solutions (pH 2, HCl and H₂SO₄) with initial concentrations of Fe(III) ranging from 9.27×10^{-3} to 3.61×10^{-2} mol L⁻¹, it was observed that (1) gypsum coating was responsible for calcite passivation, (2) passivation time in the column was dependent on the initial aqueous sulfate concentration and (3) change in porosity and permeability was due to precipitation of both gypsum and Me-oxyhydroxides. Moreover, once the columns were passivated, X-ray microtomography was used *a posteriori* to examine the precipitates responsible for the porosity changes.

To enhance our knowledge on the loss of calcite reactivity due to grain coating or clogging of porosity initially discussed by Soler et al. [27], this study presents three main innovations: The first innovation is that the column experiments were performed using calcite sand and synthetic acid solutions not only containing $Fe(III)-SO_4^{2-}-H^+$ as in Soler et al., [27], but also containing $AI-SO_4^{2-}-H^+$ as major components at pH 2. Moreover, two experiments were performed at pH 3. Concentrations of Fe(III) and Al ranged from 3.49×10^{-3} to 2.60×10^{-2} mol L^{-1} and from 3.60×10^{-3} to 3.61×10^{-2} mol L^{-1} , respectively, which fall in the range found in AMD [1,28].

The second innovation is that in the present study, in order to clarify how the secondary phases precipitate and influence the porosity change, several X-ray microtomography (mCT) measurements were carried out. mCT images were collected at different times 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:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2CO_3 \tag{6}$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s)$$
 (7)

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+$$
 (8)

or

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3(s) + 3H^+$$
 (9)

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

Table 1

Experimental	conditions	of the	aluminum	column	experiments.
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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
С	1.8	1.80E-02	3.19E-02	1.1	1.2	46	101	142	15
А	1.6	9.27E-03	1.89E-02	1.2	1.2	57	152	291	18
Μ	1.6	7.20E-03	1.58E-02	1.1	1.2	51	178	280	13
Ν	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 1×10^{-3} Lm⁻² s⁻¹; initial pH is 2 except in 4 and 2 where it is 3; all column experiments were passivated; t_{pass} denotes 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; mg Al/g limestone denotes amount of aluminum retained by limestone.

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