Applied Geochemistry 73 (2016) 13–23

Contents lists available at ScienceDirect

Applied Geochemistry

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

Effectiveness of various dispersed alkaline substrates for the pre-treatment of ferriferous acid mine drainage

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ARTICLE INFO

Article history:
Received 26 January 2016
Received in revised form
20 July 2016
Accepted 22 July 2016
Available online 25 July 2016

Keywords:
Ferriferous acid mine drainage
Iron pre-treatment
Dispersed alkaline substrate
Calcite
Dolomite

ABSTRACT

Dispersed alkaline substrates (DAS) have been successfully used in passive treatment of highly contaminated acid mine drainage (AMD) to limit coating and clogging issues. However, further optimization of DAS systems is still needed, especially for their long-term efficiency during the treatment of ferriferous AMD. In the present study, three types of DAS comprised of natural alkaline materials (wood ash, calcite, dolomite), in different proportions (20%v/v, 50%v/v, 80%v/v), and a substrate with high surface area (wood chips) were tested in 9 batch reactors. The testing was carried out, in duplicate, for a period of 91 days, to evaluate the comparative performance of the mixtures for iron pre-treatment in ferriferous AMD (2500 mg/L Fe, at pH 4). Results showed increasing of pH (between 4.15 and 7.12), regardless of the proportion of alkaline materials in the DAS mixtures. Among the tested mixtures, wood ash type DAS were more effective for Fe removal (99.9%) than calcite or dolomite type DAS (up to 66%). All tested DAS had limited efficiency for sulfate removal and an additional treatment unit, such as a sulfate-reducing biochemical reactor, is needed. Moreover, due to the similar performances of the calcite and dolomite DAS, they could be potentially substituted and rather be used in a polishing treatment unit. Based on these findings, the most promising mixture was the 50% wood ash type DAS (WA50-DAS).

1. Introduction

Environmental impacts of acid mine drainage (AMD), which is characterized by low pH ($-3.6 < pH < 6$) and high concentrations of dissolved metals, metalloids and sulfate (SO$_4^{2-}$) are largely documented (Neuman et al., 2014; Nordstrom et al., 2015). Improvement of technologies has been conducted over the last decade to limit and prevent AMD generation (Sahoo et al., 2013; Jennings and Jacobs, 2014). Several treatment technologies, including active and passive systems, have also been developed (USEPA, 2014). Passive treatment is preferred, principally for moderately contaminated water, because of its low cost, potential production of marketable sludge, and simple installation and operation (Hedin et al., 2013; Zipper and Skousen, 2014). Despite these advantages, efficiency of a single unit of passive treatment (e.g. oxic/anoxic limestone drains- OLD/ALD, passive biochemical reactor- PBR) is limited when used for the treatment of highly contaminated AMD, particularly ferriferous AMD ($Fe > 500$ mg/L) (Neculita et al., 2008; Genty et al., 2010). Hence, combinations of two or more units of passive treatment or so-called passive multi-step treatment system have been developed (Macías et al., 2012; Genty et al., 2012a). Nonetheless, coating/passivation (loss of reactivity) and clogging (loss of permeability) caused by precipitated minerals during treatment (e.g. gypsum, metal oxide-hydroxides) (Rötting et al., 2008a) are presently limiting the long term performance of such systems. Their longstanding efficiency is conditioned by removal, at an early stage, of acidogenic metallic elements, such as Fe and/or Al (Ayora et al., 2013). Indeed, during precipitation of ferric iron as hydroxide [Fe(OH)$_3$] (Eq. (1)), which starts at pH around 3–3.5, depending on Fe total concentration, the pH decreases, and the removal of divalent metals (which precipitation requires $pH > 8.5$), is inhibited.

Abbreviations: ALD, Anoxic limestone drains; AMD, Acid mine drainage; DAS, Dispersed alkaline substrate; LOI, Loss on ignition; NFOL, Natural Fe-oxidizing lagoon; OLD, Oxic limestone drains; PBR, Passive bioreactor; WA-DAS, Wood ash-dispersed alkaline substrate.

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http://dx.doi.org/10.1016/j.apgeochem.2016.07.014
0883-2927/

$$Fe^{3+} + 3H_2O \rightarrow Fe\,(OH)_3 + 3H^+ \quad (1)$$

Consequently, a pre-treatment unit for Fe removal in ferriferous AMD is a must before forwarding water into a second treatment unit for the removal of other metals and of SO_4^{2-}, if necessary. Various techniques have been developed for Fe pre-treatment, such as oxidation/precipitation (Champagne et al., 2008), oxic limestone drain (OLD) (Figueroa et al., 2007), natural Fe-oxidizing lagoon (NFOL) (Macías et al., 2012), and cascade aeration (USEPA, 2014). Most of these techniques gave promising results, but have been mostly used for Fe pre-treatment when AMD has low to moderate concentrations (40–1000 mg/L Fe). Regarding Fe concentration, the quality of water in this study is then considered as extremely contaminated (2500 mg/L Fe).

Innovative approaches using reactive mixtures composed of a coarse, highly porous material (wood chips) and small grain size of neutralizing agents (e.g. MgO, $CaCO_3$) known as dispersed alkaline substrate (DAS) have also been investigated with the aim of overcoming the coating-clogging general issues in passive treatment (Macías et al., 2012; Ayora et al., 2013). Two main types of DAS have been used to treat AMD, one comprised of MgO (MgO-DAS), for the removal of bivalent metals (e.g. Macìas et al., 2012; Ayora et al., 2013), and one of calcite (calcite-DAS), for the removal of trivalent metals (e.g. Rötting et al., 2008b; Caraballo et al., 2011).

In passive treatment, the use of economic, available and natural materials or substitute is recommended. Other selection criteria include the reaction rate of neutralizing agents, sludge production and costs (Potgieter-Vermaak et al., 2006). Hence, the dolomite DAS could be an economic replacement of the calcite/limestone DAS because it could reduce expenses up to 23% (Potgieter-Vermaak et al., 2006). Moreover, previous studies using dolomite as a neutralizing agent in the treatment of very acidic water have shown promising results (Potgieter-Vermaak et al., 2006; Huminicki and Rimstidt, 2008; Genty et al., 2012a). Depending on the grain size, some studies even presented comparable efficiency of calcite and dolomite when used for the treatment of moderately contaminated AMD under anoxic condition, with lower difference in alkalinity production (105–220 mg/L as $CaCO_3$) for a hydraulic retention time of 15 h (Genty et al., 2012a). Additional benefits of dolomite-DAS include the delaying of the neoformed minerals (e.g. gypsum $CaSO_4{\cdot}H_2O$) because of the belated release of Ca^{2+}.

Another potential replacement of MgO in DAS systems could be wood ash, principally used for its high pH (up to 12), metal retention, and neutralization capacity. The wood ash, which is usually considered as a waste, has in fact a good potential of reuse. It showed efficiency in the pre-treatment of ferriferous AMD (Genty et al., 2012b). Moreover, it is an economic material, relative to MgO which cost is up to ten times higher than limestone (Rötting et al., 2006). Then, wood ash-DAS (WA-DAS) could be advantageous and potentially give similar performance to MgO-DAS. Despite the satisfactory performance (in terms of Fe and SO_4^{2-} removal, as well as of hydraulic conductivity stability) of the wood ash, its long term performance remains uncertain (Genty et al., 2012b). Moreover, additional treatment units for sulfate removal are necessary.

The results of a very recent laboratory study, which compared the performance of calcite-DAS to witherite ($BaCO_3$)-DAS, in terms of SO_4^{2-} removal, showed that the last was more efficient, but became unreactive after only 40 days of operation, due to passivation (by coating with barite – $BaSO_4$) (Lozano et al., 2015).

Therefore, the objective of the present study is to evaluate the efficiency of WA-DAS, calcite-DAS and dolomite-DAS in batch testing, in the perspective of their use as pre-treatment units for Fe removal in a ferriferous AMD. The residual Fe concentration targeted for this pre-treatment is 500 mg/L. This concentration was reported as a threshold value based on the steady performance of a PBR, in a 15-month laboratory study (Neculita et al., 2008).

2. Materials and methods

2.1. Physicochemical characterization of materials composing the mixtures

Nine reactive mixtures made of natural materials, i.e. wood chips, and three neutralizing agents (wood ash, calcite and dolomite) were evaluated in batch tests. The wood ash was a by-product from a co-generation plant located at Kirkland Lake (Canada), the wood chips originated from P.W.I. industries (QC), the calcite from the quarry of Perth (ON), and the dolomite from the Temiscamingue region (QC). These three reagents were mainly composed of Ca and Mg (Table 1, Supplementary material). Grain size of calcite and dolomite was less than 5 mm, in order to allow almost complete dissolution, before eventual armoring during the treatment of ferriferous AMD. In this study, paste pH of the nine mixtures was determined in deionized water using a solid liquid ratio of 1:10 (ASTM, 1995). Water content was evaluated in duplicate by drying samples at 40 °C during 2 days. Specific surface area (Ss) of dry samples was determined by the BET method using 5-point N_2 adsorption isotherms with Micromeritics Gimini III 2375 surface analyzer. Particle size analysis was carried out using standard sieves (ISO R-20) in order to obtain size corresponding to 10% and 60% by weight of passing, as well as uniformity coefficient (D_{10}, D_{60} and $C_u = D_{60}/D_{10}$ respectively) (Aitcin et al., 2012). Loss on ignition (LOI), used as an indication of the organic matter content, was determined by weighing the samples before and after calcination (375 °C for 16 h). Each mixture was grinded and sieved through 0.25 mm opening before being digested in a mixture of strong mineral acids (HNO_3, Br_2, HCl, and HF) (Potts, 1987). Then, the resulting digestate was analyzed for Fe, Ca, Mg and SO_4^{2-} content by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES; relative precision of 5%) using a Perkin Elmer OPTIMA 3100 RL.

2.2. Batch testing description

The nine mixtures were set up in duplicate in 18 glass flasks of 1 L, at room temperature (around 20 °C). Each batch reactor was filled with 200 g dry mixture and 600 mL synthetic AMD (Neculita and Zagury, 2008). Mixtures consisted of wood chips and one of the following three neutralizing agents: wood ash (WA-DAS), calcite (calcite-DAS) or dolomite (dolomite-DAS) (Table 1). The batch testing was performed during a 91-day period.

The characteristics of synthetic AMD (Table 2) simulated the typical water quality of ferriferous AMD encountered at several closed/abandoned mine sites in the region of Abitibi-

Table 1
Composition and relative proportion of components of the nine reactive mixtures tested in batch reactors.

Reactors	Wood ash	Calcite	Dolomite	Wood chips	Total
	(%v/v)				
WA20	20	–	–	80	100
WA50	50	–	–	50	100
WA80	80	–	–	20	100
C20		20	–	80	100
C50	–	50	–	50	100
C80	–	80	–	20	100
D20	–	–	20	80	100
D50	–	–	50	50	100
D80	–	–	80	20	100

WA: Wood ash; C: Calcite; D: Dolomite.