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TECHNICAL ARTICLE

The Potential Use of Phosphatic Limestone Wastes in the Passive Treatment of AMD: A Laboratory Study

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Abstract In Morocco, there are many sedimentary phosphate mines that produce large quantities of phosphatic limestone wastes (PLW) that contain calcite (46 wt%) and dolomite (16 wt%). These mines are located near contaminated sites, such as the abandoned Kettara pyrrhotite mine. The surface drainage water at the Kettara mine site has a pH of 2.9–4.2 and elevated concentrations of SO_4 (from 47 to 5,000 mg/L) and Fe (from 1 to 1,200 mg/L). The efficiency of PLW was assessed in the laboratory as an alternative alkaline material for passive acidic mine drainage (AMD) treatment. A series of experiments were carried out using a synthetic AMD (pH 3) containing Fe (500 mg/L), SO_4 (3.4 g/L), Ca (220 mg/L), Al (160 mg/L), Mn (20 mg/L), Zn (15 mg/L), Cu (23 mg/L), and trace amounts of Co, Cr, and Ni. Experiments were done in both anoxic and oxic conditions, in batch and column tests, with hydraulic retention times of 24 and 15 h, respectively. The PLW efficiently increased the alkalinity and pH, inducing precipitation of most metals. The neutralizing capacity of PLW prepared at different particle sizes (0.8 mm–0.5 cm, 0.5–1, 1–2, and 2–3 cm) was found to be similar in batch tests. The initial AMD value increased from 3 to 5–6.5 during the batch tests and 6.5–8 in the columns. In batch tests under anoxic and oxic conditions, there was a significant decrease in concentrations of Fe (500–120 mg/L), Al (160–1.7 mg/L), and Cu (23–0.002 mg/L). In the column tests, Al and Cu decreased (177–2.5 and 26–0.002 mg/L, respectively), while Fe decreased less significantly (618–300 mg/L). The availability and low cost of the PLW make its use in passive AMD treatment potentially feasible.

Keywords Acid mine drainage treatment · Batch and column testing · Kettara mine site · Pollution

Introduction

Mine wastes produced during mining and subsequent ore processing can cause significant contamination of drainage water (Blowes and Ptacek 1994; Evangelou and Zhang 1995; Kleinmann et al. 1981). Oxidation of sulfide minerals and hydrolysis of their oxidation products can produce acidic mine drainage (AMD), which may drain into local waterways and groundwater, along with elevated concentrations of SO_4^{2-} and contaminants such as Fe, Al, Mn, Pb, Zn, Cu, Cd, depending on the geology and mineralogy of the mine site.

In the context of sustainable development, active treatment using chemical treatment systems to neutralize acidity (Ríos et al. 2008) is not considered a viable option for long-term remediation of AMD-generating sites (Genty et al. 2012; Potvin 2009; Ziemkiewicz et al. 2003). Passive

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methods require less energy and use natural or waste alkaline materials. Two main objectives are generally considered in designing a passive treatment system (Bernier 2005): (1) generating sufficient alkalinity to neutralize the acidity, and (2) decreasing the metal loading through oxidation/hydrolysis, and precipitation mechanisms. Passive AMD treatment methods include anoxic and oxic limestone drains (ALD, OLD), open limestone channels (OLC), successive alkalinity-producing systems (SAPS), limestone ponds, microbial reactor systems, reactive walls, and bio-sorption systems (Alcolea et al. 2012; Bernier 2005; Cravotta and Trahan 1999; Faulkner and Skousen 1994; Hedin and Watzlaf 1994; Kepler and McCleary 1994; Kleinmann 1989; Neculita et al. 2007; Ziemkiewicz et al. 1997).

Limestone ($CaCO_3$) is a common product often chosen worldwide for neutralizing AMD as it is cost-effective and often widely available in the local surrounding natural environment (Hedin et al. 1994; Nairn et al. 1991). The dissolution of one mole of $CaCO_3$ consumes 1–2 moles of acidity and releases alkalinity (as HCO_3^-) into the aqueous solution (Garrels and Christ 1965). The treatment of AMD with limestone can increase the pH to 6.0–7.5 (Pearson and McDonnell 1975; Webb and Sasowsky 1994), allowing the metals to be removed from solution via precipitation, co-precipitation, and sorption processes. Limestone is commonly used in both active and passive AMD treatments. Passive treatment systems using exclusively limestone for neutralization are generally implemented for post-closure and low-acid load treatment scenarios (Taylor and Waters 2003). They are relatively inexpensive to construct and maintain. Limestone anoxic drains are closed trenches filled with limestone, through which the AMD percolates. They are designed to exclude O_2 within the trench, thereby inhibiting ferrihydrite [$Fe(OH)_3$] precipitation onto the limestone particles and increasing partial pressure of CO_2. The initial section of the trench can be filled with organic material (Zagury et al. 2006). In OLD, the AMD influent contains relatively high O_2 (equilibrium with the atmosphere). Limestone drains, channels, and diversion wells use limestone gravel to avoid clogging (Hedin et al. 1994; Robbins et al. 1999), although this reduces the reactive surface area compared to the very fine-grained limestone used in active system reactors. During neutralization of acid drainage, several species may precipitate. If SO_4^{2-} occurs at high concentrations in the AMD (>2,000 mg/L; McDonald and Webb 2005), gypsum ($CaSO_4 \cdot 2H_2O$) can be formed. Dissolved Fe(III) and Al precipitate as metal hydroxides, mainly as ferrihydrite and gibbsite [$Al(OH)_3$]. Eusden et al. (2002) showed that the use of phosphate and lime to stabilize tailings from a mine in Colorado led to the formation of various phosphate-metallic complexes and a decrease in the metal concentrations in the pore water.

The studied Kettara mine site is one of several abandoned mine sites in Morocco that produces AMD, contaminating surface and groundwater (Hakkou et al. 2008a; Lghoul et al. 2012). More than 3 million t of mine wastes deposited on the surface of the Kettara site without any concern for environmental consequences have generated significant AMD for more than 30 years. Tailings were stockpiled in a main pond, but also in a dyke, and in smaller piles over an area of approximately 16 ha. The Kettara fine and coarse tailings are highly acid-generating, with NNPs ranging from −22 to −453 kg/$CaCO_3$/t (Hakkou et al. 2008a). Weathering and humidity cell tests were used to predict the potential for AMD and depletion of fine and coarse tailings from the abandoned Kettara mine (Hakkou et al. 2008b). Effluent water samples had low pH (2.9–4.2) and elevated concentrations of sulfate (47–5,000 mg/L) and iron (1–1,200 mg/L). Concentrations of Cu and Zn reached 58 and 45 mg/L, respectively. The pollution potential of the coarse tailings was found to be greater than that of the fine tailings due to their larger particle size distribution and greater permeability, which facilitates exposure to oxygen and percolation of water (Hakkou et al. 2008b).

Morocco is the world's leading phosphate exporting country and the third largest in terms of phosphate production after USA and Russia. At the Exploitations Minières du Gantour Company Recette VI site, 30 km north of the abandoned Kettara mine (Fig. 1a), large quantities of overburden phosphatic carbonated wastes (PLW) is removed to reach the phosphate ore layers. Trucks transport the ore to a dry screening plant for phosphate separation/concentration and manage the oversize (>40 mm) low-grade material as wastes on site. Thus, the Recette VI phosphate mine produces two waste types: the overburden waste rock (PLW used in this study) and the wastes produced during the pre-concentration process. Large amounts of these wastes are produced and stockpiled in different waste rock dumps.

The feasibility of using this PLW, which contains significant quantities of calcite (46 wt% $CaCO_3$) and dolomite [16 wt% $CaMg(CO_3)_2$], to control AMD generated by the Kettara coarse tailings was investigated in laboratory column leaching tests by Hakkou et al. (2009). The addition of 15 wt% PLW to the coarse Kettara tailings produced leachates with significantly lower acidities and metal concentrations than unamended tailings. The PLW are chemically stable and non-polluting; mixing PLW with distilled water for 2 h at a liquid/solid ratio of 2.5 led to a leachate with a neutral pH (6.5), low conductivity (0.3 mS/cm), and very low iron concentrations (Hakkou et al. 2009).

The present study was conducted to evaluate if PLW can be used as an alternative alkaline material for passive

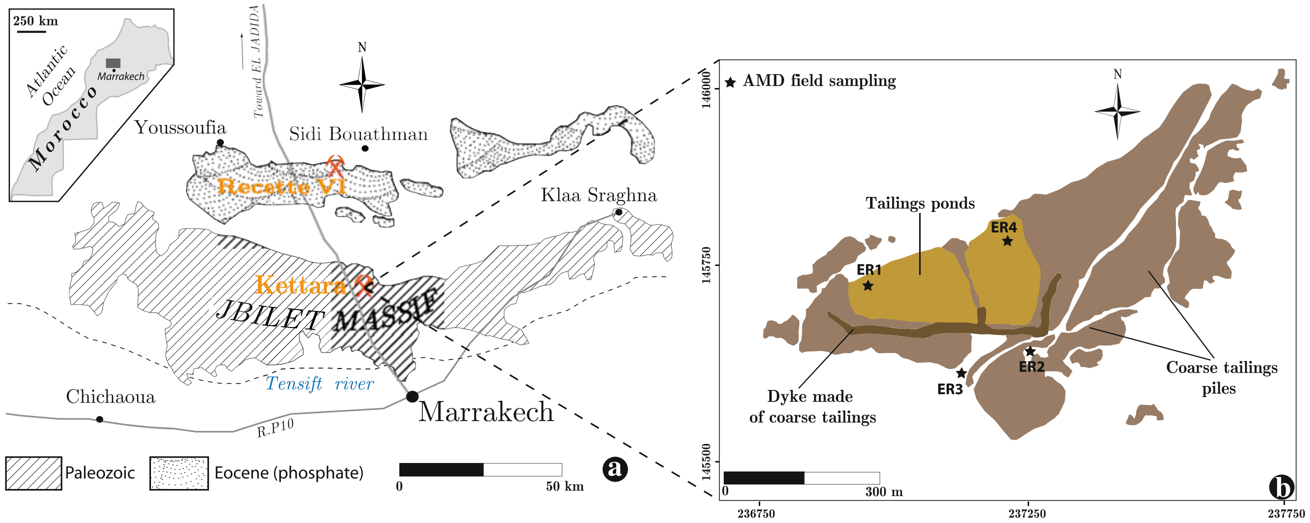


Fig. 1 **a** Simplified geological *map* of the study area and location of the Kettara and phosphate mines, **b** sample locations of the surface water runoff from the fine tailings pond (ER1 and ER4) and from the coarse tailings piles (ER2 and ER3)

treatment of AMD. It focused on the neutralizing capacity of the PLW-based system treatment and also investigated whether residual phosphate in the PLW might affect the neutralization process. Building channel treatment systems at the closed Kettara mine with PLW material would be an inexpensive way to alleviate the negative environmental effects of AMD. At laboratory scale, the capacity of PLW was evaluated to treat synthetic AMD solution. The latter had a low pH (3) and contained Fe (500 mg/L), SO_4 (3.4 g/L), Ca (220 mg/L), Al (160 mg/L), Mn (20 mg/L), Zn (15 mg/L), Cu (23 mg/L), and traces of Co, Cr, and Ni. The AMD treatment tests were conducted in both anoxic and oxic conditions, in batch and column tests with hydraulic retention times of 24 and 15 h, respectively.

Materials and Methods

AMD Field Sampling

The surface water runoff at the Kettara mine is strongly acidic (pH = 3 ± 0.1) and metal-rich due to the oxidation of sulfide minerals, and is orange-brown in color is due to the very high concentrations of dissolved ferric iron. The climate in this area is classified as semi-arid with a mean annual rainfall of approximately 250 mm. Rain can fall over short periods with high intensity. The annual potential evaporation typically exceeds 2,500 mm. AMD samples were collected at four major locations at the abandoned mine site and sealed in high-density polyethylene bottles for further laboratory analysis. Sampling locations are indicated on Fig. 1b, where ER1 and ER2 samples correspond to the water runoff from the fine tailings pond and ER2 and ER3 correspond to the surface water runoff from the coarse tailings piles.

Table 1 Composition of synthetic AMD added to the batch and the tap water used for column tests

Components	Concentration (mg/L)	Source
Ca^{2+}	283 ± 20	$CaSO_4 \cdot 2H_2O$
Al^{3+}	144 ± 10	$AlK(SO_4)_2 \cdot 12H_2O$
Fe^{2+}	539 ± 70	$FeSO_4 \cdot 7H_2O$
Co^{3+}	4.68 ± 2	$CoSO_4 \cdot H_2O$
Cu^{2+}	23 ± 4	$CuSO_4 \cdot 5H_2O$
Zn^{2+}	15 ± 3	$ZnSO_4 \cdot 7H_2O$
Mn^{2+}	20 ± 2	$MnSO_4 \cdot H_2O$
Mg^{2+}	197 ± 70	$MgSO_4 \cdot 7H_2O$
SO_4^{2-}	3,630 ± 200	–

A solution of synthetic AMD (Table 1) was prepared by adding various proportions of hydrous metal sulfates with 5 L of deionized water for batch experiments (Bernier 2005). The physico-chemical properties of the solution were: pH of 3 ± 0.2, a conductivity of 4.2 ± 0.3 mS/cm, and a total acidity of 3,670 mg/L (as $CaCO_3$). For the column experiments, 100 L of tap water was used.

Analytical Methods

The effluent obtained from the Kettara Mine, the batch tests, and from the columns tests were filtered through a 0.45 μm nylon filter and were split into two subsamples. The first was acidified with HNO_3 (to avoid metal precipitation) for metals analysis and was refrigerated at 4 °C. The second (unacidified) was used for the analyses of sulfates, total alkalinity and total acidity. The concentrations of metals were determined using inductively coupled plasma optical emission spectroscopy, ICP–AES (Perkin-Elmer Optima DV 7000 ICP–OES, relative precision of 5 %). Sulfates were analyzed using a Tomos spectrophotometer at a wavelength of 650 nm, using the barium chloride method.

The alkalinity of untreated and treated AMD (expressed in mgCaCO$_3$/L) was obtained by titration of non-filtered sample with sulfuric acid 0.02 N (precision of 1 mg CaCO$_3$/L), and the acidity by titration of non-filtered sample with sodium hydroxide 0.1 N (precision of 1 mg CaCO$_3$/L) (APHA 1995). Sample pH was measured by a combination pH electrode with temperature compensation (Instruments Hanna model 209) after calibration with standard buffer solutions of pH 4.01 and 7.01 (±0.01). Redox potential was measured using a Pt/Ag/AgCl combination electrode (thermo Orion SureFlow®), which was calibrated with a standard redox buffer solution of 220 mV. The measurements were corrected to obtain Eh expressed in mV/SHE (standard hydrogen electrode). Conductivity was determined with a HANNA HI 8773 meter.

Phosphate Limestone Wastes (PLW) Analysis

PLW materials were ground using an agate mortar. The resulting powder was analyzed by inductively coupled plasma and atomic emission spectrometry (ICP–AES PerkinElmer Optima 3100) after HNO$_3$/Br$_2$/HF/HCl digestion. Dilute HCl was used to extract sulfate from the samples, and the solution obtained was analyzed using the same ICP–AES. Total carbon and sulfur content were measured using an ELTRA CS 800 sulfur/carbon analyzer. Pulverized samples were analyzed by X-ray diffraction (XRD) analysis using a Bruker AXS D8 Advance diffractometer equipped with a scintillation detector and Co Kα radiation ($\lambda = 1.54$ Å). The data were collected at 5–70° by steps of 0.005° and a count time of 0.5 s/step.

Grain size analysis was performed in two steps: first, by sieving for the granular fractions with diameter >80 µm and second, by using a Malvern Mastersizer laser particle size analyzer for the grain fraction smaller than 80 µm. The specific gravity was estimated with a Micromeritics Accupyc 1330 helium pycnometer.

Laboratory Batch Experiments

The batch experiments were based on those proposed by Bernier (2005). The passive treatment of synthetic AMD (Table 1) was simulated in the laboratory using the alkaline PLW. The purpose of these tests was to study the effect of particle size (D1: 0.8 mm–0.5 cm; D2: 0.5–1 cm; D3: 1–2 cm; D4: 2–3 cm) on the kinetics of dissolution of PLW under anoxic conditions. The water/rock ratio was about 1 mL/g (550 mL/550 g). Each reactor consisted of a 750 mL glass jar filled with synthetic AMD and the PLW material. The reactor was hermetically sealed with a rubber seal and a top cap to maintain anaerobic conditions.

The batch test series were performed for 48 h, with the first 24 h under static anaerobic conditions. This is >15 h that correspond to an optimal hydraulic residence time (HRT) for ALDs (Hedin et al. 1994). After the first period of 24 h, the reactor was opened for another 24 h period to introduce air into the treated solution. Parameters such as pH, Eh, EC, acidity, alkalinity, metal, and sulfate concentrations were measured throughout the entire testing period (at 0, 0.5, 1, 2, 3, 5, 10, 15, 24, and 48 h).

Another test of oxic batch treatment was assessed under the same conditions. However, only one particle size of PLW (0.8 mm–0.3 cm) was tested. The batch test series were performed for 48 h (2 days) under static aerobic conditions. Parameters such as pH, Eh, EC, acidity, alkalinity, metal and sulfate concentrations were monitored throughout the entire testing period (at 0, 1, 2, 3, 5, 10, 15, 24, and 48 h).

Column Experiments

A dynamic treatment system was simulated in a column under anoxic (Fig. 2a) and oxic conditions (Fig. 2b). Twenty kg of PLW were used in the anoxic column tests, while 44 kg of PLW were used in the oxic column tests. The particle grain size fraction of PLW used in these tests was 0.8 mm–3 cm. The column was fed with synthetic AMD from the bottom to control solution flow and to have a good impregnation and targeted residence time. The up-flow was set at 5.5 mL/min to have a HRT in the column of approximately 15 h. The flow was controlled using a peristaltic pump. At the exit of the anoxic treatment column, the effluent was aerated within a glass ball before being sent to a clarifier tank. Parameters such as pH, EC, alkalinity, metal, and sulfate concentrations were determined in samples collected at the exit of the column and after aeration (Fig. 2).

Results and Discussion

Characterization of the AMD Field Samples

AMD only occurs in these regions after rainfall events. Irregular rain can fall over short periods and with high intensity. Field data for the rainy season of 2010–11 (the end of 2010 and the beginning of 2011) were: pH 2.4–3.4; EC 2.25–27.6 mS/cm (20 °C); sulfate (8,000–49,600 mg/L); Fe (40–1,650 mg/L), and Al (730–4,170 mg/L). The AMD

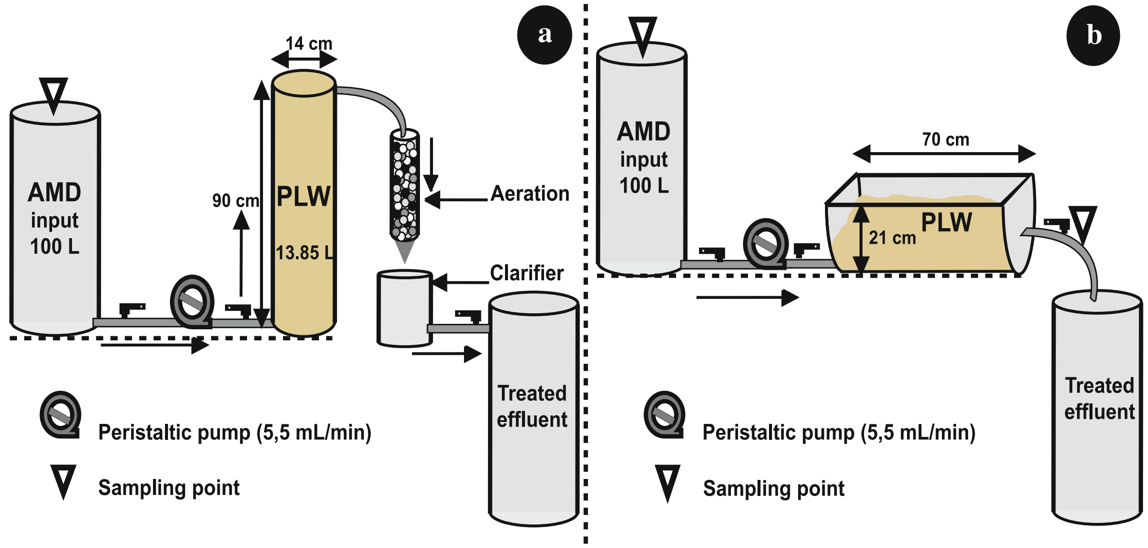


Fig. 2 **a** Schematic representation of anoxic treatment (*picture* not to *scale*), **b** schematic representation of oxic treatment (*picture* not to *scale*)

was strongly acidic and contained high levels of Co, Cu, Mn, and Zn (Table 2). Given the solution's redox potential (Eh: 600–800 mV/ENH) and pH (3), the Fe in AMD from the Kettara mine is mainly Fe^{2+} ions. The concentrations were similar to those produced during humidity cell tests done with Kettara mine wastes (Hakkou et al. 2008b). Iron release is controlled by a complex assemblage of minerals, including pyrrhotite, pyrite, chalcopyrite, goethite, and magnetite. Almost all of the dissolved Na, Al, Mg, and Si in the AMD result from the acidic dissolution of silicates (chlorite, talc, muscovite, and albite); Ca is present as gypsum and/or calcite (Hakkou et al. 2008b). Oxidation of chalcopyrite is the source of the dissolved Cu; sphalerite in the source of the Zn (Hakkou et al. 2008b); and pyrrhotite is the source of the Co (Hibti 2001). The highly acidic effluents of the Kettara Mine, with its high levels of potentially toxic metals, contaminates soil and aquatic ecosystems and consequently, human health and wildlife. This justifies the treatment of Kettara's AMD.

Phosphatic Limestone Wastes Analysis

In terms of particle size distribution, the D_{60} (Dx being the effective diameter, corresponding to x% passing on the cumulative grain-size distribution curve) and D_{80} of the PLW waste rocks were estimated to be about 8 and 31 mm, respectively (Fig. 3). The specific gravity of this material was approximately 2.83.

Table 3 summarizes the chemical analysis results and reveals high levels of CaO (42.28 wt%), P_2O_5 (12.99 wt%), SiO_2 (12.20 wt%), MgO (4.32 wt%), and C (6.7 wt%). Cr (183 mg/kg) and Zn (195 mg/kg) were potential contaminants, but had been previously shown not to be significant (Hakkou et al. 2009) in kinetic tests.

The chemical composition confirms the mineral composition presented in Table 3. PLW contains five main minerals: calcite (46.6 %), fluorapatite (27.2 %), dolomite (15.9 %), ankerite [$Ca(Mg_{0.45}, Fe_{0.55})(CO_3)_2$; 5.6 %],and quartz (4.7 %).

Anoxic Batch Tests

Figure 4 shows the experimental results related to the four particle size fractions 0.8 mm–0.5 cm (D1), 0.5–1 cm (D2), 1–2 cm (D3), and 2–3 cm (D4) of the PLW submitted to the anoxic batch tests. Clearly, the PLW particle sizes had negligible influence on AMD treatment. The synthetic AMD solution reached pH 5.5 after 5 h of contact time. The pH increased very rapidly during the first 30 min of contact time, corresponding to fast PLW dissolution, and then slowed down. A maximum pH of 6 was obtained for the synthetic AMD solution treated with particle sizes D1 (0.8 mm–0.5 cm), D3 (1–2 cm), and 2–3 cm (D4), whereas a maximum pH of 5.3 was obtained with particle size D2 (0.5–1 cm). The total acidity of the solution similarly decreased rapidly (3,600–250 mg/L as $CaCO_3$) during the first 30 min of contact, while total measured alkalinity increased substantially (reaching 100–200 mg/L as $CaCO_3$) for all particle size fractions. The pH values obtained using PLW in anoxic conditions were similar to values obtained by Bernier (2005) and Genty et al. (2012), who used calcite and dolomite under anoxic conditions. A slight decrease in the EC value (4,000–3,500 µS/cm) was observed during the contact period with all four size fractions.

Calcium concentrations within the solution using the four PLW particle size fractions increased very rapidly

Table 2 Chemical composition of the surface runoff from the fine tailings pond (ER1 and ER4) and from the coarse tailings (ER2 and ER3); concentrations in mg/L, with acidity in mg/L as $CaCO_3$, Eh as mV/ENH, and conductivity as mS/cm

	Sample					
	ER1			ER2		
Date	04/12/2010	01/02/2011	17/03/2011	04/12/2010	01/02/2011	17/03/2011
pH	2.78	2.66	2.6	2.41	2.64	2.57
Cond	4.95	13.35	8.15	7.64	27.6	2.25
Eh	795.0	759.0	745.0	837.0	726.0	753.0
Acidity	3,840.0	17,600.0	22,600.0	6,100.0	49,600.0	9,200.0
SO_4^{2-}	4,201.0	30,172.0	15,962.0	4,448.0	78,510.0	15,459.0
Ca	122.6	251.6	215.3	430.0	326.4	322.9
Al	608.9	2,228.0	937.4	824.0	3,081.0	828.8
Na	3.02	29.2	18.23	2.971	12.08	1.91
Si	3.55	11.52	4.17	53.03	11.17	15.56
Fe	188.3	459.4	205.7	767.7	886.7	258.5
Co	1.161	7.75	5.14	7.67	16.63	6.935
Cu	84.1	278.7	117.1	76.42	219.7	78.11
Zn	15.49	35.9	18.6	21.5	85.54	28.04
Mn	19.8	117.4	33.7	36.17	177.1	47.12
Mg	771.3	2,467.0	1,181.0	964.4	3,936.0	1,125.0
	ER3			ER4		
Date	04/12/2010	01/02/2011	17/03/2011	04/12/2010	01/02/2011	17/03/2011
pH	2.91	2.88	2.5	3.34	3.37	3.31
Cond	8.7	17.76	12.36	4.78	11.64	8.92
Eh	740.0	723.0	732.0	702.0	652.0	682.0
Acidity	7,550.0	24,400.0	16,000.0	4,200.0	14,600.0	14,200.0
SO_4^{2-}	12,600.0	41,904.0	24,005.0	7,411.0	43,782.0	15,207.0
Ca	220.4	350.4	266.6	122.1	341.4	240.4
Al	1,309.0	2,330.0	1,553.0	765.8	2,224.0	1,204.0
Na	<0.02	11.2	<0.02	0.0	1,707	<0.02
Si	3.508	10.79	4.158	3.76	12	4.06
Fe	528.0	1,647.0	469.6	42.37	53.3	39.58
Co	4.632	17.34	10.14	<0.003	19.76	6.01
Cu	88.78	482.5	116.5	76.44	233.9	125.4
Zn	38.71	183.4	201.8	8.154	19.26	14.89
Mn	62.49	392.8	84.44	18.89	160.6	34.5
Mg	1,715.0	6,973.0	2,217.0	708.6	2,010.0	1,257.0

during the first 30 min (280–650 mg/L) and reached 700–800 mg/L by the end of the test, indicating that the calcite dissolved rapidly in the AMD solution. A slight increase of dissolved Mg was detected during the period of anoxic treatment (200–230 mg/L), whereas Mg increased substantially after the open batch test. This is in accordance with the literature on the rate of dolomite dissolution, which is very slow compared to calcite (Plante et al. 2012; Santomartino and Webb 2007; Turner and McCoy 1990). Furthermore, P concentrations were very low (<1 mg/L), indicating that either the fluorapatite was not dissolved during the tests or that P precipitated as phosphate complexes within the column solids; iron phosphate (vivianite) is virtually insoluble.

All metal concentrations decreased in the synthetic AMD solution after treatment with the various particle size fractions. Al and Cu were both completely eliminated in the final solution. Cu disappeared only after the anoxic period. The concentrations of Fe, Mn, and Zn were only partially removed during the anoxic period, but the overall elimination rates by the end of the treatment process for the Fe, Zn, and Mn were 73, 84, and 54 %, respectively. Fe

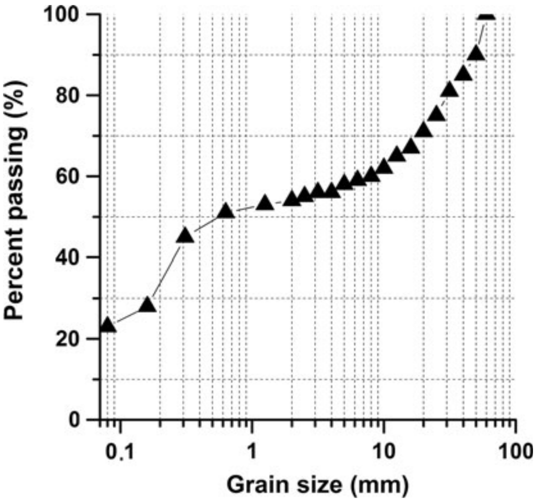


Fig. 3 Size distribution given in logarithmic *scale* for limestone wastes rocks PLW

concentration during the first day of treatment was around 335 mg/L; it decreased to 250 mg/L after approximately 15 h of treatment (see Fig. 4k). Fe removal with the PLW was higher than values obtained by Bernier (2005) and Genty et al. (2012) using calcite and dolomite.

Al removal exceeded 99 % after 30 min. Zn and Cu removals were 90 and 99 %, respectively, after 48 h. However, Mn removal was low, only reaching 54 %. Mn precipitation depends on both solution pH and Eh. Sulfate concentrations decreased moderately during the treatment process, from 3,600 to about 3,000 mg/L for all particle sizes of PLW.

Oxic Batch Tests

The anoxic batch tests showed that the PLW particle size did not significantly influence synthetic AMD treatment, so only one PLW particle size fraction (0.8 mm–3 cm) was used to evaluate the kinetic neutralization of the synthetic AMD in the oxic batch treatment tests and column experiments. The pH, EC, Eh, and concentrations of acidity, alkalinity, Ca, Mg, Fe, Zn, Cu, Mn, Al, and sulfate are shown in Fig. 5a–l. The evolution of these concentrations during oxic treatment was similar to during anoxic treatment.

During the early stages of oxic batch tests, when the synthetic AMD first contacted the PLW, pH increased very rapidly from 3 to 5 and reached 6 by the end of the treatment (Fig. 5a). This value was higher than the 5.3 observed by Bernier (2005) using calcite during his anoxic batch treatment. The redox potential of the AMD solution decreased from 650 to 490 mV/SHE (Fig. 5d), suggesting less oxidizing conditions. Alkalinity (Fig. 5b) increased during treatment but did not exceed 50 mg/L as $CaCO_3$. Acidity (Fig. 5c) is mainly linked to pH evolution and Fe precipitation, as also observed by Kirby and Cravotta (2005a, b). Acidity continued to decrease but was still significant (400 mg/L as $CaCO_3$), while iron decreased to 160 mg/L (Fig. 5k). This decrease corresponded to approximately 71 % Fe removal, which was <99.9 % obtained by Bernier (2005) using calcite and anoxic batch treatment.

During the first 30 min, the concentrations of dissolved Ca and Mg increased very rapidly, from 280 to 700 and 220 to 300 mg/L, respectively. Al and Cu were almost totally (99.9 %) removed, but Cu remained in solution until near-total depletion at around 15 h of treatment. The rates of elimination of Fe, Zn, and Mn were 67 % for Fe, 70 % for Zn, and 30 % for Mn. The dissolved sulfate remained at approximately 2.6 g/L.

Column Experiments

The evolution of physico-chemical parameters for both treatments (Fig. 6) was often similar. The pH of the treated

Table 3 Chemical composition of the alkaline phosphate limestone wastes

Major elements (wt%)

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	Na_2O	K_2O	P_2O_5	S	C	LOI	Total
12.20	0.93	0.39	0.02	4.32	42.28	0.35	0.11	12.99	0.2	6.7	26.07	99.70

Trace elements (mg/kg)

Cu	Zn	Cd	V	Cr	Ni	Nd	Mo	As	Sr	Co	Ba	Be
19.34	195.3	22.93	125.6	183.5	44.47	37.22	1.65	12.09	697.2	1.29	63.95	0.82

Trace elements (mg/kg)

Th	U	La	Y	As	Rb	Gd	Pr	Er	Zr	Sm	Ce
2.02	81.32	52.08	115.4	12.09	4.02	9.48	8.76	6.61	40.67	7.74	27.13

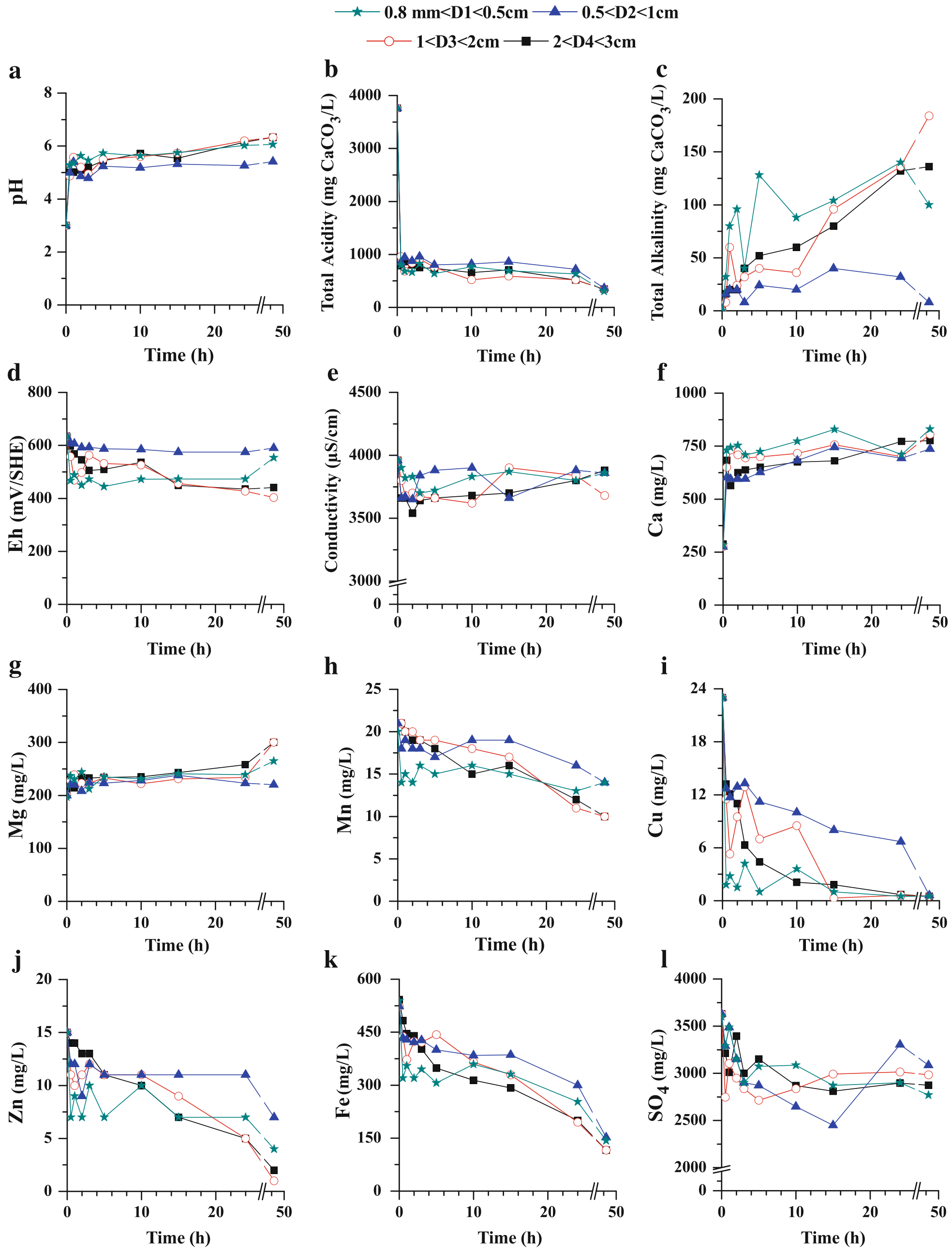


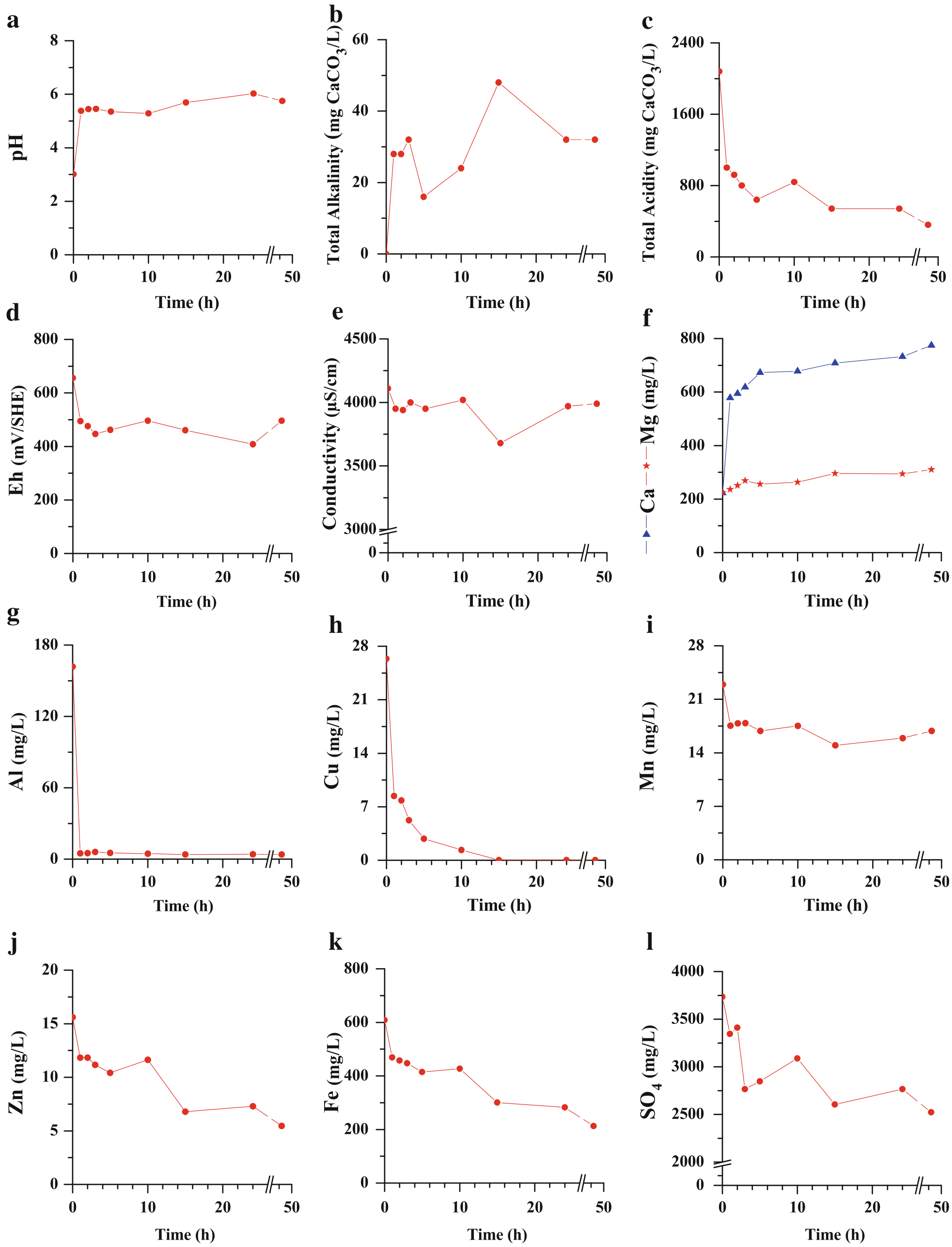
Fig. 4 Water quality evolution during the batch anoxic treatment at different PLW particle sizes

effluent was between 8 and 7 in the first 3 days and reached about 6.5 over time. This pH was higher than the one obtained by Genty et al. (2012) using limestone during AMD treatment in columns under anoxic conditions. The alkalinity of the treated solution for both columns increased by up to 700 mg $CaCO_3$/L in anoxic conditions and up to 300 mg $CaCO_3$/L for oxic treatment.

The acidity of the effluent dropped sharply from 3,000 to 2 mg/L as $CaCO_3$ during the first 2 days, after which it increased and then remained constant (at approximately 400 mg/L as $CaCO_3$) for both types of treatment. The acidity of the solution was neutralized more under anoxic conditions than in the open system and the alkalinity increase in the anoxic system was more significant than observed in the open system. This difference could be explained by the CO_2 pressure during anoxic conditions, which affects alkalinity production (Hedin et al. 1994). Furthermore, in the dissolution of PLW, calcite and dolomite, which are the principal minerals in limestone, increased the alkalinity, Ca, and Mg concentrations.

Retention of CO_2 can enhance limestone dissolution and alkalinity production because the rate and extent of the dissolution tend to increase with increased partial pressure of CO_2 and or decreased pH (Cravotta and Ward 2008; Cravotta et al. 2008; Langmuir 1997; Plummer et al. 1979; Stumm and Morgan 1996).

Fig. 5 Water quality evolution during batch oxic treatment



Conductivity reached 1,000–2,000 µS/cm during the first day, but increased during the second day to 3,500–4,000 µS/cm. The redox potential continued to decrease during treatment until the fifth day (650–250 mV/SHE), and then stabilized with time at about 250 mV/SHE.

The concentrations of Ca and Mg in the effluent decreased during the first day and then increased to a maximum of about 900 mg/L for Ca and 350 mg/L for Mg. The high Ca concentration in the effluent indicates that calcite was responsible for the neutralization. The slight increase of Mg reflects the relatively low reactivity of dolomite. P concentrations were very low (<1 mg/L) in the effluents, indicating that either the fluorapatite was not dissolved during the tests or that P precipitated (likely as iron phosphate) within the column solids.

The Cu and Al were totally (99.9 %) removed. However, the Fe and Mn, which were totally eliminated during the first 2 days, subsequently increased in the treated effluent, reaching 300 mg/L and 15 mg/L, respectively. Low Mn removal has several possible explanations (Edwards et al. 2009): precipitation is inhibited if the Fe/Mn ratio is high (as in our study), precipitates can be dissolved when ferrous concentrations are too high, and most other metals preferentially complex with sulfides before Mn. The reduction of the efficiency of the passive treatment could be attributed to precipitation and co-

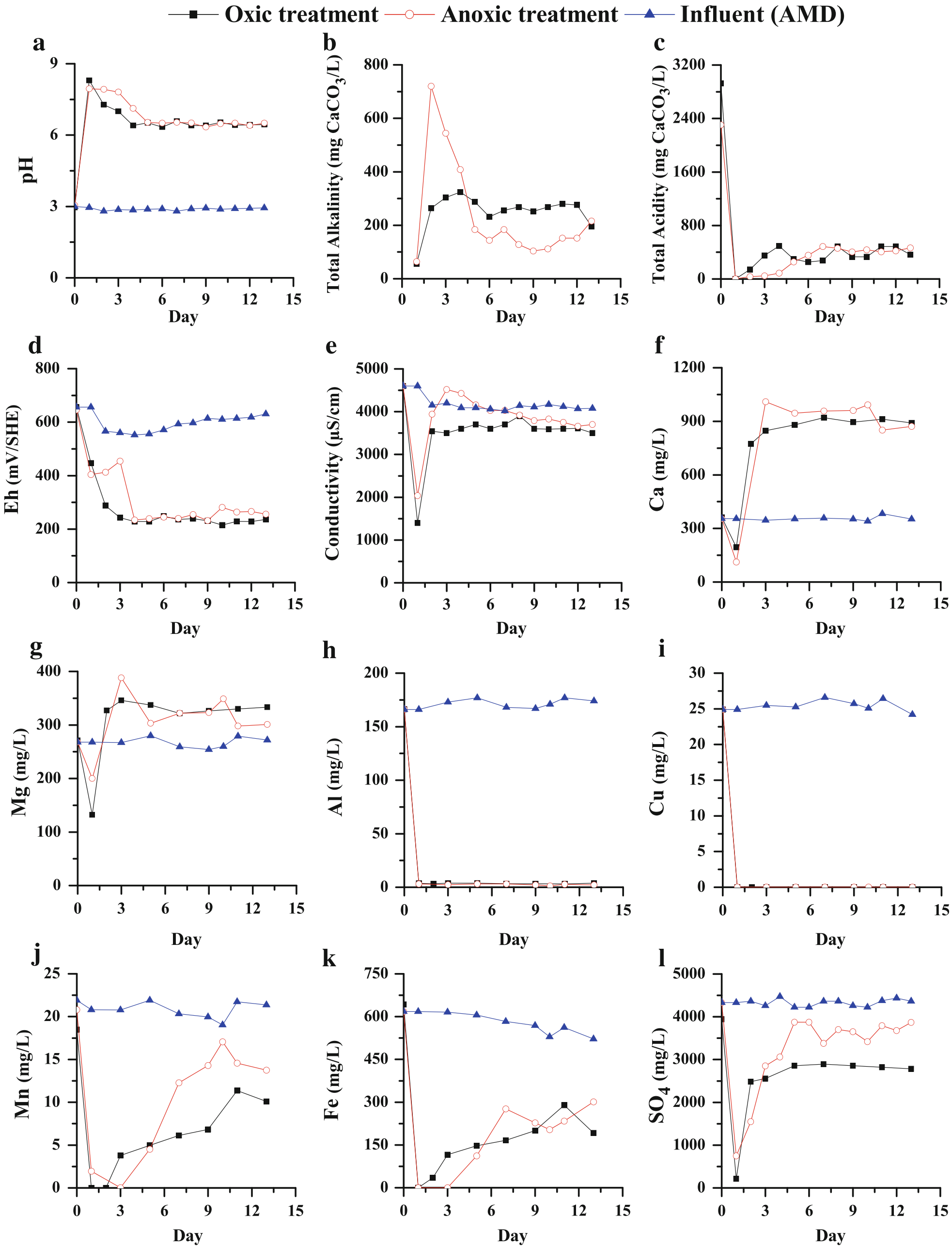


Fig. 6 Water quality evolution for the influent (AMD) and effluent columns during the treatment

precipitation of Fe hydroxides and oxihydroxide onto the PLW surface, passivating it. The ochreous color was observed on the surface of PLW.

The sulfate concentration in the effluent decreased sharply during the first day but, after 5 days, it was about 2,500 mg/L with the oxic treatment, and 3,500 mg/L with the anoxic treatment.

Conclusion

In this paper, the efficiency of PLW as an alternative alkaline material for the passive treatment of AMD was assessed in the laboratory. Field AMD waters were first characterized and then, a series of experiments were conducted for the passive treatment of a pH 3 synthetic AMD solution. The tests were performed under anoxic and oxic conditions in batch reactors and at a larger scale using columns with a hydraulic retention time of 15 h. The batch tests allowed us to evaluate the neutralization kinetics and the influence of PLW particle size (0.8 mm–3 cm). The particle size of the PLW did not significantly affect the efficiency of anoxic and oxic treatment. Dissolution of carbonates in the PLW increased the alkalinity and the pH of the AMD, causing metals to precipitate. The pH increased from 3 to 5–6.5 in the batch tests and 6.5–8 in the columns, with hydraulic retention times of 24 and 15 h, respectively. After 48 h in the batch tests, the increase in pH and alkalinity was accompanied by a significant decrease in metal concentrations: Fe (500–120 mg/L), Al (160–1.7 mg/L) and Cu (23–0.002 mg/L). Column tests results showed that Fe removal was low (618–300 mg/L).

The neutralization capacity under anoxic conditions was higher than under oxic conditions. Ca concentrations in the effluent increased rapidly, indicating that calcite was responsible for the neutralization; dolomite dissolution seemed to be negligible. P concentrations were very low in the treated solutions; this may mean that fluorapatite was not dissolved during the tests or that dissolved phosphate precipitated.

Given that more acidity was neutralized in the anoxic system, it is reasonable that the rate of metal removal was greater under anoxic conditions than in the open system. However, oxic conditions are more appropriate in a semi-arid climate since it is difficult to exclude oxygen by submerging PLW beds under water when annual precipitation is so low.

The use of PLW to generate alkalinity in passive treatment system designs appears promising, but more research and an economic study is mandatory before full-scale implementation. Passivation of limestone and the low dissolved carbon dioxide concentrations in the atmosphere limits neutralization during oxic treatment, relative to anoxic treatment. During anoxic treatment, the mounting increase of CO_2 partial pressure has a positive effect on the dissolution of limestone (Cravotta et al. 2008; Langmuir 1997; Plummer et al. 1979; Stumm and Morgan 1996). An OLC is described as a low-cost solution to the effects of intermittent AMD on the quality of surface water in Mediterranean and semi-arid mining areas (Alcolea et al. 2012). However, their usage with intermittent AMD water is very limited.

Based on these test results, a pilot-scale open limestone PLW channel will be constructed and evaluated at the Kettara tailings storage area. However, it should be noted that the channel is not expected to completely treat such a highly-contaminated, low-pH AMD; to remove all the contaminants, the channel should be combined with other treatment methods, such as sulfate-reducing bacterial bioreactors or natural solar evaporation ponds.

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