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TECHNICAL ARTICLE

Laboratory Evaluation of the Use of Alkaline Phosphate Wastes for the Control of Acidic Mine Drainage

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Abstract Pyrrhotite tailings at the abandoned Kettara mine site in Morocco are producing acid mine drainage (AMD). We investigated the use of alkaline phosphate waste (APW) rock from a nearby operating open-pit phosphate mine to control the AMD. The neutralizing potential of the APW, using the Paktunc method, was estimated between 500 and 680 kg $CaCO_3$/t. In laboratory column tests, the addition of 15 wt% APW to the coarse Kettara tailings produced leachates with significantly lower acidities and metal concentrations than unamended controls. The high calcium concentration in the flushed solutions indicates that calcite was responsible for the neutralization. Dolomite dissolution seems to be negligible and fluorapatite was stable under the testing conditions. It was also observed that when the treated solution comes in contact with unweathered Kettara coarse tailings, the pH becomes acidic, although the metal concentrations remain low.

Keywords Acid mine drainage · Column leaching test · Kettara · Mine wastes · Morocco · Neutralization · Phosphate

Introduction

Mine waste rock and tailings that contain sulfide minerals can react with atmospheric oxygen and water to produce acid mine drainage (AMD), which is generally characterized by low pH and high concentrations of sulfate, iron, and dissolved metals (e.g. Aubertin et al. 2002; Jambor 1994; Sracek et al. 2004). In Morocco, many old mine sites have been abandoned without implementation of a proper closure plan, and some of them have become environmental problems. Such is the case with the Kettara Mine, a Moroccan pyrrhotite mine located in a semi-arid area (Fig. 1). More than 3 million tonnes of fine and coarse mine waste were deposited there. Where AMD is not collected and treated, as at the Kettara mine site, it can contaminate both surface and subsurface water systems and cause severe degradation of the ecological system (El Khalil et al. 2007).

Generally, the best solution to an AMD problem is to prevent acid generation using an oxygen and/or water infiltration barrier (e.g. Aubertin et al. 2002; Ritcey 1989). An alternative approach is to add sufficient alkaline material to neutralize the acidity (Perry and Brady 1995; Rose et al. 1995) and immobilize the metals. Limestone and/or dolomite have been used to control AMD (Lapakko et al. 1997; Mylona et al. 2000), where it can be obtained inexpensively, but alkaline industrial by-products are an attractive alternative. Products that have been used as an amendment include: (1) fly ash produced by power plants (Ayala et al. 1998; Bertocchi et al. 2006; Brake et al. 2003; Dermatas and Meng 2003; Doye 2005; Pérez-López et al. 2005, 2007; Yeheyis et al. 2008), (2) cement kiln dust (CKD) produced in Portland cement manufacturing (Doye 2005; Lapakko et al. 2000; Mehling et al. 1997), (3) red mud produced by the aluminum industry (Bertocchi et al.

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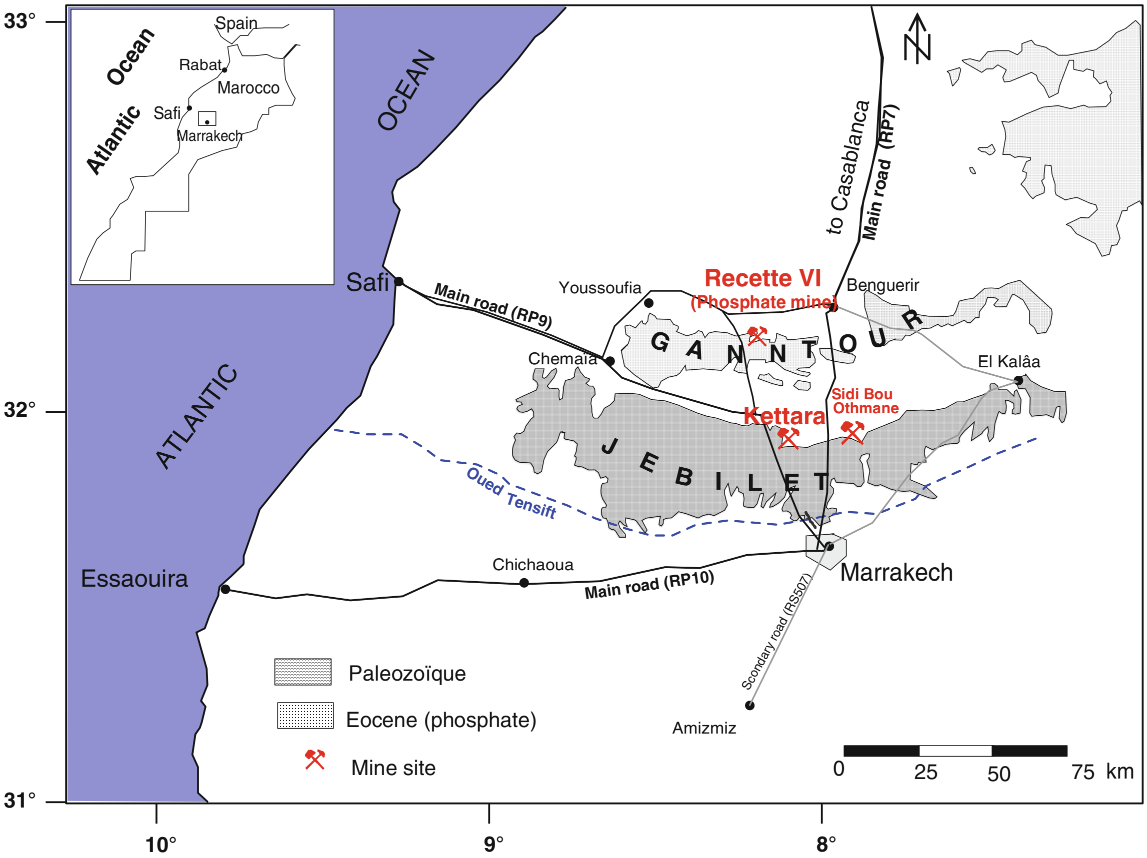


Fig. 1 Simplified geological map of the study area and location of the Kettara and phosphate mines (Hakkou et al. 2008a)

2006; Doye and Duchesne 2003; Fortin et al. 2000; Paradis et al. 2007), and (4) alkaline sludge from the paper industry (Chtaini et al. 1997).

The addition of these alkaline materials can neutralize acidity and decrease the activity of iron-oxidizing bacteria. Following neutralizing reactions, the formation of secondary minerals (sulfates, carbonates, and hydroxides) can immobilize dissolved metals by adsorption or co-precipitation (Bertocchi et al. 2006; Lapakko et al. 1997; Pérez-López et al. 2007). These secondary minerals, mainly hydroxides, often precipitate on the surface of AMD-generating sulfides, which can lead to their passivation (Lapakko et al. 1997; Villeneuve 2004), thus reducing or even stopping oxidation. With some alkaline products (e.g., fly ash and CKD), the precipitation of secondary minerals (such as gypsum, aragonite, jarosite, and iron hydroxide) also promotes the formation of a hard layer (hardpan), which can act as a barrier against water infiltration and oxygen diffusion (Blowes et al. 1991; Schippers et al. 1998; Pérez-López et al. 2007; Yeheyis et al. 2008). However, seasonal dissolution of some secondary minerals can cause variations in effluent quality.

Phosphates can also be used to precipitate some metals. Eusden et al. (2002) showed that the use of phosphates and lime to stabilize tailings from a mine in Colorado led to the formation of various phosphato-metallic phases that decreased concentrations of metals in the pore water. Phosphate materials can precipitate ferric iron (Fe^{3+}) as an iron phosphate, which prevents indirect pyrite oxidation by Fe^{3+} (Barrie and Hallberg 2005; Evangelou 1995; Skousen et al. 1998).

Morocco has three quarters of the world phosphate reserves, is first in the world in terms of exports, and third (after the USA and Russia) in terms of production (OCP 2005). Much of Morocco's phosphate reserves are in sedimentary strata that contain calcite and dolomite. Millions of tons per year of waste rock are produced during open-pit phosphate mining and beneficiation processes. Since the phosphate waste impoundments, which contain up to 20 wt% P_2O_5, adversely affect the aesthetics of the environment surrounding the mine sites, the recycling of these industrial by-products could be beneficial, in the context of sustainable development.

The main objective of this study was to investigate the feasibility of using alkaline phosphate waste (APW) from a neighboring operating phosphate mine to control AMD generated by the Kettara coarse tailings. The emphasis in this study was on the coarse tailings since these tailings have been shown to be more reactive than the fine tailings at Kettara, and contribute most of the pollution (Hakkou et al. 2008a, b). The APW contains significant quantities of calcite and dolomite that should help to neutralize the acidity generated by the Kettara tailings, and consequently reduce the activity of iron-oxidizing bacteria and fix metals. Furthermore, precipitation of minerals on the surface of the sulfides could reduce their oxidation rate by passivation phenomena (Evangelou and Huang 1992; Lapakko et al. 2000).

The rehabilitation scenario being investigated at the Kettara mine involves the use of fine APW as both an amendment (Hakkou et al. 2007) and a 'store and release' (SR) cover. This would require collecting all of the Kettara coarse tailings and placing them over the tailings pond. The coarse tailings would be amended with approximately 20 cm of APW. Then, an APW capillary barrier would be placed over the Kettara mine waste which, in a semi-arid climate, should limit the infiltration of water to the reactive mine wastes, hence reducing the production of AMD (for more details on SR covers, see Scanlon et al. 2005 and Khire et al. 2000).

In this paper, we report the results of laboratory column leaching tests, thus assessing only the amendment aspect of the APW by-products. The behavior of unweathered and oxidized coarse tailings amended with 15 and 25 wt% APW was evaluated.

Materials and Methods

Analytical Methods

The chemical composition of solid samples was analyzed with a PerkinElmer Optima 3100 RL ICP–AES following a total $HNO_3/Br_2/HF/HCl$ digestion. Dilute HCl was used to extract sulfate, and the solution obtained was analyzed by inductively coupled plasma and atomic emission spectrometry (ICP–AES). Chlorine was analyzed by absorptiometry, fluorine by potentiometry using an ion-selective electrode, and total carbon content was measured using a LECO SC144 DRPC sulfur/carbon determinator. The initial tailings mineralogy was determined by a combination of X-ray diffraction spectroscopy (XRD) and scanning electron microscopy (SEM) analyses. XRD analyses were carried out using a Bruker AXS D8 Advance diffractometer equipped with a scintillation detector and Co Kα radiation. The data were collected in 5–70° by steps of 0.005° and a count time of 0.5 s/step. Access to the JCPDS database allowed qualitative analysis of the mineralogy (e.g., phase determination); the Rietveld method was used for quantitative analyses of known phases. Compositional phases were quantified within a 0.5% error.

Kettara Coarse Tailings Sampling and Characteristics

The reactive coarse tailings considered in this study come from the abandoned Kettara pyrrhotite ore mine located approximately 35 km northwest of Marrakech in the core of the central Jebilet Mountains (Fig. 1). From 1964 to 1981, the mine produced more than 5.2 million tonnes (t) of pyrrhotite concentrate containing an average of 29% sulfide. More than 3 million t of mine wastes were stockpiled in dumps, dykes, and piles covering an area of approximately 16 ha; of these mine wastes, more than 0.4 million tonnes are coarse tailings (Hakkou et al. 2008a). These coarse tailings contain 1.6–5.6 wt% sulfur, mainly sulfide minerals (e.g., pyrrhotite, pyrite, chalcopyrite, galena, and sphalerite), and were deposited on the surface without concern for the environment. Exposure to ambient air for 25 years led to the formation of AMD that affects the surrounding ecosystems as well as more than 2,000 people living on the old mine site (Fig. 2) (see Hakkou et al. 2008a, b for more details).

An exploratory trench 1.1 m deep was excavated in the dyke, which is 15 m high and 10 m wide. Samples corresponding to unweathered coarse tailings were collected at a depth of 1.1 m while oxidized coarse tailings were collected at the surface of the dyke; they were named S_{un} and S_{ox}, respectively. The materials are generally coarse in texture and can be classified as fine gravel (Fig. 3). The D_{80} (grain size at 80% passing) was estimated to be around 14 mm for S_{un} and 10 mm for S_{ox}. Specific gravity ranges from 2.87 for S_{un} to 2.94 for S_{ox}.

Table 1 shows the results of chemical analysis performed on the unweathered and oxidized coarse tailings used in this study. Table 1 shows that the coarse tailings S_{un} and S_{ox} were high in total S (3.2 and 4.5 wt%, respectively) and iron, associated with the pyrrhotite, pyrite, and iron oxides (17.4–27.7 wt%). Other metals of interest are Cu (1,200–1,730 ppm), Zn (260–470 ppm), Cr (230–270 ppm), Pb (50–100 ppm), Co (50–70 ppm), As (120–220 ppm), and Mn (930–1,090 ppm).

Table 2 presents the relative abundance of minerals in the Kettara coarse tailings, as determined by X-ray diffraction and the Rietveld method. Pyrite and pyrrhotite remain relatively high in both unweathered and oxidized coarse tailings 25 years after mine closure. Previous geochemical and prediction studies (Hakkou et al. 2008a, b) confirmed that AMD release will continue in the future if no mitigative actions are taken. The most abundant gangue minerals are chlorite-serpentine, quartz, talc, and goethite. Muscovite and albite are present in trace proportions. Carbonates (calcite) occur in very negligible quantities.

Acid–base accounting (ABA) tests, using the modified static test proposed by Lawrence and Wang (1997), showed that coarse tailings samples have no acid-neutralizing

Fig. 2 Photographs illustrating the AMD problem at the Kettara mine site

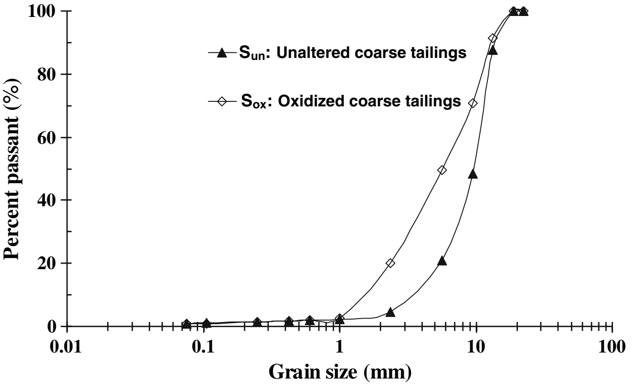


Fig. 3 Size distribution given in logarithmic scale for Kettara coarse tailings (*Un* unweathered coarse tailings; *Ox* oxidized coarse tailings)

potential (NP); their net neutralizing potential (NNP) was between −93 and −138 kg $CaCO_3$/t.

Alkaline Phosphate Waste Rock Sampling and Characteristics

At the Exploitations Minières du Gantour Company ‘Recette VI’ site, 30 km north of the abandoned Kettara mine (Fig. 1), large quantities of overburden are removed to expose the phosphate ore to be mined. Trucks transport the ore to a dry screening plant for separation and disposal of the oversize (>40 mm) low-grade material. In addition, material that does not contain sufficient quantities of economic minerals is rejected as waste rock. Thus, the Recette VI phosphate mine produces two wastes types: the overburden waste rock, hereby referred to as APW1, and the waste produced by the concentration process, hereby referred to as APW2. These wastes are produced in large quantities and are stockpiled in waste rock dumps (Fig. 4). The concentrated phosphate rock is transported by rail, either to the industrial complex located at Safi for further processing or directly to port for export.

In terms of particle size distribution, the D_{10} (grain size at 10% passing), D_{50}, and D_{80} of the APW1 waste rocks were estimated to be about 19 µm, 1.7 mm, and 10 mm, respectively (Fig. 5). The specific gravity of this material was approximately 2.83.

The studied alkaline wastes have a high concentration of Ca, P, Mg, Si, and C. As indicated in Table 3, metals such as Zn, Cr, V, and Cd are the main potential contaminants. The phosphate wastes, APW2, have higher concentrations of P_2O_5 (19.6 wt%), Zn (300 ppm), Cd (131 ppm), and Cr (275 ppm) than APW1.

Table 4 summarizes the mineral composition determined by X-ray diffraction (qualitative and quantitative, using the Rietveld method). The main phases detected by X-ray diffraction in APW1 and APW2 were calcite (40.7 and 25.5 wt%) and apatite (25.9 and 48.1 wt%). Dolomite was also abundant. The high content of fluoride and the relative absence of chloride indicates that apatite occurs as fluorapatite ($Ca_{10}(PO_4)_6F_2$). The APW2 waste from the concentration process was high in apatite. A significant amount of quartz is also present in the samples.

The mineralogical NP was estimated to be around 680 and 500 kg $CaCO_3$/t for APW1 and APW2, respectively, using the Paktunc method (Paktunc 1999). Due to their high alkaline properties, either APW1 or APW2 could be considered as a substitute for common AMD neutralizing agents. However, for this case study, the sample referenced

Table 1 Chemical composition of the coarse tailings studied

	S_{total}	S_{SO4}	Ca	Si	Mg	Na	K	Ba	Fe	Al	B	Ti	P
S_{un}	3.2	0.7	0.9	20.0	3.6	0.3	0.7	0.0	17.4	6.6	0.1	0.3	0.1
S_{ox}	4.53	0.12	0.28	17	2.83	0.26	0.39	0.02	27.7	5.69	0.09	n.d.	n.d.

	Cu	Pb	As	Cd	Co	Cr	Mn	Ni
S_{un}	1,200	100	120	30	70	270	1,090	70
S_{ox}	1,730	50	220	30	50	230	930	30

S_{un} unweathered coarse tailings, S_{ox} oxidized coarse tailings; *n.d.* not determined

Table 2 Relative abundance of investigated phases, as determined by X-ray diffraction

	Pyrrhotite	Pyrite	Chalcopyrite	Sphalerite	Quartz	Chlorite	Talc	Muscovite	Albite	Goethite	Magnetite	Calcite	Gypsum	Jarosite
S_{un}	F	F	Tr	Tr	A	A	M	Tr	Tr	F	Tr	Tr	Tr	Tr
S_{ox}	F	F	Tr	Tr	A	A	M	Tr	Tr	M	F	Tr	Tr	Tr

A abundant (30–50%), *M* medium (10–30%), *F* low (2–10%), *Tr* trace (<2%)

TA highly abundant (> 50%)

Fig. 4 Photographs illustrating mining and the origin of the alkaline phosphate wastes: **a** waste rock from open-pit mining (APW1); **b** waste from the dry screening plant (>40 mm) (APW2)

as APW1 was chosen for further testing due to its high alkalinity and its relatively low metal concentrations. A preliminary test that consisted of mixing the APW with distilled water for 2 h in a liquid/solid ratio of 2.5 led to a leachate with a neutral pH (6.5), low conductivity (0.3 mS/cm), and low ion concentrations.

Carbonate content was determined by the weight lost during thermal analysis. The TG–DTA curves were obtained at a heating rate of 5°C/min with a Thermo Cahn-Thermax 700 thermogravimetric analyzer (Fig. 6). TG curves of both samples show a total weight loss of about 28 wt% for APW1 and 22.3 wt% for APW2. These results confirm the previous XRD and chemical analyses data and correspond to the CO_2 calculated in the calcite and dolomite contained in APW1 and APW2.

Kinetic Tests Procedures

In a previous study (Hakkou et al. 2008b), humidity cell tests were used to estimate the mineral reaction rates of fine and coarse tailings from the abandoned Kettara mine. Due to the lower water retention capacity within the coarse waste, the kinetic tests showed that the coarse tailings have a greater potential to generate AMD than the fine tailings

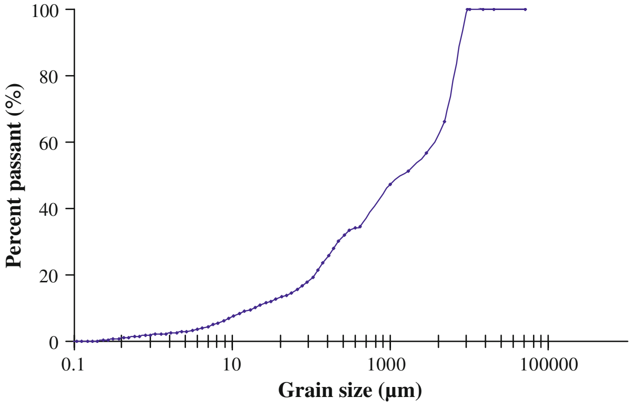


Fig. 5 Size distribution given in logarithmic scale for phosphate waste rocks APW1

(Hakkou et al. 2008b). In this paper, the coarse tailings (S_{un}) results from the humidity cell test were considered as reference results (of the geochemical behavior without an amendment) and are compared with the results of the column tests obtained in this study. Even though the two methods are different, the authors consider that comparing the geochemical results of the two approaches can give valuable information on the effect of the amendment on the AMD potential of the coarse tailings.

The humidity cell testing procedure was based on the one described in Morin and Hutt (1997) for 1 year duration (52 weekly cycles) with approximately 1.83 kg (dry weight) of unweathered coarse tailings. A full cycle consisted of 3 days of dry air circulation over the sample at 1 L/min flux, 3 days of humid air circulation at 1 L/min and flushing on the seventh day. The flush was done by inundation and soaking of the tailings for 4 h with 500 mL of deionized water. More details about the set-up can be found in Hakkou et al. (2008b).

Laboratory neutralization experiments were conducted from November 2006 to May 2007. Kinetic column tests were undertaken to evaluate the effectiveness of the APW by-products in preventing the formation of AMD from the Kettara mine coarse tailings. The leaching tests were performed using 45 cm high and 8 cm diameter Plexiglas columns (Fig. 7). The column's bottom plates were equipped with a ceramic plate (to artificially set the position of the water table, which in these tests simulated a low position below the bottom of the columns), and a water outlet to collect leachates.

Three columns were set-up with the coarse Kettara tailings mixed with 15 and 25% by mass of the fine-grained fraction of alkaline phosphate (less than 1 mm in size). As shown in Fig. 1, column A was first filled with 625 g (dry weight) of oxidized coarse tailings mixed with 15 wt% APW1, to a height of 7.5 cm, followed by a 7.5 cm layer (625 g) of unweathered coarse tailings +15 wt% APW1. Column B consisted of the same mixtures as column A, placed over a 5 cm layer of unweathered coarse tailings (395 g dry weight). Finally, column C was identical to B, the only difference being the addition of 25% instead of 15% of APW1.

Each column was flushed with approximately 500 ml of deionized water every week for 27 weeks. This rapid repetition of wet/dry cycles was used to accelerate the geochemical processes. The leachates were then analyzed by ICP–AES for major elements, minor elements, and specific metals. Water pH, Eh, and conductivity measurements were performed on freshly collected leachate samples. Acidity and alkalinity (expressed in mg/L of $CaCO_3$) of the

Table 3 Chemical composition of the alkaline phosphate wastes

	Major elements (wt%)										
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	F	P_2O_5	S	C
APW1	9.6	1.9	1.5	41.1	4.9	0.4	0.1	1.3	9.7	0.2	7.7
APW2	3.5	1.6	1.4	47.0	3.8	0.6	0.1	2.6	19.6	0.3	6.6
	Trace elements (ppm)										
	Cl	As	Ba	Cd	Cr	Cu	Ni	Pb	Sr	V	Zn
APW1	140	8	101	19	129	19	19	13	647	118	154
APW2	66	8	123	131	275	23	13	16	927	184	300

Table 4 XRD mineralogical quantification (within 0.5% error) of the alkaline phosphates wastes

	Calcite (wt%)	Dolomite (wt%)	Apatite (wt%)	Quartz (wt%)	NP (Kg $CaCO_3$/t)
APW1	40.7	25.2	25.9	8.2	680
APW2	25.5	23.0	48.1	3.4	500

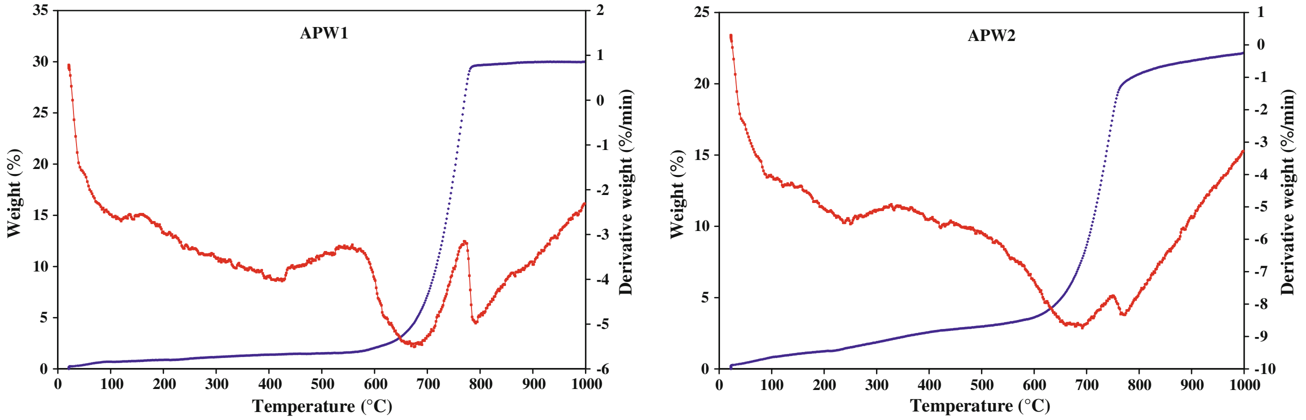
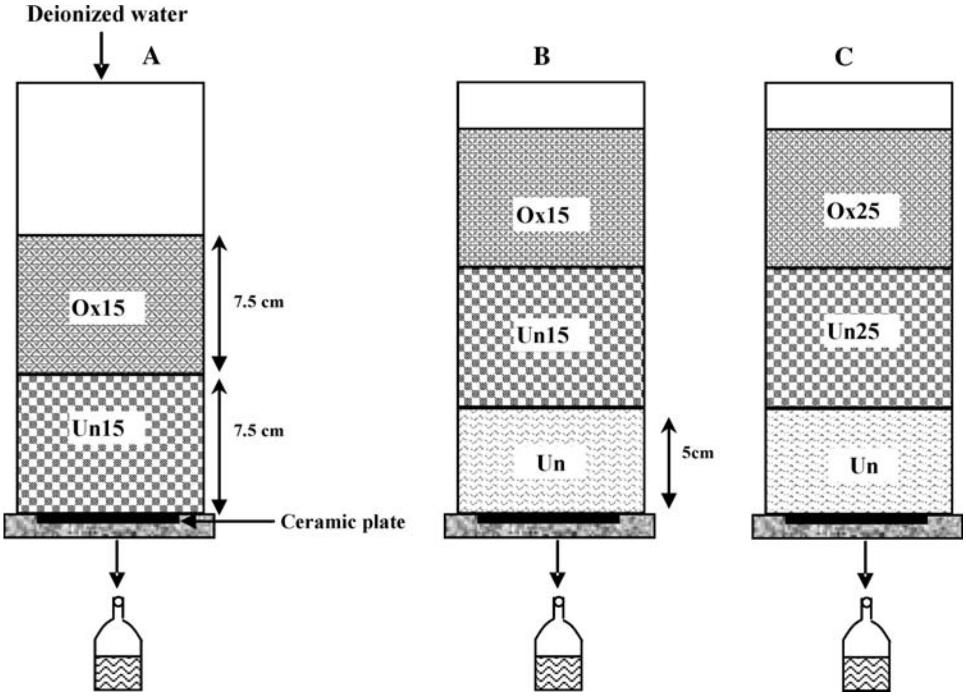


Fig. 6 Thermo-gravimetric/differential thermal analysis (TG/DTA) plot of the alkaline phosphate wastes decomposition in an oxygen atmosphere; *APW1* waste rock from open-pit mining, *APW2* waste from the concentration process

Fig. 7 Schematic diagram of the three leaching columns (*Ox15* oxidized coarse tailings +15 wt% phosphate waste; *Un15* unweathered coarse tailings +15 wt% phosphate waste; *Ox25* oxidized coarse tailings +25 wt% phosphate waste; *Un25* unweathered coarse tailings +25 wt% phosphate waste; *Un* unweathered coarse tailings)



solutions were analyzed by acid–base titration, to pH endpoints of 4.5 and 8.3, respectively. The results are expressed according to the volume of water passing through the column. The total *S* analyses are expressed as SO_4, which, although not entirely confirmed, appears reasonable, given the high Eh values.

Results and Discussion

Base Case

The water quality of the leachates from the humidity cell tests are summarized in Fig. 8a–i (Hakkou et al. 2008b). Figure 8a shows that the pH dropped rapidly to 3.1 and then to less than 3 for the coarse tailings (S1). The Eh ranged from 478 to 825 mV, favorable to sulfide oxidation. The conductivity values stabilized after 100 days at values of 1,200 µS/cm (Fig. 8b), which is typical for AMD. The acidity generated by the oxidation of sulfide minerals increased progressively during the initial flush cycles, then peaked, and declined. The acidity peaked at 3,199 mg $CaCO_3$/L and stabilized at 280 mg $CaCO_3$/L.

The dissolved sulfate concentration reached 4,900 mg/L and then decreased to 480 mg/L (Fig. 8d). Sulfate was mainly produced by the oxidation of sulfides (pyrrhotite and pyrite) and the dissolution of sulfate secondary minerals. In general, there were good correlations between

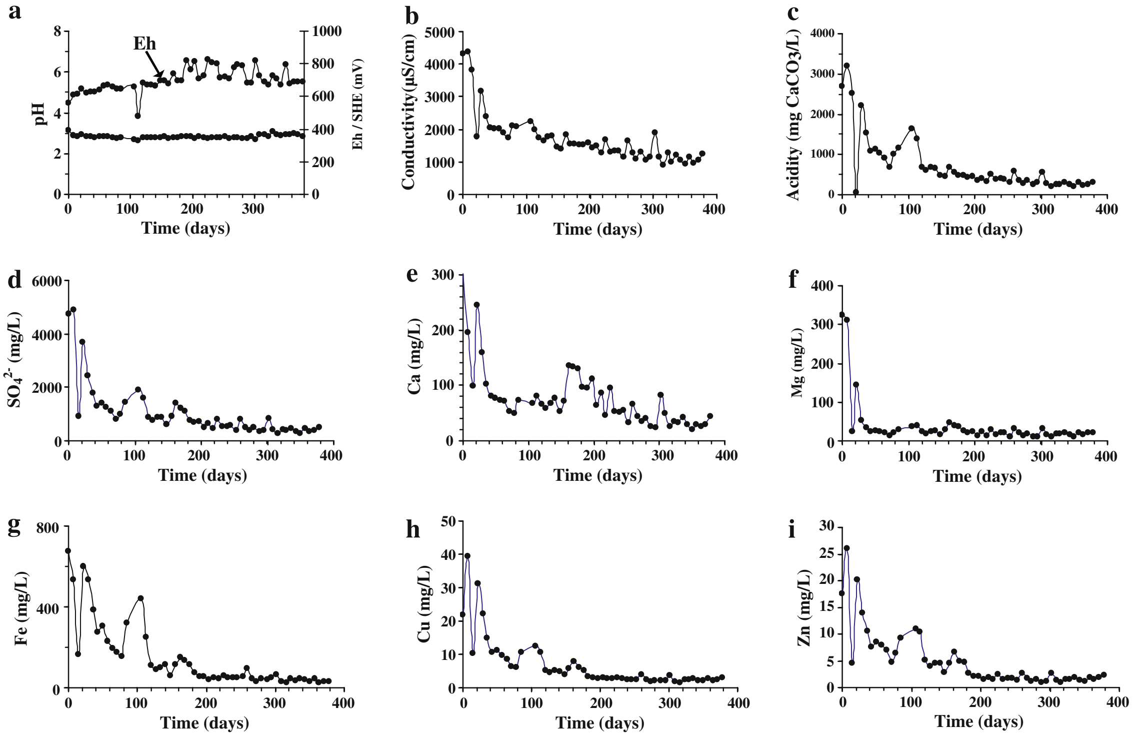


Fig. 8 Water quality from the weathering cell tests on Kettara coarse tailings samples

increases in acidity and increases in soluble metals concentration. Iron release is controlled by a complex assemblage of minerals including pyrrhotite, pyrite, chalcopyrite, goethite, and magnetite. Figure 8g shows that the iron concentrations in the flushed waters from the Kettara tailings varied between 15.1 and 1,440 mg/L. These values are much less than the theoretical values predicted from the stoichiometric oxidation of pyrite or pyrrhotite, which suggests that iron was precipitating in situ as iron oxyhydroxide.

The geochemical behavior of Ca is different from that of Mg, as demonstrated by Fig. 8e and f. The Ca could come from either calcite and/or gypsum, and even from albite–anorthite, while the Mg could be associated with chlorite or talc that dissolved in acidic conditions. Fig. 8 h and i show that the concentration of Cu and Zn reached 40 and 28 mg/L, respectively, in the flushed water. Chalcopyrite in the tailings is the primary source of dissolved Cu and sphalerite is the source of the Zn.

Column Leaching Tests

Variations in pH, conductivity, redox potential, acidity, alkalinity, and major species (viz, Al, Cu, Zn, Co) concentrations in the column leachates are shown as a function of time (Fig. 9). The values presented in this figure were not normalized by either the volume of water recovered or the weight of the materials. Concentrations of As, Ba, Be, Bi, Cd, Mo, Ni, Pb, Sb, Se, and Ti are not presented since they were not detected in significant quantities.

The initial leachates had high acidity and ion concentrations. This was most likely due to the rapid dissolution of soluble weathering products generated by some of the sulfides that oxidized before the onset of the experiments.

Leachates of column A, which contained 15% APW, had neutral pH (7–7.5) and lower redox potential (360 and 430 mV) throughout the testing period (Fig. 9a, b), presumably due to the high buffering effect of the carbonates. Columns B and C, which were filled at the bottom with a 5 cm layer of unweathered coarse tailings, produced leachates with an acidic pH (3–4.5) and higher redox potential values, favorable to sulfide oxidation. In columns B and C, the alkaline solutions resulting from the leaching of the mixed material in the upper layers became acid due to contact with the unweathered coarse tailings, and maintained these levels of acidity for the duration of the test. Note that many similarities exist between the geochemical behavior of columns B and C (Fig. 9).

Alkalinity ($HCO_3^- + CO_3^{2-} + OH^-$) is used as an indicator of the neutralizing capacity of the phosphate waste rock. As seen in Fig. 9e, column A leachates had high levels of dissolved alkalinity, ranging between 296 and 50 mg $CaCO_3$/L at the beginning of the test. After

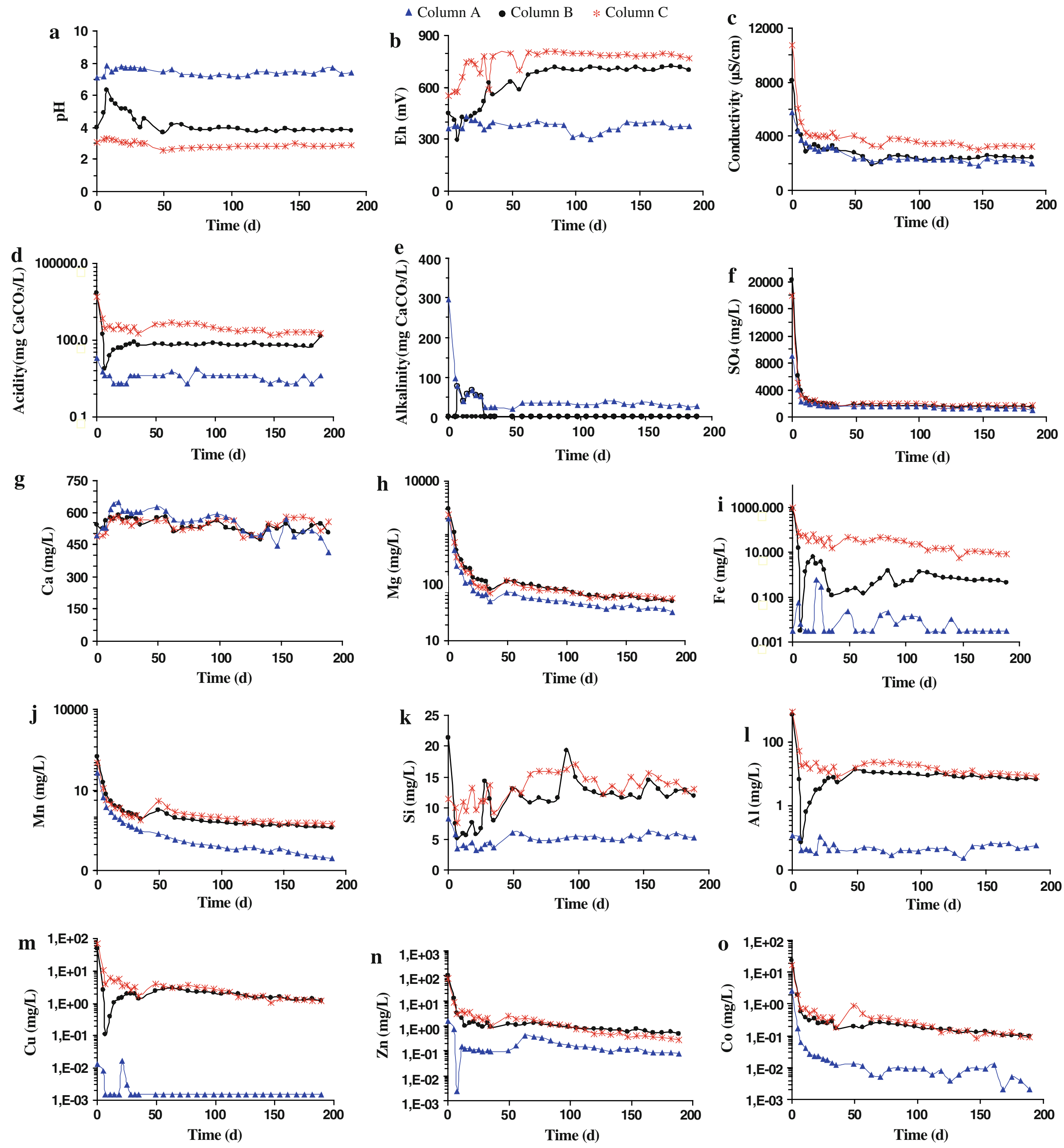


Fig. 9 Water quality from the column leaching tests on Kettara coarse tailings mixed with alkaline phosphate wastes

25 days of testing, alkalinity decreased, and leveled off at 30 mg $CaCO_3$/L. However, acidity readings were usually less than 6 mg $CaCO_3$/L, indicating that neutralization processes were important (Fig. 9d). Without the alkaline additive, pH values (Fig. 8a) were very acidic (2.6–4).

In the case of column B, after approximately 120 days, acidity ranged between 80 and 248 mg $CaCO_3$/L and then decreased to lower values (60 mg $CaCO_3$/L) at the end of the experiment (Fig. 9d). Column C produced higher acidity levels than column B, reaching 698 $CaCO_3$/L at the beginning of the test, and remained high at the end of the test (138 $CaCO_3$/L). Furthermore, alkalinity was practically absent in the leachates of columns B and C. These values of acidity are low compared to those obtained from unamended Kettara coarse tailings in humidity cell tests (Fig. 8c).

The conductivity evolution was similar in the three columns (Fig. 9c). Conductivity measurements decreased during the first few cycles (when soluble salts are usually leached) to values between 4,400 and 2,140 µS/cm. The conductivity values are mainly due to the dissolved SO_4^{2-} and Ca^{2+}, which are present at high concentrations (1,078–20,200 mg/L and 412–649 mg/L, respectively) throughout the testing period (Fig. 9f, g).

Sulfates are mainly produced by the oxidation of sulfide minerals (mainly pyrrhotite and pyrite). Figure 9f shows that the SO_4^{2-} concentrations were initially higher. After three cycles, the sulfate concentration reached 2,400, 3,900, and 3,300 mg/L, respectively, for A, B, and C, and then dropped rapidly to lower values (1,250–1,800 mg/L) at the end of the experiment.

Figure 9g shows that Ca concentrations showed little variation in the three columns. The concentrations values of Ca are high compared to those obtained with unamended Kettara coarse tailings in humidity cell tests (Fig. 8e). High Ca concentrations (545 mg/L) in the leachates throughout the experiment reflect rapid neutralization by calcite, which is present in abundance in the APW. Both the dissolution of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), which are the main minerals in the APW, could increase pH, alkalinity, and the concentrations of Ca or Mg. However, the very low Mg concentrations (Fig. 9h) indicate that dolomite did not take an active part in AMD neutralization. The Mg observed in the flushed waters may instead be associated with the chlorite or talc contained in the Kettara coarse tailings (Hakkou et al. 2008b). The literature indicates that leachate alkalinities and associated dissolution rates for calcitic limestone are approximately greater by a factor of two than those for dolomitic limestone. The dissolution rate of dolomite tends to be slower than that of calcite under the same environmental conditions (Cravotta et al. 2008; Genty et al. 2008).

In addition, P concentrations were low in the leachates, indicating that either the fluorapatite was not dissolved during the tests or that P precipitated as phosphate complexes within the column solids. Figure 9i shows that concentrations of dissolved Fe concentrations are also low for all three column leachates, in particular in columns A and B, suggesting that iron oxyhydroxides and/or iron phosphate precipitated. This observation is in accordance with the MINTEQ geochemical modeling, as discussed below. However, Table 5 shows the results of mixing APW1, unweathered coarse tailings, and unweathered coarse tailings +25 wt% APW1 with deionized water in a liquid/solid ratio of 2.5 for 2 h. The AMD from unweathered coarse tailings was also mixed with APW1 in a liquid/solid ratio of 2.5. Given the low concentration of dissolved P (less than 1 mg/L in all solutions), it seems that little iron was likely precipitated as iron phosphate.

High Si and Al concentrations in the flushed waters from columns B and C (Fig. 9k, l) most likely come from the dissolution of chlorite, muscovite, albite, and talc from the Kettara coarse tailings. Apart from calcium, the concentration of metals in the flushed waters closely correlated with the sulfate concentrations (Fig. 9f, g). As shown in Fig. 9m–o, Cu, Co, and Zn concentrations were low in the leachate from all three columns despite the acidic pH and high acidities of columns B and C. The metals have likely precipitated in all of the columns. Thus, the addition of alkaline material led to reduced concentrations of these elements (values below 1 mg/L) in comparison to the non-amended tailings (Hakkou et al. 2008b).

Using the approach proposed by Benzaazoua et al. (2004), the cumulative mass of sulfates measured in the column leachates was plotted versus the cumulative amount of calcium, magnesium, and manganese (Fig. 10). The sulfates represent the main oxidation product and the sum of Ca + Mg + Mn represents the main carbonate dissolution products. These cumulative concentrations are corrected for the recovered volume. The curves obtained, which are called oxidation–neutralization curves (Fig. 10a) represent the geochemical evolution of the ratio of acid to neutralizing element produced during the kinetic tests. The mixes studied (Kettara coarse tailings and APW) show a linear shaped oxidation–neutralization curve for columns A, B, and C. The slopes are very similar and vary between

Table 5 Results of waste phosphate rock leaching tests with deionized water and with AMD from unweathered coarse tailings in a liquid/solid ratio of 2.5

Parameter	pH	Eh	Cond.	Acidity	Alk.	P	Fe	Al	Ca	Co	Cu	Mg	Mn	S	Si	Zn
APW1	6.5	333.4	294	13	47	0.66	0.04	0.01	15.3	<0.004	0.017	6.48	0.007	13.2	1.9	0.012
Un	3.1	609.9	4,950	3,467	0	0.03	365	263	216	4.41	25.3	250	21.1	1,290	0.623	18.9
Un25	4.1	495.3	3,260	1,050	0	0.09	199	36.8	344	3.12	3.86	208	13.9	718	0.251	10.2
DMA from Un + APW1	5.9	362.1	3,960	583	0	<0.01	113	0.15	810	3.14	0.31	291	13.6	1,040	0.947	5.44

Eh is reported in mV, conductivity (cond.) in µS/cm, acidity and alkalinity (alk.) in mg of $CaCO_3$/L, and elemental concentrations in mg/L

Un unweathered coarse tailings; *Un25* unweathered coarse tailings +15 wt% APW1

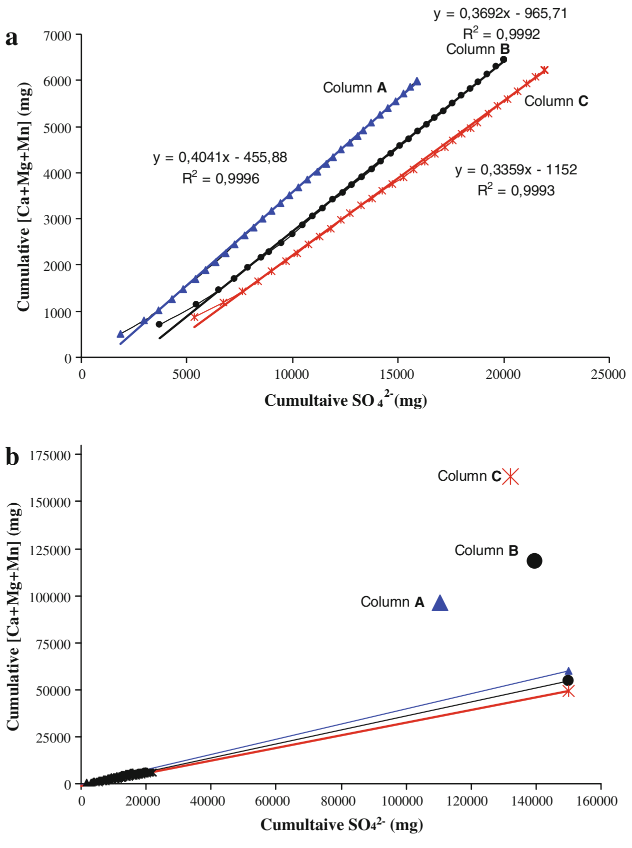


Fig. 10 Evolution of cumulative sulfate loads, sulfide oxidation rate, and neutralization curves from the column test results

0.33 and 0.40, which are very close to those found by Benzaazoua et al. (2004).

The oxidation–neutralization curves can be used to evaluate and predict the long-term geochemical behavior of mine wastes. For near-neutral tailings (as is the case of our mixtures) that show little or no precipitation of the elements concerned, it is possible to hypothetically predict the acidity potential by extrapolating the oxidation–neutralization curves and by projecting the initial sulfate (converted from sulfur content) and Ca, Mg, and Mn concentrations of the tailings. Figure 10b shows this representation for the three samples studied. The hypotheses underlying this method of interpretation are that the geochemical environment stays the same, the ratio between neutralization and oxidation products stays linear, and that mineralogy will not affect the linearity of the relation over the long-term (e.g., by depletion or precipitation of a mineral). These hypotheses are interdependent. They can be considered realistic as long as conditions (pH, Eh, temperature) remain the same. The curve extrapolation allows the evaluation of the long-term acid generating potential of the studied samples. The material will not generate acid if some carbonates remain while sulfides are depleted (in this case, the samples will be projected above the oxidation–neutralization curve), meaning that it would contain carbonates in sufficient amount to neutralize all acid that may be generated by sulfide oxidation.

Geochemical Modeling

Aqueous speciation geochemical modeling was used to test the hypotheses in terms of secondary mineral precipitation in the columns—a phenomenon that greatly affects the percolated water quality. The aqueous geochemical equilibrium model allows the calculation of the equilibrium among the aqueous species of the effluent solutions. The input (water quality) parameters were used to estimate the concentrations and activities of most of the important aqueous species in a specific water sample and to calculate the saturation indices for various minerals.

In this study, the software Visual MINTEQ, which is a Visual Basic version of the previous version of MINTEQ (Felmy et al. 1984), was used. This computer code calculates mineral saturation indices (SI) and suggests mineral phases that may control the pore water quality. An SI value greater than 0 signifies that the indicated mineral should precipitate under these conditions, while a negative SI value means that the indicated mineral should dissolve. A SI equal to 0 indicates equilibrium conditions.

Visual MINTEQ indicates that jarosite (K and H types) is the secondary mineral containing sulfates most likely to appear ($1.27 < SI < 8.2$) in columns B and C. The presence of jarosite indicates that acidic conditions occur in these columns (e.g., Blowes and Jambor 1990). In column A, where the pH was higher, the same minerals were undersaturated. Furthermore, the predicted SI of gypsum in columns A, B, and C is approximately equal to zero, which indicates that its precipitation remains probable (Villeneuve 2004).

The most probable secondary minerals containing iron likely to appear ($0.5 < SI < 9.8$) in the columns are magnesoferrite ($MgFeO_4$), hematite, goethite, magnetite, lepidocrocite, and cupric ferrite; these species all appear after the first flush. The presence of these minerals in the three columns explains the strong decrease of iron in the percolated solution. Magnesoferrite is undersaturated in columns B and C.

Saturation indices for carbonate minerals showed that in column A, calcite and dolomite might be oversaturated for the first 25 days. After this period, the same minerals were undersaturated ($SI \approx -1$). In columns B and C, the model indicates that the leachates are undersaturated with respect to dolomite and calcite for the entire test period, with SI values less than zero.

Conclusions

In this work, the generation of AMD was prevented in the laboratory by the addition of alkaline phosphate wastes to coarse tailings from an abandoned mine. This technology appears to be very promising for the control of AMD. Based on the laboratory column experiment, it appears that the addition of 15 wt% APW to Kettara coarse tailings can efficiently neutralize the acidic mine effluents. In addition, the amendment considerably lowered the metal concentrations in the leachate, compared to the unamended Kettara coarse tailings. Recycling alkaline industrial wastes to prevent the formation of AMD at its source should be one of the most sustainable solutions to the problem.

The chemistry of the effluents indicated substantial neutralization by calcitic limestone. The very low Mg concentrations in the leachates indicated that the dolomite does not take an active part in neutralization of the AMD. In addition, there was no significant difference in the drainage quality when 15 and 25% of phosphate wastes were mixed within the Kettara coarse tailings. In columns B and C, when the neutralized solution contacted the unweathered coarse tailings, the pH became acidic and acidity values increased, but the metal concentrations remained very low.

One of the options proposed for Kettara mine site rehabilitation consists of collecting all of the coarse tailings and disposing of them on the fine tailings pond. Addition of the waste rock from the phosphate mining industry as amendment would take advantage of the high carbonate content (in the form of calcite) of this material and its capacity for metal fixation.

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