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TECHNICAL ARTICLE

The Geochemical Behaviour of Mine Tailings from the Touiref Pb–Zn District in Tunisia in Weathering Cells Leaching Tests

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Abstract Flotation tailings associated with the extraction of Pb and Zn in the Touiref mining district, Tunisia, contain galena, sphalerite, pyrite, and marcasite in a carbonate gangue. The geochemical behaviour of oxidized and unoxidised tailings were consistent with their mineralogical and chemical characteristics. The leaching proceeded under neutral to slightly alkaline condition (pH 7.3–8.5), and positive Eh (250–470 mV). The concentrations of sulfate and Ca released during the leaching tests were associated with the neutralization of acidity by carbonates and the dissolution of gypsum initially present in the tailings. The iron precipitated, but significant amounts of Zn (5–3,300 μg/L), Cd (3–18 μg/L), and Pb (28–83 μg/L) were released during leaching, with the latter two exceeding international environmental norms (5 μg/L for Cd and 10 μg/L for Pb).

Keywords Contaminated neutral drainage (CND) · Flotation tailings · Metal release · Water contamination

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Introduction

The mining industry was very active during the last century in northern Tunisia and remains a fundamental component of the Tunisian economy. Mines were developed near farm lands and within the watersheds of the main watercourses, and erosion and weathering of mine wastes are a source of water and atmospheric contamination. The environmental impacts come from the extensive and prolonged interaction between the atmospheric agents (oxygen and rainwater) and the residual sulfides contained in the mine tailings above the water table. Under low pH conditions, the solubility and concentration of many metals (e.g. Fe, Al, Mn, Zn, Cu, Cd, Hg, Pb, Co) increases in the leachates and can then be easily transferred to the environment (Aubertin et al. 2002; Down and Stock 1977; Marcus 1997; Morin and Hutt 1997; Ripley et al. 1996; Ritcey 1989).

When the acidity produced by the oxidation of pyrite is neutralized by carbonates, the effluent can be neutral but contaminated with metals; this type of mine effluent is called contaminated neutral drainage (CND). Typically, CND effluents have a pH of 6–8 and high concentrations of SO_4 and HCO_3, along with high contents of Mg and Na relative to Fe and\or Al. CND mostly occurs in carbonate settings (Benzaazoua et al. 2004; Blowes et al. 1994; Bussière et al. 2004; Heikkinen et al. 2009; Jurjovec et al. 2002; Lindsay et al. 2009; Matthies et al. 2010; McCreadie et al. 2000; Nicholson et al. 2003; Pépin 2009; Percival et al. 2004; Pettit et al. 1999; Plante et al. 2010; Rinker et al. 2003; Scharer et al. 2000; Shevenell et al. 1999; Sracek et al. 2012; Stantec 2004; Xu et al. 2010) but also in silicate rocks (Day and Bowell 2005; NEDEM 2006) and coal mines (Rose and Cravotta 1998). Due to the high quantities of Ca^{2+} and SO_4^{2-} ions produced during the neutralization process, gypsum ($CaSO_4 \cdot 2H_2O$) is often present as a secondary mineral.

In this work, the authors undertook a multidisciplinary characterization (physical, mineralogical, and geochemical) of the flotation tailings sampled at the abandoned Pb–Zn mine of Touiref. The tailings were generated from ore contained in carbonate host-rocks and located in a subhumid climate latitude in northwest Tunisia. Using kinetic tests (weathering cells), we compared two segments [oxidized (OT)/unoxidised (UOT)] of the tailings to assess their geochemical and environmental behaviours and understand their long-term potential impact on the local environment.

The Touiref Mining Area

Extraction of Pb–Zn in the Touiref area stopped in 1958. The district is located in the mountainous area of Ouargha in northwest Tunisia, near the Algeria–Tunisia border, 56 km to the west of El Kef city. It is in the northern part of the Tunisian Atlas Mountains, at the southern limit of the flysch zone (Fig. 1), and corresponds to an anticline structure intruded by Triassic evaporates and surrounded by Cretaceous outcrops (Sainfeld 1952).

The climate of the region is semi-arid, with a mean annual rainfall of approximately 455 mm. High intensity precipitation commonly occurs for short durations. The annual potential evaporation typically exceeds 1,340 mm, and the average monthly temperatures in the area ranges from 8 °C in January to 29 °C in July (INM 2004).

The geology of the area belongs to the Coniacian-Burdigalian interval, which consists of alternating marls and limestone. The mineralization occurs as veins resulting from the filling of E-W to WNW-ESE secondary oblique faults and NW–SE transverse faults, and locally as fillings of stratification joints. The mineralization consists of lead (galena, cerussite), zinc (zincite at the surface, sphalerite at depth), and iron (oxides and pyrite) hosted in hard carbonate formations (SERMI 1965). More than 500,000 t of flotation tailings were deposited in a tailings impoundment (Fig. 2). These tailings continue to be disseminated by water and wind, polluting farmlands, for there are no protective or preventive measures (Fig. 2). The tailings storage area is drained by the Oued Sidi Bou Saïd, which flows in the endoreic plain of El Goreaâ.

Materials and Methods

Materials

The tailings consist of alternating centimetre to decimetre thick layers that differ from each other by colour or grain size. At the surface, the most oxidized zones are yellow to ochre in colour, while the water saturated zones are dark grey to black. 43 samples of flotation talings were collected along a vertical profile of 6.6 m deep dug with a shovel between the center and the periphery of the tailings dump: 34 samples from the oxidation zone (0–5.5 m), 7 samples from the transition zone (−5.5 to −6.2 m), and 2 samples from the unoxidized (fresh) one (−6.2 to −6.6 m). Each sample (those of the transition zone excluded) has been quartered, the two opposite quarters of all samples from the same zone are mixed to prepare a mean sample representative of the weathered zone (OT: oxidized tailings) and the zone below the water table level (UOT: unoxidized tailings) (Fig. 3) and stored in polyethylene bags prior to the kinetic testing. To ensure the representativeness of the sample fraction to be analyzed, each representative mean tailings sample was carefully separated into four equivalent

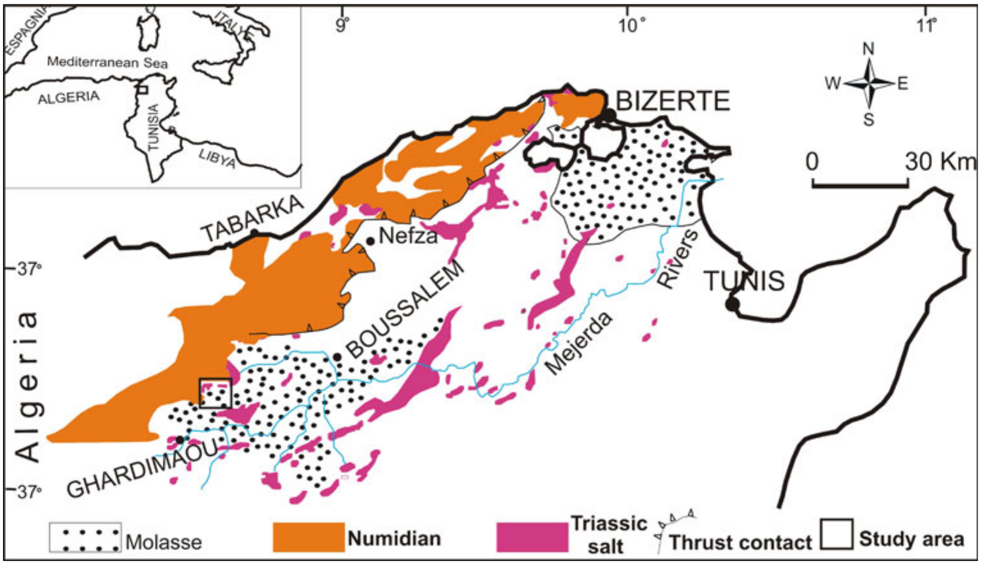
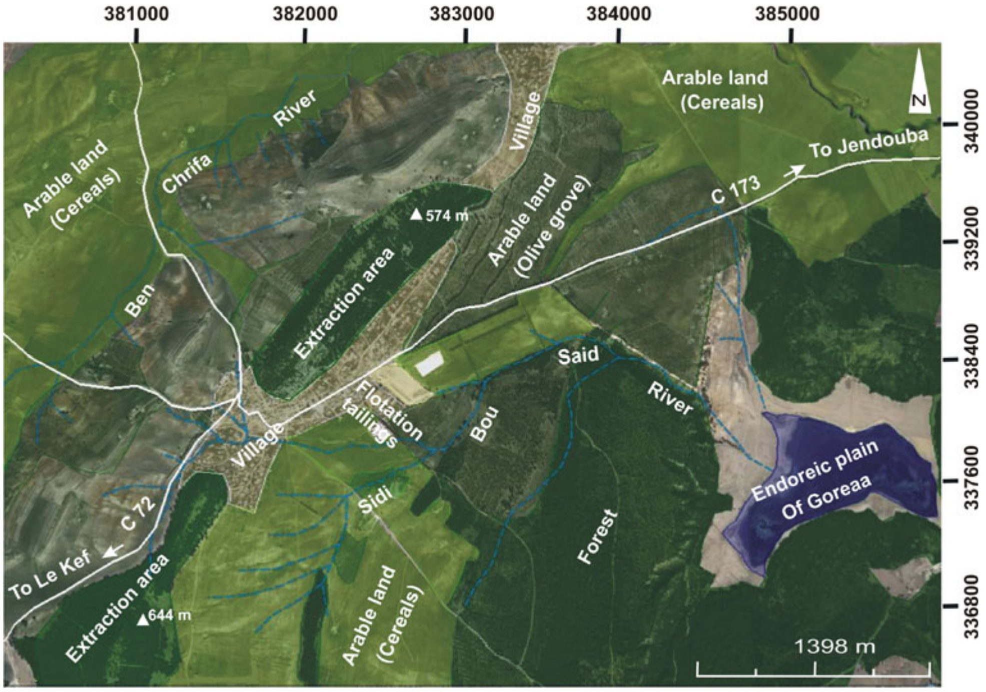


Fig. 1 Geological framework of the extreme North of Tunisia (modified after Rouvier 1977)

Fig. 2 Aerial view of the Touiref abandoned mine site, showing the flotation tailings impoundment and its surrounding areas: the protected natural wet land of El Goreaâ, large cultivated areas, a sports ground, etc



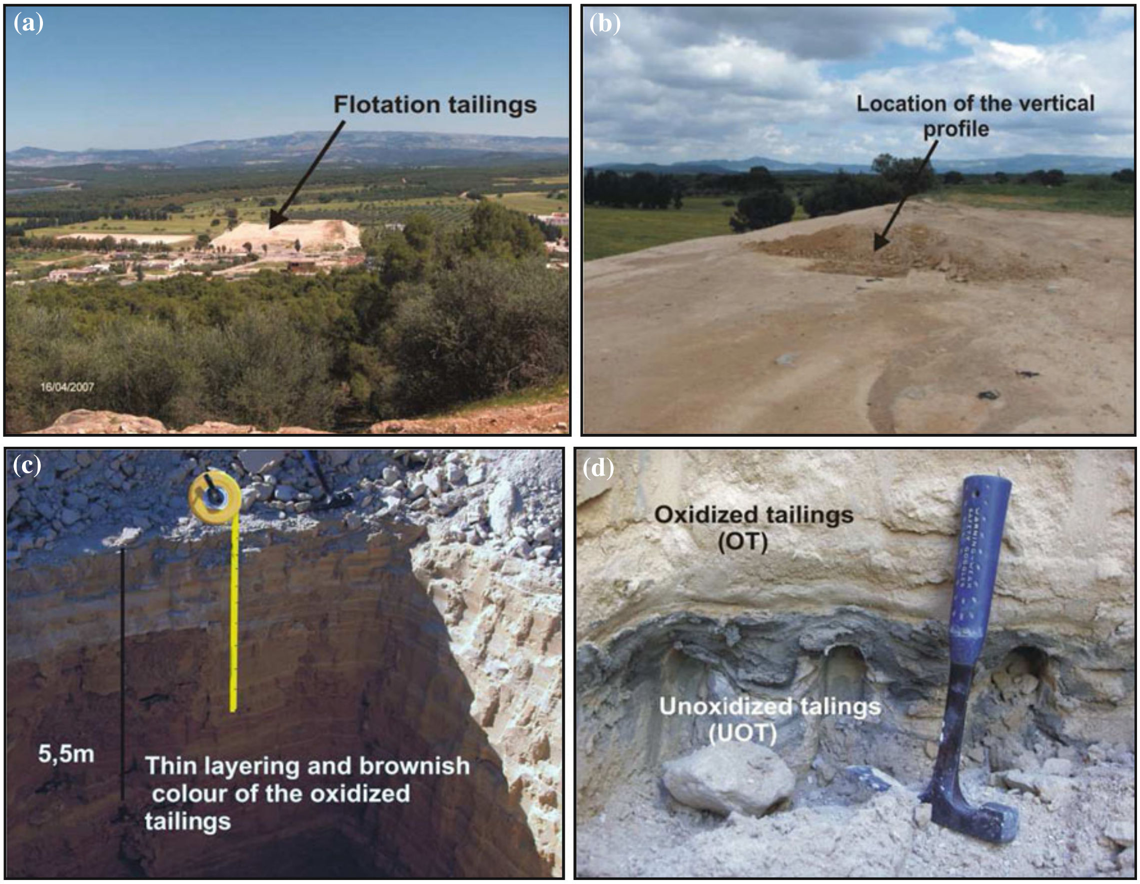


Fig. 3 The mine tailings of Touiref: **a** panoramic view of the tailings impoundment, **b** location of the vertical profile, **c** thinly bedded aspect and *brownish colour* of the oxidized tailings at the *top* of the impoundment, **d** the limit between the oxidized and the unoxidized zones of the flotation tailings, observed at 5.5 m below the top surface of the impoundment

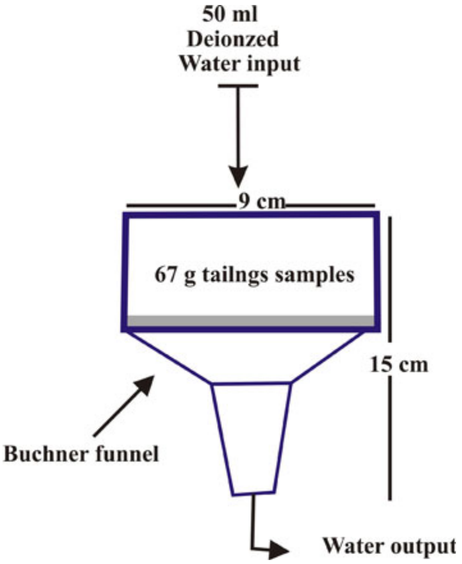


Fig. 4 Schematic illustration of a typical mini-alteration cell used in this study

subsamples. Then, two opposite subsamples were mixed and separated again into four subsamples. This procedure was repeated three times. Finally, the final representative subsamples were quartered, one subsample of which will be used for physical analysis and mini-weathering cell experiments, the second subsample will be carefully crushed in an agate mortar to be used for XRD and chemical bulk analysis. The remaining two subsamples are stored in a polyethylene bag.

Methods

Tailings Characterization

Wet tailings samples were oven dried at 45 °C for 24 h to determine their water content and to prepare dry samples for the characterization analyses. The grain size distribution was determined using a Malvern Mastersizer laser particle size analyzer. The specific gravity (G_s) of the solid phase was measured with a Micromeritics Accupyc 1330 helium gas pycnometer.

The initial tailings mineralogy was determined by a combination of X-ray diffraction (XRD) with a Bruker AXS D8 Advance, and optical microscope (Nikon optiphot-2 Pol) observations. A scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) was also used to study polished sections of tailings samples. The SEM is a pressure vacuum Hitachi S 3500-N equipped with backscattered and secondary electron detectors and a Silicon Drif Detector (X-MAX 20 mm^2) microanalysis system from Oxford Instruments.

The chemical composition (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, S, Zn, and SO_4) of the tailings was obtained with a Perkin Elmer Optima 3100 RL ICP AES following a $HNO_3/Br_2/HF/HCl$ total digestion. Sulfide sulfur was determined by subtracting the sulfate sulfur (determined by a 40 % HCl extraction; method adapted from Sobek et al. 1978) from the total sulfur (ICP-AES analysis).

These characterizations were all conducted at the Unite de Recherche et de Service en Technologie Minerale (URSTM) of the University of Quebec in Abitibi-Temiscamingue (UQAT), in Canada.

Leaching Tests in Weathering Cells

Weathering cells (Fig. 4) similar to those used by Cruz et al. (2001) were utilized in this study. The aggressiveness of the method lies in the use of a thin layer of sample, which is subjected to frequent leaching-drying cycles. About 67 g (dry weight) of tailings were placed in a 100 mm diameter Buchner funnel equipped with a 0.45 µm pore size glass-fiber filter. The experiment consisted of 20 leaching cycles, according to the following procedure: (1) the sample was rinsed with 50 mL of deionized water added at the top of the Buchner funnel, (2) after 3 h of water-tailings contact, the leaching solution was recovered by filtration, (3) the sample was left for 2 days of exposure to ambient air, before the next leaching cycle.

Leachate samples were filtered with a 0.45 µm nylon mesh filter immediately after collection. The pH of the solutions was read by a combination pH electrode with temperature compensation. Redox potential was determined with a Pt/Ag/AgCl electrode. The results were then corrected for the standard hydrogen electrode (SHE) to obtain Eh (expressed in mV).

Filtered leachates were acidified to 2 % HNO_3 to ensure metal dissolution. All chemical analyses were conducted with a Perkin Elmer Optima 3100 RL ICP-AES.

Geochemical Modeling

The Visual MINTEQ (Ver.2.14) (Felmy et al. 1984) program for aqueous geochemical equilibrium was used to evaluate the saturation indices (SI) of minerals that could precipitate during the kinetic tests. A positive SI value indicates that the mineral would precipitate, while a negative SI value means that the mineral would dissolve. A SI equal to 0 indicates equilibrium between the mineral and solution. The main model assumption is that the dissolution or precipitation reactions are rapid enough to be in equilibrium with the leaching solution.

Results and Discussion

Chemical Properties

Chemical analyses of the studied tailings samples (Table 1) show that the composition of both the oxidized and unoxidised tailings is dominated by Ca (39.5 wt% on average), due to the abundance of carbonates. The average concentration of sulfur is ≈0.3 wt%, most of which are sulfate minerals (gypsum, anhydrite). Sulfides (pyrite, sphalerite, galena) were present in both samples, with higher concentrations in the unoxidized sample (0.226 wt%) than in the oxidized one (0.212 wt%).

Mg, Fe, and to a lesser extent, Al (1.06, 0.48, and 0.28 wt% on average, respectively), were also present. It is assumed that in the oxidized part of the tailings impoundment, iron, which is initially present as sulfide and carbonate, is integrated in the secondary oxide-hydroxide minerals. The Al indicates the presence of a small amount of aluminosilicates. The concentrations of Zn, Pb, and Cd (1.23, 0.51, and 0.018 wt% on average, respectively) were relatively high. Low concentrations of other metals (Cu, Cr, Ni) and non-metals (As, Ba) were also present.

Physical Properties

Specific gravity (G_s), specific areas (SA), and particle size distribution (PSD) parameters of the studied samples are given in Table 2. The G_s is almost similar for the two samples, ≈2.75 (g/cm^3), similar to the mean density of carbonates (2.6–2.8). The SA of the oxidized sample (3.01 m^2/g) was higher than that of the fresh sample (2.86 m^2/g). This might be explained by the presence of secondary precipitates in the weathered tailings, as reported in several previous works (e.g. Benzaazoua et al. 2004).

Both the oxidized and the unoxidized samples have similar grain size properties, as shown by the D_{10} (0.65 and 0.78 µm, respectively), the D_{50} (35 and 50 µm, respectively), and the D_{90} (333 and 327 µm, respectively). Moreover, the values of the mean size (Mz: 102 and 107 µm, respectively) and the median size (Md: 35 and 50 µm, respectively) indicate a dominance of the coarse (silt and sand) fraction, which may confer to the materials a high permeability and low water retention properties, facilitating oxygen diffusion from the atmosphere. These factors favor the oxidation of sulfides. The values of the coefficient of uniformity ($C_U = D_{60}/D_{10}$: 125 and 157, respectively) show that the grain size distribution is widespread, whereas the coefficient of curvature ($C_C = (D_{30})^2/(D_{60} \times D_{10})$: 0.3 and 0.4, respectively) is an expression of a better distribution of the coarse fraction. The characteristics of both materials are typical of flotation discharges of sulfide ore-bearing hard rocks (Aubertin et al. 1996; Bussière 2007).

Table 1 Bulk chemical composition (wt%) of the studied mine tailings

Elements	Oxidized tailings (OT)	Unoxidized tailings (UOT)
Al	0.321	0.239
As	0.011	0.005
Ba	0.005	0.001
Ca	39.3	39.7
Cd	0.016	0.021
Cr	0.003	0.003
Cu	0.003	0.003
Fe	0.601	0.354
Mg	1.09	1.03
Mn	0.011	0.009
Ni	0.001	0.001
Pb	0.45	0.571
S_{tot}	0.306	0.298
$S_{sulfates}$	0.0938	0.0718
$S_{sulfides}$	0.212	0.226
Zn	1.17	1.27

Table 2 Physical properties of the two studied tailings

Property units	OT	UOT
D_r (g/cm^3)	2.754	2.750
SA (m^2/g)	3.01	2.86
% under 80 µm (%)	55.22	57.21
D_{10} (µm)	0.65	0.78
D_{50} (µm)	48.86	35.48
D_{90} (µm)	333.3	327.8
Mz (µm)	102	107
Md (µm)	35	50

Table 3 Mineralogy (in wt%) of the studied bulk sample tailings as determined by XRD

Mineral	Formula	Oxidized tailings (OT)	Unoxidized tailings (UOT)
Calcite	$CaCO_3$	84.20	87
Quartz	SiO_2	2.22	1.5
Dolomite	$CaMg(CO)_3$	3.84	4.30
Ankerite	$Ca(Fe, Mg, Mn)(CO_3)_2$	5.14	6
Gypsym	$CaSO_4$	5.14	0.23
Anhydrite	$CaSO_4$	0.17	0.30
Siderite	$FeCO_3$	1.87	0.70
Sphalerite	ZnS	0.16	0.87
Galena	PbS	–	–
Pyrite	FeS_2	–	–

–, not detected

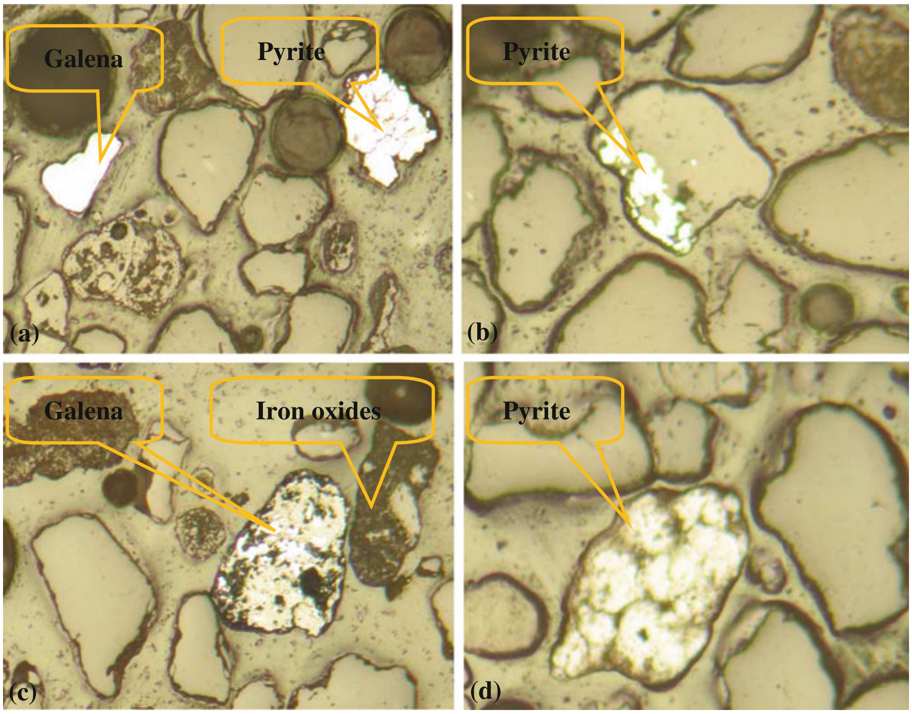


Fig. 5 Sulfides and their alteration products observed in the unoxidized (**a**, **b**) and oxidized (**c**, **d**) flotation tailings (polished sections, polarized light); **a** grain of pyrite and galena, **b** grains of pyrite included in calcite grains, **c** grain of galena partly altered into cerussite and goethite, **d** pyritospheres partly altered into goethite

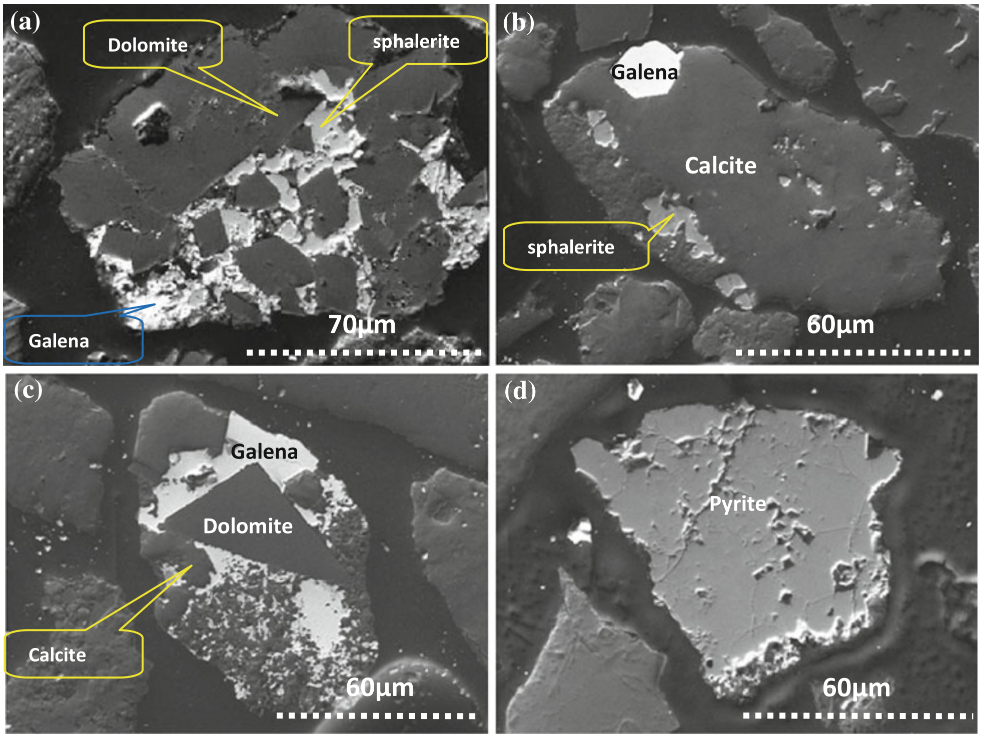


Fig. 6 SEM electron images of individual grains in the unoxidized tailings sample (**a** association of dolomite–sphalerite–galena, **b** association of calcite–sphalerite–galena, **c** association of calcite–dolomite–galena, **d** pyrite)

Mineralogical Characterization

Semi-quantitative analyses by XRD showed that both the oxidized and onoxidized tailings contain a significant amount of calcite (Table 3). Ankerite, dolomite, anhydrite, siderite, and silica were also present but in lesser quantities. Among sulfides, sphalerite dominated (approximately 0.85 wt%), whereas the other sulfides (galena, pyrite, marcasite) were not identified since they were present at low concentrations (<0.1 wt%).

Observation of the oxidized tailings (80–250 µm fraction) in polished sections under the metallographic

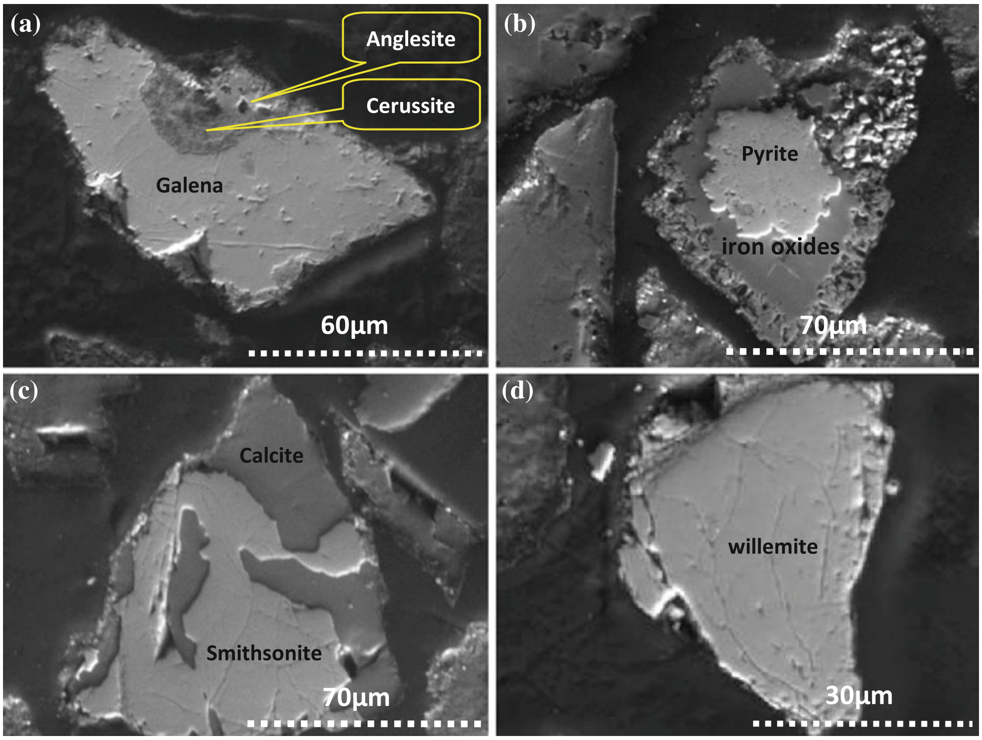


Fig. 7 SEM electron images of individual grains in the oxidized tailings sample (**a** galena replaced by cerussite and anglesite, **b** pyrite showing strongly corroded boundaries, being replaced by iron oxides, **c** sphalerite is sometimes completely replaced by smithsonite, **d** sphalerite replaced by willemite

microscope allowed identification of pyrite, marcasite, and galena as well as their alteration products (cerussite, iron oxides, etc.) and the gangue minerals (Fig. 5).

Examination of the two samples by SEM–EDS shows that in the unoxidized tailings (Fig. 6), pyrite, sphalerite, and galena are associated with a carbonate (calcite and dolomite) matrix. In the oxidized tailings (Fig. 7), the sulfides have undergone advanced oxidation.

Leaching/Kinetic Tests

The most significant parameters measured in the leachates collected after each cycle of the weathering cell test were the physico-chemical parameters (pH, Eh, conductivity) and the cumulative ionic loads. Results are normalized by kilogram (dry weight) of tailings tested and take into account the leachate volumes. Results are expressed as cumulative loads for all elements. The sulfate and Ca ions are derived from the dissolution of the carbonates (calcite, dolomite, ankerite) following acidity production, and the dissolution of calcium sulfate minerals (gypsum and anhydrite). Mg and Mn represent the by-products of acid neutralization by carbonates. The behaviour of these two groups of species define the long term acid generating potential (AGP); this criterion has been used to allow interpretation and comparison between different kinetic test protocols (Benzaazoua et al. 2001; Villeneuve et al. 2003).

pH, Eh and Conductivity

The pH (Fig. 8a) remained neutral to slightly alkaline (7.3–8.5) during the leaching tests on both the unoxidized and oxidized samples. The Eh values (Fig. 8b) varied between +303 and +471 Mv/ENH for the OT sample, and between +303 Mv/ENH and +470 mV/ENH for the UOT sample, with a slight increasing trend durins the test. These results showed that the environmental conditions favoured the oxidation of sulfides (Bussiere and Benzaazoua 1999; Bussiere et al. 2005). Conductivity measurements (Fig. 8c) were different for the two types of tailings. In the UOT tests, the values initially rose, from 249 µMhos to a maximum of 1,877 µMhos, and then decreased to about 380 µmhos from the 11th day onwards. For the OT, the conductivity steadily decreased from 1,900 to 200 µMhos at the end of the test. These observations indicate that the total ionic load in the leachates decreased during the test and that the weathered tailings progressively lost their secondary species. The same behaviour was observed for the fresh tailings at the beginning of the test.

Cumulative Ionic Loads

All of the lithophile cations (Ca, Mg, Mn, Fe, Si), sulfur (SO_4^{2-}), and multiple trace elements (MTE) were measured. The results are expressed as cumulative ionic loads versus time in Fig. 9.

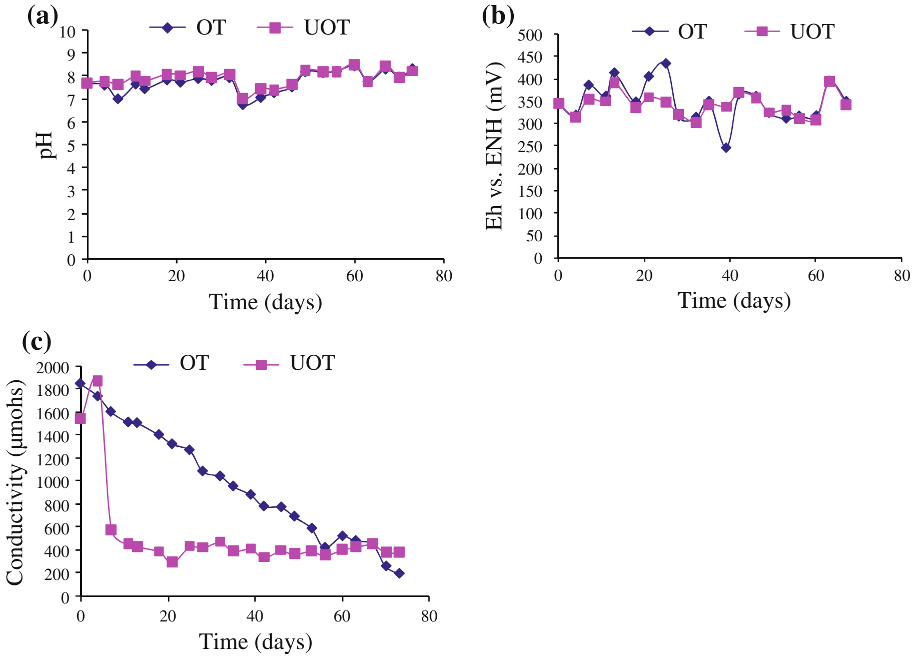


Fig. 8 Evolution of the **a** pH, **b** Eh, and **c** conductivity during the kinetic tests with the oxidized and unoxidized tailings samples

Sulfur (as SO_4^{2-})

At the beginning of the test, the sulfate load increased significantly for the OT sample (Fig. 9a), which indicates that SO_4^{2-} production, which comes from either the oxidation of sulfides or the dissolution of secondary minerals (gypsum), was a continuous and progressive process. At the 15th day, the evolution curve shows an inflection, which indicates a fall in the SO_4^{2-} production rate. This fast reduction can be associated with the dissolution of secondary minerals present in the tailings, which are more easily lixiviated in the first rinse. With regards to the UOT sample, the slope of the cumulative curve is lower, which indicates that the dissolution kinetics of sulfides is slow. Visual Minteq Software indicated that saturation indices of the sulfate compounds are negative, which implies that most of the sulfate remains in solution.

The cumulative curves for Ca, Mg, and Mn (Fig. 9b–d) decrease from the 10th day, with a more pronounced slope for the oxidized sample. This means that the tendency of calcite and dolomite to dissolve is stronger at the beginning of the test. It should be noted, however, that the OT sample released more Ca (Fig. 9b), while the UOT sample released more Mg (Fig. 9c). Mn (Fig. 9d) was almost absent in the leachates of both samples; its evolution was constant, and its release was almost equivalent for the two samples.

The concentrations Zn and Pb in the OT leachates ranged between 267 and 3,300 μg/L and 28 and 80 μg/L, respectively, whereas the UOT leachates ranged between 5 and 2,540 μg/L and 33 and 83 μg/L, respectively. The cumulative curves for these two elements (Fig. 9e, f) show that Zn was released throughout the kinetic test and in larger quantity by the oxidized sample, which means that Zn associated with the OT sample was dominantly carbonate (smithsonite), whereas in the UOT sample, Zn was mostly present as sphalerite. Lead presented a constant slope during the first 77 days of the tests, showing that its dissolution was continuous and constant, despite the difference in the mineralogical forms of the Pb-bearing minerals, which are dominantly present as carbonates (cerussite) and sulfates (anglesite) in the OT and as sulfides (galena) in the UOT.

The Cd concentrations ranged between 3 and 18 μg/L in the OT leachates and between 3 and 10 μg/L in the UOT leachates (Fig. 9g). Their cumulative concentrations didn’t exceed 0.018 mg/L, which shows that Cd is not present as individual mineral forms, but are incorporated in sphalerite (Othmani 2006).

Iron (Fig. 9h) was almost absent in the leachates of the mini-weathering cells.

Post experiment characterization

The results of the chemical analysis achieved on the two final solid samples are presented in Table 4. These results indicate a weak leaching of the elements during the test. Concerning calcium, the decrease in concentration is more important for the oxidized sample (5 %) whereas for the unoxidized one, it is about 1.4 %. As far as the total sulfur and sulfide sulfur contents are concerned, only a small decrease is observed in both species for the unoxidized sample (from 0.298 % to 0.211 % and from 0.226 % to 0.18 %, respectively), but more pronounced for the oxidized one (from 0.306 % to 0.060 % and from 0.212 % to 0.045 %, respectively).

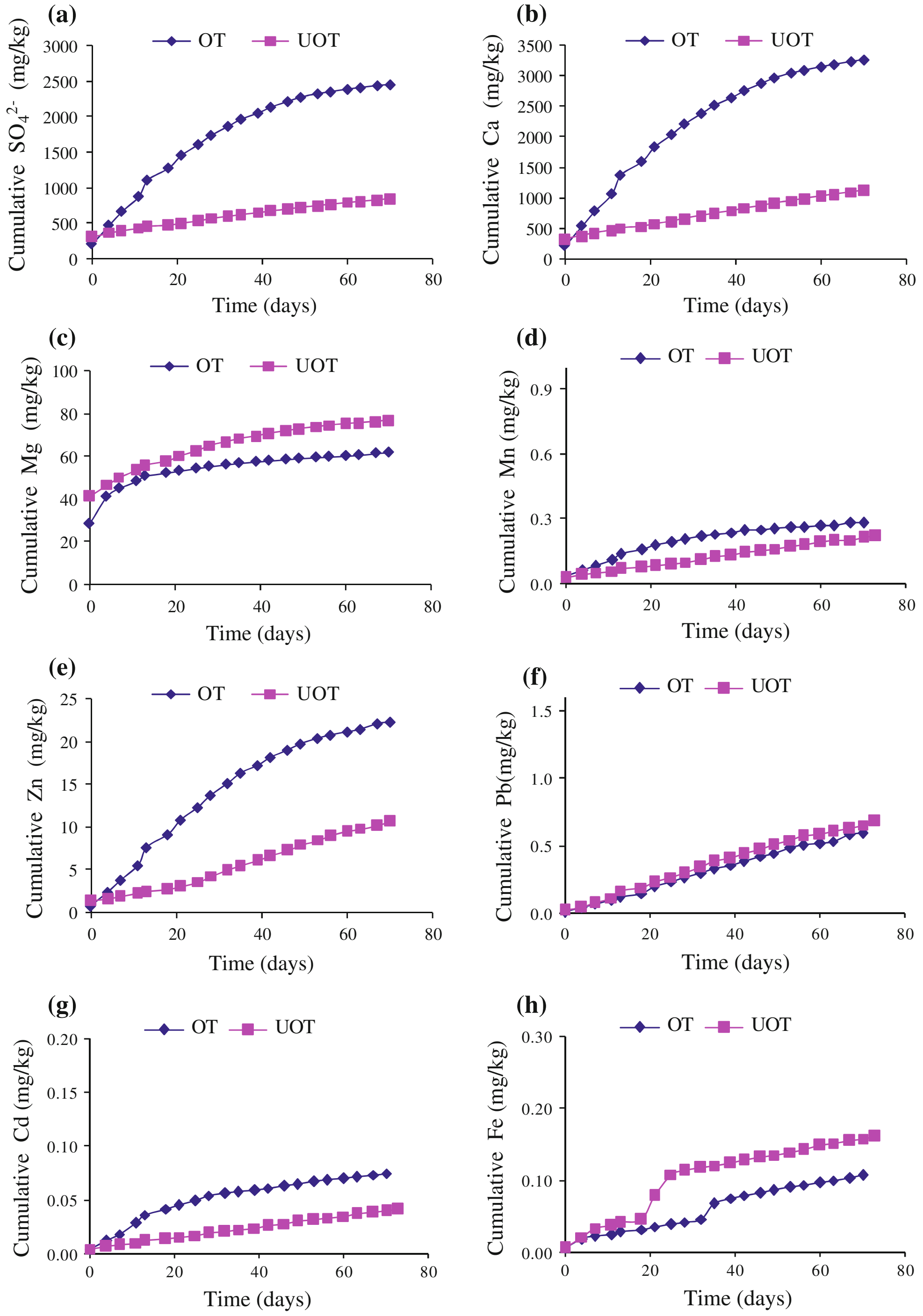


Fig. 9 Cumulative loads of **a** SO_4, **b** Ca, **c** Mg, **d** Mn, **e** Zn, **f** Pb, **g** Cd and **h** Fe, in the flushing waters of the kinetic tests conducted on the oxidized and unoxidized tailings samples

Depletion of Sulfate, Neutralizing Elements (Ca+Mg+Mn), and MTE (Pb+Zn)

Figure 10 presents the depletion of sulfate ions, neutralizing elements (Ca + Mg + Mn), and MTE (Pb + Zn) versus time. After the first 60 days of testing, the depletion of sulfate was more important for the OT (25 %) than for the UOT (7.25 %); this can be attributed to the presence of higher amounts of secondary sulfate minerals (gypsum, anhydrite, anglesite, etc.) in the OT, which are more easily leached during the initial flushes. Under the experimental conditions, the produced sulfates cannot precipitate easily, as demonstrated by the SI of gypsum for the oxidized (−0.44 to −2.42) and the unoxidized (−1.17 to −1.76) samples. However, for the neutralizing elements and MTE, the depletion was low for the two samples: less than 2 % (98 % remaining) and 1 % (99 % remaining), respectively.

Table 4 Post-experiment chemical composition (wt%) of the studied mine tailings

Elements	Oxidized tailings (OT)	Unoxidized tailings (UOT)
Al	0.233	0.260
As	0.011	0.006
Ba	0.001	0.003
Ca	34.3	38.3
Cd	0.017	0.021
Cr	0.003	0.003
Cu	0.002	0.004
Fe	0.615	0.397
Mg	1.04	1.07
Mn	0.011	0.009
Ni	0.001	0.001
Pb	0.448	0.668
S_{tot}	0.060	0.211
$S_{sulfates}$	0.014	0.031
$S_{sulfides}$	0.045	0.18
Zn	1.29	1.35

The Relationship Between SO_4^{2-} and (Ca + Mg + Mn)

The specific ionic loads of the major ionic species and MTE during the weathering cell tests were interpreted using the relationship between SO_4^{2-} and (Ca + Mg + Mn), in which both pyrite oxidation and the dissolution of calcium sulfate minerals (gypsum, anhydrite) are sources for SO_4^{2-}. However, in mining effluents and for sulfide-rich tailings, sulfur is present as sulfate ions and is the direct indicator of the dissolution of sulfides and acidification of leaching solutions (Morin and Hutt 1997). As mentioned above, it was assumed that the produced sulfates cannot precipitate easily, based on the SI of gypsum. The results show that for both samples, the sulfate concentrations correlate with those of the neutralizing elements (Ca + Mg + Mn), among which Ca is the dominant species (Fig. 11). It is assumed that these elements represent both the totality of the cations released during the neutralization of the generated acidity by carbonates (calcite and dolomite) and the dissolution of the pre-existing calcium sulfate (gypsum, anhydrite; Table 1) in the samples. So, it can be deduced that the major cations are not only released in response to the oxidation of sulfides, and consequently don't allow the assessment of the long-term acidity generating potential of the tailings, as demonstrated by Benzaazoua et al. (2001, 2004) and Hakkou et al. (2008a, b) for the Joutel (Quebec-Canada) and the Kettara (Marrakech-Morocco) tailings, respectively, for which similar weathering cell experiments have been conducted on sulfide-rich materials that do not contain pre-existing calcium sulfate.

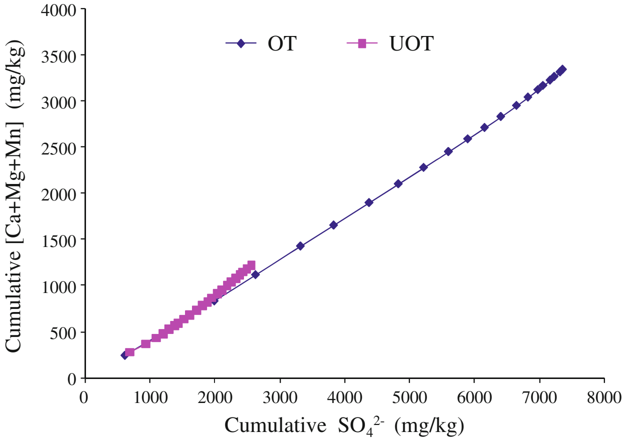


Fig. 11 The relationship between cumulative sulfate loads and the neutralizing elements produced during the weathering cell tests for the oxidized and unoxidized tailings samples

Discussion

The mineralogical analysis shows that both samples are mostly composed of calcite. Silica, dolomite, siderite, ankerite, gypsum, and anhydrite are also present, but in small quantities. Of the sulfides, only sphalerite was

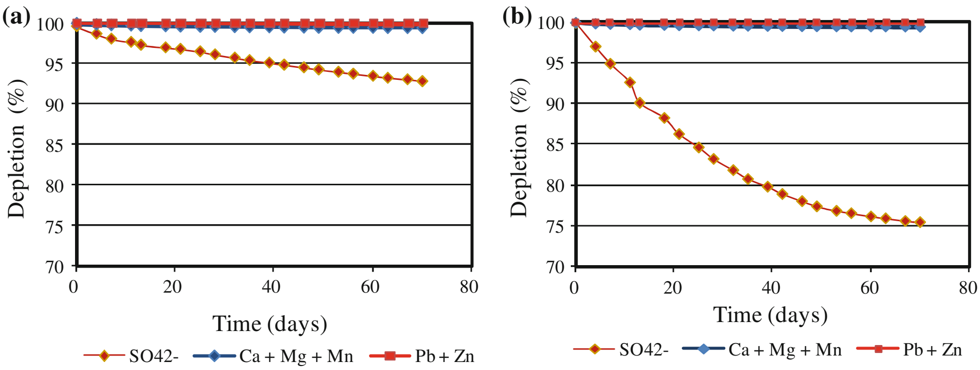


Fig. 10 Computed (%) remaining total sulfur (SO_4^{2-}), neutralizing elements (Ca + Mg + Mn), and MTE (Pb + Zn) in the tailings samples (**a** oxidized tailings OT; **b** unoxidized tailings UOT) for the weathering cell experiments

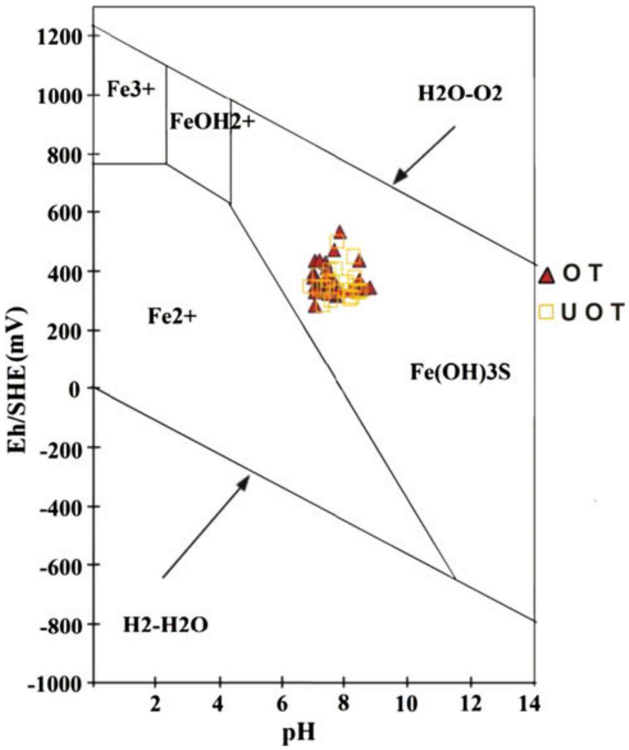


Fig. 12 An Eh–pH diagram showing the stability fields of iron species, according to Neff (2003) and Benzaazoua et al. (2004), of the oxidized and unoxidized tailings samples of Touiref

identified by XRD in both the oxidized (0.8 wt%) and unoxidized samples (0.9 wt%). Chemical analysis indicates that the percentages of Pb and Zn were 0.57 and 1.27 wt% in the unoxidized sample and 0.45 wt% and 1.17 wt% in the oxidized one, respectively. The total sulfur content in both samples was approximately 0.3 wt%, most of which is present as sulfide.

Significant concentrations of gypsum ($CaSO_4 \cdot 2H_2O$) were also detected in the oxidized tailings. The concentrations of sulfate ions and (Ca + Mg + Mn) in the leachates result both from pyrite oxidation and calcium sulfate dissolution. Since the SI shows that precipitation of gypsum is not very probable as a secondary mineral phase under the experimental conditions, these results indicate that gypsum dissolution is the major mineral phase controlling the dissolved concentration of SO_4^{2-} within the tailings impoundment, as reported for similar sites in Mexico (Romero et al. 2007) and Canada (Johnson et al. 2000; McGregor et al. 1998). A process of sulfide oxidation and neutralization by calcite takes place within the tailings pile, creating gypsum, in which case, the maximum sulfate concentration will be controlled by the equilibria between calcite and gypsum. However, our experimental studies may not have reached saturation conditions with gypsum solubility due to the fact that we focused on kinetic processes rather than equilibrium conditions.

The nearly neutral pH values measured during the tests show that the observed drainage belongs to the category of CND. Both the oxidation of sulfides and the dissolution of secondary sulfate minerals explain the high sulfate content in the leachates. Any acidity produced is immediately neutralized by carbonates (calcite, dolomite, and ankerite). Both phenomena are represented by the presence of Ca, Mg, and Mn in the leachates. However, the relative scarcity of iron sulfides considerably decreases the AMD generating capacity of the tailings, so most of the high concentrations of sulfate and Ca ions in the leachates are due to the dissolution of sulfate minerals. The higher amounts of these elements in the leachates of the OT sample than in the leachates of the UOT sample is consistent with the higher amounts of calcium sulfate in the former. The graphical representation of the cumulative ionic loads during the kinetic tests for the two samples (Fig. 11) shows that:

- For the OT sample, the initial linear increase is explained by the strong dissolution kinetics of minerals in the weathering cells during the first leaching cycles. Following this initial behaviour, the reactivity of pyrite (S), calcite (Ca), dolomite (Mg), sphalerite, and secondary sulfate minerals (gypsum) declined.
- For the UOT sample, the neutralizing elements and sulfur, as well as the metals (Figs. 9, 10), slowly dissolve during the kinetic test, whereas iron and copper are almost absent.

The concentrations of Zn, Cd, and Pb in the leachates of the oxidized sample (267–3,300, 3–18, and 28–80 µg/L, respectively) and the unoxidized sample (5–2,540, 3–10, and 33–83 µg/L, respectively) show that the former remains below the permissible maximum limit (PML) of 5,000 µg/L in water for human consumption (Lizarraga-Mendiola et al. 2009; US NPDWS 2003), whereas values exceeding the PML were recorded for Cd and Pb (5 and 10 µg/L, respectively). The excess is more pronounced for the oxidized sample (up to 4 times the PML) in the case of Cd, but almost equivalent (3–8 times the PML) in the case of Pb for the two samples. These values are comparable to those mentioned by Souissi et al. (2008) in the leachates of northern Tunisia mine tailings, but clearly below those associated with the acid solutions generated in other Pb–Zn districts, such as the Kettara mine in Morocco (Hakkou et al. 2008a, b), southwestern Sardinia (De Giudicci G (2008)), in Canada (Benzaazoua et al. 2004; Plante et al. 2010; Villeneuve et al. 2003), and in Sweden (Holmström et al. 1999).

The pH and redox potential values were plotted on an iron Eh–pH diagram (Fig. 12), which allows an understanding of the pH and Eh variations during the tests as well as the evolution of iron speciation. All of the pH–Eh projections are localized in the hydroxide stability field for both the OT and UOT. This explains the absence of iron in the leachates from the kinetic tests. The same behaviour has been observed for iron by others during kinetic test experiments (Benzaazoua et al. 2001; Blowes et al. 1998; Bussiere and Benzaazoua 1999; Bussiere et al. 2005; Cox Matthew 1998).

The quasilinear trend expressed through the neutralizing elements versus SO_4^{2-} (Fig. 11) accounts for both the oxidation of pyrite and the solubility of calcium sulfate minerals. However, a decrease in the production rate of sulfate is more evident for the UOT sample, which occurs while the pH of the leachates indicate neutral to slightly alkaline conditions. These conditions favor the precipitation of secondary minerals, such as iron oxy-hydroxides (goethite) on the surface of the grains (Fig. 12). This precipitation can decrease the rates of pyrite oxidation and dissolution of calcium sulfate. Holmström et al. (1999) and Villeneuve (2003, 2004) showed the presence of iron hydroxide precipitates on the surface of pyrite reduced its oxidation rate during a test conducted in humidity cells on a material containing high levels of sulfides and carbonates.

Conclusions

The kinetic tests showed that the leaching of the tested tailings (Pb–Zn sulfides within a carbonate matrix), produced neutral to slightly alkaline (7.3–8.5) leachates due to the neutralization of the acidity generated by the oxidation of sulfides by carbonates. High amounts of calcium sulfate were also dissolved during the experiments. Ca^{2+} and SO_4^{2-} were the major soluble species.

Under the pH conditions of the experiments, the solubility should be low for most metals, among which zinc would be the most soluble. More Zn was released by the oxidized tailings than by the unoxidized tailings. All of the iron produced by the oxidation of pyrite was precipitated as hydroxide.

Referring to the PML and to the water quality for human consumption (US NPDWS 2003), our results show that despite the high solubility of Zn, the levels recorded in the leachates did not exceed its respective PML (5,000 μg/L), while excedances were recorded for Cd (3–18 μg/L) in the leachate of the OT sample and for Pb (28–80 μg/L) in the leachates for both samples relative to their PMLs (5 and 10 μg/L, respectively). Considering the physico-chemical conditions, the leachate solutions from the studied mine tailings qualify as CND. Consequently, the MTE load transported by drainage water may pose an environmental hazard to local surface and groundwaters, as well as sediments and soils in the flood area below the mine tailings.

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