

Geochemical Behavior of Mine Tailings and Waste Rock at the Abandoned Cu–Mo–W Azegour Mine (Occidental High Atlas, Morocco)

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Abstract The abandoned Azegour mine is located in the High Atlas Mountains of Marrakesh (Morocco), and was mined for Cu, Mo, and W. About 850,000 t of waste rocks and tailings were deposited on the surface and have been exposed to weathering for 40 years. The remaining acid-producing potential (AP), acid-neutralizing potential, and geochemical behavior of the Azegour Cu- and Mo-rich tailings were investigated. The tailings were found to contain 9.6–19 wt% sulfur, mostly as sulfate (gypsum, anhydrite, and jarosite) while the waste rocks contain less (1.25–6.58 wt%) sulfur. The waste rocks and tailings contain 0.21–9.24 wt% Mo and 0.003–2.78 wt% Cu. The gangue is mostly composed of quartz, talc, chlorite, pyrophyllite, actonolite, clinoptilolite, and alusite. Lead, zinc, cobalt, arsenic, titanium, and nickel are also present. The calcium, which is mainly expressed as calcite, gypsum, scheelite, and powellite, is present at higher concentrations in the waste rocks (18–22 wt% Ca) than in the

tailings (4.7–8.6 wt% Ca). Static ABA determinations showed that the Azegour mine wastes still have high AP, 38–205 kg CaCO₃/t in the waste rocks and 46–387.7 kg CaCO₃/t in the tailings. This was confirmed in weathering cell tests, where the Azegour tailings leachate had a pH range of 1.98–3.19 and high concentrations of SO₄ (468–45,400 mg/L), Ca (230–675 mg/L), Fe (3–55,900 mg/L), Mn (0.1–1,430 mg/L), and Cu (2.3–9,000 mg/L). The Mo concentrations were high (35 mg/L) during the two first weeks of kinetics tests; W concentrations were below the 0.005 mg/L detection limit.

Keywords Acid mine drainage · Kinetic tests · Mine wastes · Sulfides

Introduction

Morocco, a country with a long mining tradition, has experienced intense mining activity due to the richness and diversity of its mineral resources, and mining is still a mainstay of Morocco's economic and social development. About 30 mine sites have been exploited in the Marrakech region and several thousand metric tons (t) of ore have been extracted. The main mine sites include the abandoned Kettara pyrrhotite mine (Hakkou et al. 2008) and the Sidi BouOuthmane mine (Pb, Zn), both located in the Jebilet Mountains. Other mines are located north of the High Atlas Mountains (Fig. 1), of which the most important are the: Azegour (Cu, Mo, W), Erdouz (Pb, Zn), and Goundafi (Zn, Pb, Cu) mines. In addition, there are barite and salt mines in the High Atlas Mountains (TichkaTafga, Seksaoua, Adouz). Most of these mines have shut down (DM 1990), but some are still active, including the Hajjar and DraaSfar (Zn, Pb, Cu) mines (El Adnani 2008).

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In Morocco, large volumes of waste rocks and concentrator tailings have been abandoned without any security and environmental protections. In the case of base metal, precious metal, and coal mines, the wastes are often rich in metal sulfides, mainly pyrite and pyrrhotite. The latter can oxidize once exposed to air and water; the resultant acidity promotes the solubilization of toxic metals contained in the mine wastes. This phenomenon is commonly known as acid mine drainage (AMD). The oxidation of sulfides can continue for long periods, from decades to centuries (Blowes and Ptacek 1994; Lappako 1990; Moncur et al. 2005; Schippers et al. 2007).

The costs of restoring sites when they contain AMD-producing mine wastes are much higher than for non-problematic sites. Hence, accurate prediction of acid generation potential is essential before the development of a closure plan or a rehabilitation strategy. Various predictive methods can be used, including static tests, kinetic tests, and mathematical models (Benzaazoua et al. 2004; Jambor et al. 2002; Lappako 2002; SRK 1989). We evaluated the pollution generation potential of mine wastes

associated with the abandoned Azegour mine. The mine waste samples were characterized for their main physical characteristics and remaining acid-generating potential. In addition, the geochemical behavior of the tailings was studied using weathering cells.

Materials and Methods

The Azegour Mine Site

The Azegour mine is located on the northern side of the High Atlas Mountains (Morocco) in the Amez Miz province of Al-Haouz, 60 km southwest of Marrakech (Fig. 1), at an elevation of 1,525 m above sea level. This mine was exploited for Cu, Mo, and W. The mineralization consists mainly of molybdenite (MoS_2), chalcopyrite (CuFeS_2), and scheelite (CaWO_4), provided by Azegour intrusive granite, which induced intense contact metamorphism (skarns) and partially transformed the limestone bands into tactites with a complex mineralogical composition (BRPM 1976; DM

Fig. 1 Location map of Azegour mine

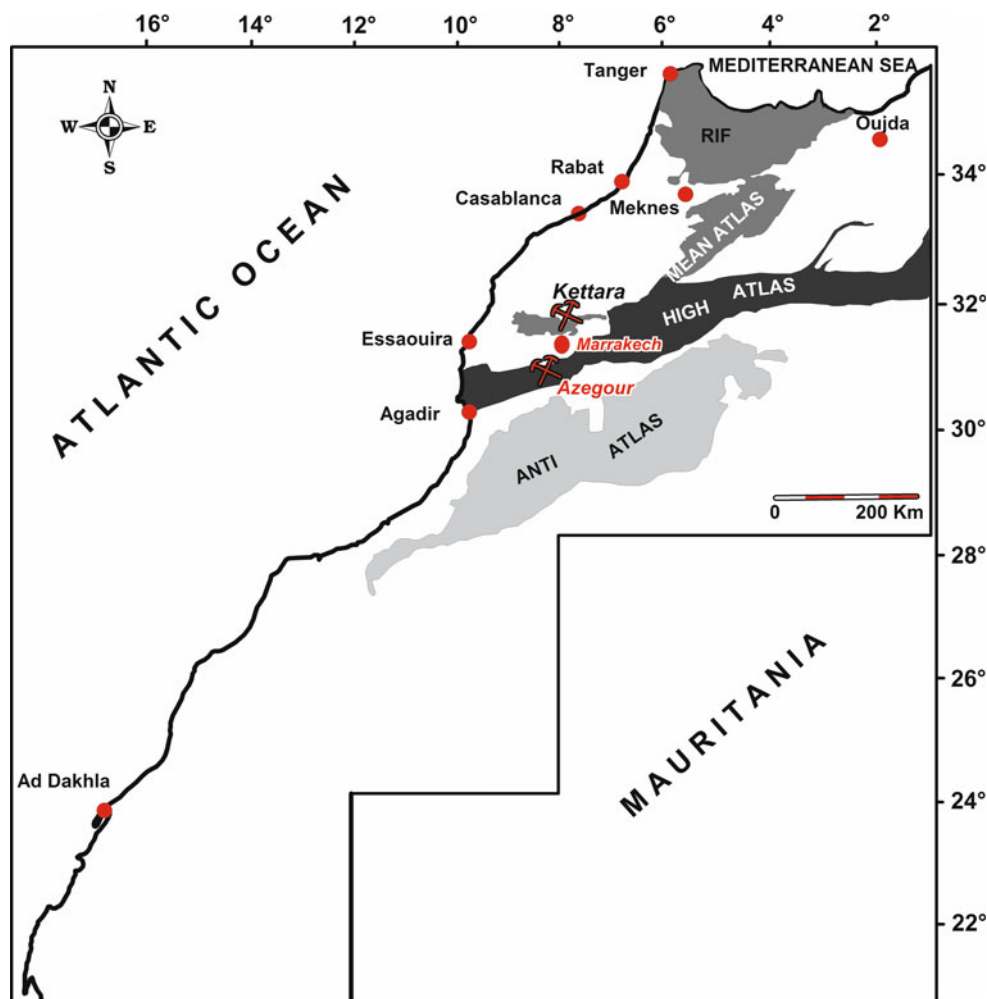
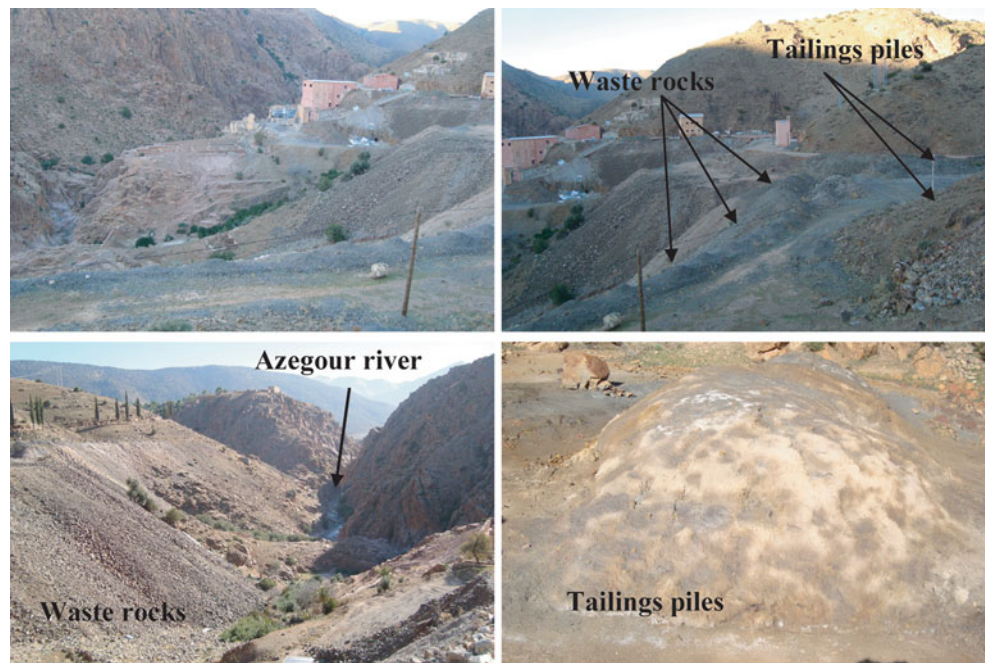


Fig. 2 Photographs showing tailings and waste rocks dispersion on Azegour mine site



1990; Prochtchenko et al. 1971; Von Der Weid 1941). It also contains pyrite (FeS_2), sphalerite (ZnS), and pitchblende (UO_2). Elements such as lead, nickel, cobalt, silver, bismuth, arsenic, and antimony also occur in the Azegour mineralization.

The Azegour mineral deposits were exploited by the Molybdène Company from 1932 until the end of Sept. 1971, almost without interruption. During this period, Azegour produced 26,294 t of concentrated copper (1941–1970), 1,570 t of concentrated molybdenum (1933–1947), 56 t of concentrated tungsten (1951–1956), and 57 t of concentrated uranium (1955–1958). The ore was processed by crushing and milling followed by froth flotation. More than 850,000 t of mine wastes (tailings and waste rocks) were deposited on the surface without concern for environmental issues. The tailings, which were deposited in tailings impoundments, and the waste rock piles have been subjected to strong weathering processes; the oxidized tailings are a rust-orange color (Fig. 2). It can be supposed that a large volume of mine wastes was discharged directly into the Azegour River (see Fig. 3).

Sampling

In January 2010, samples were collected from two waste rocks piles (samples AzS1 and AzS2; see Figs. 2 and 3; Table 1). The Azegour tailings consist of several scattered piles (Fig. 2). Two trenches were excavated (Fig. 3) and samples were collected from locations that contained very fine-grained wastes, based on field observations. Tailings samples referenced AzR1, AzR2, and AzR3 (Profile 1) and

AzR4, AzR5, and AzR6 (Profile 2) were collected at different depths in the two trenches (Fig. 4).

Samples AzR1, AzR2, and AzR3 (Fig. 4) come from a profile of the first trench. The whitish AzR1 sample was collected at the surface. The yellow–brown sample (AzR2), which corresponds to the slightly altered tailings, was taken at a depth of -15 cm. The potentially fresh waste (AzR3) was collected at -70 cm.

Samples AzR4, AzR5, and AzR6 were respectively collected at the surface and at depths of -30 and -80 cm in the second trench. Again, the white surface sample corresponds to highly altered waste (Fig. 4). The fine grain size and intense sulfide reactivity favored formation of hardpan layers at the surface. These hardpan layers were formed by metal ion adsorption and co-precipitation processes (Blowes et al. 1991), and can restrict oxygen diffusion and water infiltration into the tailings, at least partially limiting sulfide oxidation.

All samples were carefully collected, transported to the laboratory, and then stored in double-sealed plastic bags after air evacuation. The fine tailings were dried in an oven at 40 °C instead of air to minimize contact of the wastes with oxygen. A small amount of waste rock was stored at low temperature (without drying) for kinetic testing; these coarse wastes were crushed using a RETSCH PM 100 Planetary Ball Mill.

Analytical Methods

The tailings were analyzed for Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Na, Ti, Be, Ni, Pb, S, Se, Zn,

Fig. 3 Samples locations of tailings and waste rocks sampled at Azegour mine site

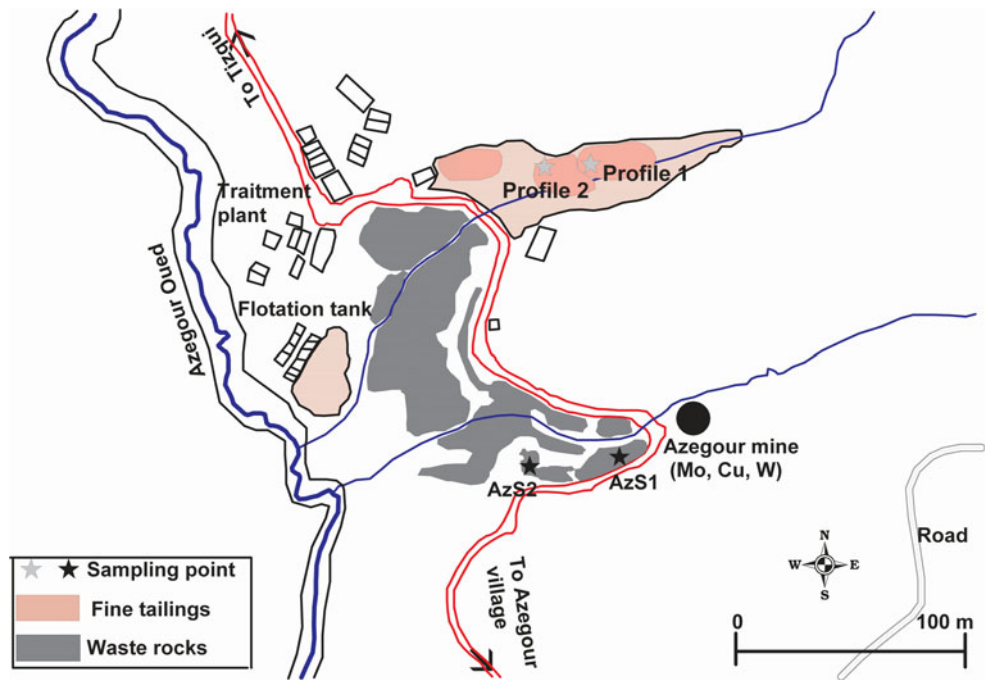
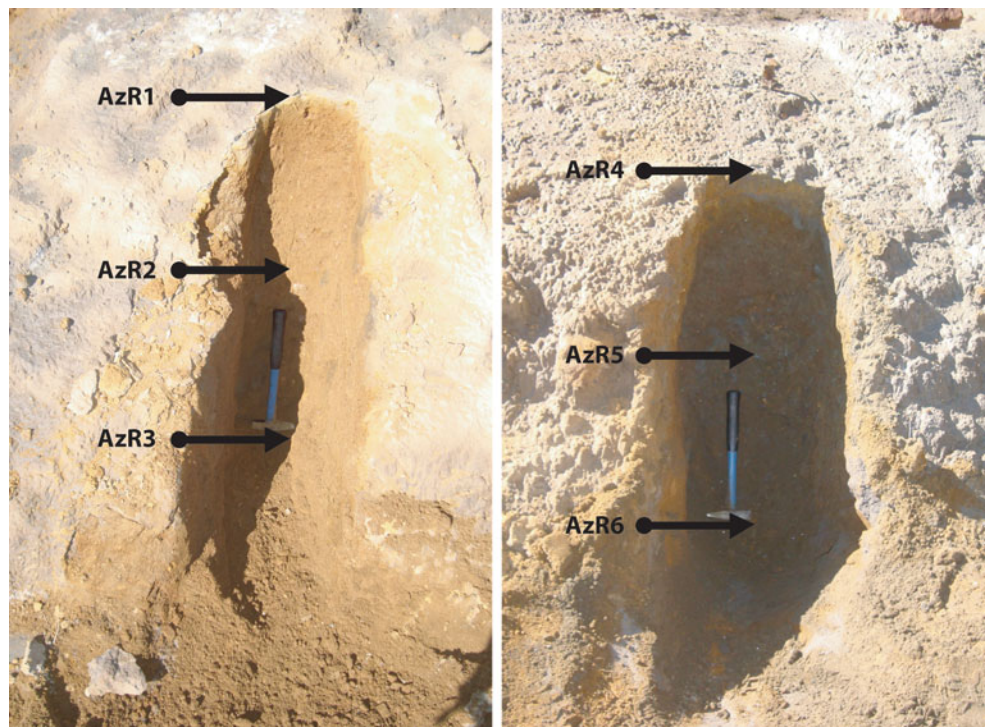


Table 1 Summary of all samples taken from the Azegour mine

Samples	Tailings						Waste rocks	
	Profile 1			Profile 2			AzS1	AzS2
Label	AzR1	AzR2	AzR3	AzR4	AzR5	AzR6		
Depth (cm)	0	15	70	0	30	80	–	–
Color	White	Yellow brown	Gray	White	Yellow brown	Gray	Dark gray	Dark gray

Fig. 4 Photos showing two profiles of sampling: AzR1 and AzR4 for surface, AzR2 and AzR4 for tailings slightly altered, AzR3 and AzR6 for fresh waste



W, U, and Mo using a Perkin Elmer Optima 3100 RLICP-AES following total $\text{HNO}_3/\text{Br}_2/\text{HF}/\text{HCl}$ digestion. Diluted HCl was used to extract sulfates and the solution obtained was analyzed by ICP-AES.

Particle size distribution was determined using a Malvern Mastersizer laser particle size analyzer. The specific gravity (G_s) was measured using a Micromeritics Accupyc 1330 helium gas pycnometer.

The initial tailings and waste rocks mineralogy was determined by a combination of X-ray diffraction spectroscopy (XRD) and scanning electron microscopy (SEM) analysis coupled with energy dispersive spectroscopy EDS. XRD analyses were carried out using a Bruker AXS D8 advance diffractometer equipped with a copper anticathode, scanning over a diffraction angle (2θ) range from 5 to 60° . Scan settings were 0.005° , 2θ step size, and 1 s counting time per step. The Diffrac Plus EVA software (v.9.0 rel. 2003) was used to identify mineral species and TOPAS software (v 2.1) implementing Rietveld refinement was used to quantify the abundance of all identified mineral species. The absolute precision of this quantification method is ± 0.5 to 1 % (Mermillod-Blondin 2005; Raudsepp and Pani 2003). In order to reach the fine size distribution required for XRD analysis, samples were pulverized in isopropyl alcohol using a McCrone micronizing mill with corundum grinding media for 15 min to obtain $\approx 90\% < 10\ \mu\text{m}$.

Sample mineralogy was further characterized by optical microscopy analysis. Polished sections from bulk samples were prepared using epoxy resin for reflected light microscopy. Scanning electron microscope (SEM) observations on polished sections using backscattered electrons (BSE) were made on a Hitachi S-3500 N microscope equipped with an X-ray energy dispersive spectrometer (EDS; Silicon drift spectrometer X-Max 20 mm²) with INCA software (450 Energy). The operating conditions were 20 keV, $\approx 100\ \mu\text{A}$ and 15 mm working distance. The detection limit can be considered as being $\approx 1\%$ (Çubukçu et al. 2006).

The static tests most commonly used to predict acid-generating potential is acid–base accounting (ABA) (Lawrence 1990; Lawrence and Wang 1996; MEND 1991). ABA measures the balance between the acid-producing potential (AP) and neutralizing potential (NP) of a given sample. The NP analyses were run in duplicate, and results were expressed in kg CaCO_3/t . AP, also expressed in kg CaCO_3/t , was calculated by using the sulfide sulfur fraction, obtained by subtracting the sulfate sulfur from the total sulfur assay. The net neutralization potential (NNP) was calculated by subtracting the AP value from the NP value. NNP values $< -20\ \text{kg}\ \text{CaCO}_3/\text{t}$ indicate an acid-producing material, whereas materials with $\text{NNP} > 20\ \text{kg}\ \text{CaCO}_3/\text{t}$ are considered to be acid consuming. Hence, an

uncertainty zone for this technique exists between $20 > \text{NNP} > -20\ \text{kg}\ \text{CaCO}_3/\text{t}$ (Miller et al. 1991; SRK 1989). Another useful tool to evaluate the AMD production potential from static tests results is the NP to AP ratio. Typically, the material is considered non-acid generating if $\text{NP}/\text{AP} > 2.5$, uncertain if $2.5 > \text{NP}/\text{AP} > 1$, and acid generating if $\text{NP}/\text{AP} < 1$ (Adam et al. 1997).

Kinetic Tests (Weathering Cells) Procedures

More representative samples, namely AzR3 and AzR6, were selected for kinetic testing using weathering cells similar to the one used by Cruz et al. (2001). This method uses a thin sample layer and more frequent flushing–drying cycles than the standard humidity cell. The main advantage of this weathering test is its rapidity (test durations range from 20 to 25 weeks) and the small volume of material required (Villeneuve et al. 2003).

Approximately 66.7 g (dry weight) of tailings were placed in a 100 mm diameter Buchner funnel equipped with a glass fiber filter. A 7 day cycle consisted of 2 days of exposure to ambient air, leaching on the third day, 3 days of exposure to air, and finally flushing on the seventh day. The flushes consisted of adding 50 mL of deionized water to the top of the Buchner funnel. The leachate was recovered by applying a slight suction on a filtering flask after 3 h of contact with the tailings. The total duration of the individual experiments was 16 cycles (16 weeks).

The leachates obtained after weathering cell flushes were filtered using a $0.45\ \mu\text{m}$ nylon filter and analyzed for several geochemical parameters to understand the sulfide reactivity, oxidation kinetics, metal solubility, and the overall leaching behavior of the tested materials. Filtered leachates were acidified with 2 % HNO_3 to avoid metal precipitation. The resulting solutions were analyzed with a Perkin Elmer Optima 3100 RLICP-AES to determine metal and sulfate concentrations (in mg/L).

For each kinetic test run, pH, Eh, conductivity, metal concentration, acidity, and alkalinity were analyzed for each leachate sample. Alkalinity and acidity (expressed in mg CaCO_3/L) were measured by acid–base titration, to pH endpoints of 4.5 and 8.3, respectively. Sample pH was read by a combination pH electrode with temperature compensation (Orion model 91–57). Redox potential was determined with an Orion Pt/Ag/AgCl electrode (model 920A). The results were then corrected to a standard hydrogen electrode (SHE) to obtain Eh (expressed in mV). Conductivity was determined with a HANNA HI 8733 conductimeter. These data was compiled as instantaneous and cumulative loads as well as elemental depletion curves based on the volume and composition of the leachates and the initial geochemistry of the solid samples.

Results and Discussion

Physical Analysis

The relative densities (G_s) of the different tailing samples were all about 2.7, while those of the waste rocks were relatively higher, about 3.6 (Table 2). In terms of grain size distribution, the Azegour mine tailings mostly fell in the silty fraction ($<63 \mu\text{m}$). The cumulative volume percentages are shown in Fig. 5 and Table 2. The grain size distribution is spread out and the grain size distribution was mostly poorly graded.

Chemical Analysis (ICP-AES)

The chemical analyses of Azegour tailings and waste rocks are given in Table 3. Elements (such as Bi, Sb, Se, Cd, W) with very low concentrations or below the detection limits of the ICP are not presented. The SO_4 content and the concentrations of most of the other elements were not significantly different in the trench 1 and trench 2 tailings profiles. Regardless of their depths in the trenches, the Azegour mine tailings have total sulfur concentrations of 9.59–19 wt%, expressed mainly as sulfate. This indicates an advanced oxidation state along the entire depth profile of the sampled stockpile. The total sulfur concentrations of the waste rock samples were 1.25–6.58 wt%, and it was mostly present as sulfides (1.22–6.56 wt%).

Fe concentrations were relatively high in the tailings (19.5–26.7 wt%) and in the waste rocks (8.01–23.9 wt%).

AzR6 samples had higher sulfate and iron content. This could be explained by precipitation of sulfates and iron after downward migration following sulfide oxidation. Si was significant in most of the tailings samples (7.20–11.13 wt%). Al was present at lower levels in the tailings (0.2–0.59 wt%) than in the waste rocks (1.82–4.22 wt%). The Si and Al indicate the presence of silicates and aluminosilicates in the gangue minerals. The tailings and waste rocks of Azegour are also rich in Ca (4.71–8.6 wt% and 17.98–22.1 wt%, respectively). Mg was also present in the tailings (1.2–1.89 wt%) and in the waste rocks (0.94–2.46 wt%).

Table 3 also lists the concentrations of other elements in the tailings and waste rock samples. There were very high concentrations of Mo in the tailings (17,800–29,700 ppm) and waste rock sample AzS2 (92,400 ppm). The tailings were also highly enriched in Cu (5,360–27,800 ppm). Other elements occur at significant concentrations in the tailings, such as Pb (1,360–1,760 ppm), Mn (830–1,720 ppm), Zn (170–1,610 ppm), As (90–420 ppm), Co (40–440 ppm), and Ni (40–250 ppm). It appears that the Azegour mine wastes could be reprocessed for their valuable metal contents, especially Mo and Cu. The feasibility of a new project would presumably require better mine waste management and restoration of the abandoned Azegour mine site.

XRD Mineralogical Characterization

Mineralogical characterization was carried out initially by XRD, which showed that the main sulfides in the wastes of

Table 2 Physical properties of the tailings and waste rocks studied

	AzR1	AzR2	AzR3	AzR4	AzR5	AzR6	AzS1	AzS2
G_s (specific gravity)	2.74	2.74	2.75	2.75	2.87	2.81	3.46	3.63
D_{80} , % under 80 mm	–	85	65.4	93.1	80.7	87.4	11.5	13.9
D_{10} , mm	–	0.9	4.7	0.7	3.1	3.6	59.6	32.4
D_{50} , mm	–	15.6	24.5	12.9	18.1	18.1	463	379.6
D_{90} , mm	–	154.3	491.1	57.4	161.8	102.9	734.1	653.3

Fig. 5 Particle size distribution for Azegour mine wastes

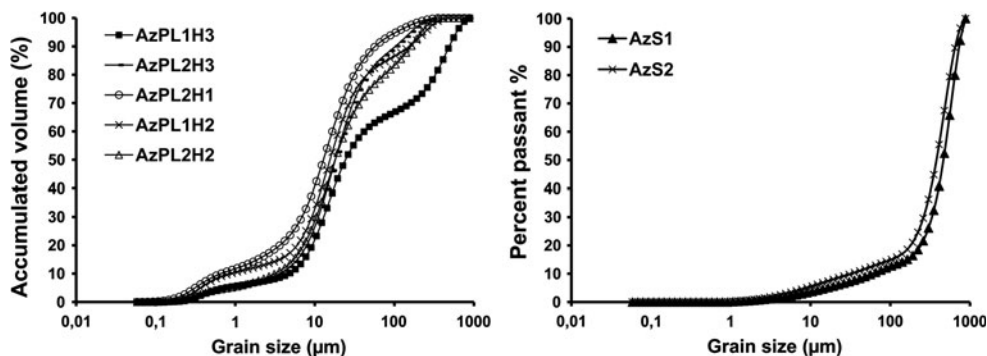


Table 3 Chemical composition of the Azegour wastes

Samples	Tailings						Waste rocks	
	Trench 1			Trench 2			AzS1	AzS2
	AzR1	AzR2	AzR3	AzR4	AzR5	AzR6		
Depth (cm)	0	–15	–70	0	–30	–80	–	–
<i>Major elements (wt%)</i>								
Stotal	9.59	9.94	11.12	19.08	14.71	18.93	6.58	1.25
Ssulfide	–	1.48	3.7	12.41	7.39	8.63	6.56	1.22
Ssulfate	–	8.46	7.38	6.67	7.32	10.30	0.026	0.029
Si	10.33	10.53	11.13	9.19	9.11	7.20	Nd*	Nd
Al	0.56	0.55	0.59	0.24	0.35	0.20	4.22	1.82
Ca	8.59	8.17	8.09	5.74	6.41	4.71	17.98	22.10
Mg	1.29	1.20	1.31	1.89	1.56	1.87	2.46	0.94
Fe	20.30	20.30	19.50	25.6	24.30	26.70	8.01	23.90
<i>Minorelements (ppm)</i>								
Cu	5,640	5,360	7,210	25,800	19,800	27,800	30	780
Mo	18,900	17,800	18,500	29,700	24,600	26,200	92,400	2,140
Zn	180	170	210	620	360	1,610	90	90
As	350	340	420	90	260	150	0	0
Pb	1,550	1,410	1,450	1,760	1,520	1,360	0	10
Ni	40	40	40	150	80	250	20	30
Ti	490	490	470	130	270	70	940	200
Mn	870	830	840	970	920	1,720	6,100	5,880
Co	40	40	50	250	120	440	0	30
Ba	150	490	130	80	110	80	100	680
Bi	70	60	70	30	30	30	0	10
Cr	20	20	10	10	10	0	30	40

* Nd not detected

Azegour stockpile and the tailings are pyrrhotite, pyrite, and molybdenite. Also, the AzS2 tailings sample contained some bornite while sample AzR4 contained some sphalerite. The Azegour mine wastes contain several silicates and aluminosilicates; quartz, talc, and chondrodite were identified in all of the samples. Calcite was the only carbonate observed. Gypsum and powellite were the main sulfate minerals in the wastes and account for the significant sulfate levels in the samples. The presence of secondary minerals (gypsum, hematite, jungite, and rancieite) confirmed the highly oxidized state of the Azegour mine wastes.

SEM Analysis

SEM analysis performed on samples AzR3 and AzR6 showed the presence of new phases not identified by XRD. Chalcopyrite as well as silicates and other trace minerals (e.g. barite) were frequently observed in both samples. The altered nature of the mine wastes was demonstrated by the fact that sulfur and various oxides and sulfates were found

partially or completely covering the surface of minerals (mainly silicates; Fig. 6). Altered pyrite grains were also observed (Fig. 6).

Based on the XRD and SEM mineralogical analysis of the Azegour mine wastes, the Ca is present as calcite, gypsum, powellite, scheelite, anhydrite, jungite, rancieite, and clinoptilolite. The Mg is not associated with carbonates but with talc, chondrodite, actinolite, fosterite, and possibly with chlorite (and other silicates observed by SEM). The Si is mainly related to quartz, pyrophyllite, chondrodite, chlorite, talc, actinolite, clinoptilolite, andalusite, and forsterite. The Al is associated with chlorite, pyrophyllite, clinoptilolite, andalusite, and boehmite.

Prediction of AMD Potential

Acid–base accounting results based on the modified Sobeck test are shown in Table 4. Azegour wastes generally show low NP (8–12 kg CaCO₃/t for tailings and 38.8–72.8 kg CaCO₃/t for waste rocks). The APs were also very different: 46–388 kg CaCO₃/t for the tailings and

Fig. 6 SEM backscattered images showing: **a** tailings texture with the main phases (molybdenite, pyrite and chalcopyrite), **b** weathered pyrite grains coated by iron oxides, **c** iron oxide precipitates covering a quartz grain, **d** secondary precipitate of sulfate, **e** secondary minerals with weathered pyrite and chalcopyrite. *Qz* Quartz, *S* sulfur, *FeMnOx* iron and manganese oxide, *FeOx* iron oxide, *FeSi* iron-silicate, *Py* pyrite, *cpy* chalcopyrite, *Mo* molybdenite

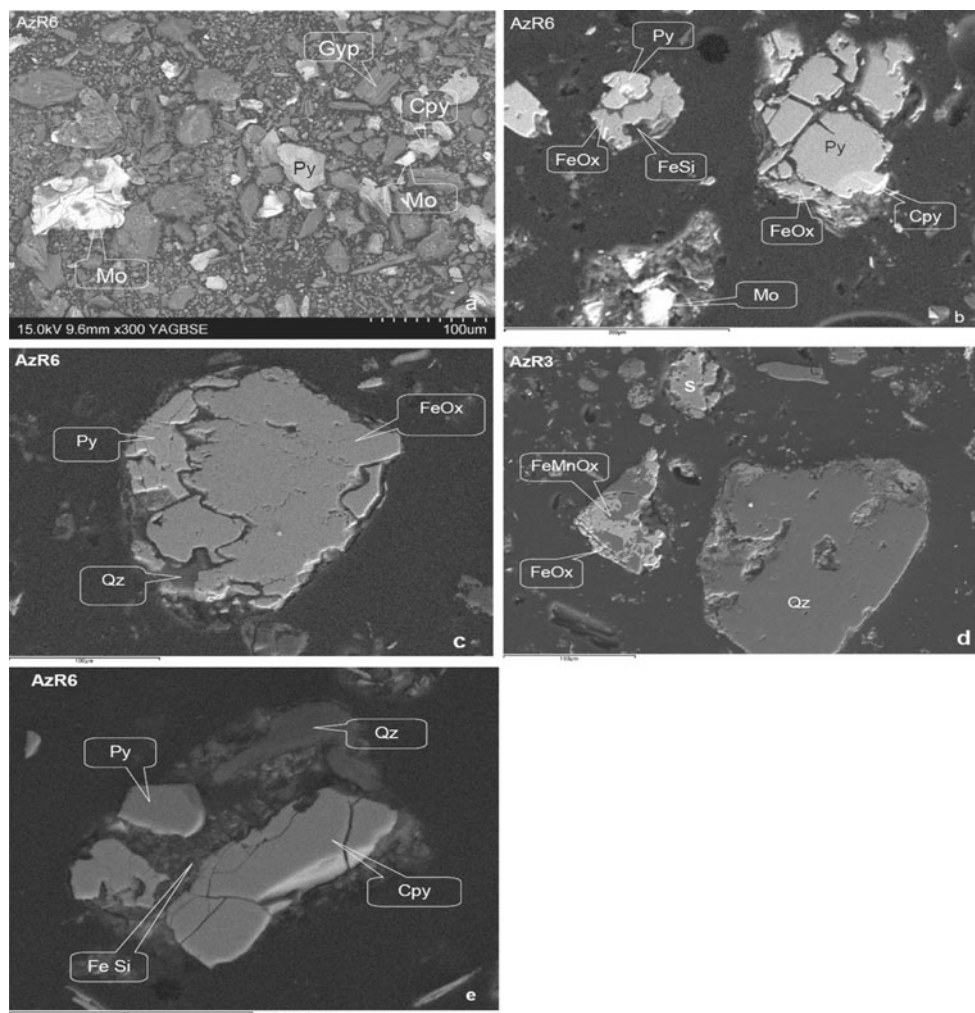


Table 4 Net neutralizing potentials of the tailings and waste rocks of Azegour Mine (n.d.: not determined)

	AzR1	AzR2	AzR3	AzR4	AzR5	AzR6	AzS1	AzS2
AP (kg CaCO ₃ /t)	n.d.	46.21	116.81	387.69	230.99	269.75	204.97	38.03
NP (kg CaCO ₃ /t)	8.96	8.23	8.38	14.95	11.96	10.1	72.83	38.83
NNP (kg CaCO ₃ /t)	n.d.	-37.98	-108.43	-372.73	-219.03	-259.65	-132.14	0.8
NP/AP	n.d.	0.18	0.07	0.04	0.05	0.04	0.36	1.02

38–205 kg CaCO₃/t for the waste rocks. According to the criteria of Miller et al. (1991), all of the Azegour tailings and waste rocks are acid generating except for AzS2, which can be ranked as uncertain (Fig. 7). The AzS2 sample was also classified as uncertain based on the NP/AP ratio (Adam et al. 1997).

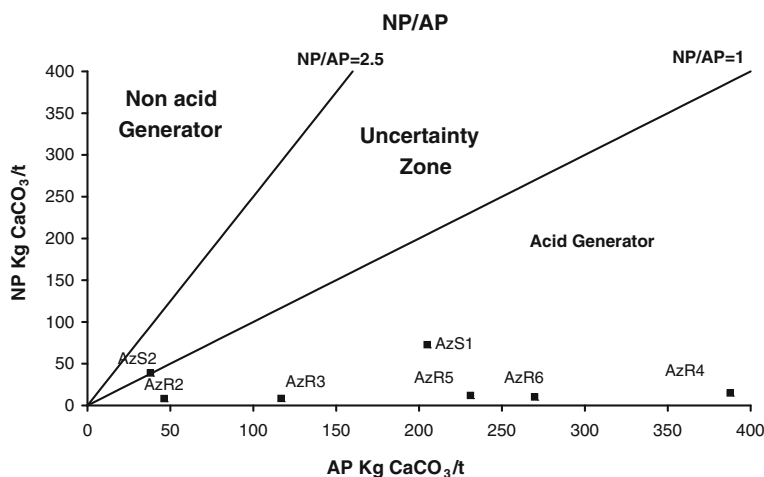
Geochemical Simulation of the Leachate

Figure 8 shows the results of leachate quality obtained during the 16 leaching cycles on samples AzR3 and AzR6. The graphs correspond to the concentrations released,

without considering either the volume or the mass of samples, for the major dissolved elements and the main parameters related to oxidation-neutralization (pH, Eh, conductivity, acidity, SO₄²⁻, Ca, Mg, Mn, Si, Al, Fe, Cu, Zn, Mo, Co). Leachates obtained during the initial cycles showed higher contaminant concentrations, presumably due to easy dissolution of oxidation products generated by weathering. Elements with low concentrations in the leachates (i.e. Pb, Ni, Cr, Cd, As, Sb, Ti, Ba) and those below the ICP detection limit (Be, Bi, Se, W) are not presented.

The elevated electrical conductivity measurements at the beginning of the test (15,260 and 44,150 μs/cm for

Fig. 7 Environmental characterization of mining wastes according to the report of Azegour NP/AP



AzR3 and AzR6, respectively) align with the major element concentrations recorded in the initial flushes. These values decrease and stabilize around the 32nd day of the test for AzR3 and the 21st day for AzR6 (Fig. 8c). These conductivities highlight the release of various ions in the leachates (SO₄, Ca, Mg), during the oxidation/neutralization reactions. The acidity is very high at the beginning of the test for sample AzR6 (11,905 mg CaCO₃/L) rather than for the sample AzR3 (8,777 mg CaCO₃/L). These values decreased progressively with time until reaching 94 mg CaCO₃/L and 210 mg CaCO₃/L for AzR3 and AzR6, respectively.

The pH was low during the first leaching cycles (2.03 and 2.1 for samples AzR3 and AzR6, respectively). A slight increase was observed thereafter, but pH values did not exceed 3.19 (Fig. 8a), presumably due to sulfide oxidation. The Eh values were high, indicating an oxidizing medium (544–728 and 557–646 for AzR3 and AzR6, respectively).

SO₄ were released at high concentrations during the early tests (3,750 and 5,750 mg/L for the second leachate for AzR3 and AzR6, respectively). Their levels begin to stabilize from the fifth leaching cycle (Fig. 8e). The SO₄ in the leachates comes from the dissolution of soluble sulfates found in the residue, especially the gypsum (Table 4) as well as the oxidation of sulfides. The SO₄ levels released by the AzR6 sample exceeded those released by AzR3, which is consistent with the initial concentrations of SO₄ stored in the two materials (Table 3) and with the SEM observations that identified more secondary sulfates in the AzR6 material than in AzR3 (mainly Fe sulfate).

The Ca levels were relatively stable (471–647 mg/L for AzR3 and 230–642 mg/L for AzR6) (Fig. 8f). Ca can be released by dissolution of both gypsum and calcite at the acidic pH of the medium (scheelite, powellite, and jungite dissolution also contribute). The Ca stability indicates that it was still far from depletion of the Ca-bearing phases.

The Mg concentrations were higher in the AzR6 leachates than those of AzR3 (Fig. 8g). The Mg concentrations were negligible (<1 mg/L) for two samples from the fourth leaching cycle. The Mg comes from dissolution of talc, chlorite, chondrodite, and the other magnesium silicates observed with SEM at the acidic conditions noted during testing.

The Al showed a significant release only during the first two to three cycles. The concentrations of Al and Si reflect the dissolution of silicates and aluminosilicates during testing. The XRD analysis appeared to indicate that a single mineral phase (namely chlorite) was responsible for the release of Al but the SEM analysis showed several minerals. The Si probably comes from the dissolution of talc, chlorite, chondrodite, and other phases observed by SEM.

The dissolution of silicates and aluminosilicates indicates that they also contributed to neutralization. However, this contribution would be less important than that of calcite, given calcite's higher reactivity (Kwong 1993). In addition, the neutralizing power of some aluminosilicates (e.g. chlorite) is controversial since the Al released following dissolution can generate acidity after hydrolysis and precipitation as hydroxides (Kwong and Ferguson 1997; Lappako and White 2000).

Fe and Cu concentrations were significant throughout the tests. Zn was released significantly during the first three cycles. Mo, Co, As, Ni, and Pb were mainly present during the first leaching cycle. Ti and Cd were present at concentrations below 1 mg/L.

Figure 8k–n show the kinetics of Fe, Cu, Zn, and Co release. The Fe concentrations ranged from 24,900 to 3 mg/L for AzR3 and 55,900 to 52 mg/L for AzR6. As the studied tailings correspond to relatively altered materials, Fe comes from the dissolution of Fe oxides (hematite identified by XRD) in addition to the oxidation of Fe

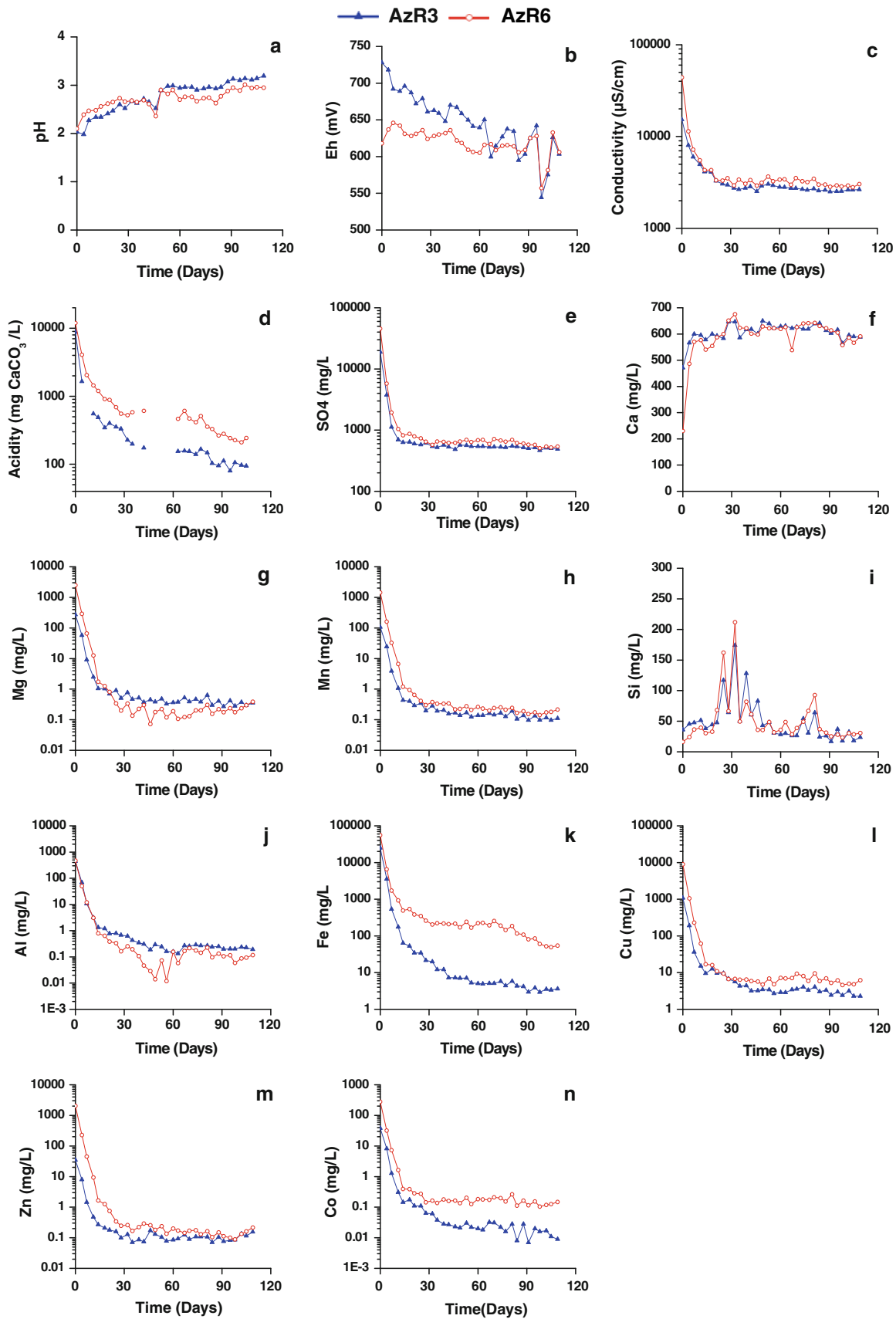


Fig. 8 Water quality corresponding to weathering cell tests realized on samples tailings AzR3 and AzR6

sulfides (pyrite and pyrrhotite) and chalcopyrite. The Cu comes mainly from the dissolution of chalcopyrite. The mineralogical analyses (XRD and SEM-EDS) showed no mineral containing Zn with the exception of jungite in AzR3, though sphalerite was also described in the mineralization of the deposit (DM 1990). However, sphalerite was identified in the AzR4 sample. The Mo was only released in the first cycle despite its high concentrations in the initial residues (Table 3) and the identification of molybdenite and powellite by XRD and SEM-EDS. This could be explained by the low reactivity of these minerals and/or rapid precipitation of Mo as a secondary phase (S, Fe, Mo, and O observed by SEM-EDS).

The leachates from the 4th and 32nd days were analyzed for U and W to check the behaviour of these two elements since Azegour mine exploited these two minerals in addition to Cu and Mo. These analyses showed that the W was below the detection limit (<0.005 mg/L). Scheelite, which was the only phase identified by mineralogical analysis to contain W, apparently did not dissolve during testing. The U occurred at concentrations of 1.37 mg/L on the 4th day and 0.09 mg /L on the 32nd day of the test. No U-bearing minerals were identified by mineralogical analysis, though pitchblende (UO₂) is described in the Azegour deposit mineralization (DM 1990).

Conclusions

In the absence of any rehabilitation strategy, the Azegour mine wastes have been exposed to weathering and erosion for 41 years. The Azegour wastes are characterized by high total sulfur (9.6–19 wt%), most present as sulfates (6.67–10.30 wt%) in the tailings, even at depth, demonstrating their advanced oxidation state. In contrast, the sulfur in the waste rocks was mainly present as sulfides (1.22–6.56 wt%). Concentrations of Mo in the tailings (17,800–29,700 ppm) and waste rocks (2,140–92,400 ppm) are very high and suggest a significant potential for reprocessing these wastes. Other elements such as Cu (30–27,800 ppm), Zn (170–1,610 ppm), As (90–420 ppm), Co (40–440 ppm), and Ni (40–250 ppm) are also present in the Azegour mine wastes.

The static test shows that Azegour wastes generally present low NP (8–12 kg CaCO₃/t for wastes and 38.8–72.8 kg CaCO₃/t for waste rocks). These wastes are considered acid-generating, with the exception of a waste rock sample (AzS2), for which the prediction is uncertain.

The results of the weathering cell tests confirmed the generation of AMD. The pH remained acidic, ranging from 1.98 to 3.19. The wastes also present a high pollution potential, mainly related to SO₄, Fe, and Cu, and secondary to Zn, Mo, Co, As, Ni, and Pb. Given their chemical

reactivity on one hand and their deposition without physical stabilization on the other, the Azegour mine wastes represent a pollution source for the surrounding ecosystems and for those downstream. Because of their relatively high Cu and Mo content, recovery of these metals could possibly be a way to fund site rehabilitation at the abandoned Azegour mine.

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