Geochemical Characterization of Tailings, Pit Lake Sediments and Waters using PHREEQC in Nador Abandoned Mine (Morocco)

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Abstract

In north of Morocco, Nador abandoned Fe-mines are well known for their acid mine drainage (AMD). Geochemical and mineralogical investigations show that tailings are dominated by jarosite, gypsum and quartz. Low quantities of hematite, magnetite, and titanomagnetite are also identified. Axara pit lake sediments comprise gypsum, quartz, langbeinite, morenosite, bianchite, and dolomite. Copiapite and jarosite are indicators of extreme acidic conditions. Fe and S constitute the main chemical composition of the studied samples. Mn is the predominant metal in tailings with values ranging from 198.49 to 638.65 µg/g, followed by As (606.93 to 16.12 µg/g); Cu (576.24 to 40.70 µg/g); Co (411.22 to 31.54 µg/g); Ni (144.70 to 16.94 µg/g); Zn (120.31 to 30.92 µg/g); and Pb (70.83 to 6.05 µg/g). Waters from Axara pit lake are characterized by acidic pH (3.12) with high conductivity (29160 µS/cm), and very high sulfate contents (31506.23 mg/l). As, Ni and Fe have exceeded the water-quality standard (WHO, 2011). PHREEQC modeling of waters shows that Fe, As, and Ni exist in solution as $FeSO_4$, As^{3+} and $NiSO_4$ species respectively.

Keywords: Acidic pit lake, PHREEQC, Jarosite, Contamination, Tailings

Introduction

Since the 1900s, the iron district of Beni Bou Ifrour-Ouixane located southwest of Nador city has played an important role in the mining history and economy of Morocco (Bouabdellah *et al.* 2016). This district consists of three highly productive iron mines, with Ouixane and Axara being open-pit mines, and Setolazar being underground (Benidire *et al.* 2022). Between 1914 and 1967, this district produced 1.5 Mm^3 of mining waste annually and over 65 Mt of ore with a Fe content of over 50% (Lakrim *et al.* 2011). The mining wastes are scattered in the landscape, resulting from abandonment without rehabilitation for more than 32 years (Tarik *et al.* 2023). The intensive mining has left pit lakes filled with water like Axara which is strongly acidic (pH = 3) (Lakrim *et al.* 2011). Tailings heaps are composed of high percentages of iron oxides, hydroxides, and sulfides (pyrite, pyrrhotite, and chalcopyrite) (Khafouri *et al*, 2011) and are directly exposed to weathering. The oxidation of sulfide-rich minerals leads to the production of sulfuric acid (H_2SO_4) and decreases in the pH of water with high contents of dissolved metals which impact soil, water, and plants (Lakrim *et al.* 2011; Air *et al.* 2021; Tarik *et al.* 2023). Thus, the main objectives of this study are to 1) investigate in detail the mineralogy and chemical composition of mine tailings and lake sediments (2) chemical speciation of PTEs in pit lake waters.

Materials and Methods

Study Area

The Beni Bou Ifrour-Ouixane mining district is close to Nador city in north of Morocco (Fig. 1). The most productive mines were Ouixane, Axara, and Setolazar (Bouabdellah *et al.* 2013). The area is characterized by a mediterranean humid climate (annual rainfall of around 346 mm/year) (El Yaouti *et al.* 2009). The geology of the study area consists of a regular alternation of schist layers interspersed with limestone lenses, along with occasional levels of acidic tuff from volcanic eruptions. All these units are covered by Barremian limestone. During the Miocene, porphyritic intrusive microdiorite was introduced into the previous sequence. Significant hydrothermal alteration halos developed accompanying the emplacement of this intrusive suite, impacting both the intrusive bodies (endoskarns) and their carbonate and sandstone-carbonate protolith host rocks (Jabrane 1993; Bouabdellah *et al.* 2013). The ore deposit is stratiform and presents banded textures where mineralized iron bands are alternated with sterile shale bands. Primary ore paragenesis is characterized by a predominance of iron oxides (hematite, magnetite) and hydroxides (goethite), locally accompanied by significant quantities of sulfides (sphalerite, chalcopyrite, bornite, marcasite, pyrite, pyrrhotite, and galena).

Sample collection and analysis

Tailings and pit lake sediments

Seven samples of mine tailings were collected in the vicinity of the Bokoya-Setolazar mine in May 2023. Samples T1, T2, T3, T4, and T5 were located on the same tailings dam. Samples T6 and T7 were collected inside the treatment unit area of Setolazar. All the mine tailings have a rust-orange color indicating their advanced oxidation state, except sample T7 which was characterized by a dark gray color. Three sediment samples were collected from the Axara pit lake (Sed 1, Sed 2, Sed 3) and one was taken from the Ouiksane pit lake (Sed 4). An additional soil sample (REF) was taken approximately 4 km far away from the mining area to serve as a non-contaminated reference sample (Fig. 1).

Mineralogical characterization was performed using X-ray diffraction (XRD) with a BRUKER Advance Diffractometer equipped with a copper anticathode. The ICP-OES Agilent 5800 VDV spectrometer was used for chemical analysis of Ca, Fe, K, Mg, Na, Al, and S. The concentrations of Mn, Co, Ni, Cu, Zn, As, and Pb were determined using ICP-MS (Perkin Elmer NexIon 300 X).

Pit lake waters

Five water samples were collected from the Axara pit lake. Samples have been collected using polyethylene bottles. Temperature (T), pH, electrical conductivity (EC), dissolved oxygen (DO), and redox potential (Eh) values were measured on-site using an HQ40d portable multi-meter. The samples were analyzed for some ions (Ca^{2+}, F^{-}, Cl^{-}, SO_4^{2}, NO^{2-}) by ion exchange chromatography using ICS 3000 Thermo Fisher detector. The total element content of As, Sn, Cr, Zn, Cd, Pb, Ni, Ca, Fe, Mg, Cu, Ti, Al, Na, and K were measured by ICP-AES (ICP ULTIMA EXPERT).

Geochemical modeling

The PHREEQC 3.7.3 software (PHREEQC. DAT) was used to examine the current speciation of PTEs in the solution. The saturation Index (SI) was calculated using temperature, pH, electron activity (pe), and metal concentration to predict precipitating minerals (Luo *et al.* 2020). SI > 0 indicates that water is supersaturated, SI = 0 indicates that the mineral and the water are in equilibrium; SI < 0 indicates that the water is undersaturated, allowing the mineral to dissolve into the solution.

Results and discussion

Mineralogy of tailings and floor lake sediment

The mineralogical compositions of mine tailings and lake sediments are represented in Fig. 2. The mineralogy of the tailings is dominated by jarosite (14-88 %), gypsum (2-80 %), and quartz (10-13%). Low quantities of hematite, magnetite, and titanomagnetite are also identified. The high content of sulfate minerals (jarosite) is produced by the oxidation of sulfide minerals (Hakkou *et al.* 2008). In tailings, high dissolved SO_4^{2-} and calcium released during silicate dissolution at low pH may lead to the precipitation of gypsum (Moncur *et al.* 2005). XRD data indicate the presence of copiapite in tailing T2. The formation of this mineral instead of jarosite is due to high concentrations of sulfate,

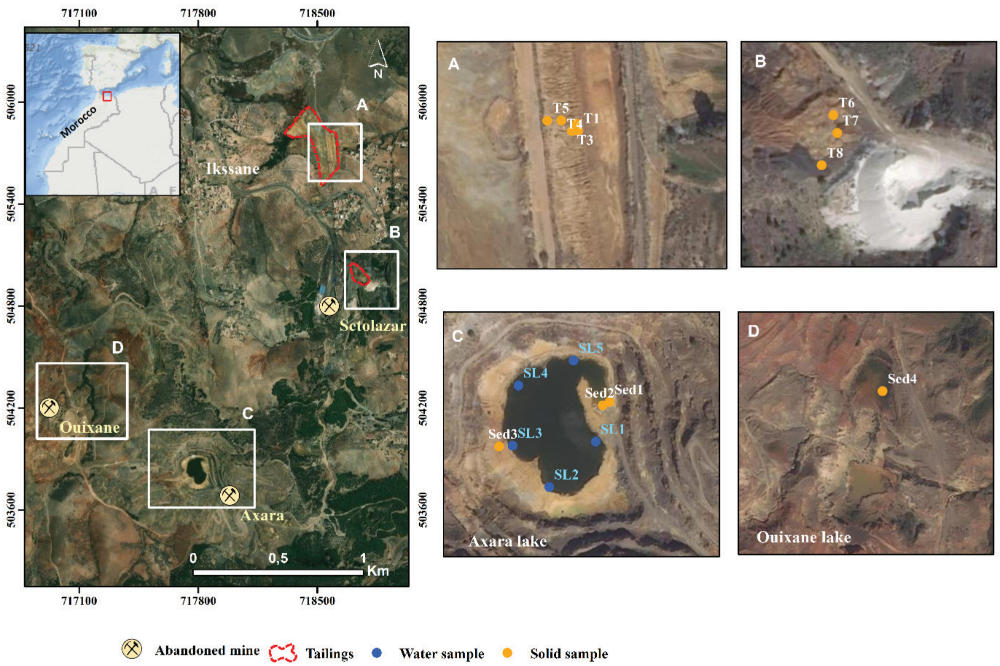

Figure 1 Samples location in the study area.

with both Fe^{3+} and Fe^{2+} in aqueous solution. Copiapite and jarosite are relatively soluble and indicate extremely acidic conditions (Nordstrom *et al.* 2015; Lim *et al.* 2024). Sample T7 presents significant quantities of hematite (69%) and magnesioferrite (22%), which explain the dark gray color of the tailing. Axara floor sediments are dominated by gypsum, quartz (32%), langbeinite (15%), jarosite (16%), and quartz (10%). The sample taken from the dried part of the lake contains morenosite (32%) bianchite (26%) and dolomite (9%). Ouiksane pit lake sediment contains aluminosilicate (albite (34%), paragonite (16%), and smaller amounts of kaolinite (5%), and clinochlore (8%)).

Chemical composition of sediments and tailings

The chemical analyses of the studied samples are illustrated in Table 1. Fe and S constitute the main chemical composition of the studied samples. The highest Mn, Zn, and Pb amounts were recorded in lake sediments. Ni, Co, and Zn concentrations in Sed 3 are related to the occurrence of the moorhouseite, Bianchite and morenosite. The Sample Sed 4 records the high value of Pb concentration (85.75 µg/g) followed by As, Cu, Co; Ni; Zn; and Pb. Sample T7 shows a high Fe content, confirmed by the presence of hematite. Significant amounts of Co, Cu, Ni, and Zn are found in sample T2. These trace elements could be associated with copiapite through coprecipitation and adsorption (Jamieson *et al.* 2005). This significant amount of As may be associated with jarosite,(Savage *et al.* 2005). All the PTEs largely exceed the reference sample.

Geochemistry of pit lake waters

The pit lake waters Axara are highly acidic (pH = 3) with high conductivity (29160 µS/cm) and less oxidizing conditions. The Eh values likely indicate variations in the dominant Fe^{2+}/Fe^{3+} redox couple, as iron concentrations are generally elevated (Yucel and Baba 2013). Sulfate is the predominant anion of Axara pit lake (31506.23 mg/l). As, Ni and Fe are found to exceed the water-quality standard (WHO, 2011), whereas the other elements amounts does not exceed their respective limits (Table 2). The high iron content can be attributed to the oxidation of pyrite (FeS_2) or other sulfide minerals, which releases Fe^{2+} and Fe^{3+} in solution. Ni could

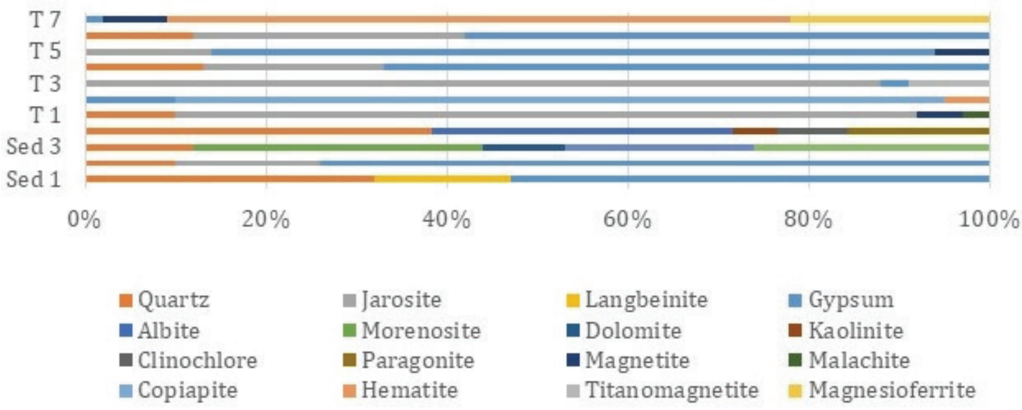

***Figure 2** Mineralogical characterizations of tailings and pit lake sediments.*

be originated from the oxidation of sulfide minerals (waste rocks, ore minerals) or from leaching from morenosite found in sediment Sed 3 in Axara pit lake.

PTEs chemical speciation in Axara pit lake

Chemical speciation was done using PHREEQC. The molalities of metal species and As that exceed the WHO standards are shown in Table 2. In this study, the main As species in solution were As^{3+}, $HAsO_2$, and $As(OH)_3$, implying a strongly reducing environment. The As^{5+} is less toxic in comparison with As^{3+} because trivalent As compounds are more soluble in water (Chaudhary *et al.* 2024).

Chemical speciation shows that Fe exists as sulfate ($FeSO_4$) and chloride ($FeCl^+$). The re-dissolution of previously formed unstable precipitates or the leaching of iron from the tailings and ore minerals are the two main causes of the higher iron contents in water (Obiefuna and Orazulike 2010). The Ni^{2+}, $NiSO_4$, and $NiCl^+$ are the predominant species. These potentially toxic metals (PTMs) can be found as sulfate species. the distribution of PTMs in water is influenced substantially by the dissolving of sulfate minerals (Hu *et al.* 2021).The calculated SI shows that Axara pit lake remains oversaturated with anatase, cassiterite, and rutile (SI>0) and they are likely to precipitate from the solution (Fig.5). These minerals require extremely little dissolved ions to reach oversaturation because of their low solubility products (K_{sp}). Gypsum (SI = -0.71) and Anhydrite (SI =

***Table 1** Chemical element concentrations in tailings and lake sediments.*

Sample		T 1	T 2	T 3	T 4	T 5	T 6	T 7	Sed 1	Sed 2	Sed 3	Sed 4	REF
Al		9.79	11.58	10.06	10.07	5.90	12.39	6.77	15.96	7.90	3.73	19.84	23.32
Ca		31.81	6.31	36.23	36.44	33.06	42.62	11.44	56.40	89.78	0.54	7.32	42.31
Fe		232.40	166.80	214.18	191.39	210.59	208.19	546.45	118.99	108.51	23.38	59.19	56.76
K	mg/g	4.81	0.90	4.34	5.14	4.83	5.87	1.33	16.94	10.81	0.01	10.81	15.67
Mg		5.54	6.73	4.29	3.72	7.78	3.73	6.21	5.92	10.09	20.99	2.25	2.77
Na		4.87	0.78	4.61	5.56	4.42	6.08	1.28	14.50	7.77	8.97	11.78	15.52
S		106.36	143.49	104.34	156.08	87.95	98.80	10.06	62.99	111.51	130.15	2.67	0.33
Mn		441.57	597.96	284.73	198.49	695.34	539.83	638.65	197.73	189.92	2130.60	507.79	881.81
Co		126.02	411.22	126.29	207.19	129.73	108.44	31.54	15.80	10.61	245.02	26.10	19.96
Ni		44.20	144.70	45.25	87.03	47.66	37.58	16.94	16.87	5.02	98.42	35.99	22.44
Cu	µg/g	361.96	576.24	329.52	152.50	307.93	234.60	40.70	206.15	305.63	413.27	146.36	25.45
Zn		66.66	120.31	51.75	30.92	84.82	70.69	51.82	31.31	40.61	330.22	245.03	82.09
As		197.72	98.59	311.61	119.88	606.93	157.11	16.12	31.11	32.36	0.92	30.67	7.24
Pb		45.53	6.05	25.82	45.39	26.79	70.83	11.26	10.22	25.21	0.00	85.75	30.74

Table 2 Hydrochemical data and chemical species molalities of the Axara pit lake water.

	Mean	WHO, 2011)	Species	Molality
pH	3.126	7.5	As^{3+}	1.47E-06
Eh(mv)	228.08		$HAsO_2$	7.87E-07
T(°C)	24.44		$As(OH)_3$	6.83E-07
Cond.(µS/cm)	29160	1500	As^{5+}	2.11E-11
Cl^- (mg/l)	3841.97		$H_2AsO_4^-$	1.94E-11
SO_4^{2-} (mg/l)	31506.22		H_3AsO_4	1.73E-12
As(mg/l)	0.10	0.01	Fe^{2+}	5.63E-04
Sn(mg/l)	0.006		$FeSO_4$	3.75E-04
Cr(mg/l)	0.03	0.05	Fe^{+2}	1.85E-04
Zn(mg/l)	3.09	3	$FeCl^+$	3.38E-06
Cd(mg/l)	0.016	0.003	Fe^{3+}	2.15E-12
Pb(mg/l)	0	0.01	$FeOH_2^+$	1.25E-12
Ni(mg/l)	1.15	0.07	Ni	2.05E-05
Ca(mg/l)	51.02	75	$NiSO_4$	1.30E-05
Fe(mg/l)	30.33	0.3	Ni^{+2}	7.44E-06
Mg(mg/l)	44.53	50	$NiCl^+$	1.99E-08
Cu(mg/l)	1.59	2		
Ti(mg/l)	0.008			
Al(mg/l)	25.33	0.2		
Na(mg/l)	32.77	200		
K(mg/l)	45.36	12		

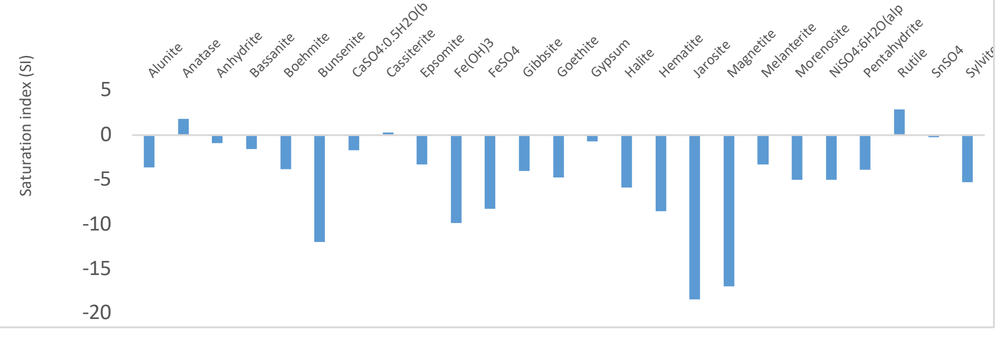

Figure 3 Saturation index of Axara pit lake waters predicted by PHREEQC

-0.88) are close to equilibrium. The pit lake is significantly undersaturated with other minerals (SI<0) indicating that they do not form or tend to dissolve (Jarosite, magnetite, and hematite).

Conclusions

In Beni Bou Ifrour abandoned mines, the tailings are dominated by jarosite, gypsum generated by AMD, and quartz, with low quantities of hematite, magnetite, and titanomagnetite. The Axara floor sediment show varying mineral compositions. They are composed mainly by gypsum, jarosite, and quartz, with Ni-Zn sulfates. Chemical analysis revealed low contents of Al, Na, K, and Mg. Fe and S occur as the main elements in both tailings and pit lake sediments. Mg occurs in mine tailings, followed by As, Cu, Co, Ni, Zn, and Pb.

In Axara pit lake the most common anion in waters is sulfate, while As, Ni, and Fe exceed water-quality Standards. A^{3+}, $HAsO_2$, and $As(OH)_3$ are the most common forms of As in water. Fe^{2+} occurs as sulfate (FeSO4) and chlorides ($FeCl^+$) where Ni+, NiSO4, and $NiCl^+$ are the most common species of Ni. The distribution of PTMs is greatly impacted by SO_4^{2-}. The SI analysis indicates that the studied waters are oversaturated with anatase, cassiterite, and rutile. Gypsum and Anhydrite are close to equilibrium, while other minerals are significantly undersaturated.

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