

# Geochemistry and mineralogy of surface pyritic tailings impoundments at two mining sites of the Iberian Pyrite Belt (SW Spain)

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**Abstract** Two pyritic tailings impoundments located in two mining areas of the Iberian Pyrite Belt (Cueva de la Mora and Minas de Ríotinto-Zarandas) were selected to assess their potential environmental impact. Mineralogical (XRD diffraction study), physico-chemical characterization (colour, particle size, pH, acid–base account, total Fe, As, Cu, Pb and Zn) as well as a speciation study (by means of a seven-step sequential extraction procedure) were performed in superficial (0–20 cm) tailings samples. Arsenic and metal contents in soils around the tailings impoundments were also studied. Zarandas dam, a reclaimed impoundment, which has been limed, partially topsoiled and planted, has supported and allowed the growth of pine trees and other plants for many years. The surface of this impoundment can be considered very acid but nonacid forming. Although total As and metal concentrations were relatively high, it is not possible to conclude that the Zarandas tailings have polluted the surrounding soils. Tailings in Cueva de la Mora showed high total and easily mobilizable concentration of toxic elements. The net

neutralization potential was strongly negative as a consequence of the acid generation caused by the sulphide oxidation, the presence of secondary acid-generating minerals and the absence of neutralizing materials. Coquimbite and rhomboclase efflorescences formed during the Mediterranean dry summers on the surface of this impoundment contained very high levels of soluble As, Cu and Zn that were easily dissolved and released to the running water in the first rains of autumn.

**Keywords** Tailings impoundments · Trace elements · Geochemistry · Mineralogy · Sequential extraction · Iberian Pyrite Belt

## Introduction

The Iberian Pyrite Belt (IPB) is one of the largest metallogenic provinces of volcanic hosted massive sulphide deposits in the world (Leistel et al. 1996). With a length of about 250 km and a width of 40–60 km, the Iberian Pyrite Belt extends from Sevilla and Huelva provinces, in SW Spain, to Beja in Portugal. The IPB comprises about 90 polymetallic sulphide deposits mainly hosted by felsic volcanic rocks in a volcanic-sedimentary sequence with original reserves in the order of 1,700 Mt (Sáez et al. 1999). Mineralizations consist of massive sulphide ore bodies containing mainly pyrite (>90% in volume) with variable amounts of other sulphides and accessory minerals such as cassiterite. The long history of metalliferous mining in the IPB (exploited since pre-Roman times) has left a legacy of abandoned mines, which represent one of the world's largest accumulations of mine wastes and acid mine drainage (AMD) discharges (Sánchez-España 2008). The province of Huelva (SW Spain) has probably the

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largest accumulations of metal mine wastes in Spain, with a total of 20 tailings impoundments containing  $109 \times 10^6 \text{ m}^3$  (Rodríguez-Pacheco and Gómez de las Heras 2006).

Abandoned flotation mining tailings impoundments may pose potential environmental hazards. After discharges stop, the chemical and physical processes in the tailings keep generating acidity, and a constant dispersion of toxic elements by wind and water erosion occurs for a long time. The acid waters resulting from the exposition of rich pyrite tailings to oxygen and moisture lead to the leaching of high concentrations of sulphates, metals and metalloids of varying composition, depending on the originating mineral deposit types and to the formation of abundant secondary ferric oxyhydroxides or hydroxide sulphates near the tailings surface. These mineral phases are of great environmental relevance due to their role in the control of pollutants' mobility.

Contamination hazards from tailings in abandoned mines can only be predicted through detailed geochemical and mineralogical studies. The aim of this study has been to study the mineralogical and chemical characteristics of flotation tailings impoundments in two important mines in the province of Huelva: Represa III in Zarandas (Ríotinto Mines) and Cueva de la Mora (Monte Romero Mine). The study was performed at the surface of the tailings, where sulphide oxidation is a major source of acidity and toxic elements. Surrounding soils, salt precipitates and efflorescences formed during summer months were also analysed as they represent major pathways for metal transportation from the tailings to ecosystems.

## Site description

### Climate and hydrology

The study area has a Mediterranean climate, ranging from subhumid to dry from north to south, with a water deficit in summer months. Annual rainfall ranges from 950 to 750 mm. Mean annual temperature exceeds  $16^\circ\text{C}$ . Annual potential evapotranspiration does not exceed 760 mm. The dry period, identified with the Thornthwaite water balance (Thornthwaite and Mather 1955, 1957), extends from June to September.

Potential vegetation is evergreen oak (*Quercus rotundifolia* and *Q. suber*) mixed forest. Land uses in the vicinity of Zarandas are dominated by old mining and industrial facilities, pine forests, derelict lands and pastures. Near Cueva de la Mora, land uses are mainly composed of *Cistus ladanifer* bush formations and *Eucalyptus globulus* and *E. camaldulensis* forest exploitations.

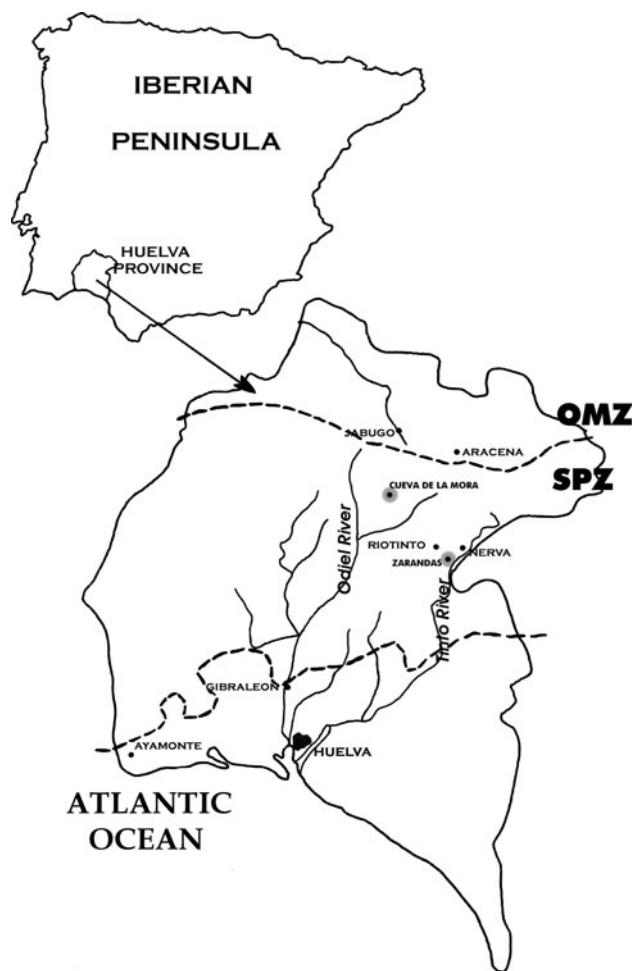
Hydrological characteristics in both areas are typical of a Mediterranean climate, with marked variations in water

discharge and water flow rates from summer to winter as well as among different hydrologic years (Sánchez-España et al. 2005). The Spanish IPB is mainly drained by the Tinto and Odiel rivers, which receive numerous inputs from small creeks arising in abandoned mines. It is well known that waters of these two rivers are very acidic and contain extremely high concentrations of iron, metals and sulphates (Nelson and Lamothe 1993; Davis et al. 2000; Olías et al. 2006; Sarmiento et al. 2004; Sánchez-España 2008).

### Tailings dams' description

The location of the studied tailings impoundments is shown in Fig. 1.

The Represa III dam (Zarandas, Rio Tinto mining district) was used for the deposition of pyrite and copper flotation tailings. This impoundment has a surface area of 14.5 ha and a maximum thickness of 15 m. It was in



**Fig. 1** Simplified scheme showing the location of the studied sulphide-bearing tailings together with towns and major rivers. The dashed lines indicate the boundaries of different geologic domains: OMZ, Ossa-Morena Zone; SPZ, South Portuguese Zone

operation from 1930 to 1973. This dam is fairly covered with planted umbrella pine (*Pinus pinea*) and spontaneous gum rockrose (*Cistus ladanifer*) (Fig. 2). According to Pérez-Blanco (1994), 40 kg/ha seeds of *Pinus pinea* were sown in February 1987. Before seeding, 3 ton/ha of finely ground lime were sprayed and mixed through surface ploughing. The eastern part of the tailings impoundment was also covered with 10 cm of stony soil material similar to those found in the vicinity. Pines have developed quite well and have reproduced from seed. A drying process has been occurring in the tailings for more than 30 years permitting the formation and continuous descent of an oxidation front (colour olive-yellow). This front has progressed to depths of 95 cm in the eastern topsoiled sector (ZTOP) and of 28 cm in the western sector (Z).

Cueva de la Mora impoundment is located in the SW area of the former old mining site of Monte Romero. Between 1965 and 1978, the ore was removed mainly via underground mining and processed by flotation to obtain copper, lead and zinc concentrates. The flotation tailings were discharged on a dam, which was constructed in the south and west sides of a natural depression. It covers an area of approximately 1.5 ha. The maximum dam height is 6 m. A natural spit divides the tailings impoundment in two bodies that are connected by water in high-level periods. Surface colour in the eastern body (CME) is grey, whereas the surface of the other (CMW) is pale yellow (Fig. 3). In the eastern body, discharge of tailings clearly continued after a period of inactivity, as shown by the presence of yellow horizons below the superficial grey layers.

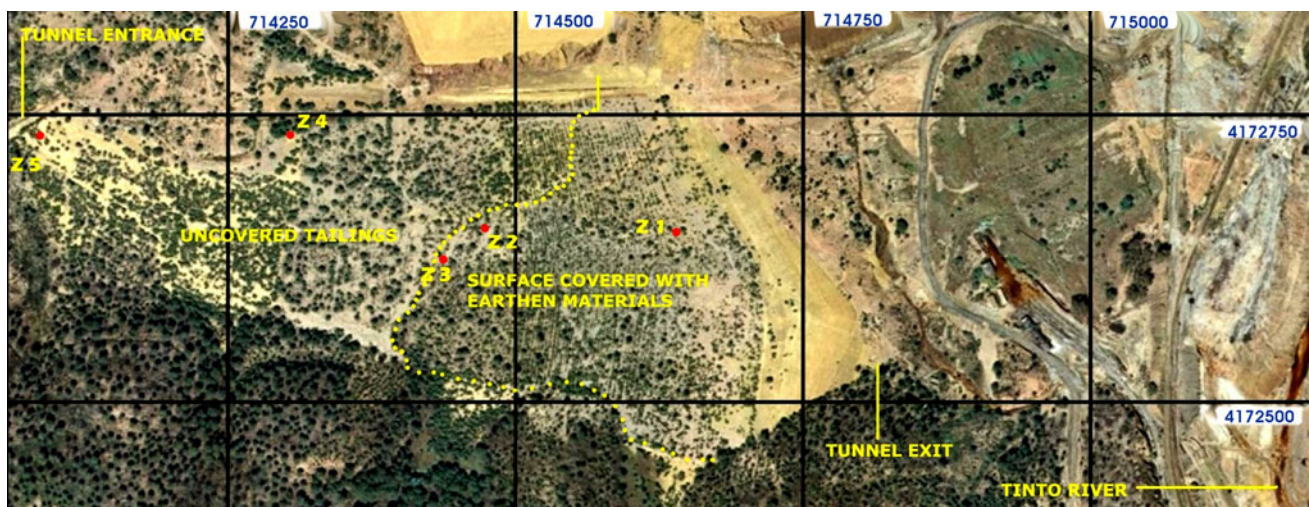
The northern limit of the impoundment cover the foot of a gentle natural hillside. As a consequence, tailings maintain a very humid condition in wet months due to rainfall and water runoff coming from the northern slope. In

autumn and winter, some areas of the dam are usually covered with water (see Fig. 3). The prolonged saturated condition of these tailings every year has resulted in a more limited alteration of the sulphide primary minerals.

**Materials and methods**

**Sampling**

Untopsoiled (Z) and topsoiled (ZTOP) tailings samples in Zarandas dam, tailings samples from the eastern (CME) and western (CMW) bodies of Cueva de la Mora dam and samples from the surrounding soils of both dams were collected. A superficial sampling of the tailings was conducted because it was expected that the superficial material is more likely to suffer runoff from rain events (Smith et al. 2006). At each sampling point, a composite sample was taken with a soil auger. Each sample consisted of five cores collected within a 1 × 1 m<sup>2</sup> area at a depth of 0–20 cm and mixed together for homogenization. The collected tailings samples were slightly wet in Zarandas (sampled in March) and completely wet in Cueva de la Mora (sampled in late October, when the western body was almost completely covered with water). Sampling points are shown in Figs. 2 and 3. A total of 16 soil samples were collected randomly at a depth of 20 cm within a maximum distance of 500 m from the tailings impoundments. Each sample was the composite of 10 sub-samples taken across a 1 × 1 m<sup>2</sup> area using a hand shovel. In summer, powder salts are formed punctually in surface depressions of Zarandas dam and well-developed cauliflower like efflorescences cover the entire surface of Cueva de la Mora tailings. Composite samples of these precipitates were taken in August.



**Fig. 2** Aerial image of Zarandas impoundment. Modified from an image downloaded from the Web page <http://sigpac.mapa.es/fega/visor/>. Blue numbers refer to 29 N UTM coordinates. The letter Z followed by a number identifies the sampling points at the tailings impoundment



**Fig. 3** Cueva de la Mora impoundment in summer (*up*) and in winter (*down*). Note the grey colour of the eastern body (*left*) and the yellow colour of the western body (*right*). Sampling points are marked on the

upper part of the image, although the sampling was performed in winter. CME: Cueva de la Mora East; CMW: Cueva de la Mora West

### Analytical methods

The tailings and soil samples were ground, oven dried (35°C) and homogenized. Mineralogical and chemical analyses were performed on the <2 mm fraction. The colour was assessed by Munsell© colours charts. Particle size distribution of the tailings was determined by standard sieving (ASTM 5000 series) for 2–0.63 mm fractions in combination with a Sedigraph particle size analyser for <0.063 mm fractions.

A routine mineralogical characterization was carried out by X-ray diffraction (XRD, powder method) using a Philips® PW-1700 equipment with monochromated CuK $\alpha$  X-radiation. Data were collected by scanning from 0° to 62° 2 $\theta$  with 0.5 s counting time per step.

Soil and tailings pH was measured in a 1:1 soil–water paste (NCRS 2004). Total S was measured using a Leco furnace. S-sulphate was determined by total reflection X-ray fluorescence spectroscopy using a TXRF Extra II spectrometer after 2 h extraction with hot 0.2 M NH<sub>4</sub>-

oxalate (Dold and Fontboté 2001). The difference between both results represents the S-sulphide content. Tailings samples were then analysed for their acid-generating potential (AP) and acid neutralization potential (NP) following the procedures of Sobek et al. (1978). AP was estimated multiplying the sulphide percentage by a conversion factor of 31.25 (Cravotta et al. 1990) to obtain the potential acidity in t CaCO<sub>3</sub> equivalent/1,000 t of material. The NP was determined from the amount of acid that the sample neutralizes in a standardized digestion-back titration procedure. The NNP (net neutralization potential) was calculated as the balance between the neutralization potential (NP) and the acidity potential (AP).

A total analysis of major and minor elements in each soil sample was performed by tri-acid digestion (concentrated HF-HNO<sub>3</sub>-HClO<sub>4</sub>) followed by ICP-MS (inductively coupled plasma-mass spectrometry) in an Elan 6000 Perkin-Elmer spectrometer equipment.

To evaluate the mobility and retention behaviour of trace elements in specific secondary minerals or mineral

groups, tailings samples were subjected to the seven-step procedure for sequential chemical extraction proposed by Dold and Fontboté (2001). This procedure consists of the following steps (fractions FI to FVII). The preferentially dissolved minerals are shown in parentheses:

(FI) Water-soluble fraction (secondary soluble sulphates): 1 g sample into 30 ml deionized water, shake for 1 h.

(FII) Exchangeable fraction (vermiculite-type mixed layer, adsorbed and exchangeable ions): 1 M  $\text{NH}_4$ -acetate, pH 4.5, shake for 2 h.

(FIII) Fe(III) oxyhydroxides (schwertmannite, two-line ferrihydrite, secondary jarosite,  $\text{MnO}_2$ ): 0.2 M  $\text{NH}_4$ -oxalate, pH 3.0, shake for 1 h in darkness.

(FIV) Fe(III)oxides (goethite, jarosite, Na-jarosite, haematite, magnetite and highly ordered ferrihydrite): 0.2 M  $\text{NH}_4$ -oxalate, pH 3.0, heat in water bath at 80°C, for 2 h.

(FV) Organics and secondary-metal sulphides (organics, calcocite, covellite): 35%  $\text{H}_2\text{O}_2$ , heat in water bath for 1 h.

(FVI) Primary sulphides (pyrite, chalcopyrite, sphalerite, galena): combination of  $\text{KClO}_3$  and  $\text{HCl}$  followed by boiling with 4 M  $\text{HNO}_3$ .

(FVII) Residual (silicates and residual fraction):  $\text{HNO}_3$ ,  $\text{HF}$ ,  $\text{HClO}_4$ ,  $\text{HCl}$  digestion.

Reagents used in the analysis were of analytical grade quality. An Elan 6000 Perkin-Elmer ICP-MS spectrometer was used for metal determinations. The average of two duplicate extractions was calculated. Using selected samples, it was found that the sum of all fractions was close to the total metal content determined by tri-acid digestion. Recoveries in the range 80–110% were obtained for these samples.

### Statistical analysis

The nonparametric Mann–Whitney test was used to identify significant differences between the elemental concentrations in the two studied tailings dams and surrounding soils. Significant differences were searched at a 0.05 confidence level for the total contents of As, Cu, Fe, Pb and Zn in tailings dams and soils as well as for the elemental concentrations in the seven fractions of the sequential extraction procedure. SPSS software was used for the statistical analysis.

## Results and discussion

### Mineralogy of tailings and efflorescences

The mineralogical composition based on X-ray diffraction on tailings samples is shown in Table 1.

The age and well-drained nature of Zarandas tailings dam have promoted extensive oxidation of primary phases.

Jarosite was present on the exposed surface of the untopsoiled sector of the Zarandas dam, but neither Fe-oxyhydroxide nor other Fe-hydroxysulphate minerals were detected by XRD analysis. In summer, white powder precipitates of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), starkeyite ( $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ ) and pickeringite ( $\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ ) could be found located in depressions of the Zarandas impoundment. A chemical analysis of these salts showed high contents of copper (598  $\text{mg kg}^{-1}$ ) and zinc (4757  $\text{mg kg}^{-1}$ ) mostly in soluble forms.

The co-existence of pyrite and secondary sulphate minerals (jarosites, alunites, anglesite) in the surface of the East body of the Cueva de la Mora (CME) confirms that short time passed since the deposition, and the water saturation conditions resulted in limited alteration of the primary sulphide minerals. In summer, well-developed secondary efflorescent salts were found covering the impoundment surface. These efflorescences included  $\text{Fe}^{3+}$  sulphates such as coquimbite ( $\text{Fe}_2(\text{SO}_4) \cdot 9\text{H}_2\text{O}$ ), rhomboclase ( $\text{FeH}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ) and copiapite ( $\text{MgFe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20 \text{H}_2\text{O}$ ). Analytical data of these efflorescences showed very high contents of soluble As (2,961  $\text{mg kg}^{-1}$ ), Cu (2,259  $\text{mg kg}^{-1}$ ) and Zn (15,824  $\text{mg kg}^{-1}$ ). Secondary minerals predominate in the more oxidized western body of Cueva de la Mora dam (CMW) and consist mainly of jarosites and gypsum. In summer, well-developed efflorescences also appeared in this body. These efflorescences also included copiapite and rhomboclase, and traces of anglesite ( $\text{PbSO}_4$ ). Chemical results showed very high contents of soluble As (1,365  $\text{mg kg}^{-1}$ ), Cu (3,765  $\text{mg kg}^{-1}$ ) and Zn (7,057  $\text{mg kg}^{-1}$ ). In addition to the high contents of soluble elements, all the sulphate minerals formed in Cueva de la Mora impoundment are considered to be acid producing and readily soluble salts (Nordstrom 1982; Bayless and Olyphant 1993). Among them, rhomboclase is possibly the most common acid sulphate occurring in nature. Because of this, every year the first rainstorms in the early autumn usually involve re-dissolution and subsequent discharge of acid, sulphate ions, As and metals to fresh waters.

### Granulometry of tailings

Grain size analysis is considered an important factor both in flotation processes and sulphide oxidation. The particle size distribution summarized by the 50 and 90 percentile for the diameter values (D50 and D90, respectively; Table 2) indicates that Zarandas tailings are coarser than Cueva de la Mora tailings, probably as a consequence of a lower efficiency of the milling process. The tailings of ZTOP presented rock fragments of chloritized shale, which were also abundant in the surrounding soils. Coarser-grained materials have a lower water-holding capacity than finer-grained materials and hence there is a higher oxygen availability for pyrite oxidation. For this reason, it is

**Table 1** Results of X-ray diffraction analysis. Chemical formulae: quartz ( $\text{SiO}_2$ ), muscovite ( $\text{KAl}_2(\text{Al,Si})_4\text{O}_{10}(\text{OH,F})_2$ ), pyrite ( $\text{FeS}_2$ ), barite ( $\text{BaSO}_4$ ), clinocllore ( $(\text{Mg,Fe})_5\text{Al}(\text{Si}_3\text{l})\text{O}_{10}(\text{OH})_8$ ), jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), hydronium-jarosite ( $\text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), plumbojarosite ( $\text{Pb}_{0.5}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ ), alunite ( $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ ), ammonioalunite ( $(\text{NH}_4)\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and anglesite ( $\text{PbSO}_4$ )

	Main minerals	Secondary minerals	Trace minerals
Z	Quartz, muscovite clinocllore	Jarosite	
ZTOP	Quartz, muscovite, clinocllore		
CME	Quartz, pyrite, barite	Jarosite, hydronium-jarosite, plumbojarosite, anglesite	Alunite, ammonioalunite,
CMW	Quartz, muscovite	Jarosite, hydronium-jarosite, plumbojarosite	Gypsum

presumable that the coarser texture of Zarandas tailings and a longer annual drought period in this area will favour the oxidation processes at the surface of the dam and the leaching of trace elements resulting from the oxidation of sulphides.

#### Sulphur forms and acid–base account

The geochemistry of the major elements (Tables 2 and 3) reflects quite well the major mineralogy of the tailings. S total contents were low in the more oxidized tailings (Z, ZTOP and CMW) probably due to the oxidation of primary sulphides and to the leaching of the sulphates during the long time of weathering. However, in CME body, sulphur was an important major element constituting as much as 32.1 wt%, reflecting the presence of pyrite and its weathering products. The rate of oxidation estimated by the percentage of sulphate-sulphur in relation to the total S content was in the order: Z (86%) > ZTOP (75%) > CMW (42%) > CME

(4%), which reflects the different oxidation degrees of the dams and confirms the higher rate of oxidation of Zarandas tailings samples.

A mining tailings can be considered acid generating when its net neutralization potential (NNP) is less than  $-20 \text{ kgCaCO}_3/\text{t}$  (Ferguson and Morin 1991). Negative NP values are possible and are sometimes derived from samples that contain residual weathering products that produce acidity upon dissolution. This occurs very prominently in CME samples. Surface tailings in the CME dam could be considered as highly hazardous due to their great potential for acidity generation and their high negative neutralization potential (Table 2). These materials contained as much sulphur as 22.9% on average, of which approximately 96.2% was sulphide-sulphur. The very strong acidic pH values of these tailings (mean value 1.32) are probably due to the oxidation processes of the high levels of pyrite present in them. These processes could be enhanced by the dissolution of the soluble Fe(III) acid-generating secondary

**Table 2** Physico-chemical characteristics of the studied tailings

Sample	Colour Munsell (dry)	$D_{50}$ ( $\mu\text{m}$ )	$D_{90}$ ( $\mu\text{m}$ )	pH	Total S (%)	S ( $\text{SO}_4^{2-}$ ) (%)	AP (kg $\text{CaCO}_3/\text{t}$ )	NP (kg $\text{CaCO}_3/\text{t}$ )	NNP (kg $\text{CaCO}_3/\text{t}$ )
Topsoiled area of Zarandas									
Z 1	2.5Y5/6	91	475	3.82	0.135	0.088	1.47	4.74	3.27
Z 2	2.5Y6/6	22	178	3.50	0.158	0.131	0.86	3.34	2.48
Z 3	10YR5/4	90	1129	4.19	0.020	0.007	0.56	1.93	1.37
Untopsoiled area of Zarandas									
Z 4	2.5Y6/8	160	350	3.39	0.305	0.225	2.50	0.00	-2.50
Z 5	2.5Y6/8	33	170	3.27	0.286	0.269	0.88	-1.14	-2.02
Cueva de la Mora East body									
CME 1	5Y6/3	27	83	1.55	12.285	0.758	360.22	-24.14	-384.36
CME 2	5Y6/2	14	57	1.40	21.700	0.681	656.84	-23.15	-679.99
CME 3	10Y6/1	36	95	1.31	25.690	0.933	773.65	-34.51	-808.16
CME 4	10Y4/1	20	62	1.03	32.095	0.736	979.96	-35.73	-1015.69
Cueva de la Mora West body									
CMW 1	5Y8/2	13	90	2.36	0.858	0.560	9.31	-3.76	-13.07
CMW 2	2.5Y8/2	65	150	1.83	1.040	0.550	15.31	-9.5	-24.81

$D_{50}$  grain size where 50% passes.  $D_{90}$  grain size where 90% passes. AP acidity potential; NP neutralization potential; NNP net neutralization potential NNP = NP-AP. AP is calculated by multiplying a factor of 31.25 by the difference between S total (%) and S ( $\text{SO}_4^{2-}$ )

**Table 3** Mean and standard deviations of total elements in the studied tailings dams

Sector/body	As (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Z ( <i>n</i> = 3)	361 ± 63	391 ± 88	393 ± 101	193 ± 48
ZTOP ( <i>n</i> = 2)	153 ± 41	297 ± 115	232 ± 148	142 ± 15
CME ( <i>n</i> = 4)	667 ± 407	316 ± 97	9380 ± 2947	879 ± 270
CMW ( <i>n</i> = 2)	853 ± 208	648 ± 159	10129 ± 1199	752 ± 205

Z untopsoiled Zarandas sector; ZTOP topsoiled Zarandas sector; CME Cueva de la Mora East body; CMW Cueva de la Mora West body

minerals such as coquimbite and rhomboclase, as shown in the XRD analysis.

Despite the low S total contents in its surface, the oxidized CMW body showed a very strong acidic pH (mean value 2.1) and some capacity to generate more acidity. This suggests that the lack of neutralizing minerals prevents the neutralization of the acidity released by the oxidation of residual sulphides.

Both the topsoiled and the untopsoiled sectors of Zarandas dam can be considered very acid, but nonacid forming materials. Sáez-Díaz (2004) determined that in areas affected by mining wastes in the IPB, a pH of 3.36 could permit healthy forest vegetation, although for *Pinus pinea* a pH around 4.7 would be desirable. With pH values between 3.27 and 4.19, the development of pine trees has been quite acceptable in the Zarandas dam. The old partial reclamation practices, which included liming, have resulted during this time in a slightly, but not significant, higher pH and a slightly positive net neutralization potential of the surface materials in the topsoiled sector (Table 2).

Total metal concentrations in soils and tailings

Of all the analysed trace elements, particular attention has been paid to As, Cu, Pb and Zn. The pollution associated with these elements has been traditionally of most interest to IPB researchers. López-Pérez et al. (2008) showed a clear Pb–Zn–As–Cu association in IPB soil total contents.

Total metal concentrations in tailings, estimated as the sum of the seven fractions of the sequential extraction procedure were higher in Cueva de la Mora than in Zarandas (Table 3). However, only statistically significant differences between Zarandas and Cueva de la Mora tailings dams could be seen at the 0.05 level for Pb. The chemical variation could be attributed to the original ore composition variability, ore recovery changes or weathering and dispersion of metals over time after the tailings were deposited.

ZTOP samples showed slightly (but not statistically significant) lower metal concentrations than the non-

topsoiled samples, due to the dilution effect produced by the addition of stony soil and mixing during reclamation.

The severity of pollution for the studied tailings was ranked by means of the pollution index (PI). This index was computed by averaging the ratios of the mean total concentrations of toxic elements in the tailings (Table 3) to the maximum phytotoxically tolerable levels (Kim et al. 2001). For As, Cu, Pb and Zn, the tolerable levels considered were 100, 500, 1,000 and 1,000 mg kg<sup>-1</sup>, respectively (intervention values for forest soils; Junta de Andalucía 1999). The calculated pollution indices for the tailings samples were in the order: 5.16 (CMW) > 4.38 (CME) ≫ 1.24 (Z) > 0.61 (ZTOP). Excluding ZTOP sector, these pollution indices are higher than 1, indicating that the average metal concentrations in the studied tailings are higher than the permissible levels in soils and can hence be considered as a potential source of environmental problems, especially in Cueva de la Mora.

The assessment of the hazard associated with polluted sites or waste deposits may be accomplished by comparing the reported element concentrations of these media to a set of toxicological benchmarks or to baseline/background data. The European Commission Decision 2009/359/CE of 30 April states that “the content of substances potentially harmful to the environment shall not exceed national threshold values for sites identified as not contaminated or relevant national natural background levels”. In view of the foregoing, As, Pb and Cu total concentrations in all the studied tailings and Zn in Cueva de la Mora were much higher than in the reported backgrounds (Table 4; Junta de Andalucía 2004). If the regional soil quality guidelines for metals are used, it is evident that the concentrations of As and Pb in Z, ZTOP, CMW and CME tailings exceed the intervention values established for natural areas and forest soils (100 mg kg<sup>-1</sup> As, 1,000 mg kg<sup>-1</sup> Pb; Junta de Andalucía 1999).

Soils

Soils located in the vicinity of the tailings impoundments (Leptosols developed on shales) were acidic (Table 4). As, Cu and Pb concentrations in samples located around Zarandas tailings dam and Cu and Zn in samples

collected around Cueva de la Mora exceeded the 95th percentile established for the background concentration of metals in regional soils and the 95th percentile of the soils of the South Portuguese Zone (Junta de Andalucía, 2004), and other values attributed to soils unaffected by mining in the IPB (Sáez-Díaz 2004). This suggests a possible effect of the tailings on the contents of these elements apart from the geological influence. These results are in accordance with the values reported in other studies about heavy metal contents in the surroundings of Rio Tinto or close to Zarandas and Cueva de la Mora impoundments (Chopin and Alloway 2007; López et al. López-Pérez et al. 2008). It could be accepted that such contamination

was caused by dispersion of elements from Cueva de la Mora dam. However, Chopin and Alloway (2007) reported that trace element concentrations decrease very rapidly with distance in the Ríotinto smelting area (near Zarandas impoundment) and that elevated concentrations in topsoils reach to a 2–3 km radius from the source. According to them, the high concentrations found in Zarandas soils would be caused by pollution. Therefore, this pollution may be due to wind dispersion from Zarandas dam (Represa III) or from other sources (dust particles transported from other tailings deposits and trace element-bearing particles volatilized during historic smelting activities).

**Table 4** pH and total concentrations of As, Cu, Pb and Zn in soils (mg/kg)

Soil data	pH	As	Cu	Pb	Zn
ZNAT1	4.67	477.2	345.1	330.3	161.8
ZNAT2	3.64	804.3	329.5	829.8	103.8
ZNAT3	3.61	40.8	204.2	106.1	89.9
ZNAT4	3.85	184.7	301.1	337.8	113.6
ZNAT5	4.42	41.6	138.1	127.7	81.2
ZNAT6	4.18	18.2	228.9	53.2	86.4
ZNAT7	4.13	95.1	235.7	195.9	84.6
ZNAT8	3.80	156.8	368.6	314.5	110.7
ZNAT (mean $\pm$ standard deviation)	4.04 $\pm$ 0.37	227.3 $\pm$ 275.8	268.9 $\pm$ 79.7	286.9 $\pm$ 245.2	104.0 $\pm$ 26.4
CMNAT1	3.76	53.3	135.2	90.5	99.7
CMNAT2	4.10	37.9	233.6	91.0	114.8
CMNAT3	6.41	42.7	253.9	77.9	332.6
CMNAT4	4.39	37.9	112.6	67.7	91.0
CMNAT5	4.53	54.2	84.5	68.2	117.2
CMNAT6	5.64	29.04	56.4	38.4	86.1
CMNAT7	4.79	34.04	268.1	140.3	233.9
CMNAT8	4.48	58.6	95.0	100.7	228.6
CNAT (mean $\pm$ standard deviation)	4.76 $\pm$ 0.86	43.5 $\pm$ 10.7	155.0 $\pm$ 84	84.3 $\pm$ 29.7	166.5 $\pm$ 75.9
Not affected soils around mines of IPB supporting healthy-looking forest vegetation <sup>a</sup>	4.5–5.2	88.0	156	120	120
Agricultural soils Riotinto area <sup>b</sup>		22	57	197	201
Agricultural soils Cueva de la Mora area <sup>b</sup>		115	159	169	227
Andalusian 95th percentile <sup>c</sup>		54	62	109	145
Geological Dominium South Portuguese Zone 95th percentile for upper soil (0–20 cm) <sup>c</sup>		157	108	117	134
Intervention values in forest soils <sup>d</sup>		>100	>500	>1,000	>1,000

ZNAT and CMNAT superficial soils samples (0–20 cm) of Zarandas and Cueva de la Mora areas, respectively. Values determined in one sample

<sup>a</sup> Sáez-Díaz (2004)

<sup>b</sup> López et al. (2007)

<sup>c</sup> (Junta de Andalucía 2004)

<sup>d</sup> (Junta de Andalucía 1999)



Element speciation

*Arsenic*

Arsenopyrite forms part of the ore mineral in the studied mining sites. It can be considered as the main source of As, although it has not been found in the XRD analysis of the studied samples. Oxidation of arsenopyrite in mine tailings is deemed as the major source of arsenic release to the environment around polymetallic sulphides mine sites. The results of the As speciation data suggest that there are two major associations of As in the studied tailings samples (Fig. 4.): Fe oxide-sulphate secondary-associated As (FIV fraction) in the oxidized tailings dams (representing 61, 66 and 80% of As total contents, in Z, ZTOP and CMW, respectively), and sulphide-associated As (FV and FVI fractions) in the grey CME surface tailings (38 and 22% respectively).

Arsenic is stable as oxyanion ( $H_2AsO_4^-$ ) under acid-oxidizing conditions and this oxyanion is mainly adsorbed to the secondary ferric minerals under low-pH conditions. Its presence in FIV fraction in the more oxidized tailings could be attributed to its adsorption onto Fe oxyhydroxides and Fe sulphates as jarosite. The association of As with Fe oxyhydroxides is well documented in different studies. As forms mono or bidentate arsenate complexes that bind to the Fe oxyhydroxides at low-pH values. Jarosite can also incorporate  $AsO_4^{3-}$  by partial replacement of  $SO_4^{2-}$  in the unit cell (Savage et al. 2000). As a consequence of its

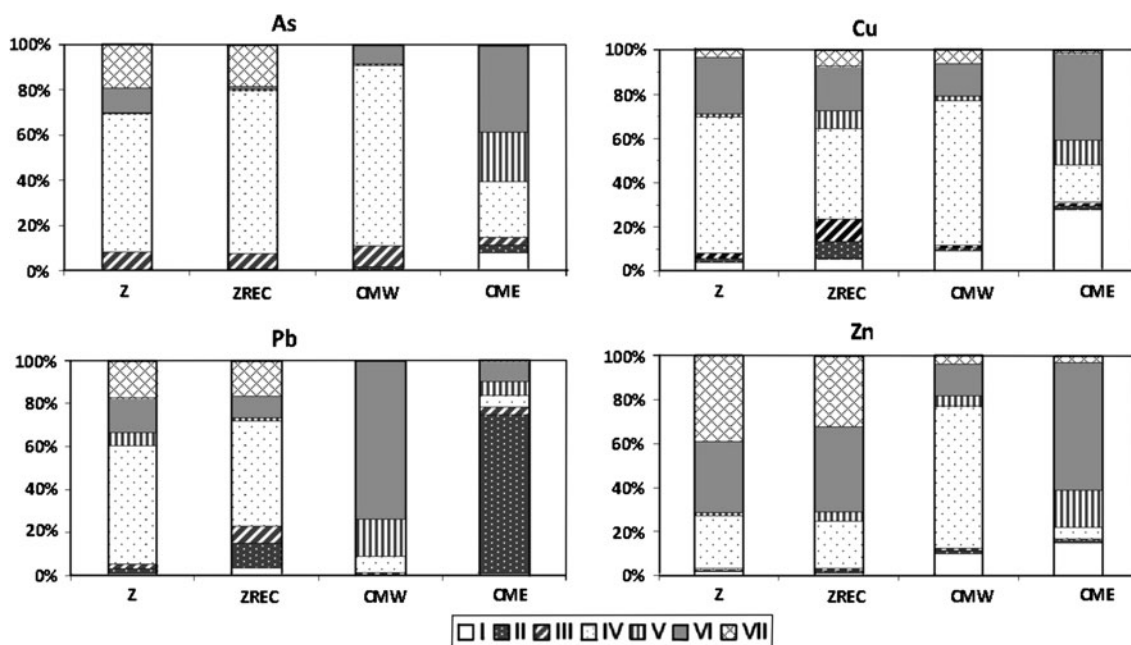
retention on the secondary ferric minerals, arsenic is less mobile in these sites, as shown by the negligible percentage of As in the water-soluble fraction (0.05, 0.28 and 0.15% of As total contents in Z, ZTOP and CMW samples).

In the more recent tailings (CME), As was mainly associated with the sulphides fractions (38 and 23% in the primary and secondary sulphides fractions, respectively). Water-soluble fraction (FI) of As represented about an 8% of total As concentration. The mineralogical analysis did not detect any As-bearing secondary soluble phase mineral, suggesting that it had been incorporated into the sulphate salts that precipitated on the surface in summer and that may be re-dissolved with the first rains of autumn.

*Lead*

Originally, galena was the main source of Pb in the studied tailings. The oxidized tailings samples exhibited different Pb partitioning pattern. Pb in the Zarandas dam samples was mainly linked to the oxidized FIV fraction (55 and 49% of Pb total contents in Z and ZTOP, respectively, Fig. 4) due to the incorporation of the Pb released by sulphide oxidation into ferric secondary minerals.

In the oxidized CMW samples, about 73% of the Pb total content was extracted in the primary sulphides fraction (FVI). However, galena was not detected in the XRD analysis of these samples. Taking into account the high total contents of Pb in these tailings (mean value 10,129 mg/kg), its high oxidation rate and the low-pH



**Fig. 4** Percentage of As, Cu, Pb and Zn extracted in each step of the sequential extraction procedure: I, water-soluble fraction; II, exchangeable fraction; III, Fe(III) oxyhydroxides fraction; IV, Fe(III)

oxides and sulphates fraction; V, organics and secondary sulphide fraction; VI, primary sulphides; VII, residual fraction

value of the tailings (1.83–2.36), which would favour galena dissolution, according to Domenech et al. (2002) and Ramos and Sieve (2007), it seems unlikely that the high content of lead extracted in fraction VI came from its presence in the sulphur form. Plumbojarosite was detected as secondary mineral in these samples (Table 1). This mineral is very resistant due to the incorporation of the  $\text{Pb}^{2+}$  into the jarosite structure (Smith et al. 2006) and could probably be dissolved under the experimental conditions used for FVI extraction (combination of  $\text{KClO}_3$  and  $\text{HCl}$  12 M following boiling with 4 M  $\text{HNO}_3$ ). Similar results were reported by Frau et al. (2009) on waste-rock dumps and tailings samples from an old Pb mine area. These authors attributed the Pb in residual fraction (obtained by *aqua regia* digestion after extraction of the sulphidic phase with  $\text{H}_2\text{O}_2$  8.8 M at pH 2.4) to resistant minerals like plumbojarosite.

CME tailings showed the highest mean values of total Pb (Table 3). This Pb was mainly linked to the exchangeable fraction (FII), the represented 74% of the Pb total contents. The abundant presence of anglesite ( $\text{PbSO}_4$ ) as an oxidation product of galena under the acidic conditions found in these tailings accounts for the Pb bound to the exchangeable fraction, extracted with 1 M  $\text{NH}_4$ -acetate (pH 4.5), according to Frau et al. (2009) and Ramos and Sieve (2007). Fanfani et al. (1997) and Leinz et al. (2000) have also reported that anglesite could be extracted over five different phases in two different sequential extraction schemes.

### Copper and zinc

In the oxidized tailings (Z, ZTOP and CMW), copper was mainly extracted in the oxidizable fraction (FIV), with mean percentages of Cu total concentrations 62, 41 and 66%, respectively (Fig. 4). Zinc was also appreciably extracted in the oxidizable FIV fraction, although in minor percentages when compared with Cu (24, 21 and 65% of Zn total content, respectively). Cu and Zn extracted in this fraction may not be interpreted as adsorbed Cu and Zn, because at pH <4 no significant adsorption of Cu and Zn on Fe(III) hydroxides takes place (Dold 2003). However, Webster et al. (1998) reported that Cu adsorption could start at lower pH at acid mine drainage precipitates (where adsorption would begin at pH 4 and at pH 6, 80–100% of the Cu would be adsorbed by schwertmannite and ferrihydrite. Kinniburgh et al. (1976) have reported that jarosite and goethite may incorporate significant amounts of Zn by co-precipitation.

In the water-soluble fraction, the contents of Zn and mainly Cu were remarkable, especially in the more acidic CME dam where 28% of total Cu and 15% of total Zn were extracted in this fraction. Different studies have reported

the coprecipitation of Cu, Zn and Cd with soluble iron hydroxysulphates precipitated during the summer periods. Olías et al. (2004) reported a higher coprecipitation of Cu together with iron oxyhydroxides and hydroxysulphates in the precipitates of the Odiel River (IPB mining district). Buckby et al. (2003) found that the most abundant hydroxysulphates that precipitate in summer in the Río Tinto basin contain high proportions of Cu and Zn. In a study of the Odiel River sediments, Galan et al. (2003) described that proportionally higher concentrations of Cu than of Zn and Cd were found associated with the reducible fraction.

### Conclusions

The application of a seven-step chemical sequential extraction procedure and a mineralogical XRD analysis with the support of acid–base accounting has permitted an acceptable characterization of flotation mining wastes. However, some limitations have been observed due to the lack of specificity of the extraction methodology to the XRD detection limits and to the presence of amorphous materials in the Zarandas tailings samples.

The calculated pollution indices for the tailings samples indicate that all the tailings, except the topsoiled sector of the Zarandas dam, contain heavy metals at a level that could be toxic to the surrounding ecosystems.

The two sectors of Zarandas dam could be considered very acidic, but not with acid-forming materials. It is possible that over the years, metals, sulphates and acidity have progressively been mobilized from the surface of this dam to the Tinto River (located at 500 m), to deep layers of the tailings impoundment or to the surrounding soils. In fact, As total contents in the vicinity of the Zarandas surpass the intervention values established by the regional authorities for forest soils. However, pollution may be also due to wind dispersion from other sources (dust particles transported from other tailings deposits and trace element-bearing particles volatilized during historic smelting activities). Liming and fertilization may be recommended to reduce the availability of toxic elements and enhance the development of pine trees and other plants growing in this tailings impoundment.

In Cueva de la Mora dam, the rate of oxidation, estimated as the ratio S-sulphate/S total, is ten times higher in CMW than in CME. Heavy metal speciation showed notable differences depending on the oxidation rate of the tailings. In the more oxidized tailings of CMW, jarosite contributes to the retention of Cu, Zn, Pb and mainly As. As a consequence, arsenic shows a very low mobility in these sites, as shown by the negligible percentage of As in the water-soluble fraction. In the less oxidized sulphidic tailings of CME, the elements are extracted mainly in the sulphidic fraction,

with the exception of lead that is preferentially extracted in the exchangeable fraction, probably as anglesite mineral. The oxidation of sulphides and the presence of secondary acid-generating minerals as coquimbite and rhomboclase in the tailings cause strong acid generation that cannot be efficiently consumed by the slow dissolution of the silicate gangue minerals. As a consequence of this, net neutralization potential is strongly negative, especially in CME tailings. The efflorescences formed during dry periods on the surface of the tailings dam contain very high levels of soluble As, Cu and Zn. These mineral salts constitute an ephemeral host of heavy metals that are easily released to the solution with the first rains of autumn. The high mobility of metals and the water-soluble mineral phases formed in summer could permit metal recovery methods such as harvesting the efflorescences with scrapers in late summer, which would reduce the risk of surface water contamination by seepage or overflow.

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