

A methodology for ranking potential pollution caused by abandoned mining wastes: application to sulfide mine tailings in Mazarrón (Southeast Spain)

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Abstract Mining wastes often contain high concentrations of toxic elements, whose mobility and dispersion may pose an environmental hazard for soils, water, ecosystems and people. This article describes the partial application of a methodology designed to evaluate the pollution potential of abandoned mining wastes, using two indices for potential pollution evaluation: an index of contamination (IC) and a hazard average quotient (CPP). Composite samples, consisting of at least 30 subsamples, were taken at three sulfidic tailings impoundments in the mining area of Mazarrón (SE Spain). Mineralogical, physical, and chemical characteristics were analyzed: color, particle size, powder XRD analysis, pH, total content of toxic elements, and concentrations in leachates by the standard procedure EN-12457-2. Tailings were extremely acid (pH 2.30–2.52). Some ranges of total content (in mg/kg) were: As (381–565), Pb (2602–4487), Sb (139–170), and Zn (3254–5652). The concentration measured in the EN-12457 leachates (µg/L) was as high as 367,000 for Zn, 2030 for Cu, and 974 for Cd. The IC and CPP values were among the most high of the tailings inventoried in Spain. The combination of the indices provided a good estimation of the potential toxicity of these wastes, and it can be useful to rank abandoned mining waste facilities.

Keywords Abandoned mine tailings · Index of contamination · Hazard average quotient · Potential pollution · South East Spain

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Introduction

When a restoration or rehabilitation of mined sites were not performed, a variety of environmental/safety hazards can occur and remain for a long time. Ideally, modern closure and rehabilitation plans should eliminate such hazards, but there are many cases of abandoned mining sites (orphaned) where rehabilitation was incomplete or neglected. These include waste rock dumps and tailings facilities, especially when wastes containing sulfide minerals have been exposed to weathering over time, releasing acid, metals, non-metals and sulfate (Nordstrom and Alpers 1999; Blowes et al. 2003; Dold 2010). Recently, the Mining Waste Directive 2006/21/EC (European Parliament and Council 2006) urges Member States to perform inventories of closed and abandoned waste facilities which cause serious negative environmental impact and serious threat to human health. In this context, the Geological Survey of Spain has developed a methodology for the systematic ranking of abandoned facilities of mining wastes, through the assessment of scenarios of potential pollution and physical instability (Alberruche del Campo et al. 2014). The methodology takes into account several issues related to the possible consequences, such as the distance of water bodies, the number of people within a specified distance, the nearby soil-use, etc. Apart from physical stability, and leaving aside pathways and receptors, the potential hazard of pollution caused by the mining wastes depend on the existing mineralogical, chemical, and physical properties. The methodology is focused on the total metals contents and the water-soluble fraction, assuming that chemical pollution of soils and sediments is a consequence of a combination of the dispersion of particles and dissolved elements by wind and water.

The purpose of this work is to investigate and evaluate the polluting potential of mine tailings using simple and

standardized methods, which are a small part of the overall evaluation methodology designed for abandoned mining waste facilities. It should be noted that field work and laboratory methods must necessarily be simple and inexpensive, because it should be implemented at many kinds of mining wastes located all over the country. The implementation of greater analytical efforts can be later invested in cases where it is considered necessary. This study evaluates the applicability and efficacy of two indices of pollution which are part of the cited methodology.

Materials and methods

Site description

Three tailings impoundments located in the vicinity of Mazarrón (Murcia, Spain) were selected (Fig. 1), because there is reliable information about the environmental effects associated with them. The impoundments studied were built to store flotation wastes from the Cabezo of San Cristobal mining area, in the vicinity of Mazarrón (Murcia, South East Spain) (Arana et al. 1993). The geological and physiographic framework of the study zone has been well described by Oyarzun et al. (2011). Basically, the most prominent relief features are the sierras of Almenara, Las Moreras, and Algarrobo. The sierras define a basin, crossed

by the Rambla of Las Moreras, which runs to the nearby Mediterranean Sea. Climate is arid Mediterranean. The annual rainfall is about 275 mm. The average temperature is about 18 °C and the annual potential evapotranspiration exceed 900 mm. Rainfall is very variable from year to year and is often torrential, causing severe erosion over bare and erodible surfaces. The hill slopes are covered with thin, stony soils and patchy scrublands. The natural soils of the study area are calcareous and poorly developed. Leptic Calcisols and Aridic Leptosols predominate on the upper and middle positions of the landscape. In the lower positions, Haplic Regosols and Haplic Calcisols are present, in transition to Calcic and Salic Fluvisols, which are developed over modern sediments on Las Moreras floodplain (Alias et al. 1990). With regard to land uses, wasteland (spoil dumps and tailings) and sparsely sclerophyllous vegetation predominate in the mined area. Urban and industrial developments, arable lands, and transport infrastructures are also found in the vicinity of the tailings impoundments.

Geology, mining, and mine tailings

Mazarrón was one of the most important mining districts located in South East Spain. The mining sites of this district are characterized by the presence of volcanic domes and tuffs (andesitic, dacitic, and rhyodacitic) that

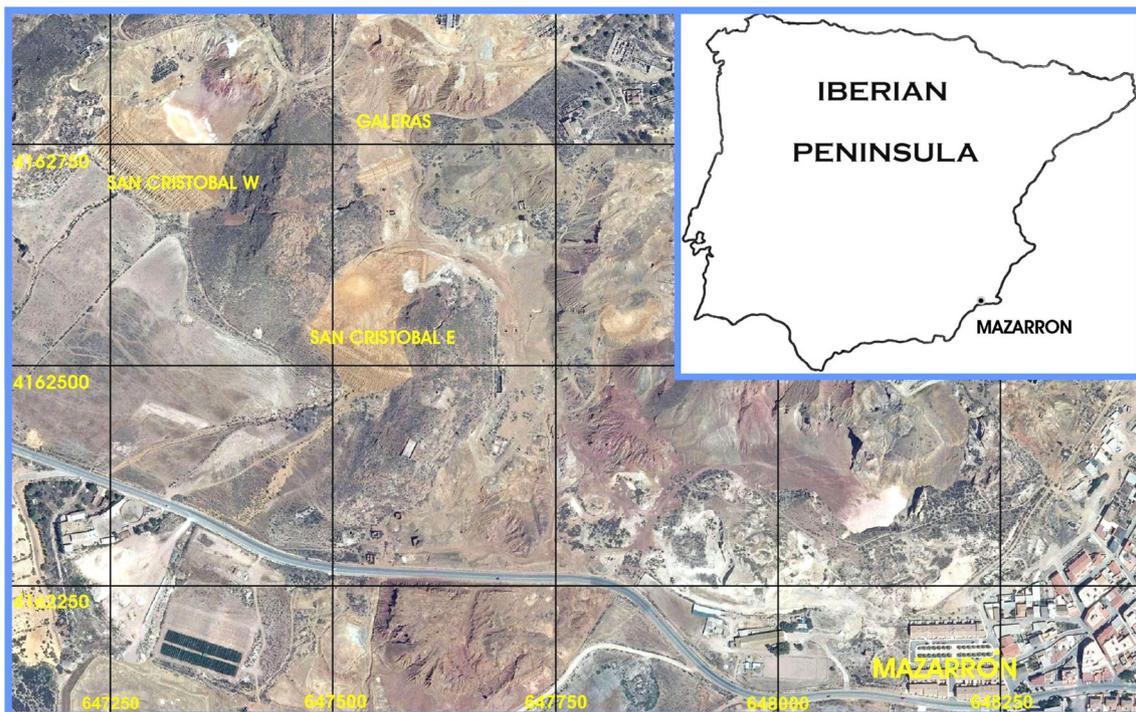


Fig. 1 Simplified map showing the location of Mazarrón and the studied tailings impoundments, superimposed on an aerial photograph downloaded from the web page <http://www2.ign.es/iberpix/>

www2.ign.es/iberpix/. Numbers refers to UTM coordinates (WGS84/UTM zone 30°N)

underwent a strong hydrothermal alteration. The orebody of San Cristobal-Perules was mined in the Roman time for the extraction of Pb, and for the beneficiation of Pb, Ag, and Zn during the 19–20th Centuries (until 1966). The main ore minerals were sulfides like galena (PbS), pyrite (FeS₂), and sphalerite [(Zn, Fe)S]. Other ore sulfides include stibnite (Sb₂S₃), berthierite (FeSb₂S₄), chalcocopyrite (CuFeS₂), arsenopyrite (FeAsS), and tetrahedrite-tennantite (Cu₆[Cu₄(Fe, Zn)₂]Sb₄S₁₃–Cu₆[Cu₄(Fe, Zn)₂]As₄S₁₃). The gangue mineralogy consists of quartz (SiO₂), calcite [CaCO₃], siderite (FeCO₃) and gypsum (CaSO₄·2H₂O) (Oyarzun et al. 2011). Due to the mining activities, this area presents a big legacy of abandoned mining wastes of various kinds (Oyarzun et al. 2011): spoils, gravity refuses, slags, calcines, and flotation tailings. These latter are the most important wastes of the study area. The flotation tailings consist of fine-grained wastes (sand to silt sized) originated by milling and flotation, which are normally discharged as slurry to a final storage impoundment. As it is known, flotation is the most widespread process for the treatment of base-metal sulfide ores in order to recovery metal concentrates. The impoundments studied were: Galeras (976-II-3-005), San Cristobal East (976-II-3-006), and San Cristobal West (976-II-3-007) (Fig. 1). The numbers represent codes of a national inventory of tailings facilities developed by the Geological Survey of Spain. The base of the tailings impoundments is located at elevations from 50 to 100 m above sea level. Taken together, they store about 350.000 m³ of sulfide-rich tailings. These tailings have been subjected to weathering and erosion for a period of more than 40 years, which has led to the generation of acid drainage (enriched in sulfate and other elements), as well as the emission of particulate matter (Arana et al. 1993; Carmona et al. 2009; Bustillo et al. 2010; Oyarzun et al. 2011; Acosta et al. 2011; Martín-Crespo et al. 2012). The slopes of the tailings dams are barren and severely eroded (Fig. 2).

Sampling method

Sampling was undertaken in general accordance with (Smith et al. 2000; Hageman and Briggs 2000). Sampling strategy entails collection of a composite sample, consisting of the combination of at least 30 subsamples taken on a random walk over each tailings impoundment. Subsamples were taken from the surface to a depth of 20 cm, assuming that the superficial material is more likely to suffer leaching and erosion. All samples were mixed and preserved in polyethylene bags. Color was determined on humid materials using Munsell[®] Soil Color Charts. Samples were labelled SCW, SCE, and GAL representing San Cristobal West, San Cristobal East, and Galeras, respectively.



Fig. 2 Barren and severely eroded slopes of the studied tailings impoundments, showing a high density of rills and gullies

Analytical procedures

The tailings samples were air-dried and homogenized. Samples were sieved through a 2 mm stainless steel sieve to remove the >2 mm fraction. Particle size distribution was measured by standard dry sieving (ASTM 5000 series) for 2–0.063 mm fractions, in combination with a Micromeritics Sedigraph 5100 particle size analyzer

for <0.063 mm fractions. From the particle size distribution, it is possible to define D_{50} and D_{90} grain diameter and USDA texture (NRCS 1993). As is known, D_{50} is the diameter that divides the distribution of particles in half. D_{90} is the diameter for which 90 % of the distribution has a smaller particle size.

Except for the leaching tests (see below), mineralogical and chemical analyses were performed on a part of the samples which was previously ground. A routine mineralogical characterization was carried out by powder X-ray diffraction (XRD), using a PANalytical[®] X'PertPro equipment with monochromated $\text{CuK}\alpha$ X-radiation. Data were collected scanning from 3 to $62^\circ 2\theta$ with a counting time of 0.5 s per step. The minerals identification was developed considering peak areas and d-spacings using the X'Pert diffractometer software and the database ICDD. Major elements (Si, Al, Fe, Ca, Ti, Mn, K, Mg, and P) were analyzed using a PANalytical[®] MagiX X-ray fluorescence spectrometer. Na was determined using a lithium tetra borate fusion and analysis by Varian Spectra AA 220FS atomic absorption spectrophotometer. pH was measured in a 1:1 soil–water mixture with a Thermo-Orion pH-meter (Peech 1965). Total sulfur content (S_{total}) was determined by sample melting in a pure oxygen atmosphere using a elemental and infrared analyzer Eltra CS-800 with induction furnace. Determination of acid soluble S_{sulfate} was performed according to the standard EN 1744-1 (Part 1, chapter 12) (CEN 2002), by gravimetric measurement of BaSO_4 , after extraction with dilute HCl, and adding an excess of precipitating reagent (BaCl_2). The difference between both results represents the S_{sulfide} content. Total analysis of trace elements (except Hg) was performed by digestion using a concentrated mixture of HF – HNO_3 – HClO_4 heated to dryness. The residue was dissolved with HNO_3 and the concentration of the elements of interest was determined by ICP-MS (inductively coupled plasma-mass spectrometry) in an Agilent[®] 7500ce spectrometer. Total mercury was measured by the cold-vapor procedure EPA 7471A (USEPA 1994), that is: a part of the samples was digested with aqua regia (three volumes of concentrated HCl plus one volume of concentrated HNO_3), and $\text{K}_2\text{Cr}_2\text{O}_7$ was added to maintain the metal in oxidized state. The released Hg was measured using a continuous flow of cold vapor by atomic absorption spectrophotometry with a Varian Spectra AA 220FS equipment. Detection limits for the analyzed elements in tailings were ($\mu\text{g/g}$): As (0.1), Cd (0.5), Cu (0.5), Hg (0.1), Ni (1), Pb (2), Se (1) and Zn (2).

In order to study the mobility of toxic elements in water, samples were leached at a solid-to-water ratio of 1:10, as described by the European standard EN-12457-2 (CEN 2002). It was not considered necessary to make any reduction of the particle size of the tailings samples prior to the leaching. Leachates were also analyzed by ICP-MS in

an Agilent[®] 7500ce spectrometer. Detection limits for the analyzed elements in leachates were ($\mu\text{g/L}$): As (0.05), Cd (0.2), Cu (0.2), Hg (0.5), Ni (0.5), Pb (0.2), Se (0.5) and Zn (1). Electric conductivity and pH of the leachates were measured with a Crison Multimeter MM41. For the determination of anions, UV–Vis absorption spectrophotometry was used, employing an Alliance-Integral-Plus autoanalyzer of continuous flow.

During the analytical procedures, all the obtained results were assessed with an internal quality control system of the IGME labs, involving duplicates, blanks, and standard samples (ALPHA AR4017 or AR4018, for S; and Environment Canada TM-28.4, TM-27.3, TMDA-51.4, or NCS DC 73310 and DC 73319, for ICP-MS).

Results and discussion

Granulometry and mineralogy

Regarding the grain-size, SCE was finer than GAL, and GAL finer than SCW (Table 1). SCW contained only 0.017 wt% and GAL had a 0.03 wt% of particles of material larger than 2 mm size. All the particles of SCE were finer than 2 mm. SCW and GAL had loamy texture (according to USDA textural triangle). In contrast, SCE was clay-loam. The D_{50} and D_{90} values of the cumulative distribution of samples particle size are given in Table 1.

Flotation produces fine-grained wastes (sand to silt sized) known as tailings that are normally discharged as slurry to a final storage impoundment. When the waste disposal activity ceased, the tailings dry up, and the weathering processes were increased, including the oxidative dissolution of sulfides. Oyarzun et al. (2011) have provided an explanation of how certain geologic and environmental features determine that the Mazarrón host rocks do not have buffering capacity, which leads to the formation of acid mine drainage in the San Cristobal mining area. With time, an oxidation front was formed at the surface of the tailings impoundments. As a result, the studied materials offer the typical appearance of oxidized pyritic tailings, in which the color is indicative of the chemical and mineralogical alteration (Table 1): brownish yellow and olive yellow.

The mineralogical results were consistent with those obtained by Martín-Crespo et al. (2012) in surface samples of similar residues located in the vicinity. The XRD results indicate that quartz (SiO_2) was the main sample components in all the samples (Table 2). Pyrite, jarosite, and gypsum were present on the three samples. Gypsum is ubiquitous at sulfide tailings, and jarosite is normally abundant at low-pH oxidized sulfidic tailings, with acidic and oxidizing conditions (Nordstrom and Alpers 1999;

Table 1 Munsell color notation and grain-size distribution (wt%) of the studied tailings

Sample	Colour	Sand	Silt	Clay	>2 mm	D ₉₀ (mm)	D ₅₀ (mm)
SCW	2.5 Y 6/6	46.4	30.0	23.6	0.17	0.35	0.024
SCE	2.5 Y 6/8	20.8	42.6	36.6	0.00	0.16	0.003
GAL	10 Y 6/8	44.6	28.9	26.5	0.03	0.26	0.020

Sand, silt and clay fractions represent respectively: 2–0.063, 0.063–0.002 and <0.002 mm

D₅₀ and D₉₀ are the diameter at which 50 and 90 % of a sample are finer (by dry weight), respectively

Table 2 Semi-quantitative mineralogical composition of tailings samples as revealed by powder X-ray diffraction

Primary minerals	Composition	SCW	SCE	GAL
Quartz	SiO ₂	XXX	XXX	XXX
Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	X		
Microcline	KAl Si ₃ O ₈	X	X	X
Pyrite	FeS ₂	X	X	X
Secondary minerals				
Jarosite	KFe ₃ (SO ₄) ₂ (OH) ₆	X	X	X
Goethite	α-FeO(OH)	X	X	
Anhydrite	CaSO ₄	X	X	X
Primary and/or secondary				
Gypsum	CaSO ₄ ·2H ₂ O	X	X	X

The term *primary* is used to refer to the minerals present in the fresh tailings deposited in the impoundment, and secondary refers to those minerals produced by weathering processes

XXX major mineral, XX minor minerals, X trace minerals

Blowes et al. 2003). Given the gangue mineralogy, it is not possible to know whether the source of gypsum is primary or secondary. The oxidative dissolution of microcline and muscovite present in the tailings can be the origin of K⁺, which is necessary to form jarosite, as well as Fe³⁺ and SO₄²⁻ which may be of various origins. Other secondary minerals like Fe-oxyhydroxides or sulfates, which may be present, were not detected, either because the XRD technique is not sensitive enough to detect low concentrations of such minerals or because they are present as poor crystalline forms. The existence of other mineral phases in the tailings of San Cristobal, such as anglesite, Pb-jarosite, goethite, have been reported in previous studies (Oyarzun et al. 2011; Martín-Crespo et al. 2012) In dry season (from May to September), acid sulfate salts are formed on the tailings surface. Bustillo et al. (2010) examined samples of crusts which were formed on the San Cristobal West impoundment during dry season, and they identified minerals such as kieserite, halotrichite, and szomolnokite.

Bulk chemical composition

Tailings samples were mainly composed of (wt%): SiO₂ (34.88–49.80), Fe₂O₃ (23.21–27.95), Al₂O₃ (3.19–5.19), K₂O (2.39–2.87) and CaO (0.98–1.16), with a relatively

high loss of ignition (19–27 %), likely attributable to water from hydrated minerals and microbial organic matter (Table 3). Total S was ranging from 4.19 to 6.57 wt %, whereas S_{sulfate} ranged between 2.59 and 4.25 wt %. These results were in general accordance to mineralogical data. The tailings have become extremely acidic (pH from 2.30 to 2.52) and enriched in jarosite and, probably, other soluble acidic sulfates as a result of the oxidative dissolution of sulfides and the lack of sufficient neutralization capacity. However, they still contained some remains of sulfur in the form of sulfide which is identified as pyrite. At these pH values, it is expected that Fe³⁺ can remain in solution and acts as a strong oxidizing agent linked to microbial activity (Nordstrom and Alpers 1999; Blowes et al. 2003), so it can be expected the formation of more acidity.

According to the European Commission Decision 2009/359/CE, of all the elements analyzed it was taken into consideration the content of: As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, V and Zn. That Decision establishes that the human and ecological risk can be considered as sufficiently low if the content of these elements not exceed national threshold values for not contaminated sites or relevant national natural background levels. In addition, it was also taken into account the content of Sb, a highly toxic element present in

Table 3 Major elements composition (oxide analysis, wt%), pH, and sulfur forms (wt%) of the studied tailings

	SCW	SCE	GAL
SiO ₂	46.65	34.88	49.80
Al ₂ O ₃	3.53	5.19	3.19
Fe ₂ O ₃	26.59	27.95	23.21
MnO	0.14	0.26	0.07
MgO	0.00	0.05	0.00
CaO	0.98	1.16	0.98
Na ₂ O	0.19	0.30	0.21
K ₂ O	2.41	2.87	2.39
TiO ₂	0.29	0.37	0.23
P ₂ O ₅	0.18	0.16	0.13
LOI	19.03	26.80	19.79
S _{total}	4.29	6.57	4.78
S _{sulphate}	2.59	4.25	2.68
S _{sulphide}	1.70	2.32	2.10
pH	2.41	2.30	2.52

LOI loss on ignition at 950 °C

San Cristobal ore. In the proposed methodology (Alberuche del Campo et al. 2014), it was considered that the benchmark levels should be background levels set for the different Spanish regions. In this case, the background values proposed by Martínez-Sánchez and Pérez-Sirvent (2007) for the Murcia Region were employed. For comparison purposes, some contents of toxic elements obtained in volcanic soils from the vicinity of the selected impoundments are also shown in Table 4 (Oyarzun et al. 2011; Faz-Cano et al. 2009). The results for total As, Cd, Cu, Ni, Pb, and Zn were consistent with previously published data of tailings sampled in the SCW and SCE impoundments (Bustillo et al. 2010; Acosta et al. 2011). There were not regional background values for the elements Mo and V, but the measured contents were not of concern: Mo (1.36–1.64 mg/kg) and V (19.4–35.4 mg/kg). The contents of Co, Cr, and Ni in the tailings samples were below the background. By contrast, the total contents of As, Cd, Cu, Hg, Pb, Sb, and Zn were higher than the background levels. For instance, the concentrations of Hg, Zn, Cd and Sb in the SCE sample were: 142, 100, 117, and 154 times the background level, respectively. Additionally, the Pb content of GAL was more than 450 times the background level, and around 275 times in the other samples.

The transport of eroded tailings can result in sediments enriched in toxic elements. Thinking about the evident erosion of the dams and the emission of sediments to watercourses, the results were also compared to the consensus-based PECs proposed by Mac Donald et al. (2000). PEC values are the Probable Effect Concentration of several toxic elements and substances in sediments. When PEC values are exceeded, harmful effects on sediment-dwelling organisms are expected to occur frequently.

Comparing the tailings contents with the PEC values, it is clear that the elements that can generate greater concern are Zn, As, and, especially Pb. In the SCE sample, the Zn content was 12.3 times the PEC and the concentration of As was 17.1 times the PEC. The concentrations of Pb measured in the three samples were between 20 and 34.5 times the corresponding PEC.

Several researchers have used different formulas to assess the combined contamination due to various toxic elements in the surface environment. With minor variations, one of the most used is called pollution index (PI) which is usually expressed as an average of the ratios of measured metal concentrations in relation to an adopted set of soil tolerable levels for the elements of interest. For example, some universal guideline values and certain intervention values have been used for these purposes in studies about pollution of soils near tailings impoundments (Jung 2001; Kim et al. 2001; Chon et al. 2011; Arranz-González et al. 2012). The developed methodology for the systematic ranking of abandoned mining waste facilities (Alberuche del Campo et al. 2014), uses a similar index, but the reference values are the regional background levels, and only taken into account the ratios that yield a result greater than one. This index was named Index of Contamination (IC, índice de contaminación in Spanish).

$$IC = 1/n \times \sum_{i=1}^n [X]_i/BL_x$$

where $[X]_i$ is the concentration of the i th element in the sample of mine waste, BL_x is the regional background level for the element X , and n is the number of element ratios that yield a result greater than one.

The greater the value of IC, the greater is the likelihood of pollutants emission to surrounding soils and sediments,

Table 4 Total concentration (mg/kg) of trace elements measured in tailings samples and extracted in three selected references

Material	As	Cd	Cu	Hg	Pb	Sb	Zn	IC
SCW	450	3.1	45.4	4.4	2762	139.0	4524	94.6
SCE	565	14.1	45.9	7.1	2602	170.0	5652	101.5
GAL	381	5.9	43.7	5.5	4487	163.0	3254	124.5
Soil background levels ^a	8.1	0.12	18.7	0.05	9.8	1.1	55.2	
Topsoil of local volcanic outcrops ^b	83	0.3	103		181	1.9	110	
	20	0.1	21		97	0.9	58	
	15	0.5	42		201	3.3	143	
Soils on local rhyodacites ^c		0.14	33.9		31.9		32.4	
PEC ^d	33	5	150	1.1	130	25	460	

PEC probable effect concentration in sediments, IC index of contamination calculated for metals included in European Commission Decision 2009/359/CE, plus Sb (explanation in text)

^a Martínez-Sánchez and Pérez-Sirvent (2007)

^b Oyarzun et al. (2011)

^c Faz-Cano et al. (2009)

^d Mac Donald et al. (2000)

which can provide a first basis for ranking. Obviously, it is not possible to know when heavy metals mobilized as particulate matter will become available, because it will depend on the chemical conditions at the sites of deposition. The calculated IC values were in the order: 124.5 (GAL) >101.5 (SCE) >94.6 (SCW). These values can be considered representative of a very high potential toxicity and are among the highest obtained for the abandoned mining wastes inventoried in Spain. This qualification is coherent with the conclusions expressed on several works developed in San Cristobal area (Bustillo et al. 2010; Oyarzun et al. 2011; Acosta et al. 2011; Martín-Crespo et al. 2012).

Leaching behavior

Tailings subsamples were subjected to the leaching test according to European standard EN 12457-2. Although this kind of waste is not subject to the Decision 2003/33/CE of the European Council (2002), it was considered interesting the comparison of the total release results (expressed in mg/kg) with the waste acceptance criteria for landfills. When one reviews several papers published relating to this leaching test (or another equivalent like the standard DIN 38414-S4 (DIN-NORMEN 1984) it is not easy to find mining wastes which may be classified as hazardous, in accordance with the above Commission Decision (Marguá et al. 2004; Cappuyens et al. 2006; Silva et al. 2011; Levei et al. 2013). The results obtained were 1360, 3674 and 1690 mg/kg for Zn in SCW, SCE, and GAL, respectively, well beyond the limit for hazardous waste (200 mg/kg). The content of Cd also exceeds the limit for hazardous waste (5 mg/kg) in SCE and GAL samples, with values of 9.75 and 5.84, respectively. Moreover, the sulfate content measured in the leachate of SCE exceeds the limit of 50,000 mg/kg, so it should be considered dangerous for this reason.

Leaching tests results are shown in the Table 5. The table also includes a very exigent standard of water quality, whose usefulness is later explained. Leachates were extremely saline and acidic, especially SWE (EC = 3.92 mS/cm and pH 2.39, for a water/solid ratio equal to 10). The major dissolved ions in the leachates were: SO₄²⁻ (3122–5104 mg/L), Ca (556–571 mg/L), Zn (136–368 mg/L), Al (141–218 mg/L), and Fe (92–185 mg/L). These high amounts of SO₄²⁻ and metals are responsible of the formation of the mentioned sulfate minerals formed during dry periods (Bustillo et al. 2010). Nevertheless, no highly soluble mineral of Fe, Al or Zn was detected. This is probably because XRD does not have the sensibility to detect low concentrations of these metal bearing minerals or because they are present in the samples as poorly crystalline forms.

Certain high levels of total elements in the tailings samples were not reflected in the corresponding leachates. This is the case of As, Sb, and Pb. At most, the maximum percentage of arsenic released with respect to the total content was 0.5 % in SCE. Sb was insignificant in the three leachates (from 0.89 to 1.74 µg/L, i.e. 0.01–0.02 %). Likewise, Pb content of the leachate was very low or negligible, despite the very high total content. Plausible explanations of the reduced solubility of these elements can be: incorporation of arsenate by substitution for SO₄²⁻ on jarosite, and retention on goethite; incorporation of Pb into jarosite, resulting in a jarosite–plumbojarosite solid solution; and probable replacement of Fe³⁺ by Sb⁵⁺ into jarosite (Fendorf et al. 1997; Dutrizac and Jambor 2000; Savage et al. 2000; Hayes et al. 2009; Courtin-Nomade et al. 2012). Furthermore, as mentioned above, the presence of anglesite (PbSO₄) cannot be excluded, which is slightly soluble in water.

To display a first approach to the polluting potential of the samples with respect to other Spanish tailings, the results obtained from leaching test have been plotted on a diagram adapted from Ficklin et al. (1992) and (Plumlee et al. 1999), together with other different types of Spanish tailings (Fig. 3).

First, the concentration of SO₄²⁻ in the leachates was 12.5–20.4 times higher than recommended for human consumption. Furthermore, thinking on water pollution likelihood, the methodology of the Geological Survey of Spain (Alberruche del Campo et al. 2014) also put special attention to the elements included in European Commission Decision 2009/359/CE, plus Al, and Se. It uses an index inspired on the named Index of Contamination (mentioned in previous paragraphs). This new index was called “Hazard Average Quotient” (in Spanish: cociente promedio de peligrosidad, CPP). The reference values are a set of selected levels for the toxic elements listed in the decision (Table 5), and they were obtained from various sources (European Council 1998; USEPA 2002; Puura and D’Alessandro 2005; USEPA 2012). This set of reference values could be considered a very exigent standard for any possible use of water or considering the health of aquatic ecosystems. The CCP is calculated as:

$$CPP = 1/n \times \sum_{i=1}^n [X_{LEACH}]_i/WQL_x$$

where [X_{LEACH}]_i is the concentration of the ith element in the leachate, WQL_x is the water quality standard for the element X, and n is the number of element ratios that yield a result greater than one. The CCP values obtained ranged from 750.5 to 1662.7. The higher CPP value obtained in SCE impoundment could be due to a higher pyrite content (a higher S-sulfide content is noticeable in SCE impoundment), the lower pH measured in leaching tests, and the

Table 5 pH, electrical conductivity (EC, mS/cm at 20 °C), sulfates (mg/L) and selected trace elements measured in leaching tests at 1:10 solid/water ratio (EN 12457-2)

	Water standard	SCW		SCE		GAL	
		Leachate conc.	wt% released	Leachate conc.	wt% released	Leachate conc.	wt% released
Al	50 ^a	153,000	6.94	218,000	7.91	141,000	8.34
As	10 ^{a,b}	18.4	0.04	284.2	0.5	93.0	0.24
Cd	0.25 ^c	346.1	≈100	974.5	68.79	584.1	98.65
Co	20 ^d	144.0	30.64	282.3	64.68	124.1	35.83
Cu	10 ^c	1127.8	24.82	2030.7	44.25	1401.0	32.06
Hg	1 ^b	<0.5	<0.11	<0.5	<0.07	8.3	1.50
Ni	20 ^b	316.8	24.88	874.1	52.02	251.9	37.89
Pb	10 ^b	<0.2	≈0	<0.8	≈0	24.8	≈0
Se	1 ^b	13.1	12.62	27.0	12.98	11.1	11.00
Zn	120 ^c	135,981	30.06	367,395	65.00	169,000	51.94
pH	6.5–8.5 ^a	2.50		2.39		3.54	
EC		3160		3920		2870	
SO ₄ ²⁻	250 ^b	3122		5104		3214	
CPP		818.4		1662.7		750.5	

Data of water-standard and leachates of tailings in µg/L. wt% released is calculated as a percentage of the content obtained by acid digestion. CPP is calculated for metals included in European Commission Decision 2009/359/CE, plus Al and Se (explanation in text)

^a USEPA (2012)

^b Council Directive 98/83/EC (1998)

^c USEPA (2002)

^d Puura and D'Alessandro (2005)

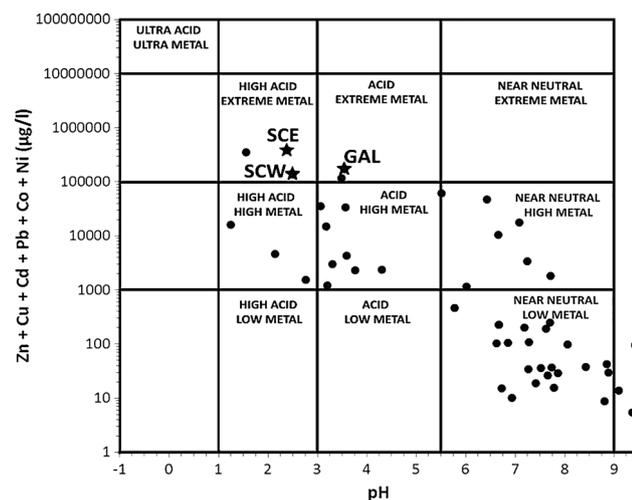


Fig. 3 Diagram showing the results of pH vs base metals (Zn, Cu, Cd, Pb, Co, and Ni) obtained by leaching (EN 12457-2) for the analyzed wastes (SCW, SCE, GAL) and for other 45 types of abandoned mine tailings in Spain (adapted from Ficklin et al. 1992, and Plumlee et al. 1999)

differences found in granulometry (notice that SCE impoundment shows the finer granulometry). These values can be considered indicative of a very high hazard of water pollution, and again they are among the highest obtained for the abandoned mining wastes inventoried in Spain. It

should be recalled that the methodology was designed to prioritize and identify the most problematic facilities in a preliminary approach, that is, these results only provide a ranking in relative terms. However, this qualification is also coherent with conclusions expressed on several works developed in San Cristobal area (Carmona et al. 2009; Bustillo et al. 2010; Martín-Crespo et al. 2012). The main elements influencing such high CPP values were Zn, Al, Cu, and Cd, and to a lesser extent: Ni, As, Co, and Se. The concentration measured in the leachates was 2820–4360 times for Al, 1384–3898 times for Cd, 1133–3067 times for Zn, and 113–203 times for Cu, with regard to the selected values. Considering the dilution of the test, the results confirm that the studied tailings have a high potential to pollute water coming into contact with them.

Conclusions

The tailings present in the Mazarrón mining area contain high concentrations of toxic elements. It is evident that erosion processes suffered by the studied tailings impoundments are severe. For this reason, it is reasonable to think that erosion processes have produced, and continue to produce, the emission of these toxic elements linked to eroded particles. According with a methodology developed

by the Geological Survey of Spain, a multi-pollutant index, named Index of Contamination (IC), was applied to the data of total content for several toxic elements: As, Cd, Cu, Hg, Pb, Sb, and Zn. These elements are those for which the measured total content was greater than the regional soil background. IC values obtained were found to be among the highest that have been calculated for Spanish mining wastes (94.6–124.5), allowing characterizing the potential toxicity of these tailings as very high.

In addition, the weathering for a period of around 40 years has generated an oxidation front in the studied tailings impoundments. As a result, the surface layers of wastes are enriched in readily soluble weathering products such as sulfate and toxic elements. The solubility of some metals in leachates obtained by the European standard EN-12457-2 was very high, especially for Zn, Al, Cu, and Cd. Furthermore, the leachates were extremely saline and acidic. An additional index Hazard Average Quotient (CCP), regarding soluble elements, was applied to leachates data, according with the aforementioned methodology of the Geological Survey of Spain. The CCP values obtained ranged from 750.5 to 1662.7, which allows characterizing the potential toxicity of these tailings as very high. The IC and CPP values obtained for the studied tailings were among the highest of the tailings inventoried in Spain.

This study has shown that there's an evident environmental hazard for soils, water, ecosystems, and people. However, this is not unique to the Mazarrón tailings, since there are numerous types of abandoned mining wastes that are more or less hazardous in Spain. Therefore, it is necessary to assess risks, even in a simple way.

It has been found that two multi-pollutant indices provided a good estimation of the potential toxicity of these wastes, using results obtained by simple analytical methods. Therefore, they can be effective tools for the systematic ranking of the pollution hazards associated to mining wastes in relative terms. This, in combination with data related to the possible consequences, such as distance from water bodies, number of people within a specified distance, land use in the vicinity, etc., helps rank mining waste facilities in a first approach to risk assessment.

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