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Critical Raw Materials recovery potential from Spanish mine wastes: A national-scale preliminary assessment

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ABSTRACT

In Spain, due to its important mining past, there are many abandoned mine waste facilities. This study evaluates the potential of Spanish mine wastes for the recovery of critical and strategic raw materials and other elements of economic relevance. For this purpose, 20 mine waste facilities have been selected in different parts of Spain based on criteria such as tonnage, element content or metal market price. Surface samples were taken at the facilities, considered representative of these, for subsequent granulometric, mineralogical and chemical analysis. The grain size data were obtained by standard sieving (ASTM 5000), while the mineralogy was obtained by X-ray Diffraction (XRD). For chemical characterization, Wavelength Dispersion X-ray Fluorescence Spectrometry (WDXRF) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were used to analyze 38 chemical elements (Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Hf, Ta, W, Tl, Pb, Bi, Th and U), many of them included in the European Union's list of Critical Raw Materials (CRMs). In addition, leachate data from mine wastes in the Iberian Pyritic Belt were analyzed to assess their bioleaching potential. The calculated enrichment factors (EF) indicate that some critical elements, as well as others with strategic and economic interest, are highly enriched in the wastes, including Sb, Bi, As, Pb, Cu, Ag, Zn, Cd, Sn, Se and Th. The most promising facilities with the highest recovery potential are located in the historic Riotinto and Tharsis mines (both in Huelva, Iberian Pyrite Belt) and the Rubiais mine in Lugo, whose tailings could contribute up to 3.2 billion dollars gross, according to the current market metal prices. This paper aims to provide a first step to promote mine waste recycling and circular mining in Spain, an initiative that would also help to mitigate the environmental damage derived from abandoned mine wastes.

1. Introduction

In the global fight against climate change, the European Union has adopted measures such as the European Green Pact and the implementation of the Ecological and Digital Transition, aimed at making Europe a fairer, more prosperous and climate-neutral region, with the year 2050 as a timeframe. These actions imply a shift from a dependence on fossil fuels to dependence on certain raw materials for the so-called *green technologies*. Taking into account that the scarcity of these raw materials could jeopardize the development of these new clean and efficient technologies, the European Commission updated, in 2020, the list of Critical Raw Materials (CRMs) for the European industry, including a total of 30 minerals (Communication COM/2020/474 final, 2020), a number that has been raised to 34 in its most recent update (European Commission, 2023), with the incorporation of minerals such as copper, nickel and arsenic. With the current global geopolitical scenario, the availability of these critical raw materials, as well as in other elements of strategic interest, has become an important issue for industrialized countries. The European Commission has raised the need to ensure that Europe has access to reliable sources of supply of these elements. In this sense, Spain and the European Union are particularly

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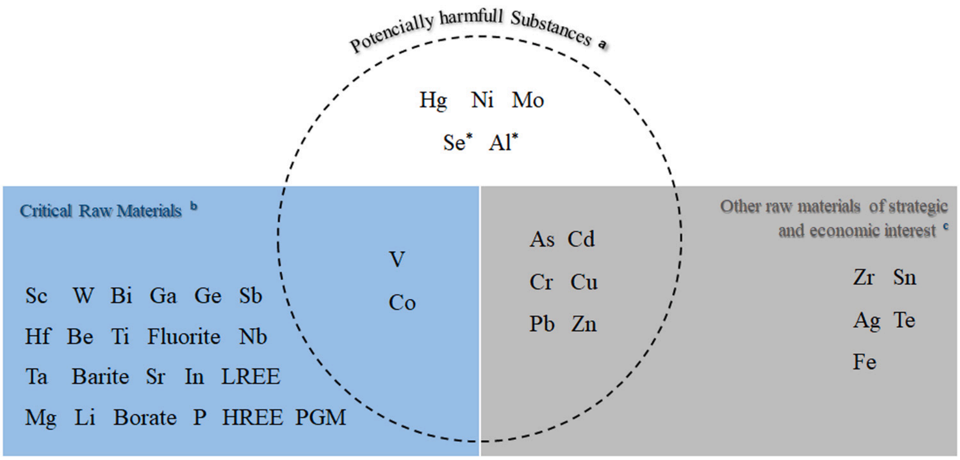

Fig. 1. Relationship diagram of potentially toxic elements within the group of critical and strategic raw materials. [a] Commission Decision 2009/359/EC (2009); [b] Communication COM/2020/474 final (2020); [c] European Commission (2020). * Substances added to the list in Commission Decision 2009/359/EC due to their proven toxicity.

dependent, as they need to import a large part of critical raw materials for their industry, an issue that has been raised for decades (Risch, 1978). However, it should be noted that Spain is also a country with a remarkable mineral wealth and a wide variety of potentially exploitable mineral resources.

The growing industrial demand for these CRMs, necessary for the development of new clean and efficient technologies, as well as the need to ensure a stable supply and the commitment made by the European Union to promote a circular economy, have led many European countries to give increasing attention to mine wastes, which are being introduced into the search circuit for secondary raw materials and, in particular, critical and/or strategic raw materials. In this regard, the European Commission produced a report on recovery of critical and other raw materials from mining waste and landfills (European Commission and Joint Research Centre, 2019). Millions of tons of minerals are extracted globally every year, which generates enormous amounts of mine wastes, mostly composed of sludges resulting from metallurgical processes such as flotation and tailings and minerals accompanying the metals or minerals of interest. It has been estimated that about 1.15 billion tons of metals (Cu, Pb, Zn, Fe, Cd and Cr) have been extracted since the emergence of primitive mining in the Stone Age (Sheoran and Sheoran, 2006). The global mine wastes market reached 189 billion tons in 2021 and it has been estimated that by 2027 a total volume of 255 billion tons will be generated worldwide (Research and Markets, 2022). For its part, Spain generated 41.8 million tons of mine wastes in 2020, according to the latest data offered by the National Institute of Statistics (INE) (INE, 2022). Mine wastes may present significant contents of substances included within the current list of CRMs (e.g., Co, Bi, V, Sb and Ta). In addition, they may contain other substances that, although not considered critical, are of interest as secondary raw materials and/or with strategic interest (e.g., Cu, Zn, Ni, Ag). Closed and abandoned mine waste facilities are also a major concern in Europe, as they often contain high concentrations of toxic elements (e.g., As, Cr, Pb and Cd), whose mobility and dispersion can pose an environmental hazard to soils, water, ecosystems and people. In fact, some of the potentially toxic elements are part of the CRMs (Fig. 1). Therefore, the use of waste, in addition to being in line with a circular economy model, offers the possibility of reducing the risk that the facilities pose to the environment and people's health, and can partially cover the costs of rehabilitating these abandoned facilities. Although reserves of these elements from mine wastes are not expected to meet current and future demand, they could help reduce the current heavy dependence of many European countries on the world's major CRMs exporters, led by China.

The investigation of mine wastes for re-mining is not new (e.g., Collings, 1978; Collins and Miller, 1979; Rampacek, 1982). However, in recent years mine wastes have gained more relevance (e.g., Ceniceros-Gómez et al., 2018; Fortes et al., 2021; Šajn et al., 2022; Villa-Gómez et al., 2022; Žibret et al., 2020), because they can represent an alternative source of critical and strategic raw materials, due to the large amounts of these elements. In addition, it is presently considered that their reprocessing is technically feasible with the currently available technologies of mineral processing (e.g., Ait-Khouia et al., 2021; Whitworth et al., 2022; Yin et al., 2018). Being already mined and crushed materials, the processing of secondary raw materials from mine wastes usually involves a notably lower cost compared to their extraction from a primary deposit that can be found even at great depth (Kinnunen and Kaksonen, 2019). According to some researchers (e.g., Marín et al., 2022), the cost of reprocessing tailings can be 40% lower compared to the primary sources. In addition, the application of physical separation techniques (which are efficient, less expensive, and more ecofriendly with respect to other techniques such as flotation) could help to further reduce the cost of mine waste reprocessing (Ait-Khouia et al., 2021). This often makes circular mining economically attractive. In addition, mine wastes can be found enriched with metals that were once not considered for utilization (e.g., rare earth elements, gallium or hafnium) and nowadays, given their increased value and utility, their recovery becomes more feasible (Falagán et al., 2017). Currently, there are several outstanding research projects on the re-mining of mine wastes in Europe, in which Spain is participating: RAWMINA (https://rawmina.eu/), NEMO (https://h2020-nemo.eu/), ETN SULTAN (https://etn-sultan.eu/), COCODRILE (https://h2020-crocodile.eu/), or TARANTULA (https://h2020-tarantula.eu/). As a particular case in Spain, the project for the recovery of tantalum and niobium from the mine wastes of the old Penouta mine, located in the central area of the Iberian Peninsula, is currently underway (European Commission and Joint Research Centre, 2019; Magdalena et al., 2021). The efficient use of mineral resources and the promotion of recycling that the European Union has set as objectives can be achieved in the mining industry if a circular economy model can be implemented. The recovery of critical elements from mine wastes represents a step in that direction, helping to minimize and reduce the use of resources through the recycling and reprocessing of wastes, moving from a linear to a circular economy (Cisternas et al., 2022; Kinnunen and Kaksonen, 2019).

This research work reviews the existing information obtained in works developed by the Geological Survey of Spain (IGME) in the last four decades (1983–2023) on the abandoned mine waste facilities existing in Spain, along with their chemical and mineralogical characteristics, which have been more comprehensively studied during the last ten years. The objective of this work is the evaluation of the potential of these mine wastes for CRMs recovery, although strategic

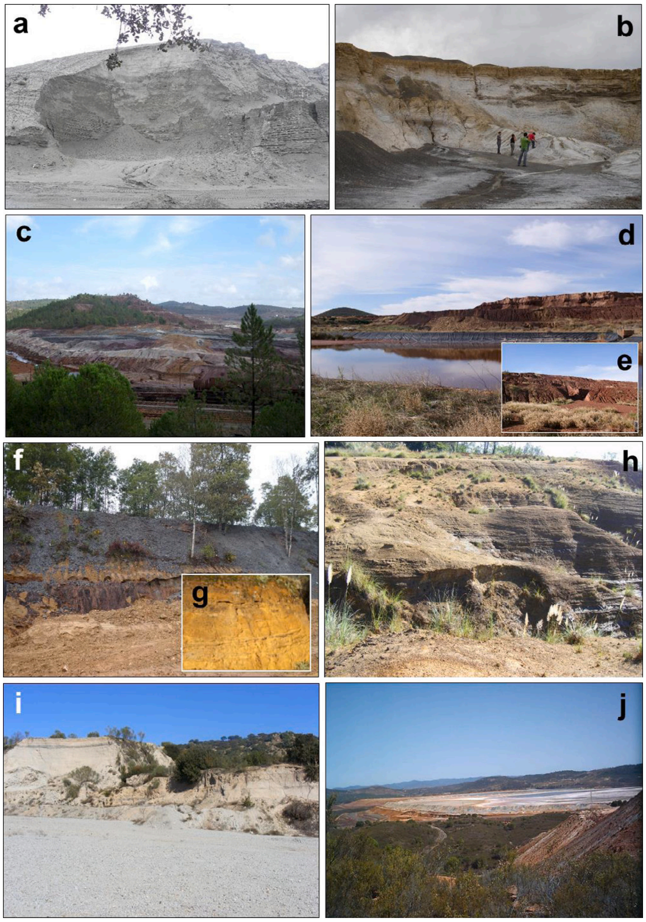

Fig. 2. Examples of existing tailings impoundments in different mines in Spain (in each case the metals extracted and the location are indicated): **(a)** El Soldado (Pb-Zn; Córdoba); **(b)** San Quintín (Pb-Zn-Ag; Ciudad Real); **(c)** Zarandas-Naya, Nerva (Cu-Zn-Pb-S-Au-Ag; Riotinto Mines, Huelva); **(d)** Leaching pile in Tharsis mine (Cu-Zn-Pb-S-Au-Ag; Iberian Pyrite Belt, Huelva) with inset **(e)** showing the internal structure; **(f)** Mina Touro (Cu; Galicia) with deailed view of the internal lamination of the tailings **(g)**; **(h)** La Luciana (Pb-Zn; Cantabria); **(i)** Casa de la Liebre (Pb-Zn; Jaén); **(j)** Riotinto main tailings (Cu-Zn-Pb-Au-Ag; Huelva).

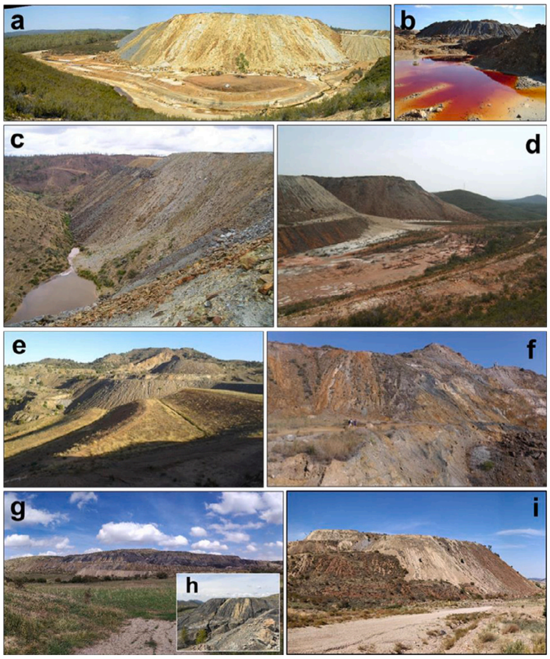

Fig. 3. Examples of spoil heaps located in different mines in Spain (in each case the minerals extracted and the location are indicated): **(a–b)** different waste rock piles in San Telmo mine (Cu-Zn-Pb-S-Au-Ag; Huelva); **(c–d)** waste piles in Aznalcóllar mine (Cu-Zn-Pb-S-Au-Ag; Sevilla);**(e–f)** spoil heaps in La Unión mining district (Zn; Murcia); **(g)** María coal mine (Teruel) with inset **(h)** showing details of erosion features; **(i)** mine in Ojos Negros (Fe, Teruel).

and other economically relevant raw materials are also considered. We selected the facilities with the highest potential for re-mining (20 facilities selected from a pool of 7162) to carry out a complete characterization (chemical, mineralogical, granulometric) of the mine wastes. The study identifies the most promising mine waste facilities from the point of view of CRMs recovery and other elements of interest, in addition to the social or environmental interest that would involve the reduction of risks that should be associated with a possible exploitation. The selected facilities should be subjected to further detailed studies (e.g., drilling, pilot-scale metallurgical assays) in order to determine the actual reserves and the most suitable processing technologies for recovery at a particular facility.

2. Materials and methods

2.1. Overview of mine waste facilities in Spain

In Spain, due to its important mining past, there are 21,673 mine waste facilities, including sludge tailings impoundments and leachate piles (the latter being a very small minority) (Fig. 2), and spoil heaps (Fig. 3) (Rodríguez-Pacheco and Gómez de las Heras, 2006).

Spain has a national inventory of mine waste facilities carried out by the IGME between 1983 and 1989, which includes some 7162 mine waste structures from different types of mining, of which 674 correspond to tailings impoundments, a figure that rose to 988 with the update of the National Inventory of Mine Tailings Impoundments between 1999 and 2002, the rest being spoil heaps (IGME, 1989; Rodríguez-Pacheco and Gómez de las Heras, 2006). These 7162 mine waste structures were characterized and their information is available in technical data sheets (IGME, 1989). These data sheets include relevant information on the facilities, such as location, main geometric parameters, volume, site typology, size, etc., as well as an evaluation of geotechnical instability processes and environmental impact. The structures inventoried, including the tailings impoundments (Fig. 4(a)) and the spoil heaps (Fig. 4(b)) from metallic mining, coal and industrial minerals are the most suitable to investigate for CRMs recovery potential, due to their high probability of still containing part of the originally exploited minerals.

2.2. Data and selection criteria for mine waste facilities

Much of the data used in this research comes from the national inventory of abandoned mine waste facilities with short or medium term risk to human health and the environment, which complies with Article 20 of the Spanish Directive 2006/21/EC (Royal Decree 975/2009, 2009) on the management of waste from the extractive industries, and which currently has some 109 facilities inventoried throughout Spain (Ministerio para la Transición Ecológica y el Reto Demográfico (MITERD), 2022; Macho-Jiménez et al., 2014). The compositional information and characterization of these wastes were obtained from the analysis of mostly composite samples taken from the surface of each facility. Spot samples were taken at some facilities. Information is also available on the location, volume/tonnage and date of waste.

Composite sampling was carried out by the method proposed by Hageman and Briggs (2000) and Smith et al. (2000), which was designed for the general characterization of abandoned mine waste facilities for contamination risk assessments. This model consists of taking

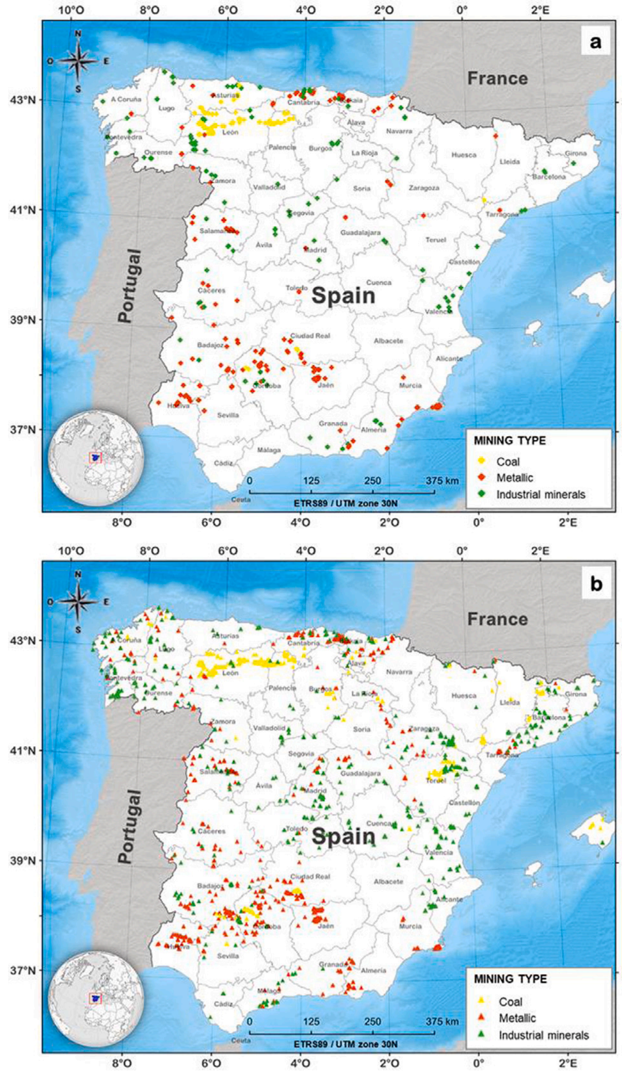

Fig. 4. Distribution of the locations of mine waste facilities in Spain: **(a)** Tailings impoundments; **(b)** Spoil heaps.

samples composed of thirty or more increments, obtained from the uppermost 20 centimeters of a given mine waste facility. A similar model proposed by Stewart and Daniels (1992) was followed for the characterization of the spoil heaps, extracting the sample by digging down to 10 or 15 cm from the surface. According to Roberts et al. (1988), the fraction smaller than 2 mm governs the soil solution chemistry, even if it only represents 21 to 35 wt%. In addition, this fraction encompasses most of the surface reactive chemical potential of mine waste facilities (Smith et al., 2000). However, from the mine waste recovery point of view, this fraction may contain valuable mineral species. Therefore, whenever possible, samples were sieved in the field with a ⌀2 mm mesh size sieve, although the vast majority of flotation residue samples pass through this sieve. When it was not possible to sieve in the field, the operation was performed in the laboratory. The coding assigned to each sample was the same as that used to identify its source facility. This code, assigned to the 7162 facilities inventoried by the IGME (IGME, 1989), is composed of several numberings separated by dashes, which were generated from the location of these facilities. For example, for coding 959-I-4-001, the first two numberings (959-I) indicate the sheet number of the National Topographic Map, scale 1: 25,000 (MTN25) of Spain (IGN, 2023), followed by the numbering indicating the quadrant of the map (from 1 to 4) in which the facility is located and, finally, the last numbering indicates an order number, assigned according to the route established in the office or field and the number of structures that may be within each sheet of the map.

As a general criterion, the selection of mine waste facilities for this study was based on choosing facilities that met the following characteristics, according to Šajn et al. (2022): (1) waste volume greater than 0.5 million tons, (2) promising chemical composition (meaning the presence of critical and strategic metals in the wastes, and whose concentrations exceed significantly their Clarke), and (3) being in an inactive, abandoned or unrehabilitated state, where old flotation methods were used and where there is a possibility of applying new and more efficient recovery methods.

As additional and important parameters to consider the potential of the mine waste facilities in this study, the granulometric (grain-size distribution) and mineralogy (identification of major mineral phases) of the mine wastes were analyzed. Although they were not considered as selection criteria, they are presented as relevant information, since both aspects have considerable influence on the design of recovery methods. Both granulometric and mineralogical information are key aspects to consider in two common treatment processes, flotation and bioleaching, in metallic mining.

2.3. Sample analysis

2.3.1. Grain size analysis

The complete granulometric (grain-size distribution) analysis of the mine waste samples, was carried out by standard sieving (ASTM 5000) for fractions between 2 and 0.063 mm. A Sedigraph 5100 particle size analyzer was used to determine the percentage of grain sizes lower than 0.063 mm and down to 0.0006 mm.

2.3.2. pH and electrical conductivity measurements

For the determination of pH and electrical conductivity, mine waste leachates were previously prepared at a ratio of 10 L of distilled water per kg of waste, according to the EN12457-2 method (“Characterization of waste leaching – Compliance test for leaching of granular waste materials and sludges – Part2”): One-stage bach test at liquid to solid ratio of 10 L/kg materials whith high solid content and with particle size below 4 mm (without or with size reduction). Subsequently, pH and electrical conductivity were both measured by Electrometry (Methods PTE-AG-001 Ed.5 and PTE-AG-002 Ed.6, respectively. Both are internal methods of the IGME water laboratory).

2.3.3. Mineralogical and chemical characterization

Qualitative mineralogical analysis was conducted by X-ray Diffraction (XRD) using the crystalline powder method in a PANalytical X’Pert Pro equipment with copper tube, graphite monochromator and automatic slit. The software used for species identification was X'Pert Data Collector with the ICDD database.

For the chemical characterization of the mine waste samples, the major elements (Si, Al, Fe, Ca, Ti, Mn, K, Mg and P) were determined in a fused bead with lithium tetraborate, sample:flux ratio (0.3:5.5) and measured by Wavelength Dispersion X-ray Fluorescence Spectrometry (WDXRF) with a PANalytical MagiX equipment with rhodium tube. Sodium was determined by Atomic Absorption Spectrophotometry (AAS) VARIAN FS-220 with lithium metaborate fusion and sample:flux (0.2:0.7).

Trace elements were determined by Inductive Coupled Plasma Mass Spetrometry (ICP-MS) and WDXRF. In the first case, Be, V, Cr, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb, Th and U analyses were preceded by digestion of the sample with concentrated HF, HNO_3 and $HClO_4$ to dryness and dissolution of the residue with HNO_3 6%. These measurements were carried out with an Agilent 7500ce equipment. Regarding the WDXRF analyses, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Hf, Ta, W, Tl, Pb, Bi, Th and U where analyzed in pressed pellets prepared with Elvacite®. Measurements were performed with a PANalytical MagiX instrument using SuperQ software and Pro Trace HR application.

2.3.4. Leachate analysis

The chemical composition of leachates emerging from 25 different mine waste facilities of the Iberian Pyrite Belt (IPB) mining district was obtained from Sánchez-España et al. (2005). These leachates were analyzed by AAS (flame operation, VARIAN FS-220) for major metal cations (e.g., Mg, Fe, Cu, Mn, Zn and Al) and by ICP-MS (ALLIANCE Integral Plus) and/or ICP-AES for trace metals (e.g., Be, Ni, Se, As, Ba, Cd, Co, Cr, Mo, Pb, Sb, U and V).

2.4. Calculation of enrichment factors

To evaluate the potentiality of the chemical elements present in the mine wastes analyzed in this study, the enrichment factor (EF) (Chester and Stoner, 1973; Zoller et al., 1974) was calculated as a tool to identify the elements that are enriched in the mine waste facilities. The general equation used to calculate the EF (Khalil et al., 2013; Li and Feng, 2012; Martínez et al., 2007) was simplified to evaluate the enrichment of the wastes as a potential ratio (Villa-Gómez et al., 2022), which indicates how many times the concentrations measured in the mine wastes exceed some established average reference values, leaving the expression:

$$EF = \frac{EL_{(\mathrm{sample})}}{EL_{(\mathrm{UCC})}} \tag{1}$$

where $EL_{(\mathrm{sample})}$ corresponds to the concentration of a given element in a mine waste sample (expressed in mg/kg or g/t) and $EL_{(\mathrm{UCC})}$ corresponds to the average concentration of that element in the earth's crust, also called Clarke and usually referred to the Upper Continental Crust (UCC). In this study, the average crustal abundance of the chemical elements were taken from Rudnick and Gao (2014). In order to get a local view of the enrichment in these facilities, this EF was also calculated using the background values for Spanish sediments as a reference. In this case, the median values of total contents in stream sediment samples ($n = 14{,}864$) were chosen as geochemical background levels (Locutura Rupérez et al., 2012). For the calculation, $EL_{(\mathrm{UCC})}$ was replaced by $EL_{(\mathrm{background})}$ in Eq. (1).

3. Results and discussion

3.1. Selected mine waste facilities

As mentioned above, the first inventory of mine waste facilities, carried out between 1983 and 1989, included non-intensive data from 21,673 mine waste facilities (including all active, closed or abandoned tailings impoundments, spoil heaps and leachate piles) throughout Spain. Subsequently, between 1989–2002, 7162 of these facilities (considered the most representative) were selected and more information was collected. In the most recent inventory (the "*National Inventory of Abandoned Mine Waste Facilities with Short- or Medium-Term Risk to Human Health and the Environment*"), carried out from 2012 to the present, more than 109 facilities of the previous 7162 have been selected and investigated, under criteria such as their volume, type of mining and environmental risk. In this work, according to the established criteria, among the more than 109 mine waste facilities inventoried to date, a total of 20 facilities have been selected, located in different provinces of Spain (Fig. 5). These facilities met at least two of these criteria and one or more samples (23 samples in total) were available from each them. Three of the 21 facilities are represented by two samples. Table 1 presents the basic data of the selected facilities, including location, type of facility, type of mining of origin, surface area, volume of mine wastes, estimated tonnage, quantity and type of samples per facility.

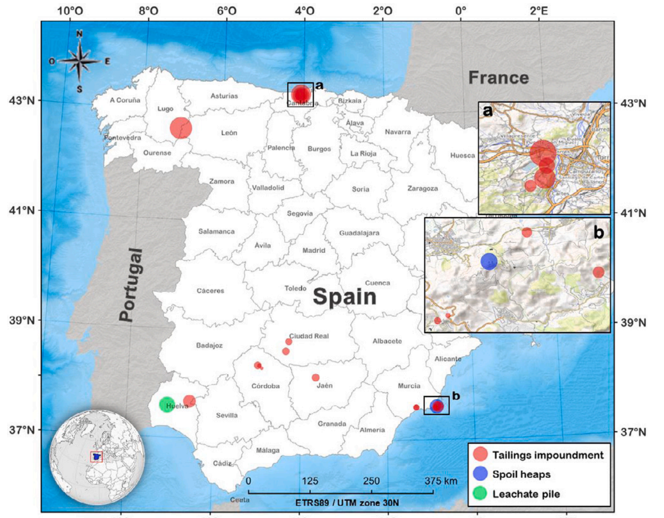

Fig. 5. Location of mine waste facilities characterized in this study. The size of the circles is representative of their volume.

3.2. Grain size distribution

Since the metal recovery efficiency is usually highly dependent on grain size of the target carrier minerals (Gupta and Yan, 2016; Petruk, 1995), the grain size distribution provides extremely useful information in any mining project focused on the reuse of mine wastes. For some cases, it may be necessary to determine the appropriate particle size to achieve for the application of a particular recovery method to the mine waste. The grain size distribution curves generated for 22 samples (Fig. 6(a)) shows the same trend for almost all the curves, which is consistent with the fact that all the samples were taken from tailings impoundments and, therefore, these wastes were subjected to the same extraction method (flotation) and resulted in similar grain sizes of the produced sludge (Bulatovic, 2007; Pease et al., 2010).

Due to the initial sieving (⌀2 mm) carried out in the field, with subsequent discarding of the material > 2 mm in the samples, the spoil heap sample 977-II-4-100 was significantly altered in terms of its grain size distribution, since in this type of structures, the percentage of material > 2 mm can be very important. Therefore, the granulometric information corresponding to this waste spoil heap sample has been disregarded in this study.

The particle composition of the different samples analyzed (Fig. 6(b)) shows some variability. Most of them, with the exception of the sample corresponding to facility 959-I-4-001, have very little or practically no gravel content (grain size > 2 mm). The average sand values (< 2 mm and > 0.02 mm) are slightly below 55%. The mean values of silt content (< 0.02 mm and > 0.002 mm) do not reach 30% while clay contents (< 0.002 mm) are slightly below 15%. The results of the textural classification, according to USDA classification, of the 22 samples (Fig. 6(c)) indicate that the most abundant textures were sandy clay loam (7 of the 22), loam (5 of the 22) and sandy loam and sandy clay loam (3 of the 22). In general, the loamy textures (crumbly residues of certain plasticity) dominate among these mine wastes, with 19 of the 22 samples showing this characteristic, and sandy fractions abounding in 15 of the 22 samples.

The parameters D_{50} (mean grain diameter) and C_u (coefficient of uniformity) of particle size distribution were obtained for the 22 samples analyzed (Table S1). The obtained D_{50} present values ranging from 0.004 to 0.20 mm, with an average of 0.057 mm, indicative of the predominance of sandy-type waste in most of the facilities. Similarly, the obtained C_u values varied between 3.4 and 194.4, with an average of 53.9; indicative of mine wastes that are not very homogeneous terms of grain size distribution. This poor grain sorting may suggest a variable efficiency of the flotation process in the former plants.

Table 1
Location, mining type, surface, volume, tonnage and other basic information of mine waste facilities selected in this study for evaluation of their CRMs recovery potential.

Province	Code waste facilities	Type of facilities	Status facilities	Mining type	Locality	X UTM	Y UTM	Zone	Surface area (m^2)	Volume (m^3)	Estimated tonnage (Mt)	Number of samples	Sample type
Ciudad Real	809-II-1-001	Tailings impoundment	Abandoned	Metallic (Pb-Zn-Ag)	Villamayor de Calatrava	388077	4296959	30	92,620	270,000	0.46	1	Composite surface
	835-II-1–001	Tailings impoundment	Abandoned	Metallic (Pb-Zn)	Almodovar del Campo	382160	4277163	30	24,200	328,000	0.56	1	Composite surface
Córdoba	858-IV-3–004	Tailings impoundment	Abandoned	Metallic (Pb-Zn)	Villanueva del Duque	324805	4248584	30	42,170	320,000	0.54	1	Composite surface
	858-IV-3-002	Tailings impoundment	Abandoned	Metallic (Pb-Zn)	Alcaracejos	327948	4247659	30	41,250	70,000	0.12	1	Composite surface
	880-II-2–001	Tailings impoundment	Abandoned	Metallic (Pb-Zn)	Alcaracejos	332954	4242928	30	15,370	50,000	0.10	1	Composite surface
Jaén	905-II-1-012	Tailings impoundment	Abandoned	Metallic (Pb-Zn)	Linares	442763	4223572	30	18,000	360,000	0.61	1	Composite surface
Huelva	938-IV-4-002	Tailings impoundment	Abandoned	Metallic (Cu)	Nerva	715216	4172364	29	81,787	1,200,000	2.04	2	Composite surface
	959-I-4-001	Leachate Pile	Abandoned	Metallic (Au)	Alosno	670264	4162502.1	29	670,000	2,000,000	3.40	1	Composite surface
Murcia	976-II-3-005/006	Tailings impoundment	Abandoned	Metallic (Pb-Ag)	Mazarrón	647588.65	4162725.27	30	20,460	160,000	0.27	2	Composites surfaces
	976-II-3–007	Tailings impoundment	Abandoned	Metallic (Pb-Ag)	Mazarrón	647320	4162804	30	18,180	180,000	0.31	1	Composite surface
	977-II-4–100	Spoil heaps	Abandoned	Metallic (Pb-Zn)	La Unión	688856	4165037	30	54,600	400,000	0.68	1	Composite surface
	978-I-1–009	Tailings impoundment	Abandoned	Metallic (Pb-Zn)	Cartagena	690166.4	4166370.12	30	49,210	600,000	1.02	1	Spot surface
	978-I-3–026	Tailings impoundment	Abandoned	Metallic (Pb-Zn)	La Unión	692748.5	4164646.43	30	74,200	750,000	1.28	1	Composite surface
	977-II-4–041	Tailings impoundment	Abandoned	Metallic (Pb-Zn)	Cartagena	687458.8	4162590.07	30	30,370	170,000	0.29	1	Composite surface
	977-II-4–043	Tailings impoundment	Abandoned	Metallic (Pb-Zn)	Cartagena	687092	4162354.5	30	24500	300,000	0.51	1	Composite surface
Cantabria	34-III-4-001	Tailings impoundment	Abandoned	Metallic (Zn)	Torrelavega	412910.4	4800702.98	30	157,300	3,200,000	5.44	1	Composite surface
	34-III-4-002	Tailings impoundment	Abandoned	Metallic (Zn)	Torrelavega	413114.4	4799739.8	30	124,600	1,250,000	2.13	1	Composite surface
	34-III-4-003	Tailings impoundment	Abandoned	Metallic (Zn)	Cartes	412180.3	4798205.33	30	79,000	700,000	1.19	1	Composite surface
	34-III-4-006	Tailings impoundment	Abandoned	Metallic (Zn)	Cartes	412994.88	4798784.70	30	160,000	2,125,000	3.61	1	Composite surface
Lugo	125-III-4-001	Tailings impoundment	Abandoned	Metallic (Pb-Zn)	Pedrafita do Cebreiro	660459	4726099.00	29	328,141	4,000,000	6.80	2	Composite surface

Mt—Million tons.

3.3. pH and electrical conductivity

The pH and electrical conductivity values of the 23 samples analyzed in this study (Table S2) range from 1.12 to 9.15, showing a great diversity from very acidic solutions (e.g., coming from acid-generating minerals such as those derived from sulfide oxidation) to alkaline ones (derived from minerals such as carbonates which are also present in some types of wastes). Similarly, electrical conductivity (EC) values ranging from 3.87 to 10,670 μS/cm were observed (Table S2). Due to the low number of samples ($n < 30$), Spearman's and Pearson's correlation has been applied in order to determine the existence of relationship between pH and EC variables. The values obtained ($R_s = 0.39$ and $R^2 = 0.42$; not shown) indicate little correlation between both parameters, which is ascribed to the very diverse origin and mineralogical nature of the studied mine wastes.

3.4. Mineralogical composition

Most of the wastes selected in this study were produced in copper, zinc, lead, silver and coal mines. Thus, it was expected that the characteristic minerals predominating in the mineralogy of the tailings were also similar and coincident with those dominating the mineral paragenesis of the primary ores. The mineralogical compositions obtained for the mine waste samples (Table S3) point to a predominance of silicates and aluminosilicates (e.g., quartz, feldspars, illite/muscovite, chlorite) and sulfides (e.g., pyrite). Sulfates (e.g., gypsum, anhydrite, jarosite, barite) and carbonates (e.g., calcite, dolomite) are also common. The latter two are considered primary minerals (i.e., abundant in the host rocks of the former ore mineralizations) and responsible for the highest pH values measured in certain wastes. The sulfates, on the other hand, are common secondary minerals in many mine tailings where primary sulfide ores are oxidized and sulfate-rich acidic solutions ascend by capillarity and evaporate near the surface (Dold, 2002). Other minerals detected in minor proportions include sulfides like marcasite, sphalerite and chalcopyrite, which denote remnants of non-recovered ore minerals in the flotation process, and oxides like goethite and scorodite, which are likely secondary minerals formed by sulfide oxidation.

3.5. Metal contents

Major elements (expressed as oxide content %) were obtained for the analyzed samples and compared with their average cortical concentration (Table 2). Most of the samples present iron oxide values above the cortical mean. Some samples also show high titanium oxide concentrations that could be considered as potentially usable (Schulz et al., 2017).

The total concentrations (in mg/kg) of twenty-nine trace elements is given in Table S4. We discarded nine elements (Sm, Ni, Ge, Rb, Br, Mo, I, Cs, and U) because they were very close to or below the detection limits of the analytical technics used in all the samples. Thirteen elements given in Table S4 are included in the current European Union's CRM list, considering the rare earth elements (REE) analyzed here as a single unit, and the remaining twelve are presented as raw materials of strategic and economic interest. As an analysis parameters, the average cortical concentration and Spanish background concentrations of each element is presented. Some facilities have significant concentrations of CRMs. For example, facility 905-II-1-012 (located in Jaén) contains the highest concentration of Sc (201 mg/kg), W (151 mg/kg) and Sb (6288–10,241 mg/kg); facility 880-II-2-001 (located in Córdoba), contains the highest concentration of Co (239–321 mg/kg), while facility 938-IV-4-002 (situated in Huelva) contains the highest concentration of Bi (347–738 mg/kg) and Ba (4799–19,212 mg/kg) respectively. Finally, facility 858-IV-3-004 (in the province of Córdoba as well) contains 77 mg/kg of Hf, being the one with the highest concentration of this element. Despite containing high concentrations of different elements with economic interest, their potential utilization will depend on several factors, including the volume of mine wastes stored in these facilities. In contrast, most facilities have low contents of Nb, Be, Zr and Cr. Because zirconium and chromium are necessary materials for the development of *green technologies* (though not considered as CRMs, European Commission, 2020) these two elements are also analyzed in this study despite their low concentrations.

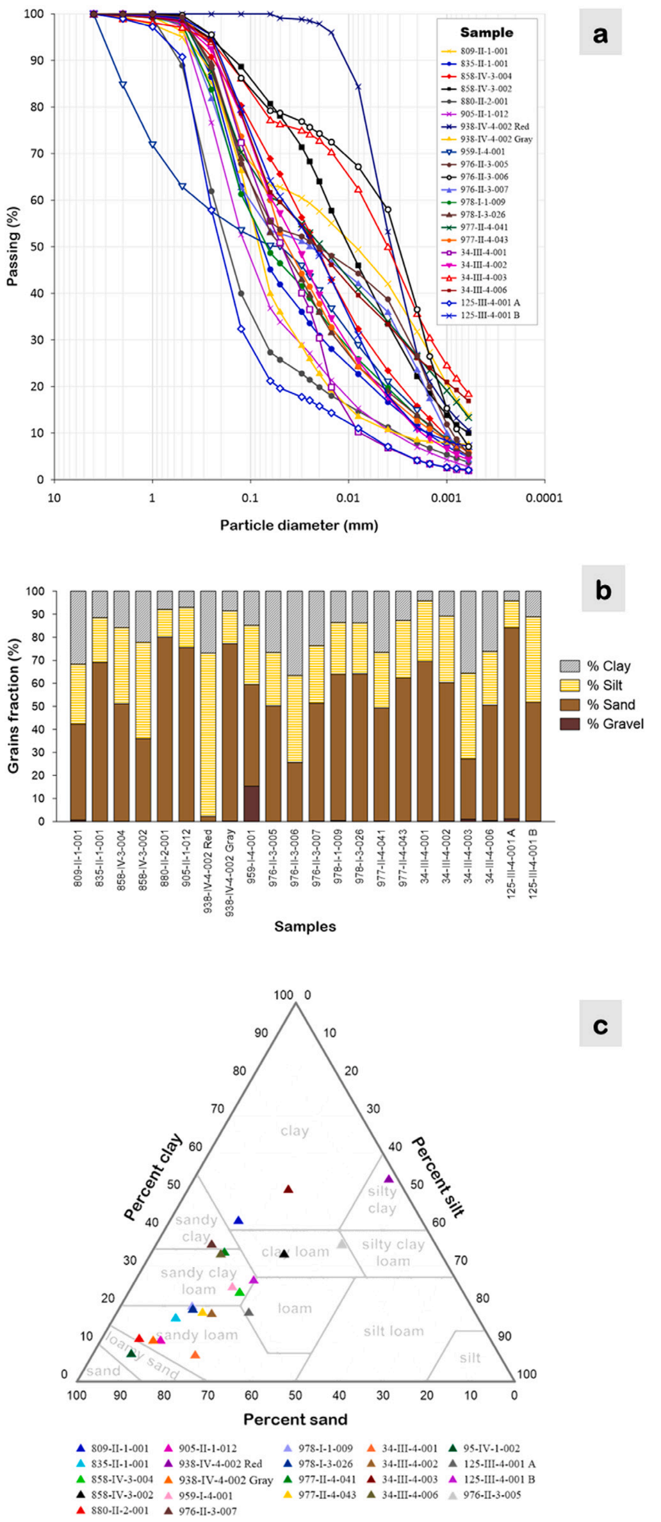

Fig. 6. Granulometric characterization of mine waste samples: **(a)** Grain size distribution curves; **(b)** Grain size distribution between clay, silt, sand and gravel fractions; **(c)** USDA Textural Classification.

Table 2
Major element oxides content (%) in selected mine waste samples.

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	MnO	K_2O	MgO	P_2O_5	Na_2O	LOI
QL	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05	<0.10	<0.10	<0.045	<0.067	
809-II-1–001	59.40	10.82	8.34	1.34	0.53	<QL	2.62	0.85	0.14	0.19	10.11
835-II-1–001	66.30	12.60	5.47	1.59	0.82	0.12	2.61	2.50	0.19	0.81	5.70
858-IV-3–004	50.00	10.90	6.26	5.76	0.53	0.32	2.17	3.95	0.13	0.28	12.08
858-IV-3-002	51.60	14.50	5.42	2.78	0.73	0.15	2.67	2.39	0.13	0.30	8.89
880-II-2–001	73.40	9.40	2.89	2.19	0.50	0.13	2.07	1.85	0.09	0.24	5.40
905-II-1–012	61.92	6.36	2.02	11.84	0.24	0.13	2.11	0.66	0.09	0.64	9.83
938-IV-4-002 Red	16.75	3.61	38.39	1.93	0.40	<QL	0.83	0.73	0.11	0.14	30.57
938-IV-4-002 Gray	27.57	0.50	43.42	<QL	<QL	<QL	<QL	<QL	<QL	<QL	23.84
959-I-4–001	40.32	7.02	41.09	1.28	0.79	<QL	0.90	0.52	0.15	0.35	7.57
976-II-3–005	49.80	3.19	23.22	0.98	0.24	0.07	2.39	<QL	0.13	0.21	19.79
976-II-3–006	34.88	5.19	27.95	1.16	0.37	0.26	2.87	<QL	0.17	0.30	26.80
976-II-3–007	46.65	3.53	26.59	0.98	0.29	0.14	2.41	<QL	0.18	0.19	19.03
977-II-4–100	33.01	7.53	34.30	1.99	0.80	0.77	0.24	1.77	0.11	0.07	12.93
978-I-1–009	24.51	3.07	41.23	3.34	0.24	1.31	<QL	2.16	<QL	0.35	16.76
978-I-3–026	55.06	7.08	15.80	3.59	0.48	0.26	0.28	2.84	0.08	3.60	0.48
977-II-4–041	41.44	9.55	21.82	3.31	0.49	0.44	0.83	2.27	0.25	0.44	14.03
977-II-4–043	39.86	6.75	19.22	8.67	0.46	0.54	0.73	2.23	0.13	0.28	11.72
34-III-4-001*	0.84	0.19	14.02	25.03	<QL	0.23	<QL	13.77	<QL	<QL	37.10
34-III-4-002	1.87	1.02	18.10	22.61	<QL	0.22	<QL	11.59	<QL	<QL	32.21
34-III-4-003	47.34	10.37	25.10	0.12	0.57	1.08	1.66	0.44	0.16	0.19	10.53
34-III-4-006	57.90	8.90	8.78	5.15	0.55	0.09	1.88	3.02	0.06	0.16	11.71
125-III-4-001 A	59.38	8.13	4.42	6.56	0.43	0.23	2.70	2.90	0.21	0.50	9.78
125-III-4-001 B	58.66	11.77	3.12	6.42	0.62	0.15	3.85	2.46	0.24	0.77	9.39
UCC[a]	66.62	15.4	5.04	3.59	0.64	0.1	2.8	2.48	0.15	2.27	–

QL—Quantification Limit; LOI—Loss On Ignition; UCC—Upper Continental Crust.

*Additionally: 6.86% SO_3, 0.55% Pb and 1.96% Zn.

[a] Rudnick and Gao (2014).

For those elements that were determined by both techniques (XRF and ICP-MS) and whose values were available, it was decided to use the concentrations obtained by XRF to estimate the tonnages of metals contained in the wastes for their economic evaluation, which will be discussed later. The choice of this technique was made on the basis that XRF does not require dissolution or digestion of the sample, thus avoiding possible errors caused by incomplete dissolution or the dilutions required in samples with high concentrations, as in our case. In addition, the measurement of a larger amount of sample (8 g in XRF), results in a more representative characterization of the sample. In this case, given that we had the possibility of using other analytical techniques for data quality control, it was use the ICP-MS technique as a complementary technique to determine some elements and corroborate their concentrations obtained by XRF.

The background values obtained for Spain are impoverished for most elements with respect to their mean crustal abundance given by Rudnick and Gao (2014). Some elements show similar values (e.g., Ce, La, Nd, Sm, Ag, Zn, Cd, Tl and Th) while others are higher (e.g., Sb, As, Pb and Se) (Table S4). The latter contents are due, as discussed in Locutura Rupérez et al. (2012), both to the rock types common in the Iberian Peninsula and to the numerous polymetallic sulfide metallogenic districts. Pb mineralizations are probably the most numerous of those existing in Spain, which may mask geochemical features linked exclusively to the dominant lithologies (e.g., granites of the Tras Os Montes domain of Galicia, black slates of the Luarca Fm). Something similar happens with As or Sb, whose contents are mainly controlled by the existence of numerous polymetallic mineralizations, while their medium to high contents are generally in accordance with the crystalline basement of the Iberian Massif.

3.6. Enrichment factor

Enrichment factors (EFs) were obtained for each element (Table 3). The elements within the group of CRMs that are most enriched in most facilities are Sb and Bi, as well as As, Pb, Cu, Ag, Zn, Cd, Sn, Se and Th within the group of raw materials of strategic and economic interest. In some mine wastes, antimony contents gave an EF of 25,603, bismuth contents gave an EF = 4613, silver contents gave an EF = 4147 and arsenic contents gave an EF = 6868. These values constitute an important starting point for the analysis of the recovery potential of these elements. The high enrichment in lead, zinc and silver in the mine wastes was expected, taking into account the mining history of most of them (more than 80% of the wastes studied here come from Pb, Zn and Ag mining). For this reason, we also calculated the enrichment factor with the values considered as background values for the Iberian Peninsula, which, as mentioned above, include samples taken throughout the entire Spanish territory (Locutura Rupérez et al., 2012). In this case, for Sb an EF = 8534 was obtained, being EF = 3690 for Bi, EF = 2748 for Ag and EF = 2772 for As (Table S5). Even though these factors have been considerably reduced with respect to those calculated with the UCC as a reference, they are still very high. This indicates that the recovery method used in the extraction of these elements during the XX century was not efficient with the technology available at the time, leaving tailings enriched with still significant amounts of these elements.

As and Pb, despite being toxic elements, are considered here as materials of strategic and economic interest. This is because arsenic, which is included in the U.S. list of critical minerals (which also includes elements such as Sn and Zn; FR Doc.2022-04027, 2022), is currently used industrially in robotics, aeronautics (drones), fuel cells and digital technologies. Pb is currently used in battery manufacturing, wind energy, photovoltaic (PV) technology, robotics, aeronautics (drones) and digital technologies (European Commission, 2020). This makes the recovery of both metals interesting and thus they are considered in this study given their implementation in *green technologies*. Similarly, Cu, Ag, Zn, Sn, Cd and Se, highly enriched in the mine wastes, are also used in the strategic technologies industry (European Commission, 2020), which makes them important resources to be recovered despite not being part of the current list of CRMs.

3.7. Economic potential of the most promising facilities

Among the studied mine waste facilities, three of them were selected as the most promising and with the highest potential for recovery (Fig. 7). These facilities are: 938-IV-4-002, from the historic Rio Tinto mine in Huelva; 959-I-4-001, from the Tharsis mine, also in Huelva; and

Table 3

Enrichment Factors (EFs) of critical and strategic metals in selected mine wastes with respect to the average cortical concentrations.

Sample	Analysis Type	CRITICAL RAW MATERIALS																	OTHER RAW MATERIALS OF STRATEGIC AND ECONOMIC INTEREST											
		REE					Other critical metals																							
		Ce	La	Nd	Sc	Y	Nb	Sr	Co	V	W	Ga	Hf	Sb	Ba	Be	Bi	Ta	As	Pb	Cu	Ag	Zn	Cd	Sn	Se	Tl	Th	Zr	Cr
809-II-1-001	ICP-MS	–	–	–	–	–	–	–	0.4	0.7	–	–	–	728	1	1	–	–	15	1,802	13	1,943	65	142	–	63	6	6	–	2
	XRF	1	1	0.8	1	3	0.5	0.1	1	1	<QL	1	7	519	5	–	210	<QL	<QL	1,362	43	1,295	106	372	2	<QL	<QL	0.4	0.8	0.9
835-II-1-001	ICP-MS	–	–	–	–	–	–	–	0.6	1	–	–	–	82	1	1	–	–	13	215	5	247	27	105	–	37	0.9	0.7	–	0.8
	XRF	1	1	1	1	1	1	0.2	0.7	1	<QL	1	<QL	76	1	–	60	6	14	173	4	258	26	<QL	2	<QL	4	0.3	2	0.9
858-IV-3-004	ICP-MS	–	–	–	–	–	–	–	1	0.8	–	–	–	323	0.4	2	–	–	75	1,614	22	543	224	972	–	170	0.9	0.6	–	0.8
	XRF	3	2	2	1	5	0.5	0.2	1	1	<QL	0.4	13	349	0.8	–	321	<QL	51	1,933	26	604	331	1,136	3	<QL	<QL	<QL	1	1
858-IV-3-002	ICP-MS	–	–	–	–	–	–	–	2	1	–	–	–	245	0.5	2	–	–	26	1,925	5	472	265	919	–	45	0.7	0.8	–	0.8
	XRF	3	2	2	2	5	0.8	0.2	2	2	<QL	0.7	15	267	1	–	346	<QL	<QL	2,189	<QL	496	420	1,022	<DL	<QL	3	<QL	1	1
880-II-2-001	ICP-MS	–	–	–	–	–	–	–	14	0.7	–	–	–	323	0.4	1	–	–	191	404	88	828	6	24	–	36	0.4	0.3	–	0.5
	XRF	1	1	1	0.7	2	0.7	0.1	19	0.9	7	0.4	3	311	0.6	–	119	6	220	432	89	853	8	<QL	<QL	<QL	<QL	0.5	0.9	0.6
905-II-1-012	ICP-MS	–	–	–	–	–	–	–	0.3	0.2	–	–	–	15,720	2	0.6	–	–	8	108	3	15	0.9	5	–	24	0.6	0.5	–	0.1
	XRF	<QL	0.9	0.9	14	1	0.4	0.4	1	0.3	79	0.6	<QL	25,603	4	–	15	<QL	8	203	5	<QL	1	106	<QL	<QL	<QL	0.4	0.6	0.1
938-IV-4-002 Red	ICP-MS	–	–	–	–	–	–	–	2	0.3	–	–	–	4,388	2	0.2	–	–	5,076	1,182	107	3,868	29	140	–	1,300	59	0.6	–	0.2
	XRF	2	2	0.8	3	4	0.6	0.2	2	1	<QL	<QL	10	5,433	8	–	4,613	<QL	6,468	1,511	152	4,147	42	277	667	1,910	44	<QL	1	0.1
938-IV-4-002 Gray	ICP-MS	–	–	–	–	–	–	–	7	0.04	–	–	–	1,553	1	<QL	–	–	128	611	12	808	7	12	–	658	24	0.3	–	0.02
	XRF	<QL	0.9	<QL	2	3	0.2	0.1	7	0.1	16	<QL	5	2,303	31	–	2,169	<QL	239	965	12	1,262	12	187	188	817	20	<QL	0.6	<QL
959-I-4-001	ICP-MS	–	–	–	–	–	–	–	1	0.8	–	–	–	620	0.5	<QL	–	–	654	480	15	245	4	<QL	–	578	<QL	–	–	1
	XRF	1	0.9	0.8	1	3	1	0.1	<QL	0.9	6	2	2	700	0.5	–	775	<QL	763	482	18	264	3	<QL	115	833	11	0.5	0.7	0.7
976-II-3-005	ICP-MS	–	–	–	–	–	–	–	0	0.2	–	–	–	408	0.7	9	–	–	79	–	2	266	49	66	–	<QL	28	427	–	0.2
	XRF	0.5	0.5	0.7	0.5	1	0.4	0.2	<QL	0.3	<QL	<QL	5	599	1	–	136	<QL	96	527	<QL	502	92	59	41	<QL	45	1	0.6	0.2
976-II-3-006	ICP-MS	–	–	–	–	–	–	–	0	0.4	–	–	–	425	0.9	2	–	–	118	–	2	300	84	157	–	23	26	248	–	0.4
	XRF	0.6	0.6	0.7	0.6	0.8	0.6	0.2	<QL	0.5	<QL	0.5	4	508	1	–	88	<QL	157	237	<LD	447	157	158	22	14	29	1	0.4	0.5
976-II-3-007	ICP-MS	–	–	–	–	–	–	–	0.3	0.4	–	–	–	348	0.7	12	–	–	94	518	2	202	68	34	–	11	28	263	–	0.3
	XRF	0.7	0.8	0.6	0.6	0.7	0.7	0.1	<QL	0.5	<QL	0.3	3	389	0.8	–	77	<QL	102	210	<QL	196	93	<QL	29	<QL	31	2	0.6	0.4
977-II-4-100	ICP-MS	–	–	–	–	–	–	–	0.7	0.8	–	–	–	653	0.1	4	–	–	169	1,197	7	408	122	304	–	24	0.5	0.2	–	0.8
	XRF	1	0.5	0.8	1	3	0.6	0.2	0.3	1	22	0.7	<QL	680	0.1	–	<QL	31	153	1,239	6	355	151	311	99	<QL	19	<QL	0.5	1
978-I-1-009	ICP-MS	–	–	–	–	–	–	–	0.4	0.2	–	–	–	305	0.1	9	–	–	136	349	2	148	82	207	–	17	2	0.2	–	0.2
	XRF	0.2	0.4	0.3	0.7	0.6	0.4	0.7	<QL	0.6	12	0.4	<QL	458	0.1	–	<QL	<QL	112	127	0.5	<QL	95	118	7.29	<QL	<QL	<QL	0.2	0.6
978-I-3-026	ICP-MS	–	–	–	–	–	–	–	0.4	0.5	–	–	–	120	0.1	0.8	–	–	34	289	3	79	156	317	–	19	1.3	0.4	–	1
977-II-4-041	ICP-MS	–	–	–	–	–	–	–	0.5	0.6	–	–	–	202	0.3	3	–	–	109	–	5	182	148	366	–	32	3	722	–	0.5
977-II-4-043	ICP-MS	–	–	–	–	–	–	–	0.6	0.4	–	–	–	149	0.3	1	–	–	45	–	4	93	111	297	–	35	3	387	–	0.3
34-III-4-001	ICP-MS	–	–	–	–	–	–	–	0.8	0.1	–	–	–	8	0.01	0.9	–	–	27	145	1	2	195	269	–	11	0.8	0.03	–	0.05
34-III-4-002	ICP-MS	–	–	–	–	–	–	–	2	0.1	–	–	–	13	0.02	1	–	–	72	231	6	2	150	271	–	<QL	1.3	0.1	–	0.2
34-III-4-003	ICP-MS	–	–	–	–	–	–	–	0.1	0.9	–	–	–	10	0.4	6	–	–	15	179	0.5	5	114	121	–	68	3	0.9	–	1
34-III-4-006	ICP-MS	–	–	–	–	–	–	–	0.5	0.9	–	–	–	6	0.4	2	–	–	16	52	0.9	<QL	52	107	–	32	0.9	1	–	1
125-III-4-001 A	ICP-MS	–	–	–	–	–	–	–	0.7	0.5	–	–	–	16	4	0.8	–	–	1	148	3	36	186	307	–	43	0.5	0.7	–	0.4
	XRF	0.3	0.8	0.7	0.8	1	0.6	0.5	0.9	0.6	<QL	1	<QL	17	4	–	<QL	<QL	<QL	124	1	<QL	186	322	1	<QL	<QL	0.5	0.7	0.5
125-III-4-001 B	ICP-MS	–	–	–	–	–	–	–	0.4	0.7	–	–	–	11	3	1	–	–	3	60	3	13	46	71	–	40	0.6	0.8	–	0.6
	XRF	0.6	0.9	0.6	0.8	0.8	0.8	0.5	0.5	0.6	2	0.9	<QL	<QL	3	–	<QL	<QL	2	42	1	<QL	39	<QL	2	<QL	<QL	0.9	1	0.5

REE—Rare Earth Elements;ICP-MS—Inductively Coupled Plasma Mass Spectrometry; XRF— X-ray Fluorescence; QL—Quantification Limit. Enrichment factor values considered high are shaded in gray.

125-III-4-001 from the Rubiais mine in Lugo. This selection was made on the basis of their volume, as well as the amount and concentration of valuable elements. We assumed that the concentrations obtained for the surface samples is representative of the totality of the wastes, especially in those of alkaline pH, which should be confirmed by drilling campaigns. Subsequently, their economic potential was analyzed, estimating the potential content in tons of each of the elements analyzed for each facility and quantifying their gross economic value, in millions of dollars, according to market prices. The price assigned to each element (in $/kg) was obtained from the average of the closing prices achieved during the 2018–2022 period. The results obtained are presented in Table 4.

This preliminary analysis provides a first approximation of the economic resources that could be potentially generated by mine wastes facilities containing critical and valuable metals, reaching figures of hundreds of millions dollars. Tailings from the selected facilities could bring 1762, 793 and 697 million dollars respectively (Table 4), based on current market metal prices. In individual terms, the highest potential value in Rio Tinto facility is generated by Tl (652 M USD), followed by Ag (285 M USD) and Sc (284 M USD). Concordantly in Tharsis Mine, the highest potential values are also generated by Tl (274 M USD) and Sc (204 M USD). In the Rubiais mine the highest potential values are generated by Sc (242 M USD) and Zn (239 M USD). It can be therefore concluded that in the three selected mine waste facilities, scandium and thallium are generally the elements with the highest economic value of all those analyzed in this study. It should be noted that these two elements are considered critical raw materials due to their very low worldwide production (10 to 20 t/year) (U.S. Geological Survey, 2022). These economic resources make these mine waste facilities the ones with the highest potential among those analyzed here. These facilities require more detailed investigations (e.g., drilling, pilot-scale metallurgical tests) in order to determine important parameters like (i) the actual reserves, (ii) the most suitable mineral processing technologies, and (iii) the expected yields. Our simplistic calculations do not consider operational costs which are inherent to any recovery project (e.g., transport and manipulation, design and construction of treatment plants, maintenance of the treatment processes, the final rehabilitation, etc.), but provides a rough estimation of the economic potential laying behind these abandoned mine wastes. Other facilities that could be of interest are 809-II-1-001 from the San Quintín mine in Ciudad Real, due to its high Ag (69–103 mg/kg) and Pb (23,152–30,632 mg/kg) content; and the 905-II-1-012 facility, the Casa de la Liebre mine in Jaén, due to its high Sb (6288–10,241 mg/kg) and Sc (201 mg/kg) content.

3.8. Acid mine drainage as a proxy of critical raw materials recovery potential from mining wastes: The example of the Iberian Pyrite Belt (IPB)

Due to different reasons (e.g., mine waste facilities located in mines that were not closed, with permits in force or with legal owners that did not allow them to be considered abandoned), there are certain mine districts in Spain for which a lesser amount of mine waste facilities were visited and substantially less samples of mine wastes were taken. These mining districts are somehow underrepresented in the National Inventory of Tailings and Waste Piles (NITWP) in which the present study is based. The clearest example is the Iberian Pyrite Belt (IPB), the most important mining district in Spain and in Europe, and one of the most important in the world according to aspects like size, history or economic potential (Leistel et al., 1998; Pinedo-Vara, 1962; Tornos et al., 2008). The IPB mining district still hosts 1700 Mt of massive sulfide with 35 Mt Zn, 14.6 Mt Cu, 13 Mt Pb, 46,100 t Ag and 880 t Au (Leistel et al., 1998). The mineralizations consisted in predominant pyrite (which can represent > 90% by volume) and variable quantities of some other sulfides like sphalerite, galena, chalcopyrite or arsenopyrite, in addition to sulfosalts like tetrahedrite or tenantite (Leistel et al., 1998; Sánchez-España, 2000; Velasco et al., 1998).

The intense mining activity developed in the IPB during more than 2000 years (Pinedo-Vara, 1962) has left an impressive legacy of large mine waste facilities (Figs. 2–3). Only in the province of Huelva exist 57 abandoned waste piles (with total volume of 107 hm^3) and 10 tailings impoundments (making up 42 hm^3), which represents one of the world's biggest accumulation of mine wastes (IGME, 1989; Sánchez-España et al., 2005). These huge heaps of mine wastes are mainly composed, in the case of the waste piles, of big fragments of barren rocks ripped from underground or open pit workings during the mining operations, though most of these wastes still contain variable quantities of pyrite and other sulfides, which made up the ore. These waste piles are very heterogeneous in composition and include all types of common rocks in the area, such as volcanic and sedimentary rocks (Sánchez-España and Velasco, 1999). According to petrological and lithogeochemical studies (e.g., Leistel et al., 1998; Sánchez-España, 2000; Sánchez-España et al., 2000), it is known that these volcanic and sedimentary rocks contain, in addition to principal components like SiO_2, Al_2O_3, Fe_2O_3, MgO, K_2O or Na_2O, a long list of trace elements in minor (but always significant) concentrations. Among these elements, there are many included in the EC's list of critical raw materials (e.g. Ba, La, Ce, Ga, Y, Sr, Nb, Co or V, in concentrations ranging from a few tens to a few hundreds of mg/kg), as well as many other elements with economic interest (e.g., Cu, Zn, Pb; also in the order of tens to hundreds of mg/kg; Sánchez-España, 2000). Recently, studies focusing on rare earth elements, which are very sensitive to pH, have also been developed, showing that acid mine waters are enriched in these elements (Olías et al., 2018).

The tailings, on the other hand, are mainly composed of muds produced in the nearby metallurgical plants, and as such, they are made of fine-grained silicates (e.g., quartz, clays and feldspars), unrecovered sulfides and other minerals like sulfates, carbonates and oxides, in accordance with findings in other tailings (Table S3). Whole-rock chemical analyses of polymetallic sulfide samples can reach very high concentrations of base metals like copper (1000–84,000 mg/kg Cu), zinc (500–305,000 mg/kg Zn) or lead (500–228,000 mg/kg Pb) and precious metals like gold (e.g., 0–3200 mg/kg Au) (Sánchez-España, 2000). In addition, the whole-rock chemistry of the mineralizations can include elevated concentrations of many critical raw materials like barium (200–251,000 mg/kg Ba), strontium (50–2300 mg/kg Sr), cobalt (20–500 mg/kg Co), antimony (40–4410 mg/kg Sb) or bismuth (5–800 mg/kg Bi), as well as other elements of potential economic interest (e.g., 600–12,000 mg/kg As), to name a few (Sánchez-España, 2000). These data are in line with those provided by a composite sample taken in a tailings impoundment of Riotinto mines in Nerva which has been included in this work (see sample 938-IV-4-002 in Table S4).

The oxidation and chemical alteration of these sulfides present in waste piles and tailings, due to the combined action of water and oxygen, leads to a chemical phenomenon known as "*acid mine drainage*" (AMD) (Nordstrom and Alpers, 1999; Singer and Stumm, 1970). These acidic effluents are characterized by a very low pH (commonly, 1.5–3.5) and very high concentrations of metals like Fe, Al, Mg, Mn, Cu, Zn, Co, Ni or Cd resulting from the dissolution of metal sulfides and accompanying silicates (Sánchez-España et al., 2005). AMD represents a severe environmental problem in mining areas worldwide, since the majority of these dissolved metals are highly toxic and represent a serious menace for aquatic ecosystems and water resources in the affected areas (Younger et al., 2002). However, at the same time, the composition of these acidic effluents provides a highly valuable information about the acid-leachable fraction of the mine wastes. In the context of circular economy and mine waste recycling, the interest of this information relies in the fact that the composition of these acidic leachates reflects the mobile fraction which is readily solubilized by a natural bioleaching process catalyzed by bacteria (Sand et al., 2022). Thus, the leachate chemistry provides a direct evidence of the critical

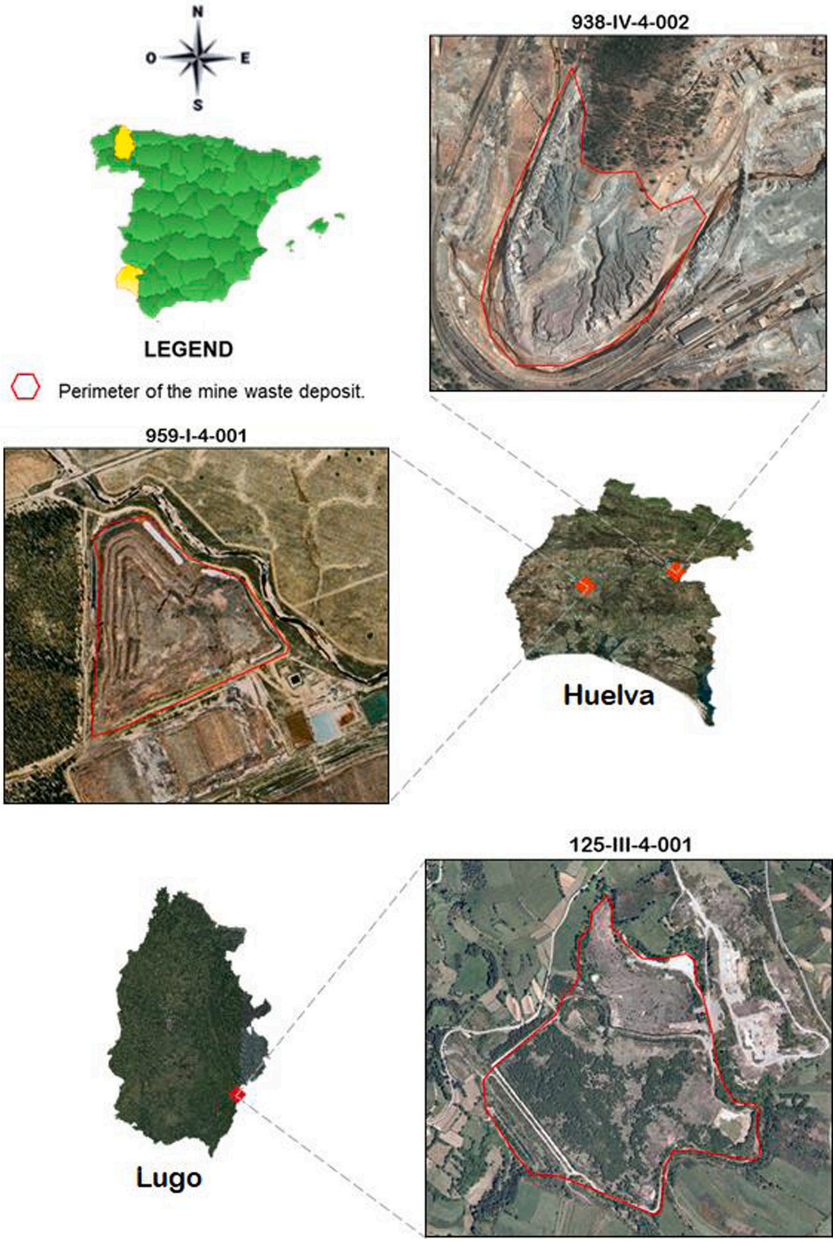

Fig. 7. Aerial view of most promising mine waste facilities.

metals and raw materials that can be successfully recovered from mine wastes by an efficient extraction method like bioleaching.

A number of studies on the chemical composition of acidic effluents seeping from mine wastes of the IPB (e.g., IGME, 2003; López-Pamo et al., 2009; Sánchez-España et al., 2005, 2008) may be highly valuable to assess the possible economic interest and technical feasibility of raw material recovery from these wastes by leaching methods. For example, a study conducted in the Odiel river basin reported the chemical composition of 64 acidic effluents seeping from 25 different mines scattered through the province of Huelva (Sánchez-España et al., 2005). This research included concentration measurements of a long list of elements, many of which are presently considered critical raw materials or elements with economic interest (Communication COM/2020/474 final, 2020). Thus, the composition of these effluents can be used as a proxy to the economic interest of many of these abandoned mine waste facilities, at least as regards to their potential to recover critical raw materials through simple bioleaching methods.

Table S6 provides the concentration of critical raw materials and other elements with economic interest for 26 acidic effluents (chiefly seeping from waste piles, in addition to one tailings impoundment) of different mines representative of the whole IPB mining district. The analyzed critical elements include major components (e.g., Mg) and also elements present in trace (though still significant) amounts (e.g., Ba, Co and V). Similarly, the elements with potential economic interest include both major (e.g., Mn, Al, Cu and Zn) and trace elements (As, Pb, Ni, Cd, Cr, U, Th, Tl). As evidenced in Table S6, there are certain critical elements like Mg or Co that present very high concentrations in many of the studied acidic liquors (e.g. values higher than 2000 mg/L Mg in leachates from Riotinto, Tharsis or San Telmo, and in the order of tens of thousands of μg/L in the case of Co), indicating that these two elements are highly soluble and readily leachable at acidic conditions. As regards to other, non-critical elements with economic interest, aluminum (maximum values exceeding 2500 mg/L Al), manganese, copper and zinc (all of them in concentrations in the order of hundreds of mg/L) are outstanding, with As, Ni, Cd and Cr being also promising elements according to their usually elevated concentrations (Table S6).

Table 4
Economic potential of the most promising mine waste facilities.

Element	Price (US$/kg)	Reference	938-IV-4-002			959-I-4-001			125-III-4-001		
			Concentration (mg/kg)	Estimated tonnage (t)	Potential value (Millions USD)	Concentration (mg/kg)	Estimated tonnage (t)	Potential value (Millions USD)	Concentration (mg/kg)	Estimated tonnage (t)	Potential value (Millions USD)
Ce	3.74	a	138	–	–	62	–	–	20	–	–
La	3.6	a	48	–	–	29	–	–	25	–	–
Nd	126.13	a	22	45	6	21	70	9	19	126	16
Sc	3,326.4	a	42	85	284	18	61	204	11	73	242
Y	35.4	c	82	167	6	54	184	6	21	139	5
Nb	70.69	a	7	–	–	12	–	–	7	–	–
Sr	13.52	d	49	–	–	30	–	–	147	1000	14
Co	49.16	b	37	76	4	–	–	–	16	107	5
V	284.13	a	56	115	33	90	306	87	56	379	108
W	44.35	a	–	–	–	12	–	–	–	–	–
Ga	180	a	–	–	–	34	116	21	20	134	24
Hf	820	c	54	110	90	12	40	33	–	–	–
Sb	8.15	c	2173	4433	36	280	952	8	7	–	–
Ba	0.18	c,*	4779	–	–	334	–	–	2595	17,646	3
Be	1025.64	a	n.a.	–	–	n.a.	–	–	n.a.	–	–
Bi	8.42	c	738	1506	13	124	422	4	–	–	–
Ta	345.22	d	–	–	–	–	–	–	–	–	–
As	1.54	c	31,046	63,334	98	3660	12,444	19	–	–	–
Pb	2.08	b	25,692	52,412	109	8200	27,880	58	2113	14,368	30
Cu	7.45	b	4268	8706	65	511	1737	13	27	–	–
Ag	635.28	c	220	448	285	14	48	30	–	–	–
Zn	2.81	b	2819	5750	16	173	–	–	12,483	84,884	239
Cd	2.42	c	25	–	–	–	–	–	29	–	–
Sn	20.38	b	1401	2858	58	242	823	17	3	–	–
Se	25.9	a	172	351	9	75	255	7	–	–	–
Tl	8067	c	40	81	652	10	34	274	–	–	–
Th	72.3	c	–	–	–	5	–	–	5	–	–
Zr	10.6	c	184	–	–	139	474	5	139	945	10
Cr	9.5	c	14	–	–	60	–	–	42	283	3
SUM					**1,762.08**			**793.58**			**697.17**

[a] https://www.metal.com/ (accessed 8 November 2022).

[b] https://www.lme.com/ (accessed 8 November 2022).

[c] https://doi.org/10.3133/mcs2022 (USGS - Mineral Commodity Summaries 2022).

[d] https://ise-metal-quotes.com/ (accessed 8 November 2022).

*Barium sulfate price.

Many of these acidic effluents are active all the year round and flow downstream to tributaries of the Odiel and Tinto river basins, carrying with them an impressive metal load to the Huelva estuary and, finally, the Atlantic Ocean (Sánchez-España et al., 2005). Based on the metal concentrations given in textcolorcyanTable S5 in combination with average flow rates measured in the different effluents, Sánchez-España et al. (2005) calculated that, only during the winter of 2003, a total amount of 4 t Al, 9 t Mg, 0.9 t Mn, 1.4 t Zn, 0.6 t Cu, 9 kg Cd, 6 kg Pb and 0.5 kg As were daily transported from the waste piles and tailings of the IPB to the Huelva estuary through the creeks and tributaries of the Odiel river basin. Taking into account the current price of some of these metals in the international metal markets (e.g., 2100–2300 $/t in the case of aluminum, 2800 $/t for zinc, or 7600 $/t in the case of copper; LME, 2022), the quantities of these metals which are being daily transported downstream from the mining areas to the Atlantic Ocean represent not only an evident environmental issue, but also a clear waste of economic resources which could be recovered and concentrated by low-cost methods.

We are unaware of any ongoing project of metal recovery from the acidic mine waters of the IPB. However, the extraction of copper by the classical cementation method has been known and utilized in the area at least since the first half of the 20th century (e.g., Taylor and Whelan, 1943), being still considered the most efficient and cost-effective method of copper recovery from these Cu^{2+}-rich mine waters (Sánchez-España et al., 2022). Copper extraction by cementation could also be performed in controlled locations, from acid sulfate efflorescences harvested from conducive areas where acidic waters flow (Cala-Rivero et al., 2018). Besides, some valuable metals like Co, Ni and Zn can be efficiently removed from the acidic solutions by oxidation of Mn(II), which produces different Mn(III/IV) oxides with a high specific surface area and good sorption capacity for all these metals (e.g., Sánchez-España and Yusta, 2019). In short, there is a big metal recovery potential in these acidic mine waters which should be further investigated in the forthcoming years through experimental studies and pilot-scale plants applying different technologies available to date (Nordstrom et al., 2017). The case of the acidic effluents of the IPB mining district represents one the most evident and paradigmatic examples of the existing need of research on efficient technologies of metal recovery (e.g., *biomining, biohydrometalurgy*) to boost circular economy.

3.9. General perspective and future directions of metal recovery potential from mine wastes in Spain

Many of the mine wastes analyzed in this study still contain significant quantities of many critical and strategic metals. A further advancement in the evaluation of the economic potential of these mine wastes would necessarily imply an increase of the geochemical information of the mine waste facilities analyzed here (which have been derived from composite surface samples), through borehole campaigns to determine whether or not the surface samples are representative of the entire volume of waste stored in a given facility. Considering that the drilling campaigns are costly, a reasonable strategy would be to choose the most promising facilities in terms of their critical or strategic metal content, and among these, those with easier access for drilling machinery. The facilities would be analyzed in detail as pilot experiences that could later be extended to other facilities if the results are satisfactory. Likewise, the number of facilities to be considered could be expanded, given that the scope of this study does not cover all the abandoned mine waste facilities in Spain, but only those included in the National Inventory of Tailings and Waste Piles. This preliminary evaluation should be also extended with the investigation of those deposits located in the IPB (whose elemental contents in acid waters have shown a great potential for recovery of certain elements), which would increase the degree of knowledge of the existing mine waste deposits in Spain.

Another future step to be considered would be to conduct mineral processing trials to evaluate the most appropriate metallurgical techniques to recover the metals of interest from these wastes. These trials should first be conducted on a laboratory scale, and could then be expanded to small pilot-scale plants at the most interesting facilities in a strategy of progressive scaling up to concentrate research efforts on those facilities that really have potential. The pilot recovery tests should also be accompanied by detailed mineralogical and geochemical investigations to establish the mineral carriers of the metals of interest, as this will also determine the choice of the metallurgical technique to be used. In this sense, electron microscopy (SEM-EDS) or electron microprobe (EPMA) studies on selected mine wastes would be extremely useful.

4. Conclusions

Based on the results obtained in the present study, it can be concluded that a significant extractive potential has been found in practically all the selected samples, highlighting several elements with possibilities of being recovered through secondary mining, especially Ag, Zn and Pb and, to a lesser extent, Sb, Cd, Bi and As. Among all the facilities analyzed, five of them are of great interest with respect to their potential benefit: 938-IV-4-002 (historic Rio Tinto mine in Huelva), 959-I-4-001 (Tharsis mine, also in Huelva), 125-III-4-001 (Rubiais mine in Lugo), 809-II-1-001 (San Quintin mine in Ciudad Real) and 905-II-1-012 (Casa de la Liebre mine in Jaen). Each of these facilities shows a potential gross profit exceeding 100 million dollars. It must be stressed that these amounts are merely indicative rough estimations based on mine waste volume, metal concentrations and the current market prices of each of the metals, and do not take into account the costs of mineral processing, transport, etc… However, they indicate an important economic potential of these tailings deposits that should encourage an increase in the amount and quality of research focused on these mine wastes.

In terms of particle size, the prevalence of fine fractions in the constituent materials of mine waste deposits is clearly an advantage, regardless of the recovery process to be applied: flotation or bioleaching. This prevalence would avoid, in many cases, the increase in the cost of the beneficiation process derived from the need to apply crushing or grinding to the treatment of the material. The metallurgical processing of mine wastes will usually require, however, a wet treatment of the material, which will necessarily entail an associated cost in raw materials (mainly water); however, the predominance of free, plastic and crumbly textures will favor the yield.

In the case of bioleaching, it is evident that the smaller the particle size, the larger the contact surface, thus facilitating the contact of sulfides with leaching microorganisms. As far as flotation is concerned, this process would a priori have worse results in terms of recovery of critical raw materials because it would generally involve reprocessing residues from a previous flotation process (which would necessarily have already obtained a large part of the material that would be extractable by flotation). However, it must be considered that given the age of most of these deposits (many prior to the 1980s), it is foreseeable that there has been a significant technological improvement of the flotation procedures with respect to those already applied at the time on the tailings.

Finally, the data on natural leachates from the IPB spoil heaps collected from previous studies show that there is a great potential for the recovery of critical elements such as Mg or Co, as well as strategic elements of economic interest such as Cu, Zn, Al, Mn or As, by bioleaching, an aspect that should be studied in detail to evaluate possible recovery strategies for these metals.

CRediT authorship contribution statement

Adrián José Rosario-Beltré: Conceptualization, Methodology, Data curation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Javier Sánchez-España:** Conceptualization, Investigation, Supervision, Funding acquisition, Writing – review & editing, Critical review. **Virginia Rodríguez-Gómez:** Investigation, Writing – review & editing, Visualization. **Francisco Javier Fernández-Naranjo:** Investigation, Writing – review & editing, Visualization. **Eva Bellido-Martín:** Methodology, Validation, Visualization. **Paula Adánez-Sanjuán:** Writing – review & editing, Visualization. **Julio César Arranz-González:** Project administration, Investigation, Funding acquisition, Writing – review & editing, Critical review.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data used in our research have been included in the manuscript as tables, either in the main text or in the supplemental information file.

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Appendix A. Supplementary data

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