

# Metal(loid) release from sulfide-rich wastes to the environment: The case of the Iberian Pyrite Belt (SW Spain)

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## Abstract

Sulfide-mining wastes may lead to severe environmental and human health risks, especially challenging in abandoned mines without environmental regulation. This work is aimed at discussing the environmental problems associated with this type of wastes, the risks posed by metal(loid) exposure to living organisms, as well as the measures available to mitigate such risks, taking the case of the Iberian Pyrite Belt (SW Iberian Peninsula), as an example, worldwide. The release of metal(loid)s from these wastes upon weathering is strongly controlled by mineral assemblage, processing technique, grain size distribution, and occurrence of highly reactive secondary minerals. Exposure to these wastes may pose a severe risk for humans and animals, and thus, remediation measures must be adopted in abandoned mines. Among these measures, recovery of valuable metals from sulfide wastes could be a promising environmentally friendly solution; however, grade and mineralogical siting of valuable metals, as well as selective recovery methods, must be site-by-site investigated.

## Addresses

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## Keywords

Sulfide wastes, Weathering, Metal(loid) release, Bioassimilation, Simulating body fluids, Metal recovery.

## Introduction

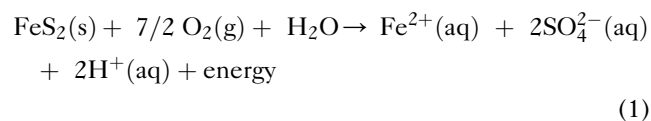
Although sulfide minerals are small contributors to the Earth's crust composition, they tend to concentrate in certain geological environments, forming valuable components in metallic ores. Inefficiencies caused by mining, mineral processing, and metallurgical extraction produce different types of unwanted wastes with nonrecoverable sulfides that are dumped at disposal sites and hopelessly exposed to weathering [1]. As a result of mining, sulfide mineral reactivity is also greatly enhanced, and under atmospheric weathering conditions, these minerals release metal(loid)s causing environmental pollution. This pollutant process, known as acid mine drainage (AMD), is the major potential long-term environmental effect of sulfide mining, which can last for hundreds or even thousands of years. The oxidation of sulfides leads to the formation of different secondary minerals such as Fe oxides, Fe oxyhydroxysulfates, and hydrated metal sulfates, which may constitute transient or permanent sinks of metals in wastes heaps [e.g. Refs. [2,3]]. This environmental concern is especially important in historical mine sites, where uncontrolled mining activities can even date back to hundreds or thousands of years. This is the case of the Iberian Pyrite Belt (IPB), which is one of the most important sulfide-mining regions in the world, with more than 100 abandoned mines. The long history of metal mining in the region has left a legacy of derelict mines and enormous amounts of mining wastes; around 4800 ha of surface are occupied by waste rock piles, pits, tailings impoundments and other mining facilities only in the Spanish sector of the IPB [4]. In volcanogenic massive base metal deposits, only a few percent of the valuable metals is recovered, and thus, more than 90% of the ore becomes a waste after processing. This environmental situation has attracted the interest of many researchers in the last years; however, to the best of our knowledge, there is no exhaustive review of the different works dealing with mineral and geochemical characterization, the potential capacity to release metal(loid)s, possible impact to living organisms, and the mitigation measures needed to limit environmental and health risks. For this reason, the main aim of this

work is to critically discuss these issues to provide the readers a full picture of the environmental quandary associated with sulfide mining wastes, illustrated with the example of the IPB.

### Metal(loid) release upon weathering

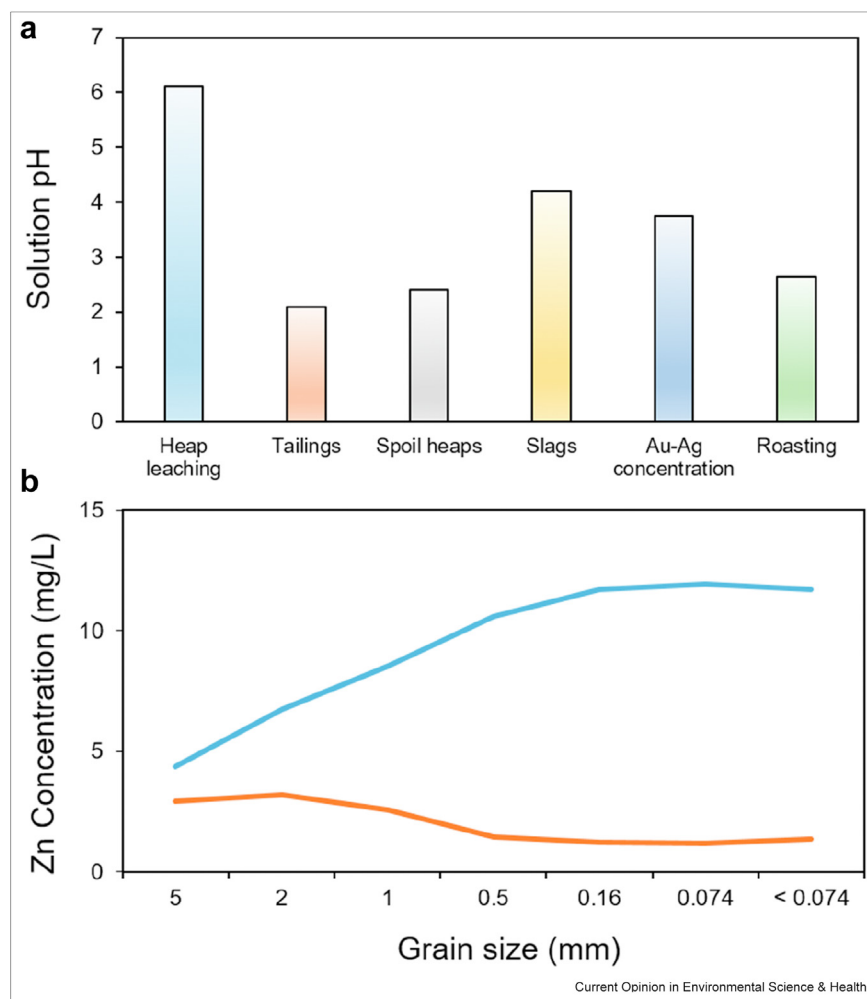
The weathering of wastes in historical sulfide mines leads to chronic pollution by metal(loid)s release [e.g. Refs. [5,6]\*. Probably, the most important factor controlling the release of contaminants in mining wastes upon weathering is the predominant mineralogy. Sulfide mining wastes are composed of sulfides and other gangue minerals such as silicates, oxides, hydroxides, phosphates, halides, or carbonates, exhibiting commonly an extremely heterogeneous distribution [1]. Most of the mining, processing, and metallurgical wastes such as spoil heaps, tailings, and roasted pyrite,

respectively, contain residual sulfides, mainly pyrite, whose oxidation causes the release of acidic effluents ( $\text{pH} < 3$ ) after rainfalls (Figure 1a) if the acid-producing capacity of Fe-sulfides is larger than the buffering capacity of host rocks in the wastes, according to the general equation:



The oxidation rate depends on several factors, including oxygen availability, temperature, pH, bacterial activity, and surface area of pyrite grains, and will control the acidity of the drainages. Nevertheless, different

Figure 1



Reactivity of different wastes of the IPB to leaching with distilled water (solid:liquid ratio 1:20) mimicking rainfall weathering, according to (a) solution pH and (b) Zn release for different grain size fractions of two roasted pyrite wastes (lines orange and blue).

additives during the mineral processing can also play a critical role in the acidity of the resulting leachates. For instance, during the heap leach process to extract Au, lime is added to the wastes to increase the metal extraction. The oxidation of Fe-sulfides in alkaline environments results in neutral drainage waters (Figure 1a), with elevated concentrations of sulfate and anions, while most cations are secondarily retained by adsorption to mineral surfaces at  $\text{pH} > 6$ .

A detailed knowledge of mineralogical composition, chemical composition and physical properties such as grain size, porosity and hydraulic conductivity of the different waste types is necessary for reliable predictions of acid mine drainage formation and efficiency of mitigation measures. In this sense, the abundance and reactivity of the different minerals in each type of waste may control its potential capacity to release not only acidity but also contaminants into the environment [7]. For example, gossaniferous wastes are mainly dominated by goethite and hematite, which despite hosting considerable amounts of metal(loid)s, exhibit a low reactivity [8]. On the other hand, slags comprise glass and crystallized minerals, such as fayalite, magnetite, and quartz, which may host significant concentrations of metal(loid)s, especially in historical slag deposits due to inefficient metal recovery technologies [1]. Although the general belief is that metal(loid)s are trapped in the silicate glasses and other minerals, thereby conferring a nonreactive nature, slags are not totally chemically inert due to the presence of highly reactive secondary minerals such as residual sulfides and efflorescent Fe sulfate salts that are known to play a crucial role in the release of contaminants [1]. The presence of these acidic secondary minerals may also lead to the generation of acidic effluents in these low-reactive slag wastes (Figure 1a). These secondary minerals are chiefly dominated by soluble sulfates such as copiapite, melanterite, alunogen, gypsum, or hexahydrate, which may serve as temporary sinks for acidity and trace metal(loid)s in mining wastes during dry seasons, while they are redissolved again during rainfall events releasing back the contaminants [e.g. Refs. [9–11]].

Another critical factor controlling metal(loid) release from wastes is the grain size, being the smaller particles more reactive due to large specific surfaces, leading to increasing metal(loid) release rates [12–14]. Although grain size plays a dominant role in metal(loid) mobility from sulfide mining wastes, the partitioning of highly soluble secondary minerals among grain size fractions may, in some cases, be the key factor controlling the metal(loid) release from these wastes, especially in semiarid climates [14]. This fact is shown in Figure 1b, where the release of Zn from roasted pyrite wastes after leaching with distilled water is represented. As can be seen, inverse relationships between grain size and Zn release are observed in two nearby roasted pyrite heaps,

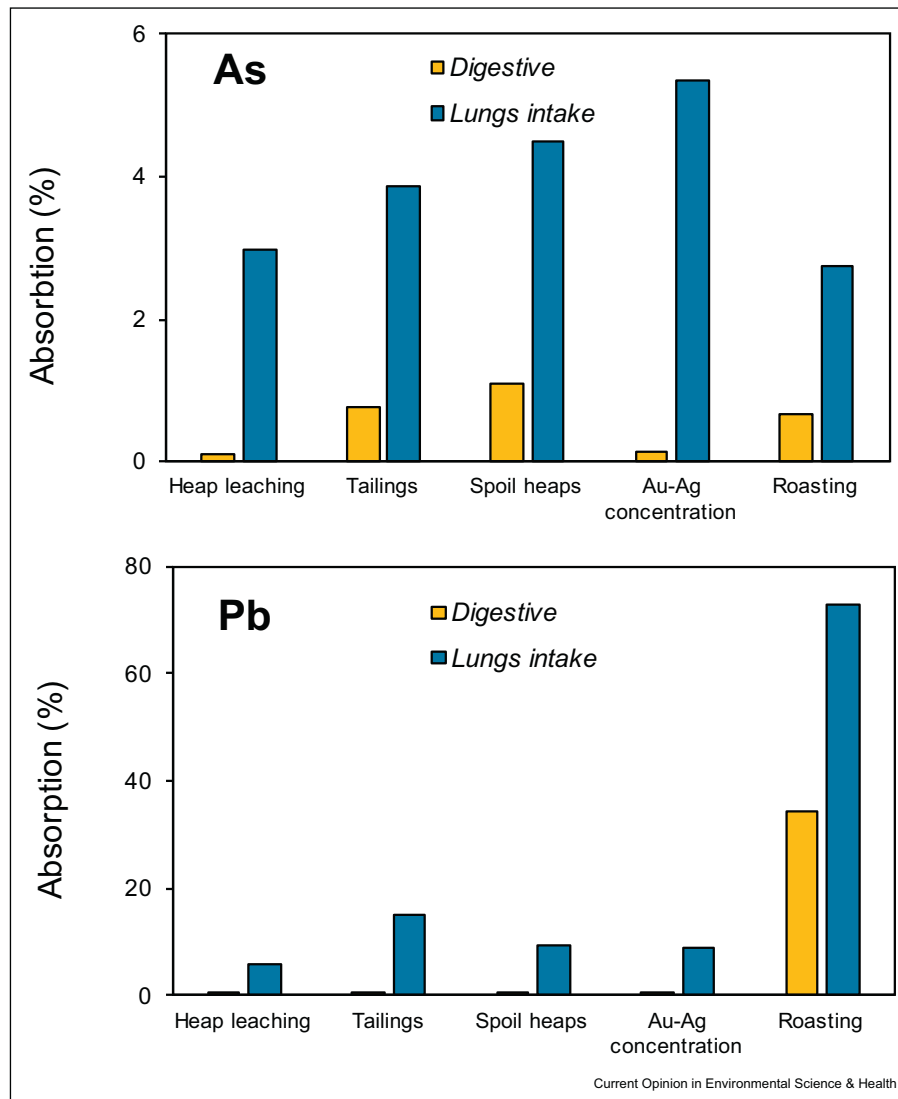
attributed to the preferential accumulation of secondary minerals between grain size fractions.

A simple approach to assess the metal(loid) release upon weathering of mining wastes relies on sequential extraction schemes to determine the soluble, reducible, oxidizable, and residual components [e.g. Refs. [7,15]]. However, Caraballo *et al.* (2018) [16] reported an underestimation of metal mobility in metal-rich wastes and recommended the use of alternative approaches for assessing toxic metals mobility in highly polluted mining residues.

### Bioaccessibility and bioavailability of metal(loid)s in wastes

As a consequence of the high reactivity of sulfide mining wastes, there is a growing concern about the bioaccessibility of metal(loid)s in living organisms. The impact of sulfide mining wastes on wildlife, especially on small birds and mammals, has been reported in different mine sites worldwide [e.g. Refs. [17,18]], including the IPB [19]. These authors described increased levels of metal(loid)s in hair, feathers, and tissues of rabbits, mice, partridges, and shrews in mine sites compared to reference areas. However, a greater concern is the direct ingestion by human beings. Unlike in animals, where invasive techniques have been traditionally used to monitor the internal levels of pollutants, implying sacrificing individuals, bioaccessibility in humans must be studied by nondestructive techniques. In this sense, many studies reported elevated concentrations of metal(loid)s in human blood, hair, gallstones, toenails, or urine upon exposure to mining wastes [20–24]. The human body may interact both physically and chemically after exposure to mining waste particles through inhalation, ingestion, and dermal absorption [25]. For this reason, many studies commonly approach the bioaccessibility and bioavailability of metal(loid)s using solutions simulating body fluids (e.g., respiratory, gastrointestinal, perspiration, or blood serum). For instance, Gray *et al.* (2010) [26] studied the potential human exposure to Hg due to inhalation of airborne and hand-to-mouth ingestion of Hg-bearing sulfide roasted particles. These authors reported high Hg concentrations (1.6–9.2 mg Hg leached/g) using simulated gastric, lung, and serum-based fluids, being the leaching capacity controlled by mineralogy, particularly by the presence of soluble compounds. In the case of the IPB, to the best of our knowledge, there are no studies reporting metal(loid) bioaccessibility from mining wastes using these fluids; however, preliminary results evidenced that the exposure to sulfide mining wastes could pose a serious risk for inhabitants in the surroundings of mining areas. Figure 2 shows the human absorption of As and Pb through different biological routes from different wastes in contact with simulating body fluids (i.e. pulmonary and digestive). It is clearly

Figure 2



Absorption (%) of As and Pb contained in different wastes of the IPB through digestive and pulmonary routes. Simulating body fluids made according to Ruby et al. (1996) [27] and Stopford et al. (2003) [28].

seen that metal(loid) absorption is highly dependent on mining waste, element, and route. In this case, the pulmonary absorption of As is up to 5 times higher than digestive (below 1% of total As; Figure 2). This enhanced pulmonary absorption is also observed for Pb, where up to 73% of Pb was absorbed in roasted pyrite samples. Therefore, detailed studies on metal(loid) absorption after mining wastes exposure in the IPB are urgently required.

### Mitigation measures to avoid metal(loid) release from mining wastes

The dumping of enormous amounts of highly reactive sulfide wastes and their exposure to atmospheric

conditions may lead to dramatic contaminant episodes. For avoiding AMD generation, different measures are commonly adopted for the treatment of mining wastes aimed at minimizing oxygen diffusion or advection/convection in waste heaps, minimizing water infiltration and leaching, removing or isolating sulfide minerals, providing acid-neutralizing minerals, and controlling bacteria and biogeochemical processes. Among these measures, the most common are wet and dry covers, encapsulation, blending, and addition of organic wastes or bactericides [1]. These techniques, however, also have some drawbacks such as the enhancement of mobility of metals after an intervention (e.g. reductive dissolution of metal oxides, increased metalloid mobility

at circumneutral pH values), the limited effectiveness of bactericides and organic compounds that require continuous addition, or the indirect pollution of waters by coating and encapsulating agents [29]. In addition, not all measures may be applied in all geographical locations (e.g. wet cover in dry areas), and no independent measure is appropriate to all mine site conditions, so a combination of them is commonly applied to reach success [1].

Other measures are focused on limiting metal mobility and bioavailability in wastes, such as phytostabilization, which is a phytoremediation strategy based on immobilizing metal(loid)s in soil or roots [30]. This technique has been profusely studied in the IPB. For instance, *Erica andevalensis* and *Erica australis* plants have been found to grow spontaneously over sulfide mining wastes, tolerating high acidity, and metal(loid) concentrations, and even bioaccumulating Mn in their aerial parts [31,32]. Other studies reported the rehabilitation of mining waste areas in the IPB by combining technosols implementation and phytostabilization [33]. Although it has not been previously applied in the IPB, artificial inoculation may be an efficient and cost-effective phytostabilization route [34].

Restoration measures should be performed based on a detailed risk assessment of each waste repository, aiming at deactivating the pollution sources and rehabilitating the contaminated areas with remedial actions [2]. Owing to the orphan nature of most mine sites in the IPB, environmental liabilities are often assumed by the public administration, and thus, the scarcely reported cases of restoration measures were put in practice by the regional government [35,36]. Notwithstanding, the reopening of mines in the IPB may suppose a breaking point in this environmental quandary since permits require that mining companies must take over the environmental liabilities from past mining, and thus, a remarkable improvement of environmental conditions is expected in the short term [37,38].

### Recycling and recovery of valuable metals from sulfide mining wastes

Despite all measures aimed at isolating and inactivating sulfide mining wastes, other promising environmentally friendly treatments can be considered. For instance, the reuse of mining wastes as construction materials constitutes an innovative management approach in accordance with the principles of circular economy [e.g. Refs. [39,40]], which may recycle large volumes of mining wastes deposited in mine sites. On the other hand, sulfide mining wastes usually have relatively high metal(loid) concentrations due to the inefficient mineral processing techniques used in the past that yielded poor metal recoveries, and thus, they could be a secondary source of elements of economic interest. For

example, smelter slags historically deposited in the IPB were inefficiently smelted and show Cu contents above 2.5% [41]. In addition, sulfide oxidation products, such as gossans and precipitates from acid waters (Fe and Al oxyhydroxysulfates or evaporitic sulfate salts), can also host significant metal concentrations [42]. In this sense, only a few works dealing with the metal content of wastes deposited in the IPB have been reported. For example, Alvarez-Valero *et al.* (2008) [43] reported a pool of around 6 Mt of Fe, 55,295 t of Zn, 29,000 t of Cu, 2613 t of V, and 513 t of Ni, only in mining wastes deposited in São Domingos (Portugal). Mateus *et al.* (2011) [44] suggested the recovery of base metals in roman and modern slags of this same mine. This recovery would also be feasible for other elements considered as critical raw materials (CRMs) such as rare earth elements (REE), as evidenced by Pérez-López *et al.* (2008) [7], who reported concentrations of up to 544 mg/kg in gossans and mining soils of São Domingos. Martín-Crespo *et al.* (2011) [45] also reported concentrations of Sb, an element of industrial interest, higher than 800 mg/kg in sulfide tailings. Others, such as the platinum group elements (PGE; i.e., Ru, Rh, Pd, Au, and Pt), may be related to sulfides in the IPB [46]. Indium (In) and Germanium (Ge), together with Fe and Cu can replace Zn in the structure of sphalerite, a common sulfide in the northern deposits of the IPB [47]. In this sense, Benzaazoua *et al.* (2003) [48] found high concentrations of In associated with stannite in the Neves Corvo mine (Portugal), which resulted in an added value to the mineral concentrate obtained in this mine. More recently, Wierzbicka-Wieczorek *et al.* (2019) [49] have reported average In contents of 6 mg/kg in sulfide waste rocks of historical mine sites of the IPB. For this reason, it is essential to investigate the CRMs content in the mining wastes deposited in the IPB to assess its potential recovery. This investigation, together with the development of selective recovery methods [e.g. Ref. [50]] may open the door for the cost-effective recovery of CRMs (REE, Sb, Be, Co, Ga, Ge, In, PGM's, Nb, Ta) and other elements of interest from sulfide wastes of the IPB.

### Concluding remarks

The weathering of sulfide wastes dumped in historical mine sites, like the IPB, may pose a risk for the environment and human health. The transference of metal(loid)s from these wastes to the hydrosphere is strongly controlled by the mineralogical composition of wastes, the processing technique applied, the grain size distribution, and the occurrence of highly reactive secondary minerals. The existence of towns in the surroundings of abandoned mines may lead to the indirect intake of metals by humans and animals through different metabolism pathways. In order to limit metal pollution from mining wastes and bioassimilation problems, remediation measures must be adopted in

abandoned mines; however, these measures have been scarcely practiced in the IPB and are mainly developed and funded by the regional government. The reopening of the mines in the IPB and the compulsory acceptance of the environmental legacy by the operating mining company may imply a significant improvement of the environmental situation in the short term. Sulfide wastes, however, may be not only an environmental problem but also a source of elements of economic interest, as evidenced by the high concentrations of valuable metals found. This could be a promising environmentally friendly solution to waste management in abandoned sulfide mines, like those of the IPB. However, in some cases the processing may be difficult due to the encapsulation of metals in the mineral assemblage. In other cases, the presence of impurities may difficult the development of selective recovery methods or cause the increase of waste management costs, turning the activity sub-economic. For this reason, a deep investigation of the mineralogical siting of valuable metals and the occurrence of environmentally significant elements in wastes rocks is required to assess the cost-effective and environmentally friendly valorization of these wastes.

### 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.

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This paper reviews different approaches to recover valuable metals using innovative and selective recovery methods.