



## Research Article

# Metal mobility and bioaccessibility from cyanide leaching heaps in a historical mine site

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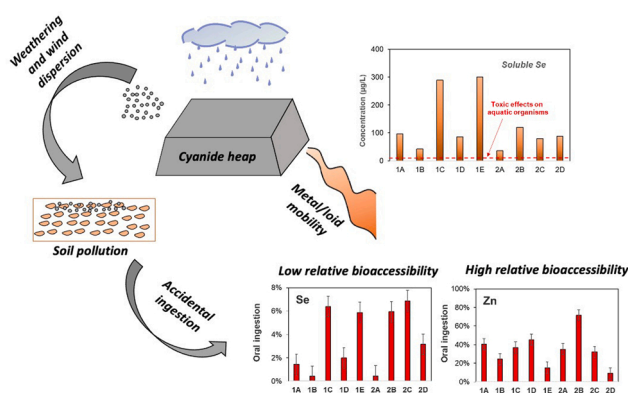
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## HIGHLIGHTS

- The high release of Se makes cyanide leaching wastes to be hazardous.
- High release of Fe, Pb, and Al observed during the simulation of oral ingestion.
- Mn and Zn exhibited a high relative bioaccessibility (52–72% of total content).
- Silicates and goethite may release V and Cr during accidental oral ingestion.
- Water-soluble secondary minerals host high amounts of Se, Pb, Tl, Mn, Co, Ni, or Zn.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Unlike acidic sulfide mine wastes, where metal/loid mobility and bioaccessibility has been widely studied, less attention has been paid to alkaline cyanide heap leaching wastes. Thus, the main goal of this study is to evaluate the mobility and bioaccessibility of metal/loids in Fe-rich (up to 55%) mine wastes resulting from historical cyanide leaching activities. Wastes are mainly composed of oxides/oxyhydroxides (i.e. goethite and hematite), oxyhydroxysulfates (i.e. jarosite), sulfates (i.e., gypsum, evaporitic sulfate salts), carbonates (i.e., calcite, siderite) and quartz, with noticeable concentrations of metal/loids (e.g., 1453–6943 mg/kg of As, 5216–15,672 mg/kg; of Pb, 308–1094 mg/kg of Sb, 181–1174 mg/kg of Cu, or 97–1517 mg/kg of Zn). The wastes displayed a high reactivity upon rainfall contact associated to the dissolution of secondary minerals such as carbonates, gypsum, and other sulfates, exceeding the threshold values for hazardous wastes in some heap levels for Se, Cu, Zn, As, and sulfate leading to potential significant risks for aquatic life. High concentrations of Fe, Pb, and Al were

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released during the simulation of digestive ingestion of waste particles, with average values of 4825 mg/kg of Fe, 1672 mg/kg of Pb, and 807 mg/kg of Al. Mineralogy may control the mobility and bioaccessibility of metal/loids under rainfall events. However, in the case of the bioaccessible fractions different associations may be observed: i) the dissolution of gypsum, jarosite and hematite would mainly release Fe, As, Pb, Cu, Se, Sb and Tl; ii) the dissolution of an un-identified mineral (e.g., aluminosilicate or Mn oxide) would lead to the release of Ni, Co, Al and Mn and iii) the acid attack of silicate materials and goethite would enhance the bioaccessibility of V and Cr. This study highlights the hazardousness of wastes from cyanide heap leaching, and the need to adopt restoration measures in historical mine sites.

## 1. Introduction

Cyanide leaching is currently the dominant process used by mining companies to extract precious metals (i.e. Au and Ag) from ores, especially through heap and tank leaching [23]. Since around 1970's heap leaching has developed into an efficient procedure to beneficiate a variety of low-grade, oxidized Au ores, showing significant advantages with respect to tank leaching such as the simplicity of design, lower capital and operating costs, and shorter startup times [34]. This cost-effective process, based on the selective dissolution of precious metals by cyanide solutions, generates large amounts of cyanide-bearing wastes. In order to assure an effective performance of cyanide solutions, the pH of solutions has to be maintained at alkaline values of around 10.3, which often requires the addition of lime or other alkaline materials [23]. More acidic conditions may lead to cyanide losses through hydrolysis, reaction with carbon dioxide, or with hydrogen to form volatile hydrogen cyanide (HCN), while more basic conditions slow down the process [34]. Leaching typically takes from several weeks to months, depending on the permeability and size of the pile. The cyanide anion not only dissolves Au and Ag but also other metals and metalloids (e.g. As, Cd, Co, Cu, Fe, Ni, Pb and Zn), however most of them are hosted in secondary minerals.

Owing to this widely used mining technique, large quantities of alkaline cyanidation wastes are stockpiled in the vicinity of processing plants. Circumneutral mining leachates can transport high concentrations of metals and metalloids. This is the case of heap leaching wastes produced during Au and Ag recovery, in which acidity is neutralized during mineral processing in order to optimize the metal recovery. Most metals have low solubility at basic pH, however the occurrence of some weakly hydrolyzing metals such as Ni, Cd and Zn can remain in solution as they usually require more elevated pH values (higher than 8.5) to be transferred in solid forms. In addition, some metalloids of potential concern (e.g. As, Sb, Se) can enhance their solubility under basic conditions, forming anionic complexes that are poorly sorbed at neutral to basic pH values [2]. For this reason, the potential release of metal/loids upon weathering conditions and metal/loid bioavailability from these wastes must be studied. Unlike acidic sulfide mine wastes, alkaline wastes such as those of cyanide leaching, have attracted less interest and existing works focus on the chemical characterization and treatment of these leachates during the mineral processing (e.g., [26,12]), instead of the mobility and bioaccessibility of metal/loids after stockpiling.

The Iberian Pyrite Belt (IPB) is one of the most important polymetallic sulfide-mining regions in the world. The long history of metal mining in the region has left a legacy of derelict mines and an enormous amount of mining wastes. Among them, it stands out the occurrence of large piles of cyanidation wastes in the surroundings of Tharsis Mines, which has been scarcely studied. The processed ores corresponded mainly to Fe oxides/hydroxides contained in gossans and/or obtained from roasting pyrite. Gossans refers to the oxidation product by weathering and leaching of a sulfide body by geological processes. Mineral assemblages of these rocks are quite similar to those obtained by roasting pyrite. During the mineral processing performed until 2001, cyanidation wastes were stockpiled in different levels of variable height (Fig. S1). No remediation measures were performed on the leaching heaps and thus were subjected to weathering agents after the cease of

the activity. The main goals of this work are to study the release of metals and metalloids under rainfall occurrence, the potential impact on the aquatic life and the bioaccessibility of metal/loids in case of accidental ingestion. The results obtained and the methodology used in this study may contribute to adequate management of this type of wastes worldwide.

## 2. Methodology

### 2.1. Site description

The Au and Ag recovery complex of the Tharsis mines in Filon Sur took place initially from 1937 to 1968 through tank leaching. Gossans were initially processed by vat tanks, after crushing. In order to avoid the excessive consumption of cyanide, lime was added to reach appropriate alkaline conditions. After cyanide leaching, the cyanide-rich solution was separated from a thick sludge. The Au/Ag cyanide-rich solution went into a concentration tank while the sludge was brought to 3 different stirring reactors. There, fresh cyanide solution was added together with oxygen in order to enhance the formation of Au and Ag cyanide complexes. In this step, the sludge was deprived of Au and Ag and dumped into heaps by means of pipes. The efficiency of this process was estimated around 60%, with a consumption of 27 kg of cyanide for each kg of concentrate. The treatment capacity of this plant was around 200 t/day of gossan ore [32].

The activity of the treatment plant restarted in 1982, eventually ending in 2001, due to the low Au concentration observed in the reserves. The minerals processed during this period were gossans outcropping in the mining area and roasted pyrite from close derelict exploitations. Ore minerals were crushed and milled until reaching a grain size between 0.1 and 7 mm. Then, lime and cement were added to the minerals and afterwards were transported to the heap leaching floors. The treatment production started with 200,000 ton/yr but even reached productions close to 1 million tons after the plant extension in 1998. The heaps had an extension of 100 × 70 m. In 2001 the ore processing ceased, and the leaching heaps were left without any restoration measure (Fig. 1).

### 2.2. Sampling and chemical characterization

A vertical profile was sampled in two different leaching heaps (Fig. S1) in order to study the heterogeneity of the wastes. A composite sample of approximately 5 kg was collected from each level (Fig. 1a and b) using a polypropylene shovel previously washed with distilled water and transferred to polypropylene sterile bags. In the laboratory, samples were oven-dried at 30 °C to avoid mineralogical transformations (Fig. 1c). Afterwards, samples were sieved at different grain sizes (i.e., 5, 2, 1, 0.5, 0.16, and 0.074 mm) and stored in sterile polypropylene bags to determine the grain size distribution, except aliquot samples which were powdered in a ring mill and stored for chemical and mineralogical analysis. The chemical composition of samples was determined at MS Analytical (Langley, Canada) for major and trace elements following a multi acid digestion procedure with a mixture of HCl, HNO<sub>3</sub>, HClO<sub>4</sub> and HF. Thus, 1 g of sample in a microwave digestion system following a temperature ramp. After cooling, the digests were transferred into clean

tubes, diluted to 50 mL with high purity Milli-Q water, and filtered to remove the insoluble particles. Then, acid solutions were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). The analytical accuracy was verified by the analysis of reference materials (OREAS 904), and the analytical precision was determined by duplicate analysis, with differences < 5% for all elements. Total sulfur, N and C were analyzed using a C-S-N LECO Analyzer by combustion at 1300 °C.

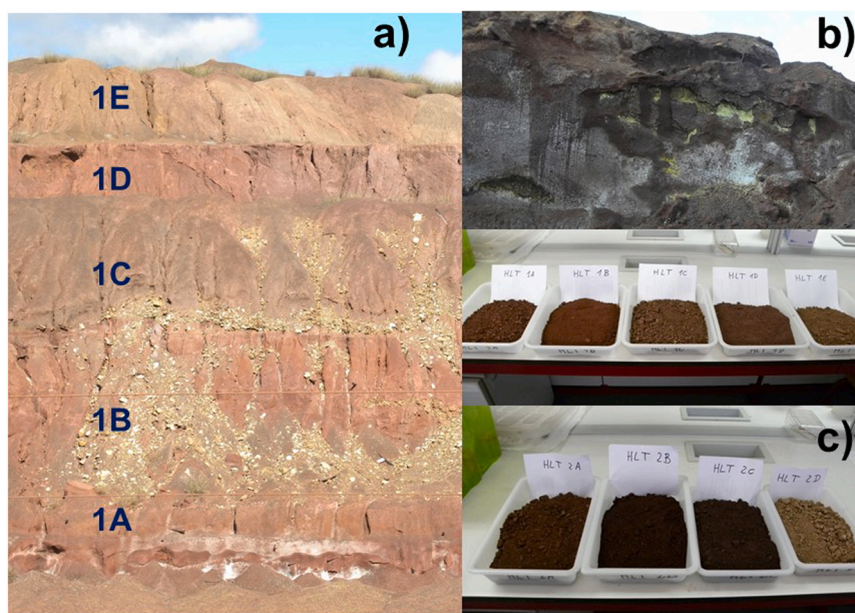
### 2.3. Mineralogical characterization

X-ray diffraction (XRD) patterns were obtained from powder samples with a Bruker D5005 X-ray Diffractometer with Cu K $\alpha$  radiation. Diffractometer settings were 40 kV, 30 mA, a scan range of 5–65° 2 $\theta$ , 0.02 2 $\theta$  step size, and 2.4 s counting time per step. Analysis of diffraction patterns was performed with the X Powder software [25]. Samples were also examined by scanning electron microscopy (SEM). Thus, semi-quantitative chemical analyses and imaging of samples were obtained by using a SEM coupled with energy dispersive spectroscopy (SEM-EDS; FEI-Quanta 200 equipped with a microanalyzer EDAX Genesis, 2000) at the R+D Services of the University of Huelva. In addition, detailed information on mineralogy and Fe speciation was obtained by Mössbauer spectroscopy at the Campus Tecnológico e Nuclear (CTN-IST) from the University of Lisbon. Mössbauer spectra were collected between 295 and 4 K in transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi <sup>57</sup>Co source in a Rh matrix. The velocity scale was calibrated using  $\alpha$ -Fe foil. Isomer shifts, IS, are given relative to this standard at room temperature. The absorbers were obtained by packing the powdered samples into perspex holders. Absorber thicknesses were calculated on the basis of the corresponding electronic mass-absorption coefficients for the 14.4 keV radiation, according to Long et al. [22]. Low-temperature measurements were performed in a bath cryostat with the sample immersed in liquid He for measurements at 4.1 K and in He exchange gas for temperatures > 4.1 K. The spectra were fitted to Lorentzian lines using a non-linear least-squares method. The estimated parameters from the Mössbauer spectra taken at 295 K, 80 K and 4 K of the heap leaching samples can be seen in Table S1.

### 2.4. Assessment of metal mobility and bioaccessibility from cyanide leaching heaps

The behavior of the heap leaching wastes during rainy events was studied by performing a 24-h distilled water leaching (ratio 1:10) following the EN 12457-2 leaching protocol [13]. This test has been commonly applied for evaluating the acceptance for waste disposal in European landfill sites, including different type of mine wastes (e.g., [24,36]). This standardized test considers the fraction below 4 mm with or without size reduction, so in this study the same size (<250  $\mu$ m) used in bioaccessibility determination was selected. The effect of storm magnitude on metal release was also studied by increasing the ratio to 1:20. In addition, the pH paste method (ratio 1:1) according to EC [15] was applied to samples and physico-chemical parameters (i.e., pH, EC and ORP) were measured at different times (i.e., 15 min, 4, 24 and 48 h) to study porewaters chemical composition. Solutions were subsequently filtered at 0.45  $\mu$ m using cellulose nitrate Millipore filters, acidified to pH < 2 and analyzed at the R+D Services of Huelva University using ICP-AES (Jobin Yvon Ultima 2) for major elements and ICP-MS (Agilent 7700) for trace elements. Detection limits were 0.2 mg/L for S; 0.1 mg/L for Na; 0.05 mg/L for Fe, K, Mg and Si; 0.02 mg/L for Al and Ca, and 2  $\mu$ g/L for trace elements. The analytical precision was checked by triplicate analysis of selected samples with values below 5% in all cases. Blanks were also analyzed in each analysis sequence, being all elements below the detection limit. The analytical accuracy was evaluated by the analysis of reference materials (NIST-1640), with differences below 6% of referenced concentrations.

On the other hand, metal/loid bioaccessibility from wastes was determined using the Simple Bioaccessibility Extraction Test (SBET) [35]. Synthetic gastric fluid was synthesized using a 0.4 M glycine buffer extraction solution adjusted to pH 1.5  $\pm$  0.5 with ultrapure HCl to simulate human gastric solution. Samples (< 250  $\mu$ m fraction) were put into contact with the solutions applying a ratio 1:100. The size fraction below 250  $\mu$ m was used because this particle size is representative of that which adheres to children's hands [35]. The containers were hermetically sealed to avoid the loss of liquids when placed in a shaker incubator (37  $\pm$  0.2 °C and 120 rpm) for 1 h to perform the extraction process. After centrifugation, samples were filtered through a 0.45  $\mu$ m cellulose acetate filter and stored at 4 °C until analysis, which was completed before 7 days. The analysis was performed by ICP-AES and



**Fig. 1.** a) Picture of the leaching heap 1, showing the different levels sampled in this study; b) picture of level 2 C with the occurrence of yellow efflorescent salts and c) picture of the different collected samples in the laboratory.



ICP-MS as previously commented.

A Principal Component Analysis (PCA) has been performed using the XLSTAT (Addinsoft) software to infer relationships between the mineralogy and the reactivity and bioaccessibility of metals in studied wastes. The use of PCA allows reducing the number of variables in a multivariate dataset but retaining as much variation as possible in the dataset. Variables were standardized to z-scores to fit a normal distribution and thus, the Pearson ( $n - 1$ ) correlation matrix was used [9]. In addition, the chemical speciation and mineral saturation indices using the PHREEQC code v2.12.01 [31], with the WATEQ4F database [4].

### 3. Results and discussion

#### 3.1. Chemical and mineralogical characterization

Grain size plays a key role in mineral reactivity, which is usually enhanced as a consequence of different processes such as blasting, crushing and grinding occurred during mining activities, leading to the increase of their reactive surface area [6]. As can be seen in Fig. S2, some differences can be observed between studied leaching heaps. While evident differences in grain size are observed in the first heap, a more homogeneous grain size distribution is observed in the second heap. Thus, levels 1A and 1C turned out to have the coarser grains with values around 18% passing through the 0.5 mm sieve, while the finer grains were observed in level 1D with around 35% of particles below this value (Fig. S2). In the case of the second heap, where more homogeneous grain size distribution is observed, all samples exhibited values of around 25% of particles smaller than 0.5 mm. Regarding the mineralogical properties of the studied wastes, they are mainly composed by Fe oxides/oxyhydroxides (i.e. goethite and hematite), oxyhydroxysulfates (i.e. jarosite), and quartz (Table 1). Gypsum was also identified in some levels of the heaps. The low crystallinity and minor presence (below 5%) of other minerals precluded their identification by XRD. An additional examination of samples by SEM (Fig. S3) allowed identifying some minerals such as calcite and siderite in some samples and pyrite in the level 2C, whose concentration may be < 5% of abundance. Some techniques such as Mössbauer spectroscopy may provide additional information such as Fe speciation in samples and the characteristics of Fe minerals, especially in environmental samples (e.g., [27]). Spectra of selected samples are shown in Figs. S4-S7. In these samples, all the Fe is present as Fe(III) except in levels 1E and 2D where there is 4% and 2% of Fe(II), respectively (Table S2). The main Fe(III) containing mineral phase is hematite followed by goethite. At least 14% of Fe is present in goethite except in level 2B where the fraction of Fe(III) in pure hematite reaches 91%. Fe(III) in jarosite is also present in all these samples in low amounts. The fraction of Fe in nanosized oxides is also very low < 3% for most samples except for levels 1C, 1E and 2D where it reaches values around 5–7%. In several samples the fraction of Fe in hematite and goethite is similar but differing the relative amounts of pure and impure hematite. Samples with Fe(II) and Fe(III) in silicate phases are those with higher fraction of nanosized oxides, jarosite and lower fraction of pure hematite.

The chemical composition of studied wastes is consistent with the mineralogical assemblage. Accordingly, the wastes showed high concentrations of Fe (16–55%; Table 1) with the lowest values observed in the bottom piles. The content of S in wastes ranged from 0.58% to 4.8%, due to its lack in gossan ore or its removal during roasting process of sulfides. It is striking that the higher content of S was found in the level 2C, where the occurrence of evaporitic salts was visually observed (Fig. 1b), and even the presence of pyrite by SEM (Fig. S3), which indicates an incomplete roasting process. The content of other major elements in leaching heap wastes ranged from 0.13% to 5.5% for Al, 0.31–2.5% for Ca, 0.1–1.5% for K, 0.06–0.43% for Na, 0.03–0.19% for Mg and 0.24–0.05% for C (Table 1). Regarding trace metals, the leaching heap wastes turned out to be especially enriched in these elements. For example, the capacity of Fe minerals to retain As and Pb is evidenced by

**Table 1**  
Chemical and mineralogical composition of cyanidation wastes. Gt: goethite; Ht: hematite; Jt: jarosite; Q: quartz; Gyp: gypsum; Cl: clinocllore.

Sample	Mineralogy	Major elements (%)											Trace elements (mg/kg)												
		Al	Ca	Fe	K	Mg	Na	S	C	N	As	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Se	Sn	Sb	Tl	V	Zn
1A	Gt, Ht, Jt, Q	0.51	0.31	46	0.12	0.03	0.11	0.64	0.08	0.03	4110	0.15	4.0	96	181	36	9.7	4.6	11,256	77	23	1094	2.3	41	112
1B	Gt, Ht, Jt, Q	0.88	0.42	55	0.14	0.03	0.08	0.61	0.06	0.01	6944	0.08	5.3	79	395	88	5.4	2.8	12,543	79	51	986	0.58	92	208
1C	Gt, Ht, Jt, Gyp, Q	3.0	1.4	46	0.57	0.17	0.17	2.4	0.10	0.01	5212	0.49	53	73	1167	235	8.7	16	9492	63	31	892	14	122	753
1D	Gt, Ht, Jt, Q, Cl	1.5	0.46	45	0.18	0.03	0.13	0.68	0.19	0.02	6406	0.15	18	87	263	25	6.2	8.7	6460	59	28	342	5.6	132	97
1E	Gt, Ht, Jt, Gyp, Q	3.3	0.66	25	0.94	0.17	0.43	1.3	0.13	0.13	3957	0.65	23	86	641	403	9.5	16	13,421	62	51	866	7.7	91	404
2A	Gt, Ht, Jt, Gyp, Q	1.8	0.34	36	0.28	0.09	0.09	0.58	0.05	0.05	4468	1.0	19	85	429	179	8.3	9.3	11,234	80	34	840	2.5	86	428
2B	Gt, Ht, Jt, Gyp, Q	0.13	1.7	50	0.06	0.12	0.24	2.2	0.05	0.12	1453	2.9	64	27	797	89	11	8.4	15,672	35	130	792	30	24	1517
2C	Ht, Jt, Gyp, Q	0.31	2.5	42	0.11	0.09	0.06	4.8	0.05	0.01	1479	1.7	44	17	1174	47	7.1	5.9	11,980	28	20	707	24	116	679
2D	Gt, Ht, Jt, Q	5.5	0.86	16	1.49	0.19	0.26	0.82	0.24	0.06	1932	0.45	12	86	423	263	6.6	23	5216	35	102	308	8.4	24	308

the high concentration of both elements (1453–6943 mg/kg for As and 5216–15,672 mg/kg; [Table 1](#)) and the evolution along the profile, similar to that observed for Fe. The cyanidation wastes also contained high concentrations of other elements such as Sb (308–1094 mg/kg), Cu (181–1174 mg/kg), Zn (97–1517 mg/kg) or Mn (24–403 mg/kg). Lower concentrations were found for Sn (20–130 mg/kg), V (24–132 mg/kg), Cr (17–96 mg/kg), Se (28–80 mg/kg), Co (4.0–64 mg/kg), Ni, Tl (0.6–30 mg/kg), (2.8–23 mg/kg), Mo (5.4–11 mg/kg), and Cd (0.1–2.9 mg/kg) ([Table 1](#)).

### 3.2. Simulations under rainfall events

The fundamental processes that control the mobility of potentially toxic elements in mine wastes involve mineral–water interactions [Jamieson et al. \[18\]](#). For this reason, the behavior of the heap leaching wastes during rainy events was studied by performing a 24-h distilled water leaching following the procedure contained in the Council [\[10\]/EC](#) of the EU. As can be seen in [Table 2](#), the leachates exhibited circumneutral pH values (from 5.7 to 7.4), except for 2 C level, which showed acidic values (pH of 2.3). The wastes displayed a high reactivity, with EC values ranging from 0.47 to 5.4 mS/cm, with the maximum values found in levels 2 C (5.4 mS/cm) and 2D (4.0 mS/cm). These values coincide, considering the different ratio, with those observed during the pH-paste procedure, with circumneutral values (5.9–7.7) except for level 2 C (2.2–2.3), with decreasing values with time ([Fig. S4](#)). In this sense, the acidic nature and high reactivity of level 2 C may be due to the accumulation of other type of wastes, with a higher content of pyrite and other soluble minerals, as evidenced the mineralogical information ([Table 1](#) and [Fig. S3](#)). This malpractice, based on the mineralogical characterization of mine wastes of different nature, was commonly applied in historical mine sites when environmental controls were lacking. The high EC values observed in the leachates may be related to the dissolution of the more soluble secondary minerals enclosed in the cyanidation wastes such as carbonates, gypsum, and other sulfates, as evidenced by the high concentrations observed of sulfate (180–4424 mg/L), Ca (54–604 mg/L), Na (up to 282 mg/L), Mg (up to 110 mg/L) and K (up to 23 mg/L) ([Table 2](#)). Regarding trace metal/loids, the release from levels 1C, 2B and 2C stands out, with 7226, 1291 and 956 µg/L of Mn, respectively, 6120, 11,560 and 16,380 µg/L of Zn, or 764, 461 and 706 µg/L of Co. [Figs. S5–S8](#) shows the saturation indices (SI) of waters with respect to Al and Fe oxides/oxyhydroxides, sulfate and carbonate minerals. As can be seen, waters are generally oversaturated with respect to Al and Fe oxides and oxyhydroxides, except for jarosite which occurrence was reported by XRD in all level and exhibited subsaturated values (IS from –1 to –9.5; except in level 2 C; [Fig. S6](#)) in solution. In this sense, [Welch et al. \[39\]](#) reported a dissolution rate of 1 µmol/g jarosite/day after studying the dissolution of jarosite-rich soils with time in waters. These authors also reported an initial pulse in metal concentrations linked to the dissolution of secondary sulfates. The geochemical model predicts the dissolution of different metal (Fe, Pb, Cu, Zn, Ca and Mg) sulfates, with an apparent equilibrium with respect to gypsum in levels 2B and 2C ([Fig. S7](#)). The alkaline nature of heaps could be also a source of metals upon carbonate dissolution. [Fig. S8](#) support this hypothesis, with SI below 0 for all heap levels.

It is especially striking the release of metal/loids from level 2C upon acidic conditions with high concentrations of Fe (970 mg/L), Al (24 mg/L), As (7972 µg/L), Cu (5083 µg/L), Cr (277 µg/L) or V (4.4 µg/L) ([Table 2](#)), which are scarcely mobile at circumneutral pH values recorded in the remaining waste levels. It is also worth noting the release of other metal/loids such as Se (289 µg/L for 1C and 300 µg/L for 1E), Tl or Pb (up to 866 and 555 µg/L, respectively in 2B; [Table 2](#)). In the case of Pb, this metal is not very mobile in acid conditions due to the low solubility of secondary minerals and the tendency for Pb to be attenuated through adsorption on Fe oxyhydroxides and other mineral surfaces. However, in circumneutral, oxidizing environments, Pb may be hosted

in carbonate minerals such as cerussite (PbCO<sub>3</sub>) or hydrocerussite (Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>), which are more soluble than secondary minerals found in acidic conditions ([Jamieson et al., 2015](#)). Although subsaturation of waters with respect to these minerals was observed ([Fig. S8](#)), they were not identified by mineralogical techniques in these wastes. In the case of Tl, this metal may be related to the presence of original sulfides and secondary minerals formed after smelting and roasting of sulfide ores ([\[19\]](#); [Liu et al. \[21\]](#)).

The high mineral reactivity of these wastes may be dangerous for the environment. To assess their hazardousness, a comparison with threshold values established by Europe to allow waste disposal in European landfills [\[10\]](#) was performed. It is remarkable that most levels of wastes (except 1B and 2A) would have a hazardous nature due to the exceedances in Se values (from 0.80 to 3.0 mg/kg; [Table 2](#)). In addition, wastes deposited in levels 1C and 1D exceeded the limits established for As and Zn ([Table 2](#)) to be considered as hazardous wastes, while those deposited in level 2B exceeded the limits for Zn and sulfate. However, wastes deposited in the level 2C, of acidic nature, exhibited the highest number of exceedances, with values of Cu, Zn, sulfate and As above the threshold values for hazardous wastes ([Table 2](#)). In the case of As, even exceed the maximum values allowed for disposal in hazardous landfills. Therefore, wastes deposited in the level 2 C must be treated before disposal.

A comparison of the percentage of metal/loids released regarding the total content can be made in order to know the potential mobility of metal/loids from the cyanidation waste heaps. [Fig. 2](#) shows the release of different pollutants from these wastes in contact with waters, considering two different ratios (i.e., 1:10 and 1:20). As can be seen, sulfate exhibited a high mobility, with values between 10% and 52%, linked to the occurrence of highly soluble sulfates. The release of Mn and Zn was also significant in levels 1C, 2B and 2C, with values ranging from 14% to 36% for Mn and from 7.5% to 28% for Zn ([Fig. 2](#)). Some metal/loids such as Fe, Al, Cu, As, and Tl ([Fig. 2](#)) exhibited a very low mobility from wastes, except in the level 2C, where the acidic conditions enhanced the mobility of these elements upon contact with waters, although remained below 8% of total content. These elements are commonly hosted in Fe and Al oxides/oxyhydroxides and their mobility is commonly low in sulfide mine wastes (e.g., [\[3,1\]](#)). A similar release was observed for some other metal/loids such as Pb (<0.04%), Sb (<0.04%), Mo (<1.87%), and Se (<5.3%) ([Fig. 2](#)). Regarding the different solid:liquid ratios employed, differences in metal/loid release were recorded. As can be seen in [Fig. 2](#), slight differences were observed for sulfate, Zn, Mn, Mo, Se, Pb and Sb, with higher values for the 1:20 ratio due to relatively more mineral dissolution at higher volumes of solvent. Conversely, slightly higher values were observed using the 1:10 ratio for Fe, As, Tl and to a lesser extent Al, which may be due to re-precipitation/sorption processes. This re-precipitation processes were observed by [Welch et al. \[39\]](#), where secondary Fe minerals precipitate after jarosite dissolution.

Metal/loid concentrations in leachates were compared with the threshold values of the Criterion Continuous Concentration (CCC) and the Criterion of Maximum Concentration (CMC) established by the aquatic life criteria of the US EPA [\[33\]](#). The CCC is the threshold concentration above which a contaminant poses a significant risk to most aquatic organisms upon persistent exposure, while CMC represents the acute exposure to a metal (highest 1 h average concentration), which should not be exceeded to avoid undesirable impacts on aquatic organisms. Concerning those elements considered toxic for the aquatic life, the interaction of these wastes with water turned out to release metal/loids such as Sb and As. Highest Sb concentrations were observed in the bottom and top levels of the wastes while As followed a saw teeth evolution. In the case of As, samples from 3 levels (1B, 1D and 2C; [Table 2](#)) exceeded the criterion continuous concentration (CCC), that is, the threshold value above which a certain element pose a significant risk to the majority of species in freshwaters if chronic exposure is maintained. On the other hand, the level 1C also exceeded the CCC for Zn, Ni

**Table 2**  
Chemical composition (in mass/vol and mass/mass) of leachates after performing the EN 12457–2 leaching protocol [13] and their comparison with threshold values of acceptance for waste disposal in European landfill sites, and the aquatic life criteria of the US EPA [33]).

	pH	EC mS/cm	ORP mV	Alkalinity mg/L CaCO <sub>3</sub>	Major elements (mg/L)										Trace elements (µg/L)													
					Al	Ca	Fe	K	Mg	Na	SO <sub>4</sub>	V	Cr	Mn	Co	Ni	Cu	Zn	As	Se	Mo	Cd	Sn	Sb	Tl	Pb		
1A	6.2	1.3	210	20	0.22	221	0.07	8.7	4.6	81	660	< 2	< 2	< 1	29	< 1	12	14	33	97	15	< 2	< 2	19	< 1	< 1		
1B	7.3	0.47	149	25	0.09	54	b.d.l	3.5	0.56	31	180	< 2	< 2	< 1	13	< 1	2.6	5.7	145	43	3.0	< 2	< 2	9.2	< 1	< 1		
1C	5.7	2.4	260	0	0.30	593	0.03	2.4	82	27	1789	< 2	< 2	7226	764	111	118	6120	2.9	289	1.5	< 2	< 2	< 1	9.9	7.5		
1D	7.2	0.82	156	23	0.10	108	b.d.l	5.9	0.61	56	339	< 2	< 2	< 1	39	< 1	2.5	3.9	245	87	3.1	< 2	< 2	10	< 1	< 1		
1E	7.1	2.8	159	21	0.21	463	0.05	23	4.1	282	1517	< 2	< 2	13	191	3.1	3.7	8.3	9.5	300	6.9	< 2	< 2	28	< 1	< 1		
2A	7.4	1.3	147	28	0.11	212	0.05	7.2	30	42	572	< 2	< 2	2.4	2.2	< 1	2.0	5.8	23	36	2.7	< 2	< 2	6.7	< 1	< 1		
2B	6.7	4.0	200	5	0.29	604	0.12	6.6	110	219	2038	< 2	< 2	1291	461	27	17	11,560	< 1	121	1.5	15	< 2	< 1	866	555		
2C	2.3	5.4	545	0	24	569	970	0.05	75	< 0.1	4424	4.4	277	956	704	65	5083	16,380	7972	80	1.5	49	< 2	< 2	5.4	< 1	12	
2D	5.9	1.7	349	17	0.24	334	0.02	9.6	2.3	92	905	< 2	< 2	< 1	46	< 1	2.8	4.2	25	88	4.9	< 2	< 2	4.1	< 1	< 1		
<i>Impact on the aquatic life:</i>																												
Freshwater criterion maximum concentration (CMC)																												
Freshwater criterion continuous concentration (CCC)							1						74				52		120	150		0.72		5			2.5	
<b>Major elements (mg/kg)</b>																												
1A					2.2	2207	0.70	87	46	863	6595	< 0.02	< 0.02	< 0.01	0.29	< 0.01	0.12	0.14	0.33	0.97	0.15	< 0.02	< 0.02	0.19	< 0.01	< 0.01		
1B					0.85	536	< 0.01	35	5.6	307	1787	< 0.02	< 0.02	< 0.01	0.13	< 0.01	0.03	0.06	1.5	0.43	0.03	< 0.02	< 0.02	0.09	< 0.01	< 0.01		
1C					2.9	5927	0.34	24	817	268	17,890	< 0.02	< 0.02	72	7.6	1.1	1.2	60	0.03	2.9	0.01	< 0.02	< 0.02	< 0.01	0.10	0.07		
1D					1.0	1082	< 0.01	59	6.1	561	3387	< 0.02	< 0.02	< 0.01	0.39	< 0.01	0.02	0.04	2.4	0.87	0.03	< 0.02	< 0.02	0.10	< 0.01	< 0.01		
1E					2.1	4628	0.48	228	41	2818	15,167	< 0.02	< 0.02	0.13	1.9	0.03	0.04	0.08	0.10	3.0	0.07	< 0.02	< 0.02	0.28	< 0.01	< 0.01		
2A					1.1	2118	0.52	72	299	416	5716	< 0.02	< 0.02	0.02	0.02	< 0.01	0.02	0.06	0.23	0.36	0.03	< 0.02	< 0.02	0.07	< 0.01	< 0.01		
2B					2.9	6039	1.2	66	1097	2187	20,378	< 0.02	< 0.02	13	4.6	0.27	0.17	116	< 0.01	1.2	0.01	0.15	< 0.02	< 0.01	8.6	5.5		
2C					242	5687	9694	0.50	749	< 1	44,236	0.04	2.8	9.6	7.0	0.65	51	164	80	0.80	0.01	0.49	< 0.02	0.05	< 0.01	0.12		
2D					2.4	3335	0.18	96	23	918	9051	< 0.02	< 0.02	< 0.01	0.46	< 0.01	0.03	0.04	0.25	0.88	0.05	< 0.02	< 0.02	0.04	< 0.01	< 0.01		
<i>EC Maximum values in landfills (mg/kg):</i>																												
Inert											6000					0.4	2	4	0.5	0.1	0.5	0.04		0.06		0.5		
Non-hazardous											20,000					10	10	50	50	2	0.5	10	1	0.7		10		
Hazardous											50,000					70	40	100	200	25	7	30	5	5		50		

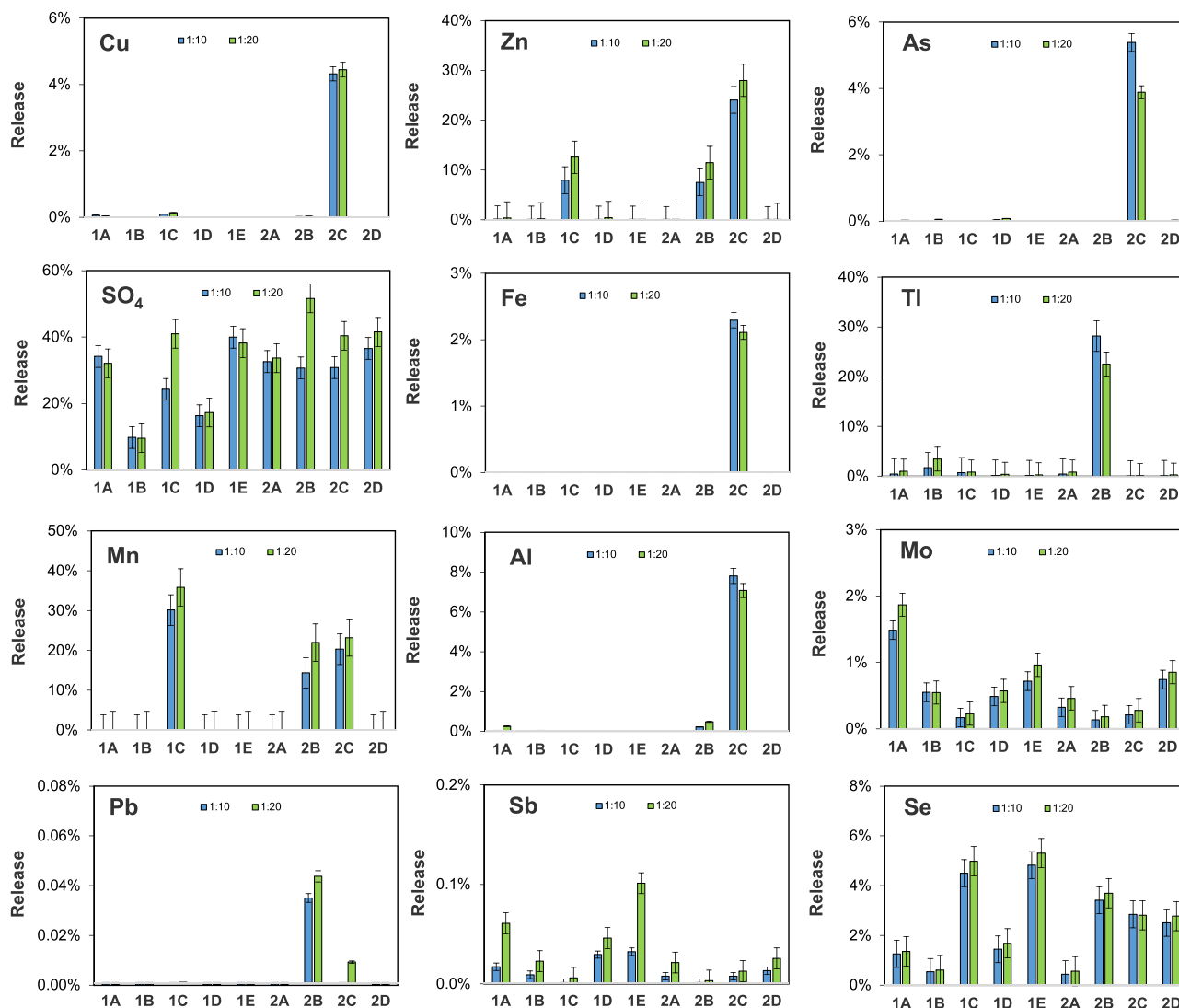


Fig. 2. Release (in %) of metal/loids from cyanidation wastes in contact with waters upon different solid:liquid ratios (i.e., 1:10 and 1:20).

and Pb with maximum values of 8.1 mg/L, 111 µg/L and 7.5 µg/L, respectively. The level 2C, with acidic conditions, also showed exceedances for Cr, Ni, Zn, As, Cd, Sb and Pb. In the case of the criterion maximum concentration (CMC), which represents the highest concentration that is not expected to pose a risk for aquatic life in case of acute exposure, exceedances for Zn were observed in levels 1C, 2B and 2C. Once again, this latter level (2C) exhibited the highest risk for chronic exposure to metal/loids, with additional exceedances of CMC for As and Cd. Although no values of CCC and CMC are indicated for Tl, elevated dissolved concentrations (> 1 µg/L) may cause gill and liver tissues damages in zebrafish, leading to the final death of these aquatic

organisms [37]. In this study, concentrations of up to 866 µg/L (Table 2) were observed.

### 3.3. Simulations of bioaccessibility by accidental ingestion of cyanidation wastes

The resuspension of waste particles may pose a health risk to humans if they are accidentally ingested and pass through the digestive system where metals may be absorbed. The term bioaccessibility has been commonly defined as the percentage of the total intake of pollutants available for absorption into the human body digestive system [29]. In

Table 3

Release of metal/loids (in mg/kg) during the simulation of accidental ingestion of cyanide heap leaching waste particles.

	Al	Fe	V	Cr	Mn	Co	Ni	Cu	Zn	As	Se	Mo	Cd	Sb	Tl	Pb
1A	611	2289	11	23	6.4	0.71	2.2	27	45	50	1.1	< 0.2	< 0.2	2.2	0.45	1055
1B	336	389	11	4.8	9.2	0.55	0.47	4.3	51	44	0.33	< 0.2	< 0.2	0.30	0.10	500
1C	1413	2720	11	5.8	123	20	4.7	134	279	31	4.0	< 0.2	< 0.2	1.2	1.5	322
1D	645	1079	11	3.5	7.6	1.1	0.66	15	44	44	1.2	< 0.2	< 0.2	0.62	0.93	288
1E	1988	8767	11	11	173	14	7.5	182	62	35	3.6	< 0.2	< 0.2	6.9	0.51	628
2A	986	1182	11	9.2	82	7.4	1.7	24	149	26	0.36	< 0.2	0.50	0.81	0.34	1570
2B	108	10,290	7.4	5.9	41	16	1.3	185	1087	76	2.1	< 0.2	1.5	6.1	16	10,321
2C	290	15,542	7.4	4.1	11	8.2	0.88	65	217	235	1.9	< 0.2	0.62	1.2	0.10	114
2D	890	1169	8.1	5.2	116	3.1	2.1	76	28	17	1.1	< 0.2	< 0.2	0.48	0.26	251

this sense, children have been considered as vulnerable targets to metal/loid uptake from unintentional hand-to-mouth action (e.g., [17, 28]). Table 3 shows the total amount of metal/loids absorbed during the simulation of accidental oral ingestion of mine waste particles. As can be seen, high quantities of Fe, Pb, and Al were released during the simulation of digestive ingestion of waste particles, with average values of 4825 mg/kg of Fe (389–15,542 mg/kg), 1672 mg/kg of Pb (114–10,321 mg/kg), and 807 mg/kg of Al (108–1988 mg/kg). Lower quantities were released of other metals such as Mn (6.4–173 mg/kg), Zn (28–1087 mg/kg) or Cu (4.3–185 mg/kg). During the simulation, other metalloids were released. Average values of 62 mg/kg of As (17–235 mg/kg), 10 mg/kg of V (7.4–11 mg/kg), 8.1 mg/kg of Cr (3.5–23 mg/kg), 7.9 mg/kg of Co (0.71–20 mg/kg), 2.4 mg/kg of Ni (0.47–7.5 mg/kg), 2.2 mg/kg of Sb (0.3–6.9 mg/kg), 2.2 mg/kg of Tl (0.1–16 mg/kg), or 1.7 mg/kg of Se (0.3–4.0 mg/kg) were found. In the case of Mo and Cd, most values were below the detection limit, although values between 0.5 and 1.5 mg/kg were observed for levels 2A–C (Table 3). Fig. 3 shows the relative absorption (with respect to total content) of metal/loids during the simulation of the accidental ingestion of waste particles. As can be seen, Zn and Mn exhibited a high bioaccessibility during gastric assimilation of mine waste particles, with values ranging from 11% to 52% for Mn and 9.1–72% for Zn. The release of other metals such as Tl and Pb remained below 20% of total content,

except for the level 2B, which exceeded these values (i.e., 51% for Tl and 35% for Pb). Helsner et al. [16] reported a high Pb bioaccessibility by the easily dissolution of cerussite from mine wastes and a lower bioaccessibility in samples where sulfide predominated. This would explain the variable values of Pb bioaccessibility found, with the lowest values recorded in the acidic 2C level.

The release of Cr and Cu also reached values below 20% except for levels 1A, 2B and 2C for Cr and levels 1E and 2B for Cu, which slightly surpassed these values (Fig. 3). The same pattern was also observed for V, with most values below 20%, but exceedances in levels 1A, 2B and 2D. On the other hand, elements such as Se and Al exhibited values below 15% for all samples (1.6–12% for Al and 0.2–6.9% for Se). The metal/loids which displayed the lower bioaccessibility were Fe, Sb and As, with values below 5%, although in this latter case exceedances were observed in level 2C (16%; Fig. 3), of acidic nature.

#### 3.4. Relationship between waste mineralogy and metal/loid release

The mineralogy of studied wastes was mainly dominated by Fe minerals such as goethite, hematite and to a lesser extent jarosite, Fe silicates and carbonates (Table 1 and S2, and Fig. S3), with a significant proportion of impure hematite (16–40%) and nanosized goethite (up to 7%). These minerals have high sorption capacities for metals/loids such

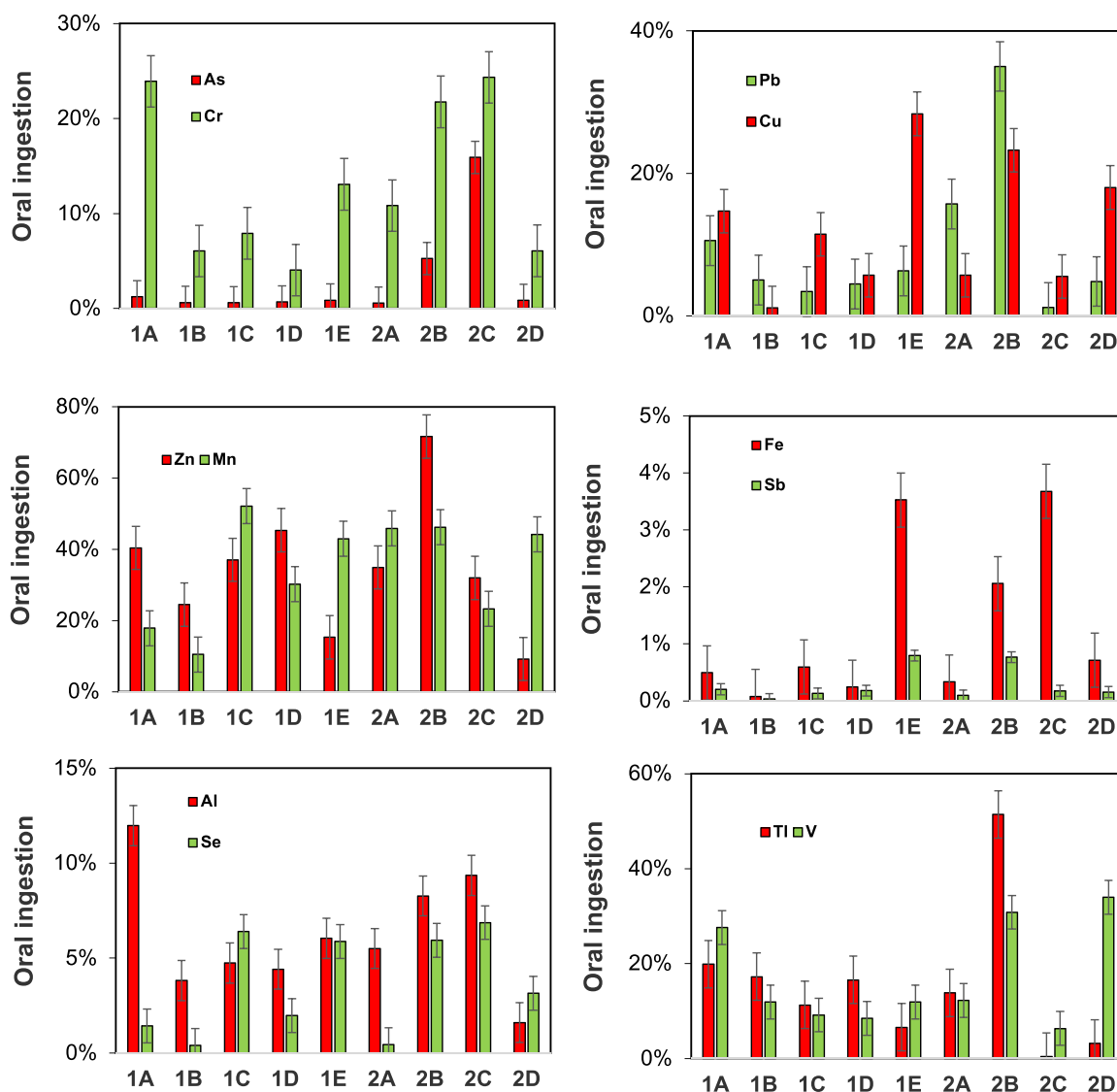


Fig. 3. Relative absorption (with respect total content) of some metal/loids during the simulation of accidental oral ingestion.



as As, Cr, Pb, or Se, especially if they are present as nanoparticles due to their larger surface area and different structure [38].

Fig. 4 shows the results of the PCA performed on bulk composition and mineralogy of studied wastes. Three different groups can be observed according to the position of minerals and elements in the PCA; i) a group dominated by Fe minerals such as hematite, jarosite and gypsum, where elements such as Ca, S, Cu, Zn, Cd, Tl, Pb, Fe or Sb would be hosted; ii) a group mainly dominated by goethite, where elements such as As, Se, V, Fe and Sb are found; and iii) a group dominated by quartz and carbonates, where the presence of elements such as Mg, Na, K, Al, N, Mn is observed. Groups related to goethite and hematite are

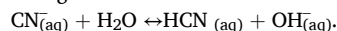
placed close each other in the PCA, with Fe and Sb located in both groups (Fig. 4).

The solubility of minerals contained in the wastes is critical to control the weathering of mine wastes and the release of metal/loids into the water bodies. Fig. 4 also shows different groups depending on the soluble compounds during the interaction with water and the mineralogy of wastes. On the one hand, a group formed by levels 1C, 2B and 2C, dominated by the presence of hematite, gypsum and jarosite, which has a great potential of metal/loid release, especially the level 2C, of acidic nature and high concentrations of Fe, Al, Cu and As. The dissolution of gypsum and other metal sulfates (not detected by XRD) may have caused the release of high concentrations of  $\text{SO}_4$ , Ca and metal/loids such as Se, Pb, Tl, Mn, Co, Ni, or Zn. Although jarosite was present in most levels and waters exhibited subsaturation (Fig. S7), the dissolution of this mineral may play a minor role considering the low concentrations of Fe observed during the leaching tests. On the other hand, a group comprising the remaining waste levels, which exhibited a lower reactivity due to the predominance of silicate materials and goethite, is observed in Fig. 4. Despite this lower reactivity, elements such as Mo and Sb would be preferentially released due probably to the dissolution of alkaline minerals (e.g., carbonates), as evidenced the presence of K and Na together with higher pH values in this group.

In the leaching test with water (i.e., soluble; Fig. 4) pH conditions were close to neutrality for most waste levels (pH of 5.9–7.4; Table 2), except for 2C which exhibited acidic conditions (pH 2.3; Table 2), and the higher metal release potential. Therefore, the release of metal/loids during the simulation with gastric fluids upon more acidic conditions (pH 1.7) is expected to be higher than in the previous leaching with water. As can be seen in Fig. 4, three different groups can be identified according to the metal/loid bioaccessibility; i) a group composed of levels 2B and 2C, with predominance of gypsum, jarosite and hematite, which seems to be related to the bioaccessibility of Fe, As, Pb, Cu, Se, Sb or Tl; ii) a second group formed by the 1E level, with remarkable bioaccessibility of Ni, Co, Al and Mn; and finally, iii) a third group including the remaining levels, with predominance of silicate materials and goethite and enhanced bioaccessibility of V and Cr. Davis et al. [7] studied the bioaccessibility of As and Pb in mine soils using simulating digestive fluids, reporting the preferential dissolution of anglesite ( $\text{PbSO}_4$ ) and enargite ( $\text{Cu}_3\text{AsS}_4$ ) as most likely phases controlling Pb and As solubility. However, in some cases encapsulation by less soluble phases, like jarosite, may reduce the release of these elements [8]. This variable mobility among elements was also observed by Lin and Quvarfort [20] who reported a high release of Fe, Cu, and Zn associated with secondary sulfate minerals but a low release of Pb due to the incorporation of this metals into altered silicates during roasting.

### 3.5. Mechanisms of metal mobilization in the leaching heaps

Cyanide and its degradation in leaching heaps may play an important role in metal mobilization. The dissolution of solid sodium cyanide leads to the formation of  $\text{Na}^+$  and  $\text{CN}^-$ , which forms complexes with target (i. e., Au and Ag) and unwanted metals (e.g., Fe, Cd, Zn, Ni, Cu or Co) within the heaps. However, it can also follow hydrolysis according to the following reaction:



The amount of cyanide converted to hydrogen cyanide depends on the salinity and especially the pH of the solution. At  $\text{pH} > \sim 10.5$ , most of the free cyanide is present as  $\text{CN}^-$ . However, at  $\text{pH} < \sim 8.3$  all free cyanide is present as HCN which is certainly volatile and can be released into the atmosphere [23]. Therefore, during the hydrometallurgical process, the addition of alkaline reagents (e.g., CaO or  $\text{Ca}(\text{OH})_2$ ) to cyanide solutions is required, especially in sulfide heap leach piles. Once the mining operations cease, the concentrations of free cyanide in pore waters of sulfidic heap leach piles may increase over time due to decreasing pH conditions caused by rainfalls and the uptake of carbon dioxide from the atmosphere, which leads to the transformation of

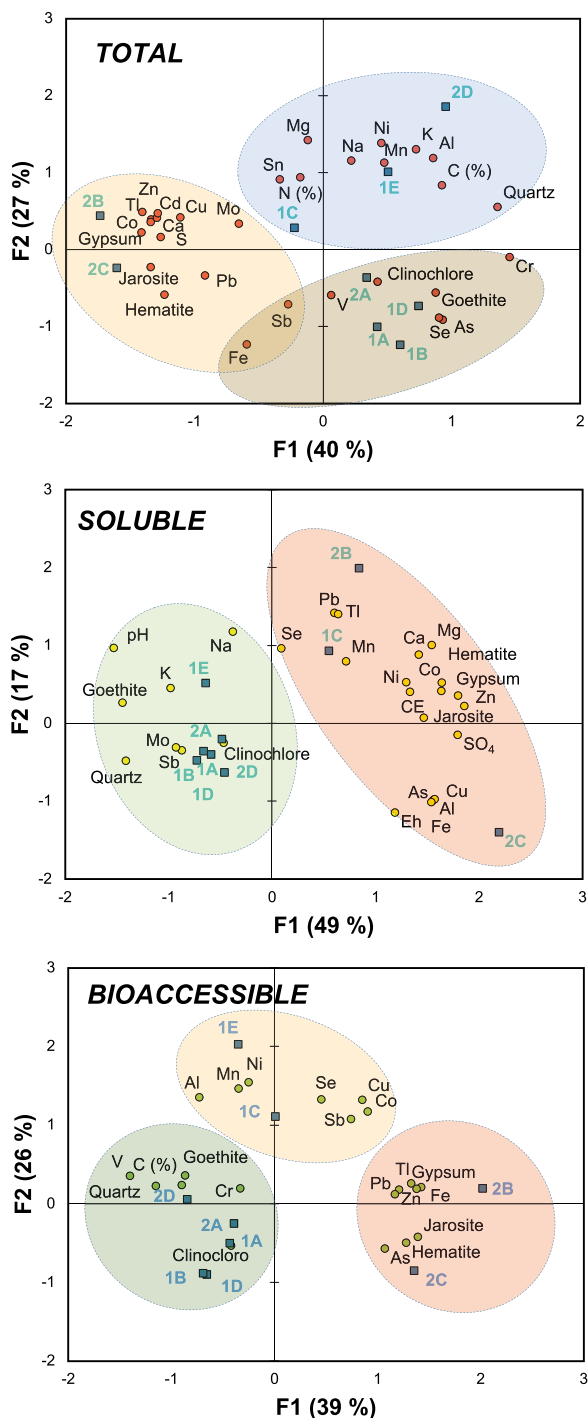
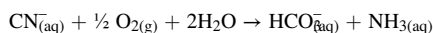


Fig. 4. Results obtained after applying a Principal Component Analysis (PCA) to the bulk, soluble and bioaccessible metal/loid contents of wastes studied.

stable cyanide complexes into HCN, which will be subsequently volatilized [23]. Thus, volatilization is the major mechanism of natural cyanide attenuation in leaching heaps, accounting up to 90% of the cyanide removed from heaps, while the other 10% losses occurring through other processes such as biological oxidation, degradation through UV radiation or formation of thiocyanate [5]. In this sense, certain bacteria such as *Pseudomonas* naturally present in the heaps can degrade cyanide to obtain nutrients for their growth following this simplified equation:



The rates of these processes are site-dependent and are affected by numerous factors such as the intensity of light, ore mineralogy, rainfall regime, temperature, pH, salinity, oxidant concentration, and complexes concentration [5]. For example, the effectiveness of natural degradation of cyanide in leaching heaps was evaluated by Engelhardt [14], indicating that 85% of cyanide originally present after leaching had been naturally degraded after 18 months. A longer period was documented by Declercq et al. [11] who modeled the natural degradation of cyanide in a leaching heap. These authors reported a total degradation of cyanide in the upper part of the heap, mainly by volatilization, after 13 years, highlighting a reduced rate in the lower part of the heap, where these removal processes seemed to be limited. Therefore in derelict mine sites, where mineral processing ceased long time ago, residual cyanide may play a minor role in metal mobilization compared to dissolution/precipitation of secondary minerals. This fact was highlighted by Parbhakar-Fox, [30] at the Croydon Au-mines, where heap leaching operations were performed in 1984–1985 on mineralized rhyolites hosting sulfides. Thus, the occurrence of secondary minerals beudantite, hidalgite, kintoreite and Fe-As-Pb oxides controlled the metal mobilization from these heaps. In the present study, the leaching ceased in 2001, so it is reasonable to think that cyanide may also play a minor role in metal mobilization from these heaps and the dissolution/precipitation cycles of secondary minerals associated to climate regime may control instead the mobility of these metals. In addition, microbiological processes play an important role not only in cyanide degradation, but also in metal mobilization, biomineralization, precipitation, and mineral transformation. For example, the oxidation of residual sulfides in the heaps is catalyzed by bacteria, enhancing the metal release from the heaps, especially with time. This can be seen in the pH-paste results (Fig. S4), where the total dissolved solids increase notably with time (e.g., from 8.9 to 20 mS/cm in level 2B). Thus, the long-term weathering and leaching of these heaps would lead to an increased metal/loid release as Yin et al. [40] reported for Tl in uranium mine tailings containing sulfides.

#### 4. Conclusions

The mobility and bioaccessibility of metal/loids in Fe-rich (up to 55%) mine wastes resulting from historical cyanide leaching activities was evaluated in this study through chemical analysis (i.e. total composition, and leaching and bioaccessibility tests) and mineralogical techniques (i.e., XRD, SEM-EDS, and Mössbauer spectroscopy). These wastes are mainly composed of oxides/oxyhydroxides (i.e. goethite and hematite), oxyhydroxysulfates (i.e. jarosite), sulfates (i.e., gypsum, evaporitic sulfate salts), carbonates (i.e., calcite, siderite) and quartz, highlighting the abundance of impure hematite, which in some cases exceeded that of pure phases, and variable amounts of nanosized goethite.

The chemical composition of studied wastes is consistent with the mineralogical assemblage, with high concentrations of Fe (16–55%) and low content of S (0.58–4.8%). The leaching heap wastes turned to be especially enriched in trace elements (1453–6943 mg/kg of As, 5216–15,672 mg/kg; of Pb, 308–1094 mg/kg of Sb, 181–1174 mg/kg of Cu, 97–1517 mg/kg of Zn, and 24–403 mg/kg of Mn).

Leaching test with distilled waters revealed the neutral pH values of leachates (pH 5.7–7.4), except for level 2 C of acidic nature (pH 2.3) due to the presence of sulfides and other acid-generating minerals (i.e., Fe sulfates). The wastes displayed a high reactivity, as evidenced by the high electrical conductivity (EC) values in leachates, ranging from 0.47 to 5.4 mS/cm, and high dissolved concentrations (180–4424 mg/ of sulfate, 54–604 mg/L of Ca, up to 282 mg/L of Na and up to 110 mg/L of Mg) associated to the dissolution of secondary minerals such as carbonates, gypsum, and other sulfates. In addition, high concentrations of Se (up to 300 µg/L), Tl or Pb (up to 866 µg/L) were observed. On the other hand, it is especially striking the release of metal/loids from the acidic level 2 C with high concentrations of Fe (970 mg/L), Al (24 mg/L), As (7972 µg/L), Cu (5083 µg/L), Cr (277 µg/L) or V (4.4 µg/L), which are scarcely mobile at circumneutral pH values recorded in the remaining waste levels. This high release of metal/loids is associated to the dissolution of evaporitic Al and Fe sulfate minerals formed after sulfide oxidation in the heaps. The studied wastes must be treated before disposal in safe conditions as the Se concentrations exceeded threshold values for hazardous wastes in all leachates (and other metal/loids such as Cr, Ni, Cu, Zn, As, Cd, Pb and Sb in other levels). These wastes would also pose a significant risk for aquatic life due to the release of As, Zn, Ni and Pb.

High concentrations of Fe, Pb, and Al were released during the simulation of digestive ingestion of waste particles, with average values of 4825 mg/kg of Fe (389–15,542 mg/kg), 1672 mg/kg of Pb (114–10,321 mg/kg), and 807 mg/kg of Al (108–1988 mg/kg). Lower quantities of Mn (6.4–173 mg/kg), Zn (28–1087 mg/kg), As (17–235 mg/kg), V (7.4–11 mg/kg), Cr (3.5–23 mg/kg), Sb (0.3–6.9 mg/kg), Tl (0.1–16 mg/kg), or 1.7 mg/kg of Se (0.3–4.0 mg/kg) were released. Regarding the relative bioaccessibility, base metals such as Zn and Mn exhibited high values (up to 72% and 52% of release).

Mineralogy may control the mobility and bioaccessibility of metal/loids in cyanide leaching heaps. A multivariate statistical analysis performed on bioaccessible fractions links the dissolution of gypsum, jarosite and hematite to the bioaccessibility of Fe, As, Pb, Cu, Se, Sb or Tl. On the other hand, the bioaccessibility of Ni, Co, Al and Mn seems to be related to the dissolution of an un-identified minerals (e.g., aluminosilicate or Mn oxide), while the acid attack of silicate materials and goethite enhanced the bioaccessibility of V and Cr. Upon weathering conditions (i.e., rainfall events), the dissolution of highly soluble secondary minerals such as carbonates and sulfates controls the metal/loid release (e.g., such as Se, Pb, Tl, Mn, Co, Ni, or Zn) from cyanide leaching heaps.

#### CRedit authorship contribution statement

**C.R. Cánovas:** Writing – original draft, Conceptualization, Funding acquisition, Investigation, Supervision, Writing – review & editing. **R. Moreno-González:** Methodology, Visualization, Writing – review & editing. **B.J.C. Vieira:** Methodology, Visualization, Writing – review & editing. **J.C. Waerenborgh:** Methodology, Visualization, Supervision, Writing – review & editing. **R. Marques:** Methodology, Visualization, Writing – review & editing. **F. Macías:** Formal analysis, Validation, Writing – review & editing. **M.D Basallote:** Methodology, Visualization, Writing – review & editing. **M. Olías:** Conceptualization, Validation, Investigation, Supervision, Writing – review & editing. **M.I Prudencio:** Conceptualization, Funding acquisition, Investigation, Supervision, Writing – review & editing.

#### 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

Data will be made available on request.

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## Environmental Implications

Unlike acidic sulfide mine wastes, alkaline wastes such as those generated during cyanide leaching to obtain Au and Ag have received less attention. These wastes exhibit a high reactivity upon rainfall weathering due to the dissolution of secondary minerals such as carbonates, gypsum, and other sulfates, exceeding the threshold values for hazardous wastes in some heap levels for Se, Cu, Zn, As, and sulfate leading to potential significant risks for aquatic life. The accidental ingestion of resuspended particles may also lead to the absorption of metal/loids, especially Fe, Pb and Al.

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2023.130948.

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