

## Mineral reactivity in sulphide mine wastes: influence of mineralogy and grain size on metal release

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**Abstract:** The aqueous oxidation of sulphide minerals leads to the generation of acid mine drainage (AMD), one of the main causes of water pollution worldwide. Mineral reactivity is greatly enhanced as a result of extraction and processes such as blasting, crushing, and grinding that increase rock surface area. The exposition of sulphide mine wastes to atmospheric conditions enhances AMD generation. However, a large number of processes and factors (*e.g.*, pH, redox conditions, aqueous and surface complexation reactions) may control the mobility of elements in solution. In particular, the formation of soluble secondary minerals may act as transient storage of metals and acidity during AMD generation, leading however to their release upon rainfalls. To study the influence of mineralogy and grain size on the metal release from a variety of sulphide mine wastes collected in the Iberian Pyrite Belt, different grain size samples were treated with distilled water (S:L ratio 1:10) for 24 h simulating rainfall weathering. Results reveal that grain size plays a major role on metal mobility from sulphide mine wastes. However, mineralogical and geochemical evidence points at the partitioning of highly soluble secondary minerals among grain size fractions as the key factor controlling the metal release rate from these wastes. The results obtained show the importance of grain size on the reliability of the different leaching test procedures, and thus encourage standardizing these procedures worldwide.

**Key-words:** metal release; leaching test; grain size mineral fractionation; secondary minerals; sulphates; acid mine drainage.

### 1. Introduction

Sulphides are stable and very insoluble under reducing conditions, but exposure to atmospheric conditions through mining enhances sulphide oxidation, leading to a process known as acid mine drainage (AMD), considered as one of the main causes of inorganic water pollution worldwide. AMD is an environmental challenge, especially in areas affected by sulphide and coal mining, where the release of acidity, sulphates, iron and other metals and metalloids (*e.g.*, Cu, Zn, Co, Cd, Ni, As, *etc.*) commonly affects the quality of receiving streams and groundwater (*e.g.*, Resongles *et al.*, 2015; Cánovas *et al.*, 2017). A detailed description of reactions controlling sulphide oxidation can be found in Nordstrom (2011). On the other hand, AMD also has a strong economic impact; costs for total worldwide liability associated with the current and future remediation of AMD were estimated at approximately \$100 billion (Tremblay & Hogan, 2001).

Sustainable mining requires tools to predict future drainage quality at mine sites. The results of laboratory leaching tests are strongly controlled by several variables such as solution pH, redox condition, mineralogical composition, specific surface area, contact time, and liquid-to-solid ratio,

to name a few. Among them, the mineralogical composition of samples seems to play a critical role (Benvenuti *et al.*, 2000). The potential release of toxic elements from mine wastes upon weathering involves mineral–water interactions and, thus, a complete characterization of reactive minerals present in fresh and weathered material is required to understand the chemical reactions involved (Jamieson *et al.*, 2015). Soluble sulphate salts may act in dry seasons as temporary sinks for acidity and minor elements such as Cd, Co, Zn, Ni, Cu and Mn, which are again released during rainfall events in wet seasons (*e.g.*, Bigham & Nordstrom, 2000; Hammarstrom *et al.*, 2005; Cánovas *et al.*, 2008). The identification of these mineral phases by conventional techniques of mineralogical characterization (*e.g.*, X-ray diffraction [XRD]) is often difficult since they tend to precipitate within a set of more crystalline minerals and requires a detailed examination of samples.

On the other hand, grain size may also have an important influence on mineral reactivity, which is usually enhanced as a consequence of extraction and processing (*e.g.*, blasting, crushing and grinding) during mining activities, leading to the increase of reactive surface area and a higher exposure to water and oxygen. In this sense, the grain size of mining wastes may also have a strong influence on environmental

policies as particle-size reduction is often recommended during predictive dissolution tests of mining wastes aimed at fulfilling environmental regulations (Lapakko *et al.*, 1995). Leaching test procedures commonly used by environmental agencies to assess the reactivity of materials usually limit the maximum grain size; however, different grain sizes are established. These limitations could lead to contradictory results for the same tested material upon diverse tests using different grain sizes and treatments (*i.e.*, crushing), as leaching is a surface-controlled process and smaller grains have a greater specific surface area (Karius & Hamer, 2001). There is a lack of studies dealing with the role of grain size on metal release from sulphide wastes. The influence of the grain size on the metal release under weathering conditions must be therefore properly addressed.

These issues are especially relevant in derelict mines, with absence of control measures, such as most of those existing in the Iberian Pyrite Belt (SW Spain), where intense mining developed since antiquity has left a huge volume of AMD-producing wastes deposited in the vicinity of mine sites and exposed to weathering. Thus, the main goal of this work is to study the influence of mineralogy and grain size on the metal release upon rainfall weathering from a variety of sulphide mine wastes.

## 2. Methodology

### 2.1. Sampling

The Iberian Pyrite Belt is one of the most important polymetallic sulphide-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. This area has the largest accumulation of metal mine wastes in Spain, with a total of 20 tailings impoundments containing 109 Mm<sup>3</sup> (Rodríguez-Pacheco & Gómez de las Heras, 2006). Samples were collected from the Zarandas mineral processing plant (Riotinto mining district; Fig. 1), where the mined mineral, mainly pyrite, was crushed and roasted in order to produce sulphuric acid *via* SO<sub>2</sub> recovery with water. A smelter and a plant for sulphuric acid production were located in this mine site, the latter being in operation until the 70s of the last century. This site, characterized by the occurrence of large tailing dams and spoils heaps, is close to the pyritic tailing dam “Represa III” previously studied by Arranz-González *et al.* (2012). Three different waste typologies were selected in this study; 1) wastes from pyritic tailing dam (ZA1), 2) roasted pyrite wastes (ZA2) and 3) spoil heap wastes (ZA3) (Fig. 1).

A composite sample of approximately 2 kg was collected from each waste typology using a polypropylene shovel previously washed with distilled water, and transferred to polypropylene sterile bags. Surface samples, more exposed to weathering, were discarded. Samples were oven-dried (30 °C), sieved in the laboratory at different grain sizes (*i.e.*, 5, 2, 1, 0.5, 0.16, and 0.074 mm) and stored in sterile polypropylene containers until analysis. Aliquots of each raw sample were also milled up to obtain powder size for geochemical and mineral characterization.

### 2.2. Chemical characterization

Bulk samples were analysed at MS Analytical (Langley, Canada) for major and trace elements after a multi acid digestion (*i.e.*, HCl, HNO<sub>3</sub>, HClO<sub>4</sub> and HF). The resulting solutions were analysed by inductively coupled plasma optical emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). Analytical accuracy was confirmed by the analysis of reference materials (OREAS 904). The analytical precision was assessed by duplicate analysis and differences were <5% for all elements.

The behaviour of the wastes samples upon rainfall weathering was studied by performing the EN 12457-2 leaching test (CEN, 2002), which is based on submitting samples to leaching with distilled water for 24 h (ratio 1:10). This procedure has been commonly applied to assess the acceptance for disposal of a waste in European landfill sites, including its use for a wide variety of mine wastes (*e.g.*, Vemic *et al.*, 2015; Macías *et al.*, 2017). Leachates were analysed, after filtering at 0.45 µm and acidification to pH < 2, 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 20 µg/L for trace elements. A triplicate analysis was performed to evaluate the analytical precision and the measurement error was <5% in all cases. In each analysis sequence, blanks were analysed, and all elements were below the detection limits. Analytical accuracy was confirmed by the analysis of reference materials (NIST-1640).

### 2.3. Mineralogical characterization

XRD patterns of each grain size sample after soft grinding were carried out at the R + D Services of the University of Huelva using 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. Semi-quantitative chemical analyses and imaging of samples were obtained by scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS; FEI-Quanta 200 equipped with a microanalyser EDAX Genesis, 2000). XRD patterns and SEM information were obtained before and after submitting samples to EN 12457-2 test in order to assess mineralogical changes in samples during the leaching test.

### 2.4. Data treatment

A Principal Component Analysis (PCA) has been performed on samples to infer patterns of behaviour in selected variables. The use of PCA allows the number of variables in a multivariate data set to be reduced, whilst retaining as much as possible of the variation present in the data set. Variables were standardized to z-scores to fit a normal distribution, thus the Pearson ( $n - 1$ ) correlation matrix was used (Davis, 2002).

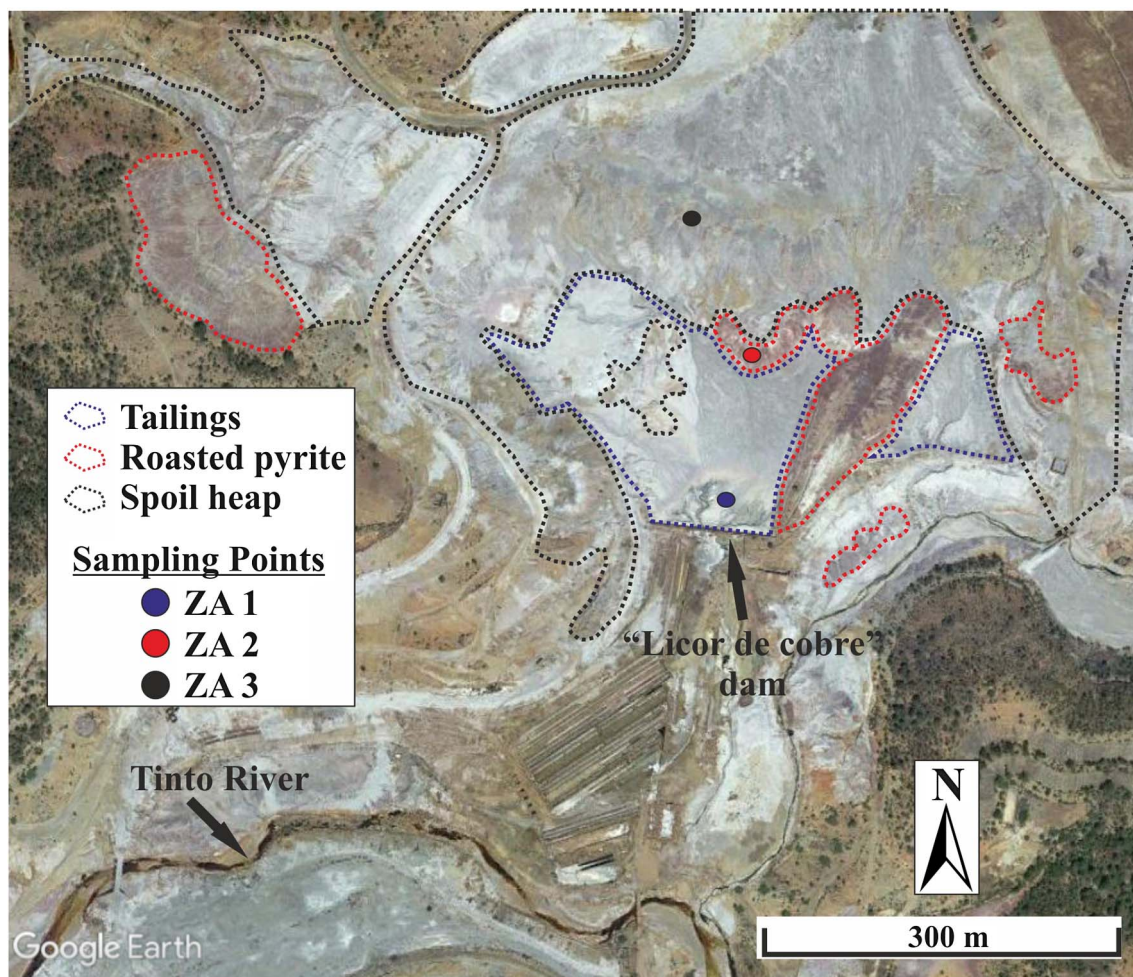


Fig. 1. Location map of the sampling site, showing the total area covered by each waste type studied.

### 3. Results

#### 3.1. Chemical and mineralogical characterization

The main chemical and mineralogical characteristics of the studied mine wastes can be seen in Table 1. Wastes from the pyritic tailing dam (ZA1) are composed of a fine grain size and grey colour pyritic sludge (Fig. S1 in Supplementary Material linked to this article and freely available at the GSW website of the journal: <https://pubs.geoscience-world.org/eurjmin>). These wastes arise from the ore processing activities (*i.e.*, crushing, grinding, and flotation) developed in this mine site, and have a high water content. The erosion of the nearby and even overlying wastes (Fig. 1) causes the transport and deposition of fine-grained wastes. The sample is mainly composed of pyrite, hematite and quartz (Table 1), although the high crystallinity of these minerals may mask the presence of other less abundant minerals. Roasted pyrite samples (ZA2) are composed of red colour wastes of different grain sizes, characterized by the presence of salt efflorescence at the surface (Fig. S1). The XRD patterns revealed the presence of quartz and hematite and the absence of pyrite. On the other hand, samples collected from the spoil heaps (ZA3) are composed of grey colour wastes, showing small red mineral grains embedded in

the surface (Fig. S1), which could come from the weathering of the surrounding roasted pyrite spoils. The XRD patterns reveal a composition similar to ZA1, with the presence of quartz and pyrite (Table 1).

The lowest S concentrations were observed for the roasted pyrite samples (ZA2), around 2.1 wt% S, whereas the other wastes studied exceeded 10 wt% S content (Table 1). Despite being apparently spoil heap wastes, the sample ZA3 exhibited a higher Fe concentration (39 wt%, Table 1) than tailing and roasted pyrite wastes (around 25 wt%). As expected, the highest concentrations of other metal and metalloids were observed in pyritic tailing samples; *e.g.*, around 20 200 mg/kg of Pb, 2679 mg/kg of As, 1863 mg/kg of Zn, and 1083 mg/kg of Cu. (Table 1). On the other hand, the metal content observed in spoil heaps wastes (ZA3) exceeded those observed in roasted pyrite samples (ZA2), due to the existence of sulphides in the spoil heaps (Table 1).

#### 3.2. Leaching tests performed on bulk and grain-size fractions

The mineral reactivity of samples was assessed simulating rainfall weathering in laboratory. Table 1 shows the release of metals during the EN 12457-2 leaching test and the

Table 1. Chemical and mineralogical characteristics of bulk samples, and release of S and metal/loids (expressed as % soluble) during the 12457-2 leaching test.

Mineralogy	Al	Ca	Fe	K	Mg	Na	S	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Sb	Sn	Sr	Tl	V	Zn	
	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	
ZA 1 Q, Py, Ht	2.3	0.04	25	0.73	0.07	0.44	11	2679	7.1	55	49	1083	133	13	20	200	520	180	55	40	45	1863
% soluble	11	40	7.6	0.40	57	3.2	17	2.0	26	9.0	40	53	40	27	0.10	0.11	0.01	2.3	0.5	7.3	34	
ZA 2 Q, Ht	0.68	0.03	27	0.32	0.03	0.1	2.1	737	2.3	23	142	747	52	13	6961	266	153	28	30	31	551	
% soluble	32	80	3.4	0.02	62	0.05	55	16	54	23	42	43	45	44	0.01	0.07	0.02	3.8	0.03	7	62	
ZA 3 Q, Py	0.09	0.01	39	0.03	0.01	0.07	10	1893	4.7	79	381	749	124	27	11	200	683	238	8.4	59	47	1062
% soluble	29	45	6.2	31	33	2.1	18	7.0	28	5.1	46	18	18	42	0.24	4.0	0.03	3.0	3.1	19	39	

comparison with the total concentration of the samples. Despite the high concentrations of Fe found in samples, this element exhibits a low mobility under rainfall conditions (3.4–7.6% of total; Table 1). Other elements such as Sb, Tl, Pb and Sn also reveal low soluble percentages during the test (generally below 1%, Table 1). On the other hand, other elements such as Al (11–32%), Co (5–23%) or V (7–19%) were moderately soluble during the test. In this sense, sulphur also showed a moderate mobility (around 18%) in tailing (ZA1) and spoil heaps samples (ZA3), while noticeably higher values were observed in roasted pyrite samples (ZA2) (55%; Table 1). Elements commonly associated with host rocks such as Ca (40–80%) and Mg (33–62%) also showed a high solubility, whereas K, Na or Sr were scarcely released (0.02–3.8%; Table 1).

Figure 2 shows the concentration of some elements after submitting the different grain-size aliquots of samples to the same procedure (*i.e.*, EN 12457-2 leaching test) as applied to the bulk sample. A progressive increase in concentration of most elements (*e.g.*, Fe, As, S, Ni, Co, Cu, Zn, Mn or Al) is observed with decreasing grain size, which is especially evident below 0.16 mm (Fig. 2). This tendency is observed in roasted pyrite samples (ZA2) and especially in spoil heaps (ZA3; Fig. 2). In the case of roasted pyrite samples (ZA2), a sharp increase in concentration is observed in the finest grain size (below 0.074 mm), especially for Fe, S, Al, Zn, As, Ni and Co.

However, in the case of tailing samples (ZA1) a different tendency is observed. A progressive increase can be initially seen for most elements linked to the medium grain size. However, a decrease in concentration is observed in most elements thereafter, although related to different grain size fractions. In this way, the decrease in concentration for Ca and As is observed below the 0.76 mm grain size, S and Al below 0.16 mm and Fe, Zn and Ni below 0.5 mm. On the other hand, the decrease in concentration for Cu is noticed even at higher grain sizes (*i.e.*, below 1 mm).

## 4. Discussion

### 4.1. Influence of mining activities on mine wastes properties

The study site is strongly affected by mining activities, as shown by the occurrence of tailing dams and waste heaps of different nature. Such activities determine the physico-chemical properties of mine wastes. For example, tailings

(ZA1) show the highest content in fine-grained particles due to the mineral processing performed (*i.e.*, crushing, grinding, and flotation). The influence of mining activities on the chemical properties is also significant. The lowest values of S were observed in roasted pyrite samples (ZA2), which is consistent with the absence of pyrite since this waste results from the roasting of pyrite-rich ores to remove S for mineral beneficiation. The remaining S may thus arise from an inefficient roasting, the formation of secondary sulphates undetected by XRD, or even from sorption processes. As previously reported by Pérez-López *et al.* (2009), iron oxides resulting from the roasting usually present a porous texture with high surface area able to adsorb SO<sub>2</sub> during the roasting process (Lin & Qvarfort, 1996). In some cases, inappropriate waste management policies commonly observed in derelict mine sites lead to the occurrence of waste piles with unexpected high metal concentrations. This is the case of spoil heap samples (ZA3), which show very high concentrations (of *e.g.* Fe, Cr, Sb; Table 1) as compared to other wastes, due to the presence of pyrite-rich material within the spoil heaps.

### 4.2. Mineral reactivity

Mineralogy seems to control the metal release in sulphide mine wastes. Thus, the low release of some metals (*i.e.*, Fe, Sb, Tl, Pb and Sn) during the leaching test must be linked to their presence as oxide and sulphide phases, while others commonly found in insoluble minerals (*e.g.*, Al, Co or V) show a moderate solubility, probably linked to their occurrence in sulphate salts. The differences observed among wastes in the release percentages of S must be related to the different minerals hosting S in samples; while S may be mainly hosted by sulphides in tailings (ZA1) and spoil heaps (ZA3), soluble sulphates or adsorbed SO<sub>2</sub> may be the main contributor of S in roasted pyrite (ZA2). This adsorbed S would be readily released when iron oxides react with infiltrating water, which explains the high S concentrations leached during the leaching test and is consistent with the mineral processing performed.

The release of metals from these mine wastes seem to be controlled by the dissolution of previously precipitated efflorescent sulphates, mainly of Fe. These minerals are formed by evaporation of AMD in mining environments and incorporate other metal/loids (*e.g.*, As, Cu, Zn, Co, and Ni) as impurities (Buckby *et al.*, 2003). Divalent metals such as Cu, Zn, Ca or Mg have been reported to substitute Fe(II)

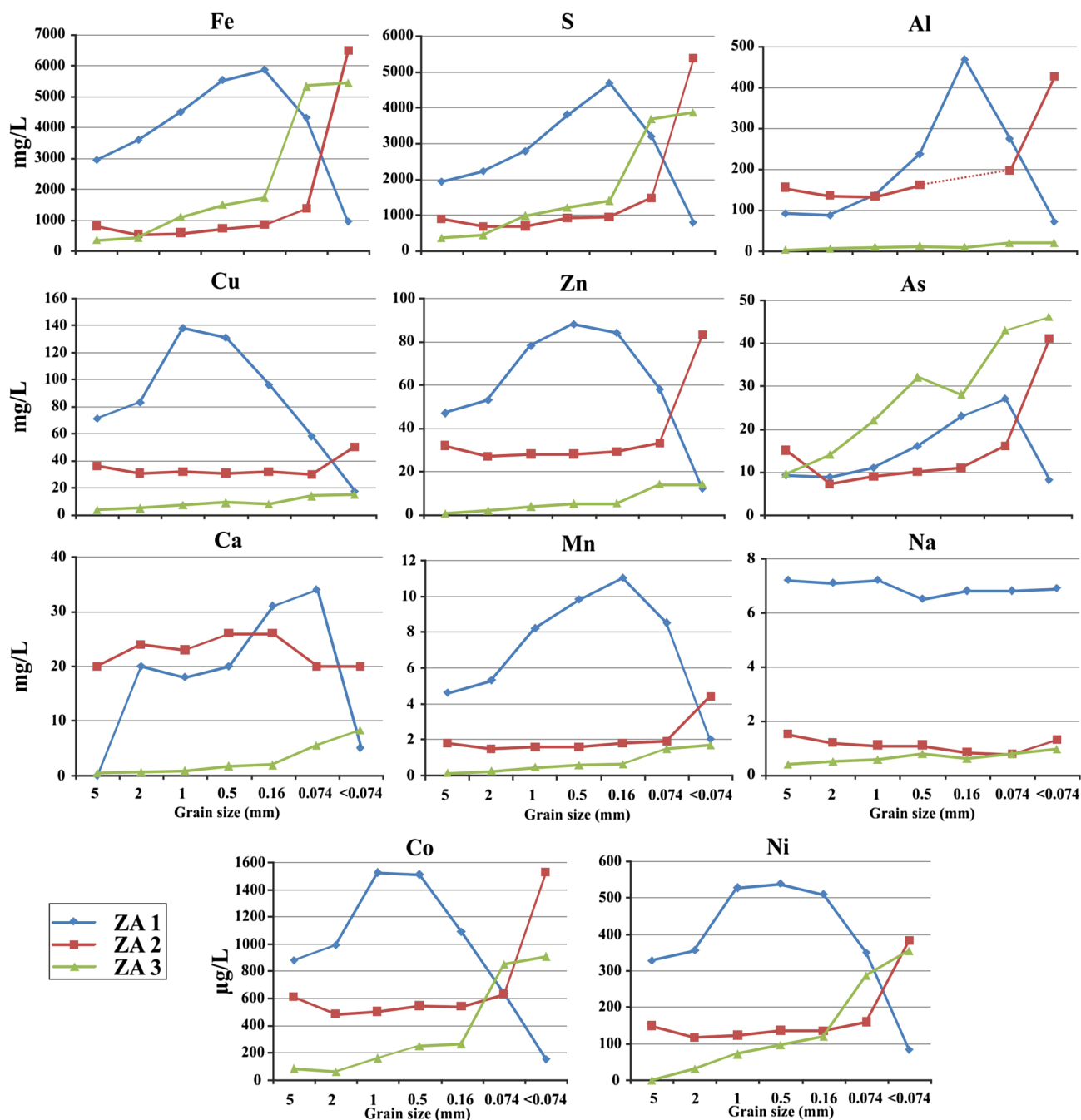


Fig. 2. Release of S and selected metal/loids during the leaching test performed on each grain-size fraction of studied samples.

in the structure of these minerals (*e.g.*, Jamieson *et al.*, 1999; Jambor *et al.*, 2000; Buckby *et al.*, 2003). The high solubility of these minerals upon weathering conditions converts them into temporary storage of metal/loids, leading to severe episodes of pollution upon their dissolution (*e.g.*, Keith *et al.*, 2001; Hammarstrom *et al.*, 2005; Cánovas *et al.*, 2008, 2010). The capacity of these minerals for storage of metals and their release back to the environment after rainfalls have been reported worldwide. Smuda *et al.* (2007) reported the mobility of metals from a sulphide waste rock dump from Cerro del Pasco (Peru). These authors reported a similar release of metals (*i.e.*, Fe, Cu, Zn, Mn, and Cd) than

that observed in our study, as well as the low mobility shown by Pb. On the other hand, Lin & Quvarfort (1996) reported a high release of Fe, Cu, and Zn associated with secondary sulphate in roasted pyrite wastes in central Sweden. These authors also reported a low release of Pb because roast-derived altered silicates acquired Pb, showing a low solubility. In the Iberian Pyrite Belt, Arranz-González *et al.* (2012) obtained lower values of Cu (28%) and Zn (15%) in sulphide tailings from Cueva de la Mora and Zarandas. These authors also reported low percentages of As release (<0.3%) due to the fact that As is stable as oxyanion under acid and oxidizing conditions, being mainly

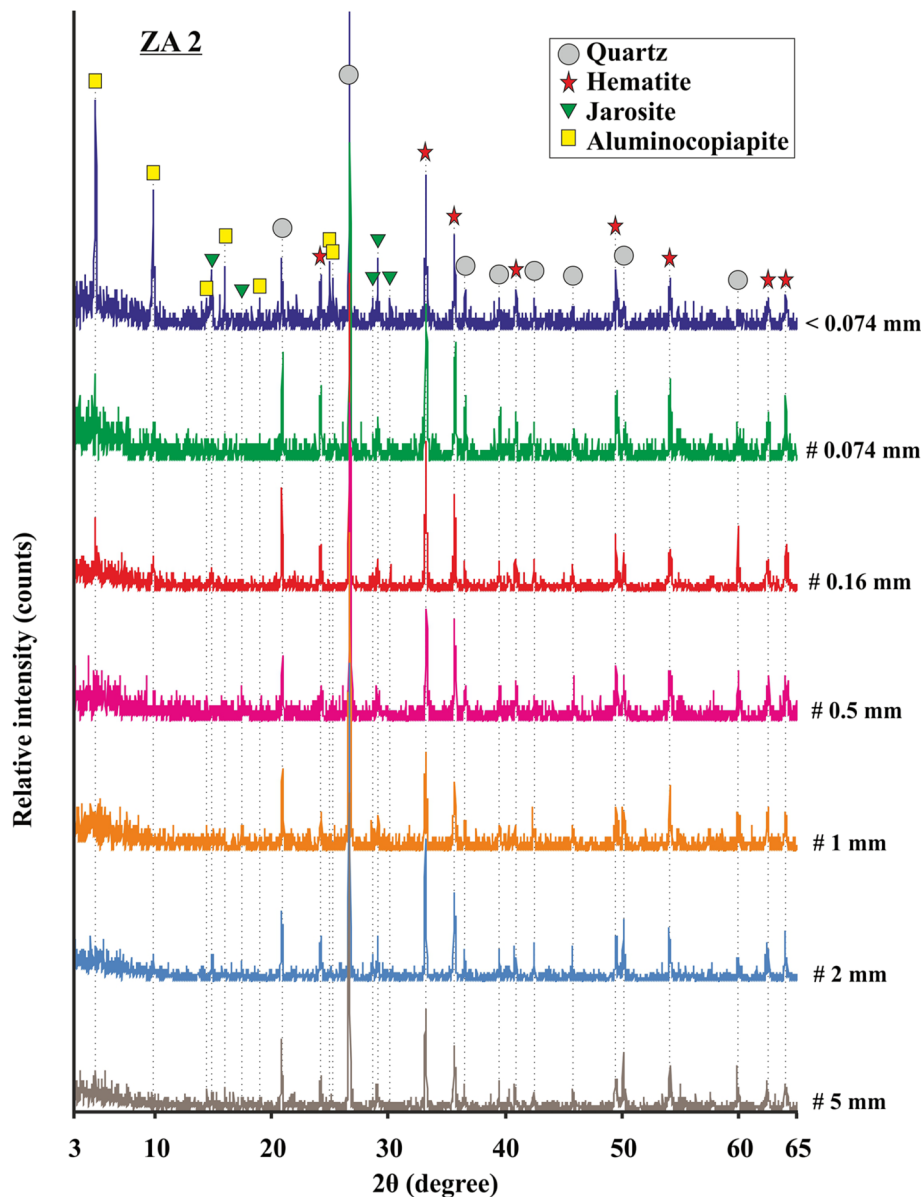


Fig. 3. X-ray diffraction patterns of each grain-size fraction of roasted pyrite wastes (ZA2).

adsorbed onto the secondary ferric minerals, insoluble in water.

#### 4.3. Influence of grain size on metal leaching

Mineral reactivity is also strongly affected by particle size, porosity and surface area. In this sense, sulphide tailings are much fine grained and have a much higher specific surface area available for oxidation and leaching reactions than waste rocks (Lottermoser, 2010). Therefore, the general belief is that the decrease in grain size would lead to increasing levels of mineral reactivity due to the higher specific surface area of minerals. This tendency was observed for roasted pyrite (ZA2) and spoil heap samples (ZA3). However, a different pattern was observed for tailing samples (ZA1, Fig. 2).

These different patterns suggest the existence of other factors controlling the leaching behaviour of studied mine wastes. One possibility could be the existence of mineralogical differences among grain size distributions. Figures 3–5 show the XRD patterns of the different grain sizes in each sample. The XRD patterns of the grain size fractions reveal the presence of minor minerals that did not show diffraction effects in the bulk sample (Table 1). The coarser fractions of roasted pyrite (ZA2) are characterized by the occurrence of quartz, hematite and jarosite. However, as long as the grain size decreases, the presence of aluminocopiapite ( $\text{Al}_{2/3}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$ ), a highly soluble efflorescent sulphate, is more abundant (Fig. 3). The presence of this mineral would explain the increase of S, Fe and Al observed in the fine grain sized samples during the leaching test (Fig. 2). The concentration of other metal/loids such as As, Zn, Ni or

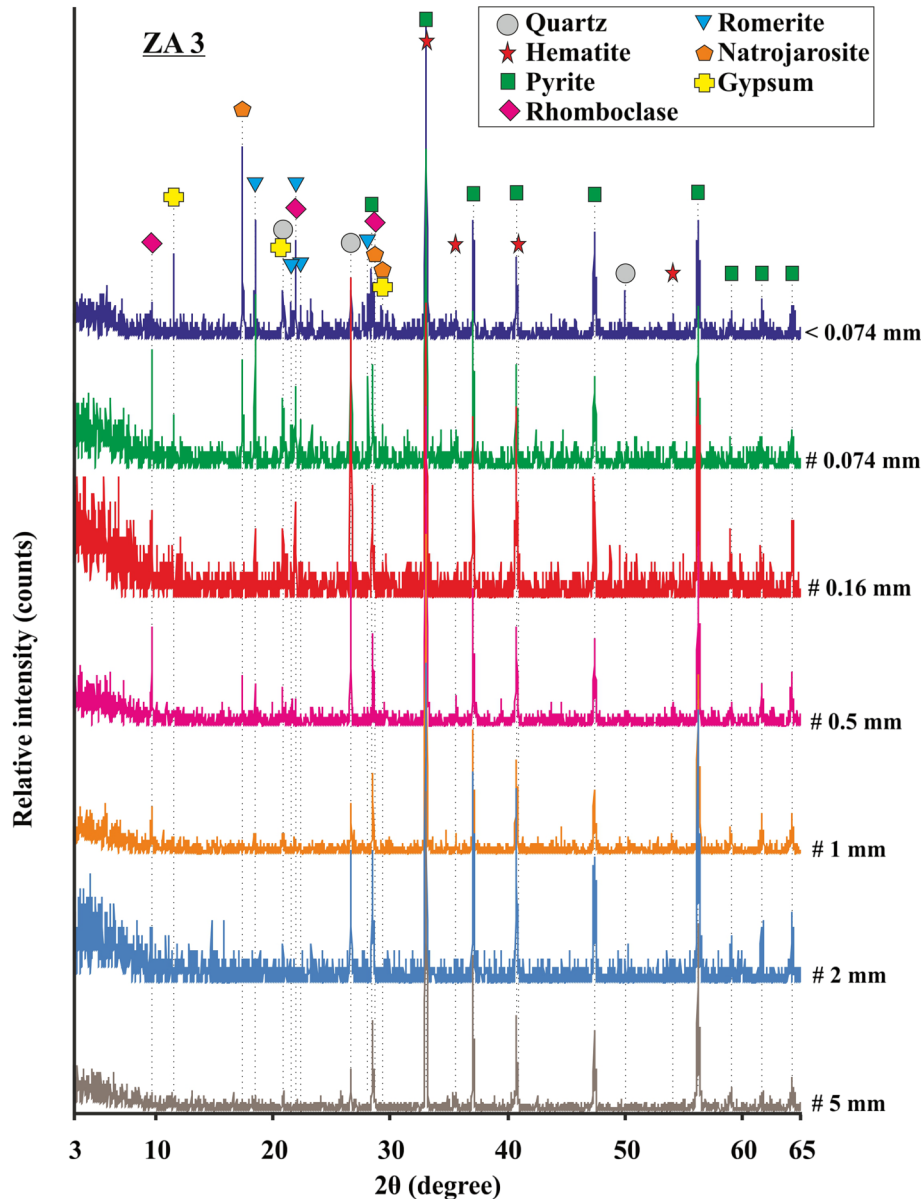


Fig. 4. X-ray diffraction patterns of each grain-size fraction of spoil heap wastes (ZA3).

Cu also increases in the fine grain-size fractions (Fig. 2), which host significant amounts of aluminocopiapite.

A similar pattern is observed in spoil heap samples (ZA3), where the coarse grain-size fractions are characterized by the presence of quartz, hematite and pyrite (Fig. 4), while the fine grain-size fractions are characterized by the occurrence of other efflorescent salts such as römerite ( $\text{Fe}^{2+}\text{Fe}^{3+}(\text{SO}_4)_4 \cdot 14(\text{H}_2\text{O})$ ) and rhomboclase ( $\text{H}_3\text{Fe}^{3+}\text{O}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ). In addition, the presence of other less soluble sulphates such as natrojarosite and gypsum was also identified in the XRD patterns of the fine grain-size fractions. In the same way as in roasted pyrite samples (ZA2), the dissolution of these efflorescent minerals contained in the fine grain-size fractions led to the sharp increase in sulphate and metal concentrations. The dissolution of gypsum may also have caused the increase in Ca concentrations observed in the fine fractions of roasted pyrite samples (ZA2), but not that

observed for spoil heaps (ZA3) where this mineral was not identified in the XRD patterns (Fig. 4).

Conversely, the absence of XRD peaks of efflorescent minerals in the fine and coarse grain-size fractions of tailing samples (ZA1) is striking. In this sense, only the 0.16 mm fraction shows intense peaks of copiapite (Fig. 5), which may explain the highest concentrations of most metals linked to this medium grain size in relation to fine and coarse fractions (Fig. 2).

These results can be compared with other studies worldwide. Embile *et al.* (2016) tried to characterize the effects of grain size on drainage production of samples from the Recsk porphyry skarn Cu–Zn deposit in Hungary, an area known to generate AMD. These authors reported that grain size correlated with the sulphate release: the highest sulphate release was observed for lower grain sizes. However, the leaching of metals established an increasing concentration

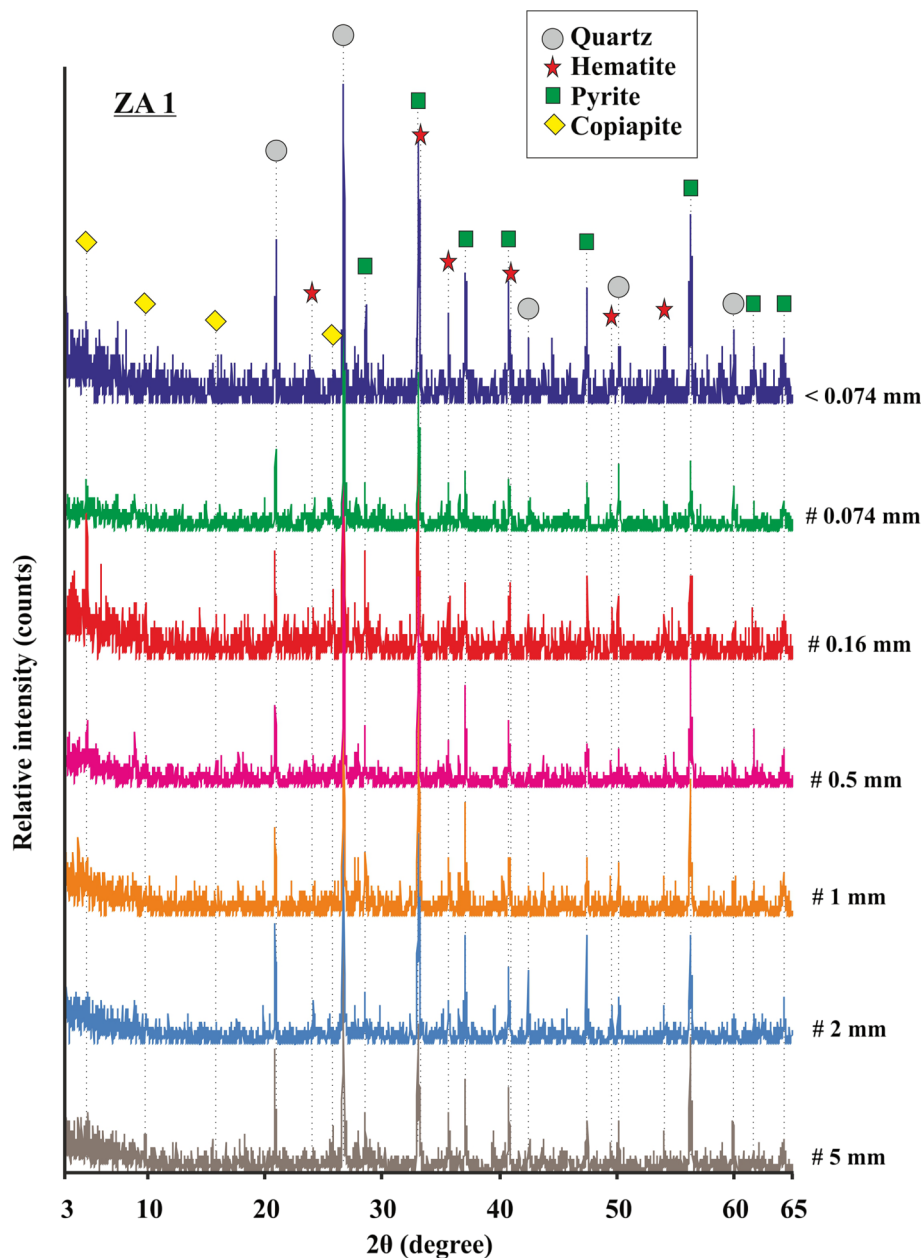


Fig. 5. X-ray diffraction patterns of each grain-size fraction of pyrite tailing wastes (ZA1).

with increasing acidity, without a very clear relationship to grain size. In this sense, they reported that finer grains produced the highest concentration of Zn, while the coarser grains produced the highest concentrations of Fe. Just the opposite finding was reported by [Silva \*et al.\* \(2014\)](#) in cinnabar mines in Asturias (NW Spain), who found a clear tendency of As to be accumulated in the finest particle-size.

#### 4.4. Mineralogical and grain-size fraction controls on metal release

As discussed in [Sections 4.2 and 4.3](#), the potential release of metals from the studied wastes may be strongly controlled not only by their grain size but also by their mineralogical composition. This finding is also supported by the results

of PCA ([Fig. 6](#)). The spoil heaps (ZA3) leaching behaviour, characterized by high release of trace metals such as As, Se, Pb, Sb or Tl, may be strongly controlled by the presence of soluble sulphates (*i.e.*, römerite, rhomboclase or gypsum); thus, the finer the grain size, the higher the release. On the other hand, sulphide tailings (ZA1) proved to be a significant source of sulphate and metals (*e.g.*, Fe, Al, Cu, Zn, and Mn) because of the presence of copiapite ([Fig. 5](#)) although, unlike the spoil heaps, the higher potential release is not linked to the fine grain-size fractions but to the medium ([Fig. 6](#)). In the case of roasted pyrite (ZA2), the high contents in hematite and jarosite, a sulphate less reactive to water, confer this sample a lower release potential than the other wastes studied. However, the presence of copiapite in the fine grain-size (<0.074 mm; [Fig. 3](#)) provides



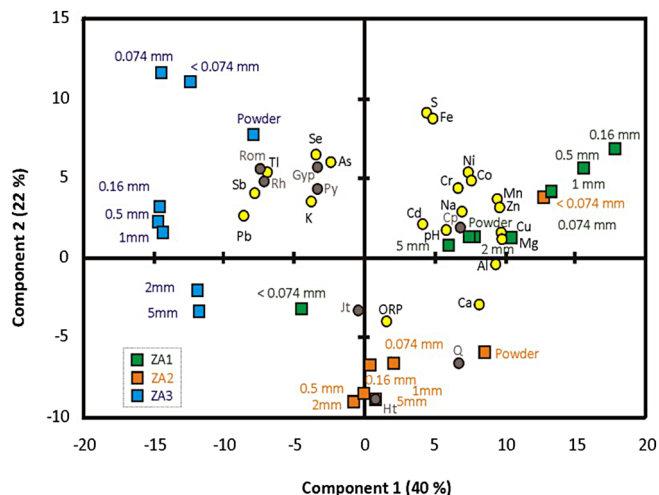


Fig. 6. Principal Component Analysis (PCA) performed on each grain-size fraction submitted to leaching tests. Mineralogical abundance was obtained from semi quantitative values.

this fraction a higher capacity to release metals, similar to tailing samples (ZA1).

The dissolution of these minerals during the leaching test is illustrated by the SEM-EDS images of selected grain-size fractions before and after the test (Fig. 7). The presence of sulphates coating the surface of quartz and pyrite grains can be clearly appreciated in bulk tailing samples (ZA1, Fig. 7a). However, these efflorescent sulphates have

disappeared from the surface of these minerals after the leaching test, as shown, *e.g.*, by the quartz grain in Fig. 7b, which seems to be very clean. The same fact is observed in roasted pyrite (ZA2) and spoil heaps (ZA3) samples. The SEM image of roasted pyrite samples (ZA2) before the test (Fig. 7c) proved the presence of Fe-sulphate crystals with a chemical composition close to copiapite, previously identified by XRD, as well as jarosite, coating the surface of other minerals such as quartz. However, the dissolution of the more soluble sulphate during the leaching tests causes the clearance of the mineral surfaces, leaving only the more insoluble minerals such as quartz and low-solubility sulphates (*i.e.*, anglesite and barite; Fig. 7d). The SEM image of the spoil heap sample (ZA3) reveals a high abundance of acicular crystals of Fe sulphate (Fig. 7e), confirming the XRD results, which identified the occurrence of r merite and rhomboclase in this grain-size fraction. Together with these efflorescent minerals, the SEM image also revealed the presence of less soluble S minerals such as anglesite and pyrite. In turn, when the sample is submitted to the leaching test, the sulphate crystals disappear (Fig. 7f).

## 5. Environmental and policy implications

Although the waste handling practices are continuously improving, environmental problems that need to be addressed remain in abundance (Majzlan *et al.*, 2006, 2018). The exposure of sulphide-rich mine wastes to

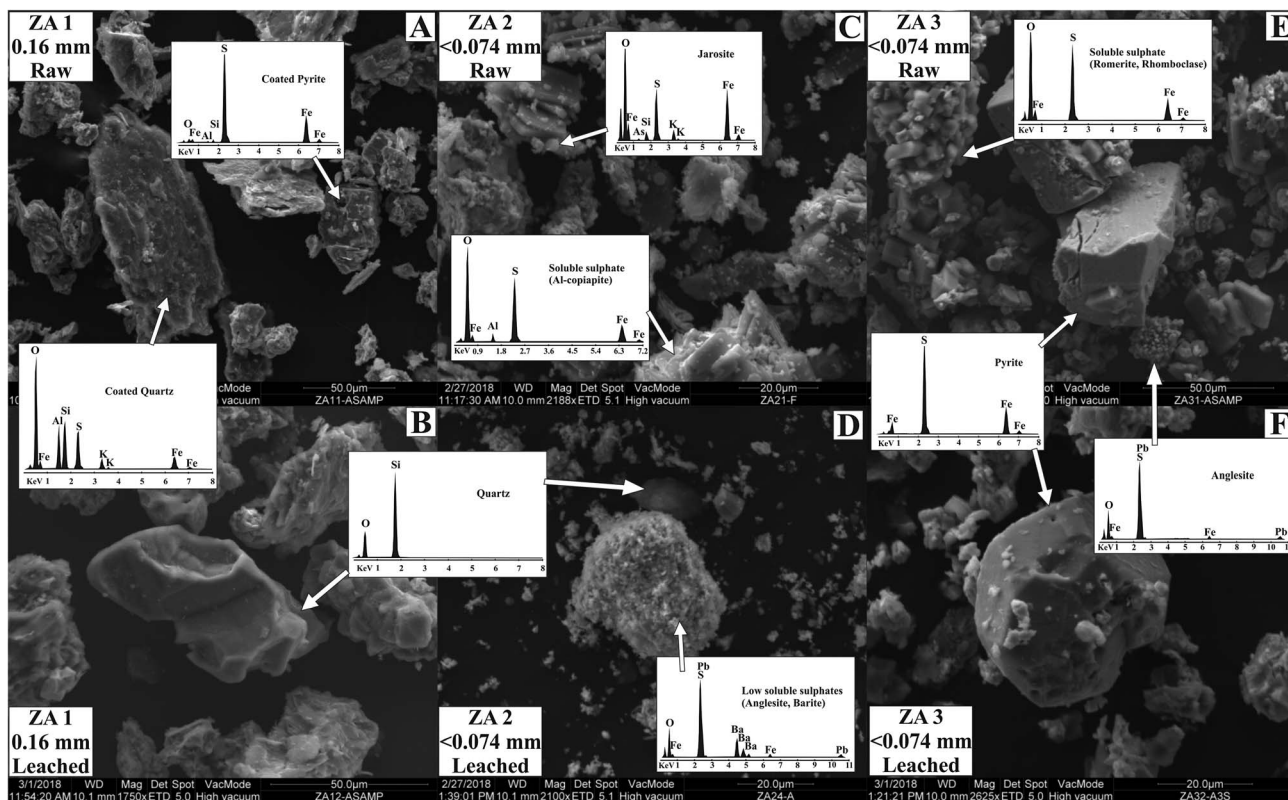


Fig. 7. Scanning electron microscope (SEM) images of selected grain-size fractions of samples before (A, C, E) and after (B, D, F) being submitted to the leaching test. EDS spectra of selected grains are included (insets).

atmospheric conditions leads to the formation of AMD and secondary minerals. In some cases, these minerals evidence a high solubility upon rainy events, thus affecting water bodies in different climatic settings (Hammarstrom *et al.*, 2005). This phenomenon is especially relevant in semiarid climates, where long dry periods give way to short but intense rainy events, which constitute severe episodes of pollution (Cánovas *et al.*, 2010). The formation of secondary minerals constitutes a temporary storage of metals during sulphide oxidation; however, when rainfall takes place these metals are remobilized. The longevity of AMD processes guarantees the recurrence of these pollutant episodes in AMD affected environments for a long time to come. Thus, the adoption of restoration measures is urgently needed, especially in derelict mine sites, where mine wastes are commonly widespread without any type of isolation which could limit the release of metals to the hydrosphere.

On the other hand, the results obtained in this study highlight the importance of grain size and mineral distribution among grain sizes as factors controlling the metal release during weathering reactions. This fact could have significant policy implications due to the different procedures adopted by environmental agencies to evaluate the potential release of metals from environmental matrices. Leaching test procedures usually limit the maximum grain size for practical purposes, but there is no unanimous consensus about the size needed to apply such procedures. Some methods propose crushing the sample to obtain powder while others submit the raw sample to the test. This could provide different results for the same tested material, due to different mineral specific surface exposed to reactions. In addition, it is not unusual to find procedures that apply different maximum grain sizes. For example, Hageman *et al.* (2015), describe the requirement of crushing the samples below 9.5 mm before performing the EPA procedures of Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) (USEPA, 2004). Even in the case of the procedure followed in this study (EN 12457-2; CEC, 2002) to evaluate the reactivity of the sulphide mine wastes, different grain sizes are proposed (10 and 4 mm). In the case of the Japanese Standardized Leaching Test, the particle size cut-off is 5 mm, reducing by crushing those particles above this limit. The Australian Standard Leaching Protocol (ASLP) is derived from the USEPA TCLP, allowing the use of distilled water and reducing the particle size to be tested down to 2.4 mm. This fact therefore encourages standardizing these procedures worldwide, after a detailed investigation of different matrices, trying to mimic as close as possible real conditions found in the field.

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