Title:

Management strategies and valorization for waste sludge from active treatment of extremely metal-polluted acid mine drainage: a contribution for sustainable mining

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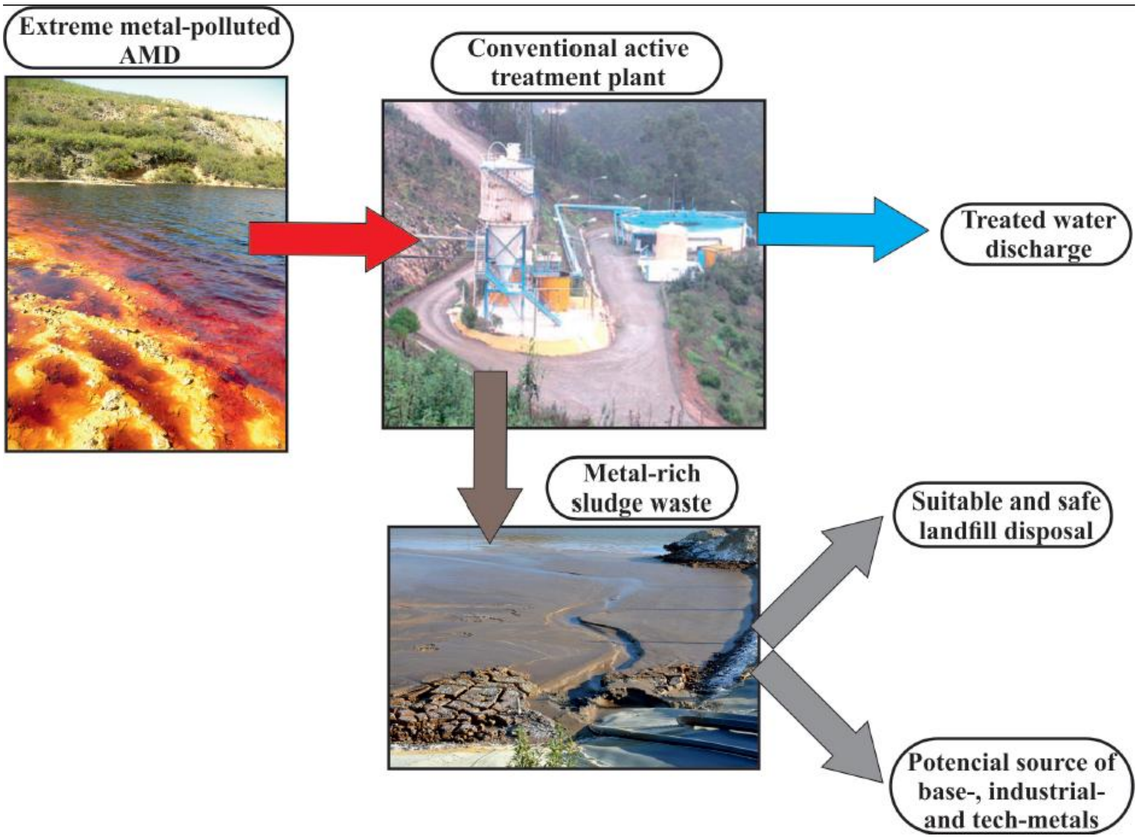
Abstract

This study assesses the environmental impact and the potential valorization of metal-sludge waste generated by the active neutralization of extremely metal-polluted acid mine drainage (AMD). To this end, two regulated leaching tests (EN 12457-2 and 1311 USEPA TCLP), a standardized sequential extraction protocol (BCR sequential extraction) and single leaching tests were performed using dilute common industrial acids. The results of the two standardized leaching tests showed a complete discrepancy, classifying the waste as both inert (according to the TCLP) and not suitable for disposal at landfills for hazardous waste (according to EN 12457-2). In this regard, the environmental characterization of the waste using the BCR sequential extraction lined up with interpretations made by the EN 12457-2 leaching test, reinforcing the hazardousness of this type of residue. This waste requires careful management, as evidenced by the release of high concentrations of metals (e.g., Cd, Zn, Al) when interaction with rainfall and organic acids take place, exceeding the risk threshold values for aquatic life. The easy extraction of base, industrial- and tech-metals that is possible with dilute acids encourages the consideration of this type of sludge as an interesting alternative metal source with great economic potential. The joint application of remediation treatments and metal recovery schemes could contribute to the goal of zero waste production in mining activities, which would help to develop sustainable mining practices worldwide.

Keywords:

metal sludge; acid mine drainage; environmental assessment; waste valorization

Graphical abstract



1. Introduction

Water resources can be severely damaged by mining activity, especially when no action is taken to prevent pollution. In working and orphan sulfide-bearing mining sites, exposure of mining waste to oxygen and water leads to the generation of acidic waters with high concentrations of sulfate and metal(loid)s, known as acid mine drainage (AMD). These highly polluted waters become a serious environmental concern (Akcil and Koldas, 2006). AMD generation processes are very long-lived and can persist for hundreds and even thousands of years after cessation of the mining activities (Younger, 1997). Mine waters can be treated by two generic approaches, active or passive treatment systems (Johnson and Hallberg, 2005). Both in active and passive treatment systems, acidity and metals are removed from the solutions using different (bio)geochemical reactions that lead to the generation of a solid waste (generally as a metal-rich sludge) (Johnson and Hallberg, 2005).

Zinck and Griffith (2013) conducted a detailed study on the waste production from conventional active and passive treatment technologies at 108 working mine sites in Canada and other countries. On average, these sites produced about 9,500 tons of dry sludge per year, with production ranging from 20 to 135,000 dry tons per year depending of the site. These figures are not exhaustive but indicative of the huge worldwide production of waste from AMD neutralization. In addition, this production is expected to rise due to the foreseen increase in metal mining and the expected generation and/or implementation of stricter environmental regulations around the world.

This waste should be properly disposed of in order to avoid environmental impacts. To this end, the stability of this waste under different disposal and weathering scenarios must be addressed. In this regard, several scenarios have been proposed (e.g., Zinck, 2005; Zinck and Griffith, 2013); however, to date no studies on leaching behavior under different weathering conditions have been performed; thus, there are no information of the suitability of disposal according to environmental regulations. In this sense, static and dynamic, single and sequential leaching tests are well established and widely accepted methods to determine the potential metal release of mining waste (Hageman et al., 2015). However, to our knowledge, these types of leaching tests have not been properly performed in waste that derives from the neutralization of acidic waters, mainly in conventional active treatment plants, which are the most common technology used for AMD depuration.

The recycling and reuse of mining and mineral processing waste can be considered one of the main challenges for future waste management (Lottermoser, 2011). A few investigations focused on the reusability of this waste have been reported, mainly in construction, agriculture or carbon dioxide sequestration (Zinck, 2005), also as neutralizing material for AMD-generating waste rocks and tailings (Demers et al., 2015) or directly for mine waters remediation (Wolkersdorfer and Baierer, 2013). Nevertheless, such practices could be limited by the high content of toxic impurities, and so most waste remains stored in disposal areas, causing environmental problems. Recent researches report a fractional precipitation of metals of economic interest by active neutralization of AMD which could be a promising metal source from AMD (Chen et al., 2014), which potential recovery is being still tested at pilot scale (Yan et al., 2015).

The mining industry currently faces a challenge of global significance: the development of sustainable mining (Laurence, 2011, Moran et al., 2014). Developed countries such as those of the European Union (EU) or United States of America emphasize the need of supplying the growing demand for base-, industrial- and tech-metals, by reducing its dependence on external suppliers (Silberglitt et al., 2013), while ensuring the environmental safety (EU Commission, 2016). Among them, the reuse of mining and mineral-processing wastes is one of the most promising secondary sources (Bian et al., 2012). To our knowledge, the reuse of conventional active treatment wastes as a potential source of metals has not been properly assessed until now.

To bridge these gaps, the present study aimed to explore environmental risk, management strategies for land disposal and the valorization of metal sludge waste generated by AMD neutralization at active treatment plants. With this purpose, sludge formed by the active neutralization of an extreme metal polluted AMD from the Almagrera mining industrial complex (Iberian Pyrite Belt, IPB) was characterized. This characterization included different leaching tests evaluating the land disposal options proposed by the current European (EN 12457-2, 2002) and US environmental regulations (US EPA, 1998). The potential mobility of metals contained in the sludge was assessed by the standardized sequential extraction procedure proposed by the European Community Bureau of References (BCR, Ure et al., 1993a), while the exposure of aquatic life to metals by an uncontrolled leachate from the sludge was studied under several scenarios (e.g., rainfall, co-disposal with municipal wastes). Finally, the potential valorization of the sludge was investigated by leaching experiments to extract elements of technological and industrial interest. This novel approach based on the joint application of environmental tests (single and sequential, static and dynamic), and metal recovery schemes on these metal-rich residues may contribute to a sustainable mining of sulfide ore deposits.

2. Materials and methods

2.1 Metal sludge from the AMD neutralization at Almagrera Industrial Complex

From 1982 to 2001 polymetallic sulfide ores were processed in Almagrera Complex (SW Spain) by flotation to obtain Cu, Pb and Zn concentrates. In addition, crude pyrite refuses were processed (by roasting and SO_2 recovering) to produce sulfuric acid, oleum and Cu sulfate. As a consequence of these mineral processing activities two tailing ponds were built to accommodate the generated wastes (sulfide tailing pond and roasted pyrite pond, Fig. 1A). Despite restoration in 2006, two AMD discharges (AMD1 and AMD2, Fig. 1A) emerged from both impoundments. AMD1 exhibits remarkable extreme metal concentrations (especially Al, Cu, Fe, Mn and Zn; Table 1), whereas AMD2 could be considered a typical moderately polluted AMD within a sulfide mining district like the IPB.

Due to the severity of the mentioned AMD pollution, the regional authorities implemented a conventional active treatment plant which comprised a first step of alkaline dosing (CaO and/or MgO) followed by an agitation/sedimentation tank (Fig. 1B). Due to the low flow rates of AMD1 (annual mean of 1.5 L/s) and AMD2 (0.4 L/s), both discharges are pumped out to a storage pond near to the treatment plant (Fig. 1A). Thus, the treatment plant works temporally when enough combined AMD has been accumulated. The resulting metal-rich waste sludge is pumped out to a pond built over the surface of the tailing ponds, where around 39,000 tons are stored (Fig. 1A and C). In the metal-sludge pond, a representative sample (approximately 2kg) of the first 20 cm from the shallowest part was collected close to the discharging point during an inactive period of the treatment plant, using a polypropylene shovel previously washed with distilled water, and transferred to polypropylene sterile bags. In the laboratory, the sludge was oven-dried (30 ºC), ground and stored in sterile polypropylene containers until analysis. Subsamples were used for the different analytical procedures.

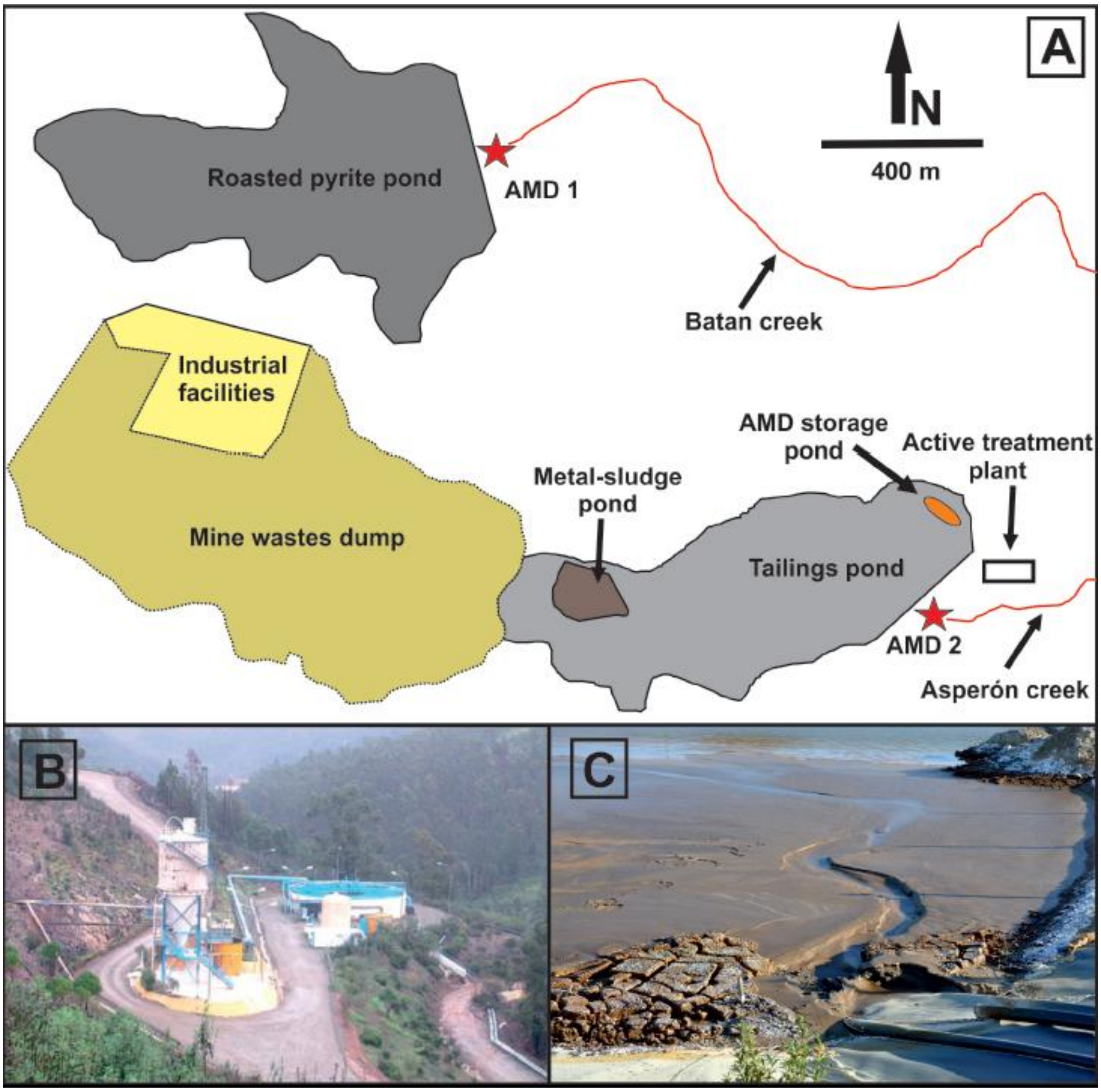
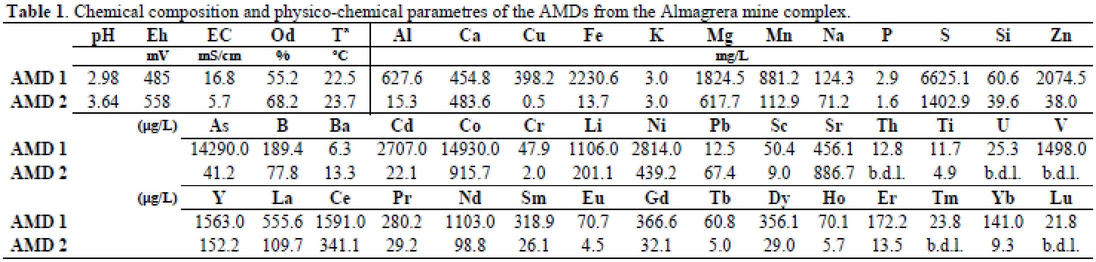


Fig. 1.

Table 1. Chemical composition and physico-chemical parametres of the AMDs from the Almagrera mine complex.



	pH	Eh	EC	Od	T^a	Al	Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Si	Zn
		mV	mS/cm	%	°C	mg/L											
AMD 1	2.98	485	16.8	55.2	22.5	627.6	454.8	398.2	2230.6	3.0	1824.5	881.2	124.3	2.9	6625.1	60.6	2074.5
AMD 2	3.64	558	5.7	68.2	23.7	15.3	483.6	0.5	13.7	3.0	617.7	112.9	71.2	1.6	1402.9	39.6	38.0
		(µg/L)	**As**	**B**	**Ba**	**Cd**	**Co**	**Cr**	**Li**	**Ni**	**Pb**	**Sc**	**Sr**	**Th**	**Ti**	**U**	**V**
AMD 1			14290.0	189.4	6.3	2707.0	14930.0	47.9	1106.0	2814.0	12.5	50.4	456.1	12.8	11.7	25.3	1498.0
AMD 2			41.2	77.8	13.3	22.1	915.7	2.0	201.1	439.2	67.4	9.0	886.7	b.d.l.	4.9	b.d.l.	b.d.l.
		(µg/L)	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
AMD 1			1563.0	555.6	1591.0	280.2	1103.0	318.9	70.7	366.6	60.8	356.1	70.1	172.2	23.8	141.0	21.8
AMD 2			152.2	109.7	341.1	29.2	98.8	26.1	4.5	32.1	5.0	29.0	5.7	13.5	b.d.l.	9.3	b.d.l.

b.d.l. (below detection limit).

2.2 Leaching protocols for management and hazardousness assessment

As stated before, management assessment and hazardousness classification of the sludge were addressed according to the EU standard EN 12457-2 (2002) leaching test and the US standard TCLP leaching test (US EPA, 1998). The EN 12457-2 leaching test assesses the suitability of wastes for disposal in a landfill site. The experimental concentrations obtained in the test can be compared with the limit threshold values established by the European Council (EC Decision 2003) for the acceptance of wastes in three types of landfill sites: inert, non-hazardous and hazardous wastes. Given that it is the first time that static tests are used in sludge from active AMD treatment, and following the suggestions of the European rule (EC Decision 2003), the EN 12457-2 leaching test was repeated three consecutive times in a same sample aliquot to have information on the effluent quality and extractability over time.

The Toxicity Characteristic Leaching Procedure (TCLP) (US EPA, 1998) was originally designed to simulate co-disposal with municipal wastes but also used for the hazardousness classification of mineral-processing wastes (e.g., Vemic et al., 2015). Additionally, metal concentrations in TCLP leachates can be also employed as limits to determine if a specific waste needs to be submitted to a universal treatment standard (UTS) to accomplish with Land Disposal Restrictions (LDR, EPA 530-R-01-007) (US EPA, 2012). A detailed description of both tests can be found in Supplementary materials.

2.3 BCR sequential extraction procedure

The procedure, detailed in Supplementary materials, is based on the method proposed by the European Community Bureau of References (Ure et al., 1993a). This methodology has been previously applied to assess metal mobility in mining residues (e.g., Pérez–López et al., 2008) and wastes generated by passive AMD neutralization (Macías et al., 2012).

2.4 Valorization experiments

Two sets of leaching experiments using dilute HCl and H_2SO_4 at solid/liquid ratios of 1:20 and 1:40 were conducted. Both experiments were performed under agitation (3h) with reactive grade acids at 0.5M and 1M concentrations. Following the extraction, samples were centrifuged; the supernatant filtered and kept refrigerated until analysis.

2.5 Analytical techniques

Concentrations of dissolved major and trace elements were determined at the Central Research Service of the University of Huelva by inductively coupled plasma atomic emission spectrometry (ICP-AES Jobin–Yvon Ultima2) and inductively coupled plasma mass spectrometry (ICP-MS Agilent 7700), respectively. All analysis was performed by triplicate. Several blank samples were carried through the complete leaching procedures and all elements were below the detection limit of the equipment. Certified Reference Material SRM-1640 NIST fresh-water-type and inter-laboratory standard IRMM-N3 wastewater test material were also analyzed. Detection limits were calculated by average and standard deviations from 10 blanks for each experimental procedure. The reproducibility of the results obtained by this procedure are described in Supplementary materials while specific detection limits obtained for each element in the different methodologies employed are listed in Tables S1-S4.

X-ray diffraction (XRD) patterns were obtained with a BrukerD5005 X-ray Diffractometer with Cu Kα radiation. Diffractometer settings were 40 kV, 30 mA, a scan range of 3-65º 2ϴ, 0.02 2ϴ step size, and2.4 s counting time per step. Additional mineralogical information was obtained by scanning electron microscope coupled with energy dispersive spectroscopy (SEM-EDS; FEI-Quanta 200 equipped with a microanalyzer EDAX Genesis 2000). The density of the metal-sludge was measured by a picnometer. The moisture content was measured by drying the sample until reaching a stable weight.

3. Results and discussion

3.1 Physical, chemical and mineralogical properties of metal sludge

The solid waste from the AMD neutralization is metal-rich sludge with a dry density of 1.9g/cm^3 and moisture content of around 30%. The pseudo-total chemical composition of the metal-sludge is detailed in Supplementary material (Table S1). Calcium and Mg from the neutralization reagent, and metals (e.g., Zn, Mn, Fe, Al, Cu) and S from the AMD solution clearly dominate the sludge composition.

The mineralogical composition obtained by XRD of the raw sample and of that obtained after 24 h of contact with deionized water (EN 12457-2 leaching test) only showed gypsum as newly-formed mineral (Fig. 2A). SEM-EDS observations also confirmed the appearance of newly-formed gypsum as well-developed euhedral monoclinic crystals with tabular habit (Fig. 2B and D). The high concentrations of Ca from the neutralization reagent and sulfate from the AMD must favor the gypsum precipitation. On the other hand, the pH increase by alkaline addition would cause the decrease in solubility of metals, and the subsequent precipitation by hydrolysis of oxy-hydroxides and/or oxy-hydroxy-sulfates. However, the rapid nucleation and precipitation of secondary metallic phases by AMD neutralization in treatment systems promote a very small crystal size and poor crystallinity that makes difficult their mineralogical identification by XRD (Pérez-López et al., 2011). A more detailed examination with SEM-EDS confirmed that metals precipitated as microaggregates (Fig. 2B and C), with variable chemical composition, but mainly formed by Zn, Fe, Mn, Cu, S and Al; in this microaggregates high concentrations of Mg from the neutralization reagent are also detected. The high sulfate concentrations analyzed in some of these metallic microaggregates could be indicative of the presence of evaporitic sulfate salts formed in the sludge due to its exposure to weathering conditions. Finally, at a lesser extent, detrital grains of sulfides were also observed (Fig. 2C and E), which is not surprising considering the proximity of the pond to other sulfide-rich mining wastes (Fig. 1A).

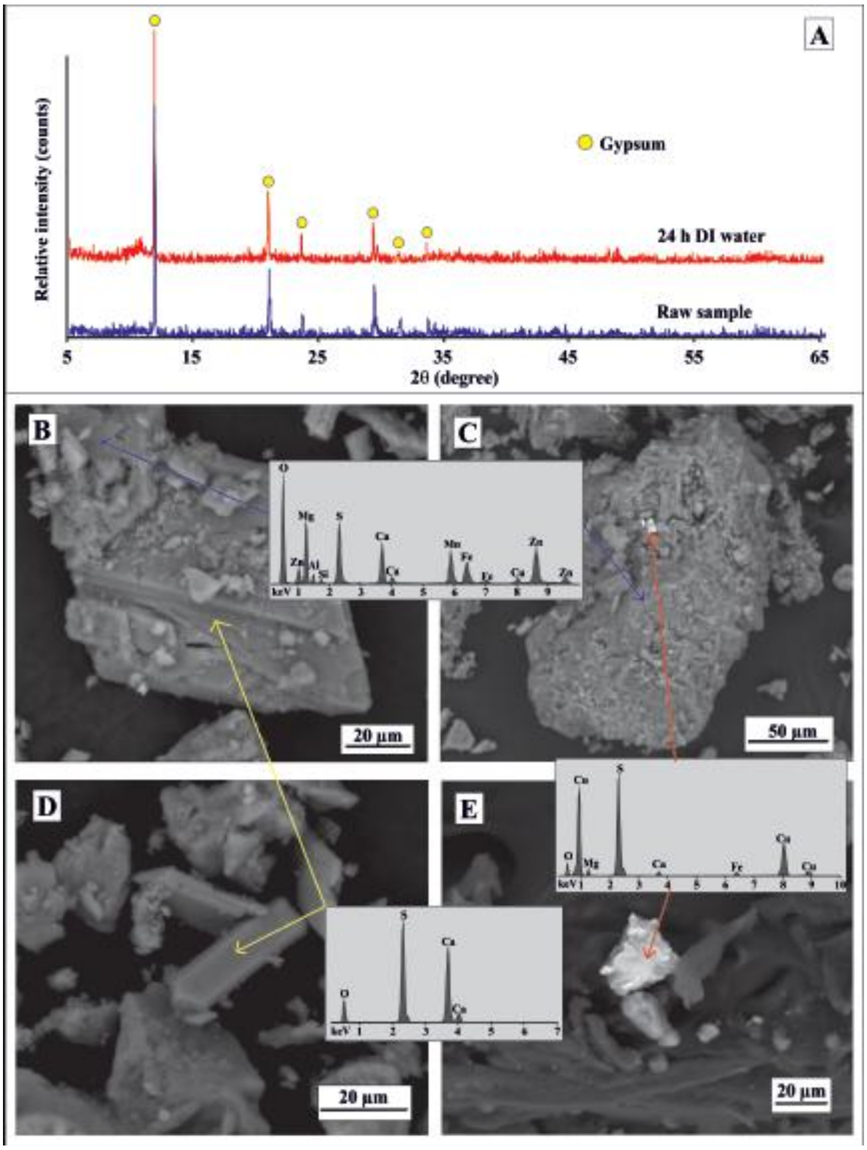


Fig. 2

3.2 Environmental assessment

The environmental mobility of metal pollutants in the Almagrera sludge was addressed by the BCR sequential extraction procedure. The concentrations of all the elements analyzed in each step of the BCR sequential extraction are detailed in Supplementary materials (Table S2). These results have been summarized and plotted in Figure 3, where total concentration and relative percentage of the main major and trace elements along the different steps of the BCR are shown. As it is well-defined in the literature (e.g., Ure et al., 1993b), the elements released in each step of the procedure must be associated with the mineral phases identified by XRD and SEM-EDS.

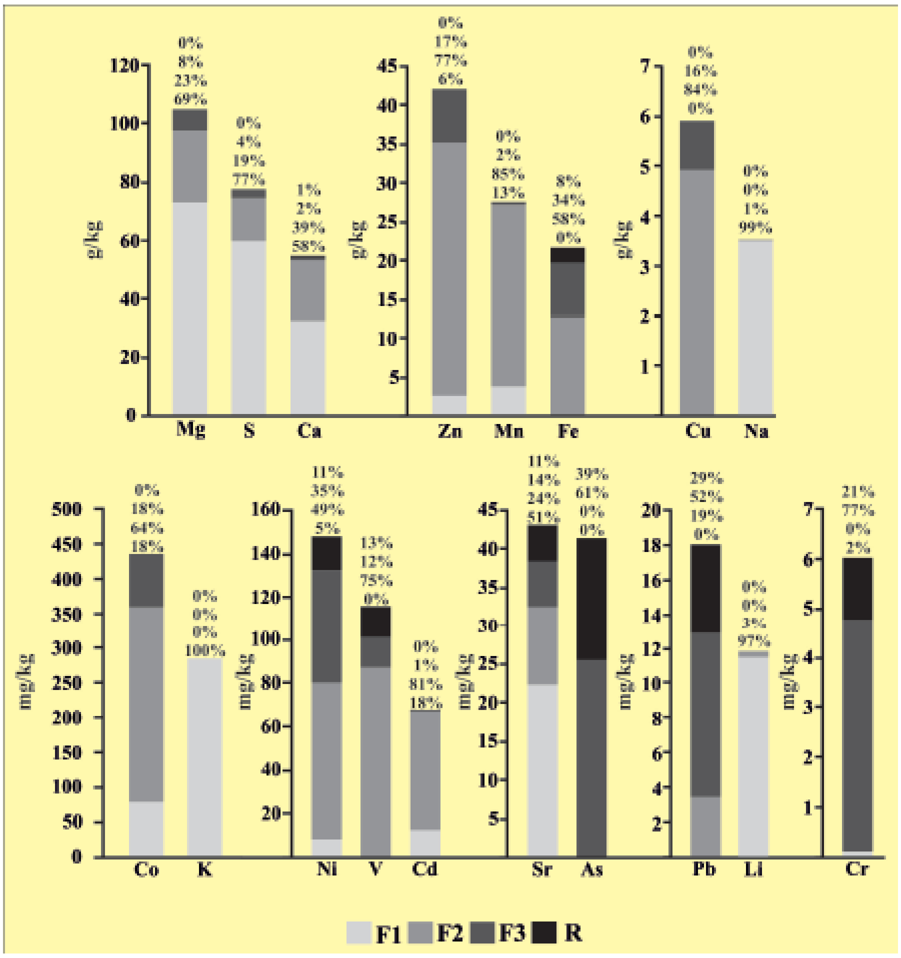


Fig. 3

In the Almagrera metal sludge, high total concentrations and relative percentages of S, Mg and Ca are leached in the most labile fraction (F1). In addition, minor percentages of metals such as Zn, Mn, Co, Ni and Cd were also found in the F1. Consistent with the mineralogy, F1 must correspond to gypsum and other sulfate-salts formed by evaporation (Fig. 2). These evaporitic sulfate salts are readily soluble and act as sinks for these divalent trace elements (Jambor et al., 2000). The rest of the alkaline elements (Na, K, Sr and Li) showed a behavior similar to Mg and Ca during the extraction, with high percentages leached in F1. Additionally, the sludge released an important percentage of S and metals such as Zn, Mn, Fe and Cu in the F2, which could be related to oxy-hydroxides and/or oxy-hydroxy-sulfates precipitated as metal-rich microaggregates during the neutralization process (Fig. 2B and C). Finally, S and other metals (e.g., Zn, Fe and Cu) extracted in F3 could be related to the detrital sulfides inherited from the nearby mining facilities (Fig. 2C and E).

Thereby attending to this interpretation two groups of metals can be distinguished during the BCR extraction: (1) Zn, Mn, Cu, Co, V and Cd whose distribution is associated with percentages above 60% for the reducible fraction (F2), formed by oxy-hydroxy-sulfates generated during AMD neutralization; and (2) As, Pb, and Cr with values in the oxidizable fraction (F3) higher than 50%, linked to sulfides inherited from the surrounding wastes. Iron and Ni are mainly released in the F2, although considerable amounts are also associated with the F3, so they could be associated with both groups.

Table 2 shows an estimation of the total metal content of Almagrera sludge (39000 tons), as well as the stock of bio-available, reducible, oxidizable and non-labile fractions according to the BCR results. Considering the high toxicity of Cd and its affinity to the most labile fraction (18% for Cd in F1, Fig. 3) in respect to the total content (497 kg of Cd, Table2), Almagrera sludge wastes can be considered hazardous for the environment. If the rest of the mobile fractions (F2 and F3) are included, the potential environmental risk is highly increased, although this risk will depend on the environmental conditions. Other important toxic pollutant in Almagrera sludge is As, with a total amount of 1673 kg (Table 2), mainly contained in the oxidizable fraction (61% in F3, Fig.3), which correspond to 1021 kg (Table 2) that could be released to the environment if the sludge is subject to oxidizing conditions.

Table 2. Quantified amount of total, bio-available, reducible, oxidizable and non-labile metals content in Almagrera waste sludge.

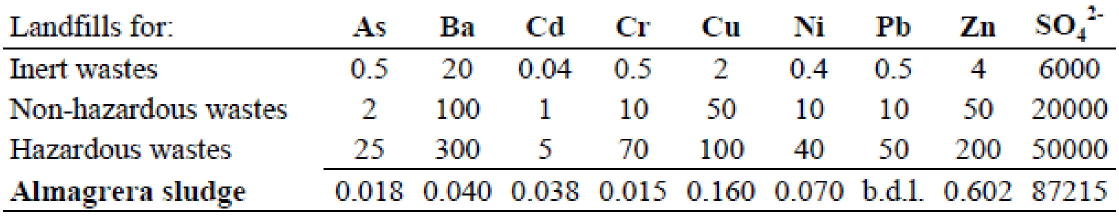
	Elements (t)						Elements (kg)				
	Zn	Mn	Fe	Al	Cu	Co	Ni	Cd	As	Pb	Cr
Total	**1673.3**	**1089.6**	**856.1**	**467.0**	**233.5**	**17.2**	**5564.6**	**2762.8**	**1673.3**	**778.3**	**233.5**
Bio-available	100.4	141.6	0.0	0.0	0.0	3.1	278.2	497.3	0.0	0.0	4.7
Reducible	1288.4	926.1	496.5	9.3	196.1	11.0	2726.6	2237.9	0.0	147.9	0.0
Oxidizable	284.5	21.8	291.1	448.3	37.4	3.1	1947.6	27.6	1020.7	404.7	179.8
Non-labile	0.0	0.0	68.5	9.3	0.0	0.0	612.1	0.0	652.6	225.7	49.0

These results highlight the propensity of toxic metals to be released under changing conditions (i.e. rainfalls, redox changes) and the importance of controlling disposal conditions to prevent any environmental risk.

3.3 Management assessment and hazardousness classification

Table 3 shows the regulatory limits for waste acceptance at landfills in EU (EC Decision, 2003) and the element concentration for the Almagrera sludge after EN 12457-2 leaching test. According to the results, the sludge could be considered as inert if only metals are considered due to concentrations in leachates are below the limits established for inert wastes landfills. This fact is indicative of the high stability of the waste for potentially toxic metals under the chemical conditions induced by EN 12457-2 leaching test. However, considering SO_4 concentration, the sludge cannot be disposed in any type of regulated landfill due to the high release of SO_4 (87,215 mg/kg), being the limit of acceptance at landfills for hazardous wastes 50,000 mg/kg. Under this situation, the UE regulation (EC Decision, 2003) demands a further treatment (additional neutralization, encapsulation, etc.) for these wastes prior to be tested again by EN 12457-2. Given that SO_4 is the main component of the vast majority of the AMDs, this fact could have important implications for sludge management generated by active treatment plants. Landfill disposal of the resulting sludge would require further treatment and, hence, considerable additional expenses of waste management.

Table 3. Regulatory limits for waste acceptance at landfills in EU (council decision 2003/33/EC), and Almagrera sludge concentration after EN 12457-2 leaching test. Data in mg/kg.



Landfills for:	As	Ba	Cd	Cr	Cu	Ni	Pb	Zn	SO_4^{2-}
Inert wastes	0.5	20	0.04	0.5	2	0.4	0.5	4	6000
Non-hazardous wastes	2	100	1	10	50	10	10	50	20000
Hazardous wastes	25	300	5	70	100	40	50	200	50000
Almagrera sludge	0.018	0.040	0.038	0.015	0.160	0.070	b.d.l.	0.602	87215

b.d.l. (below detection limit)

Furthermore, Figure 4 shows the release of the major metals and sulfate over time after applying the EN 12457-2 test three times consecutively. With the exception of Ni, sulfate and the remaining metals are leached between 60 and 100% after 24 h of contact, which suggests that the first contact of the metal-sludge with rainwater would be the most potentially dangerous for the environment. These results also guarantee the applicability of this static test for assessing the landfill disposal options in the wastes from AMD treatment.

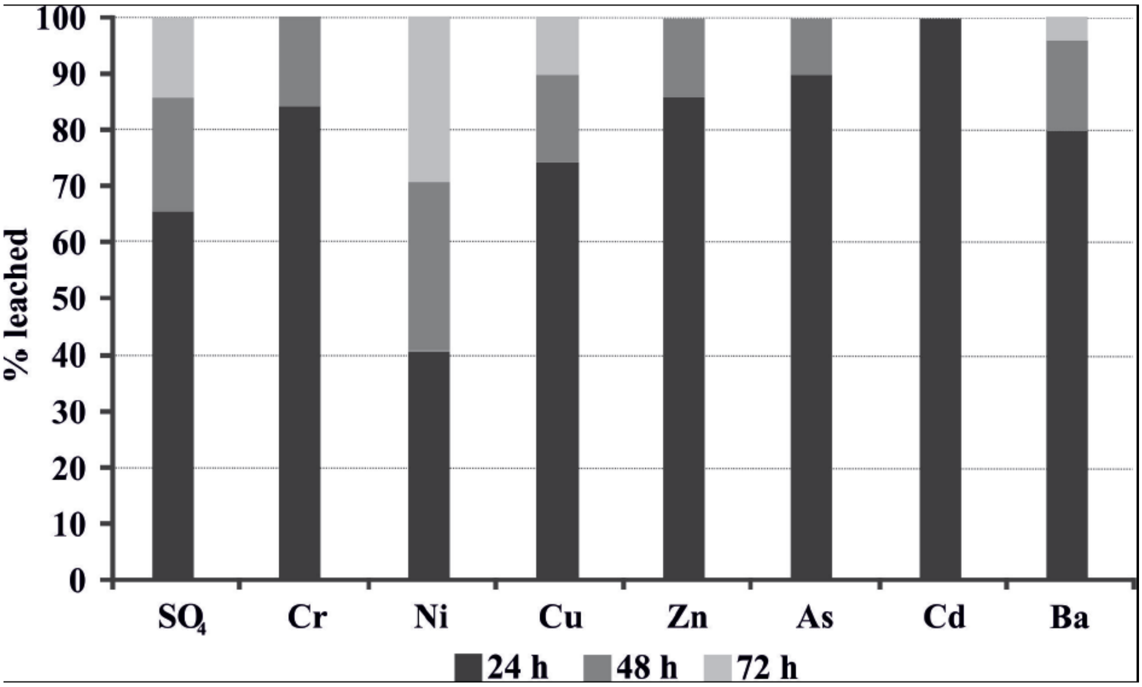


Fig. 4

According to the US EPA regulations the Almagrera metal-sludge can be considered as no hazardous waste because TCLP and UTS limits are not exceeded (Table 4). Consequently, there is no need to be treated (before land disposal) to accomplish with Land Disposal Restrictions (US EPA, 2012). These results would be congruent with those obtained in the EU landfill disposal classification considering only some released metals. However, EPA rules disregard the sulfate concentration after leaching test, thus the final recommendations comparing the EU and US tests completely disagree. This discrepancy has been previously reported for management assessment and hazardousness classification of the wastes generated by passive treatment systems (Macías et al., 2012).

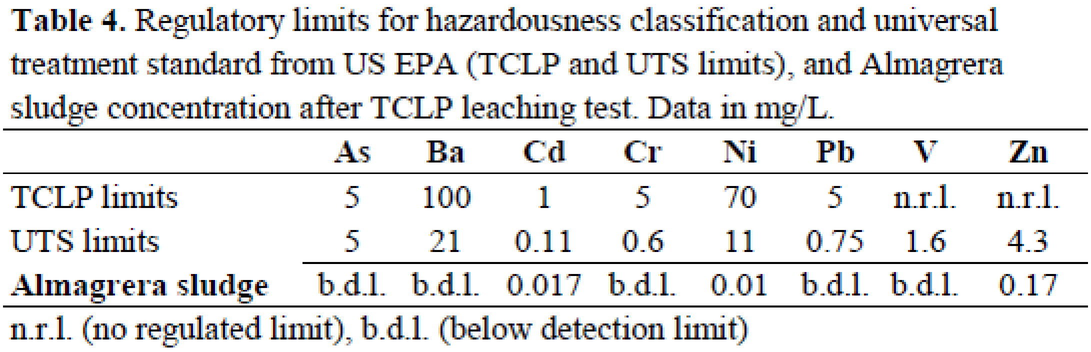


Table 4. Regulatory limits for hazardousness classification and universal treatment standard from US EPA (TCLP and UTS limits), and Almagrera sludge concentration after TCLP leaching test. Data in mg/L.

	As	Ba	Cd	Cr	Ni	Pb	V	Zn
TCLP limits	5	100	1	5	70	5	n.r.l.	n.r.l.
UTS limits	5	21	0.11	0.6	11	0.75	1.6	4.3
Almagrera sludge	b.d.l.	b.d.l.	0.017	b.d.l.	0.01	b.d.l.	b.d.l.	0.17

n.r.l. (no regulated limit), b.d.l. (below detection limit)

3.4 Landfill disposal options and environmental concern

Potential negative effects for the aquatic life of uncontrolled leachates from an inappropriate disposal of the metal-sludge could be simulated by comparing data obtained in the different leaching protocols (EN 12457-2, TCLP and BCR fractions) with limit values established by the criterion continuous concentration (CCC) from the National Recommended Water Quality Criteria of the US EPA (US EPA, 2016). The CCC is defined by EPA as: "*an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect*".

The following weathering scenarios have been evaluated in this study: (1) contact of the sludge with rainwater (simulated by the EN 12457-2 test) which may occur in uncovered disposal facilities; (2) contact of the sludge with organic acids (TCLP test) which would simulate co-disposal with municipal wastes in urban landfills; (3) interaction between the sludge and weak acidic leachates in reducing environments (F1+F2 BCR fractions), which may occur in underground disposal facilities; and finally (4) interaction between the sludge and weak acidic leachates in oxidizing environments (F1+F3 BCR fractions), which would simulate disposal in surface impoundments or waste piles.

Figure 5 shows CCC limits and extracted metal concentrations for the different scenarios. As can be observed, only Cd exceeds the CCC limit in case of contact of the metal sludge with rainwater (EN 12457-2); which evidences a potential risk for the aquatic life by this metal. For the simulation of co-disposal with municipal wastes (TCLP), concentrations of Cd, Zn and Al are higher than the CCC limits, thus being a more dangerous weathering scenario than the rainwater leaching. By summing effects of weakly acidic leaching plus reducing (F1+F2) or oxidizing (F1+F3) environments, both the number and concentration of released metals are markedly increased. Some of these metals (Cd, Zn, Al or Fe) exceed CCC limits by several orders of magnitude, highlighting that the environmental conditions of the disposal are of paramount importance for metal release control.

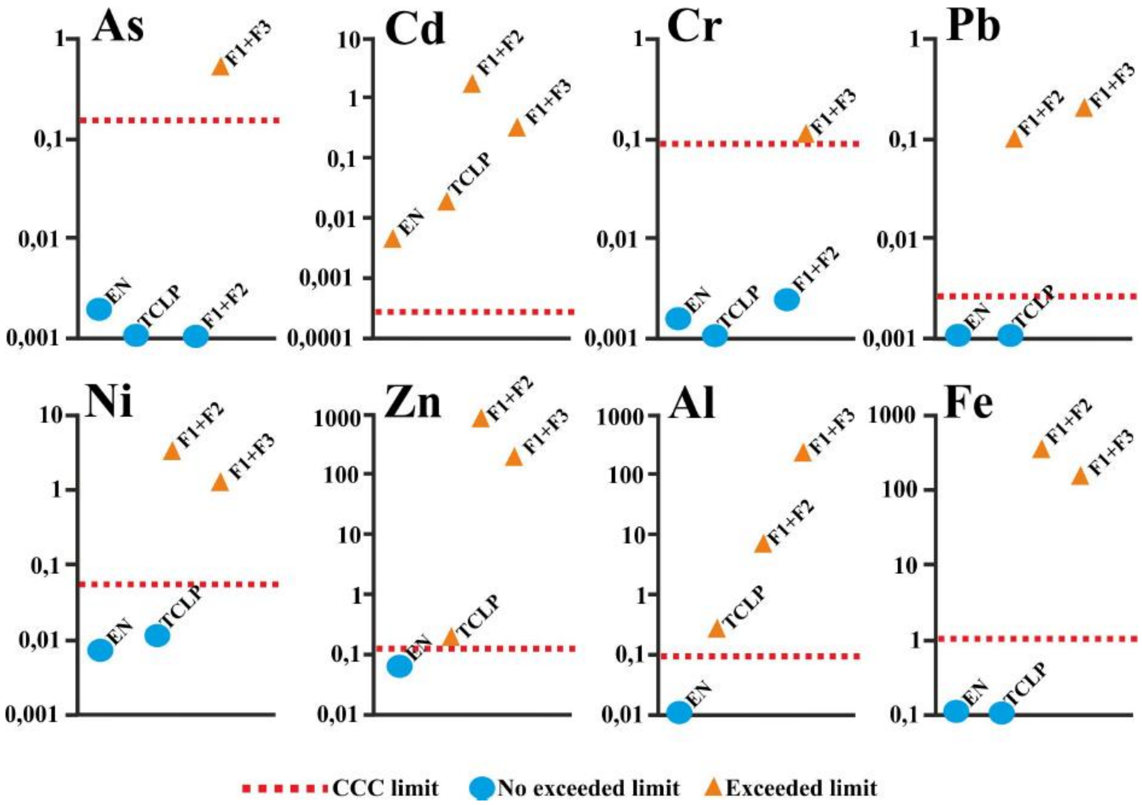


Fig. 5

3.5 Potential valorization

The presence of potentially recoverable metals in mine waters and treatment-derived sludge has previously been reported elsewhere (Smith et al., 2013). As stated before, metals of the sludge from AMD treatment would be mainly contained in poorly-crystalline oxy-hydroxides and/or oxy-hydroxy-sulfates. As a first approximation, these mineral phases may be solubilized under soft acid conditions and thus, elements of economic interest may be subsequently recovered. Under these premises, the potential recovery of metals from Almagrera sludge was studied.

The concentrations of all elements analyzed in the sludge are shown in Supplementary materials (Table S1). There are some base metals with very high concentration, such as Zn or Cu with around 43 g/kg and 6 g/kg respectively, which account for approximately 1,673 and 233 tons of Zn and Cu in Almagrera sludge pond (Table 2). In mining terms, ore grades deduced from these values would correspond to 4% for Zn and 0.6% for Cu, which are clearly mineable in current market conditions. These findings are even more significant if one considers that the sludge concentrates the metals of interest by an order of magnitude in relation to the treated AMD (for comparison, see Tables 1 and S1). Other base metals such as Co (443 mg/kg, total amount of 17 tons) and industrial metals such as Mn (28 g/kg, total amount of 1,090 tons) could increase the potential value of this waste. Moreover, the waste sludge contains remarkable concentrations (200 mg/kg, total amount of 7.8 tons) of high-tech metals such as rare earth elements and yttrium (REY), which could be also considered as valuable by-products.

Considering the estimated annual production of metal sludge (4,300 tons of dry sludge) by AMD neutralization in Almagrera site, the annual output of the marketable metals can be deduced: 186 tons/yr for Zn, 121 tons/yr for Mn, 26 tons/yr for Cu, 1.9 tons/yr for Co and 0.9 tons/yr for REY. The high worldwide annual production of this type of wastes and the scarcity and economic interest of the host metals, highlights its potential recovery.

Dilute acids (HCl and H_2SO_4, 0.5 and 1M) at different ratios (1:20 and 1:40) were used to obtain a first approach of metals extractability from the sludge. The use of 1:40 ratio only slightly increased the extractability. Therefore, and for the sake of simplicity, only 1:20 ratios are shown in Figure 6. For base metals, the H_2SO_4 leaching is the most effective extracting solvent in comparison to that of HCl for the same molarity, which is reasonable considering the proton activity in solution. Thus, the recovery percentages of the H_2SO_4 leaching were higher than 90% for Zn, Cu, Co, Ni and Cd. There are not significant differences between 0.5M and 1M H_2SO_4 concentrations to extract these metals (Fig.6A), which is indicative of that the solid-solution saturation was already reached at 0.5M concentration. The HCl extraction showed also noticeable recoveries, except for the case of Cu with 0.5M solutions which showed recovery percentages lower than 60% of the total content (Fig. 6A). Only around 40% of the Mn content was recovered from the sludge (Fig. 6A), regardless of the leaching reagent and concentration, so this method employed is less effective for this metal. On the other hand, the most effective REY extraction took place with 1M HCl leaching (Fig. 6B), with recovery values up to 90%, with the exception of Ce (around 60%). By using H_2SO_4 as extracting reagent, irrespective of the molarity, low recovery values are obtained, mainly for light rare earths.

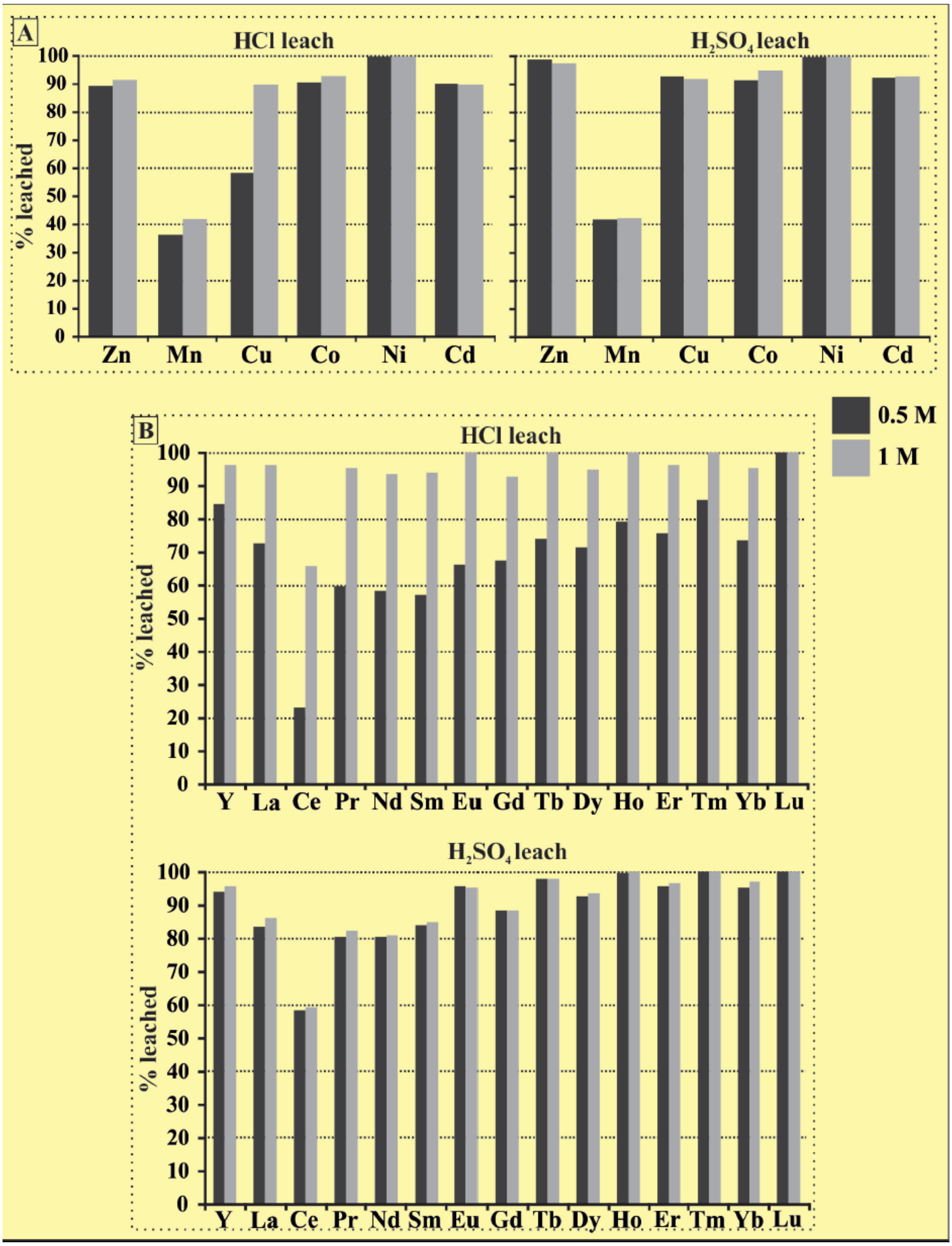


Fig. 6

These experimental results suggest the potentiality of these wastes as source of metals. However, the recovery of these economic metals may be limited by the technical feasibility; acidic leaching of the sludge generates leach liquor with a high content of impurities, which generally is not suitable for any market specifications. In this sense, much research has been recently done on selective recovery methods of target metals contained in several waste streams. At this respect, Cui and Zhang (2008) provide a review of metal recovery methods from electronic wastes. Chen et al. (2015) achieved high recovery rates for base metals (i.e. Ni, Mn, Co and Li) from sulfuric acid leaching liquor of spent lithium-ion batteries by selective precipitation and solvent extraction. Mansur et al. (2008) report the selective extraction of Cu(II) over Fe(II) in a HCl leaching liquor from industrial wastes by liquid-liquid extraction. Nayl (2010) recovered selectively Co and Ni from sulfuric solutions by organic solvent extraction. Once technical difficulties have been overcome, other questions should be addressed before valorization by the industrial sector. Further studies are needed in order to answer these questions.

4. Conclusions

The environmental risk, management strategies for land disposal and valorization of metal sludge wastes generated by AMD neutralization in an active treatment plant was explored. According to the metals mobility after EN 12457-2 and TCLP leaching tests, the Almagrera metal-sludge could be considered as an inert waste. However, the additional presence of sulfate in the regulatory limits of the EU generates a complete discrepancy in the final classification of the residue between both regulations; the metal sludge should not be accepted even at landfills for hazardous wastes according to EU regulations and must be treated prior final disposal. This complete discrepancy between both international regulations strongly advises to use other complementary assessment techniques to obtain an optimum characterization and classification of this type of waste. The results obtained after the BCR sequential extraction procedure revealed a potential environmental risk due to the high concentration of pollutants released in the most labile, reducible and oxidizable fractions, highlighting the hazardousness of this type of residue.

The leachate concentrations were compared with the limits proposed by the criterion continuous concentration (CCC) to evaluate the potential exposure of the aquatic life to the contaminants eventually released from Almagrera sludge under different disposal scenarios (i.e. co-disposal with municipal wastes in urban landfills, disposal in underground facilities; and disposal in surface impoundments or waste piles). The comparison revealed a noticeable environmental risk for all the simulated landfill options, which recommends avoiding the direct contact of the waste with any leaching solution. The use of these complementary techniques could improve the waste management and prevent potential environmental risks.

A more sustainable approach was performed by testing the possibility of reuse these wastes as secondary source of metals of economic interests; the high concentrations of some base, industrial and high-tech metals could transform this residue into a valuable resource. The readily extraction of all these metals with dilute acids was proven; i.e. around 90% of Zn, Cu, Co, Ni and Cd with 0.5M H_2SO_4 and nearly 90% of REY using 1M HCl. Considering the growing production of these wastes worldwide (i.e. 9500 tons per year), this type of sludge is an interesting alternative metal source in our always metal demanding/consuming economy. The joint application of AMD treatment, environmental characterization and stabilization of wastes and further metal recovery may constitute a promising step towards the zero waste goals pursued by the sulfide mining sector.

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FIGURE CAPTIONS

Figure 1. Sketch of the Almagrera industrial-mine complex where can be noted the roasted pyrite pond, tailing pond, the waste dump and the acidic discharges, i.e. AMD1 and AMD2 (A), image of the conventional active treatment plant composed by an alkaline dosing system and an agitation/sedimentation tank (B), and detailed image of the metal sludge waste pond (C).

Figure 2. XRD patterns of the original sample (Raw sample) and of the sample obtained after 24h of contact with deionized water (24h DI water) (A); and SEM images and EDS spectrums of tabular gypsum crystals and amorphous metal-rich microaggregates (B), amorphous metal-rich microaggregates and cooper sulfide (C), tabular gypsum crystals (D), and cooper sulfide detrital particle (E).

Figure 3. Concentrations obtained for some selected pollutants leached after each step of the BCR sequential extraction. The numbers on the top of each element´s column correspond to the fraction (%) of the element extracted in each step, in ascending order: F1, F2, F3 and R.

Figure 4. Histogram with the percentages of some pollutants leached after EN 12457-2 leaching test at different times (24h, 48h and 72h).

Figure 5. Charts for As, Cd, Cr, Pb, Ni, Zn, Al and Fe with values obtained after EN 12457-2 (EN) test, TCLP test, F1+F2 BCR steps and F1+F3 BCR steps; and Criterion Continuous Concentration (CCC limit) from US EPA National Recommended Water Quality Criteria. Data in mg/L. Circular symbols indicate no exceeded limit and triangular symbols indicate exceeded limit.

Figure 6. Metals extractability by HCl and H_2SO_4 leaching tests at 1:20 ratio for base- and industrial-metals (A), and for REY tech-metals (B).

TABLES

Table 1. Chemical composition and physico-chemical parameters of the AMDs from the Almagrera mine complex.

Table 2. Quantified amount of total, bio-available, reducible, oxidizable and non-labile metals content in Almagrera sludge.

Table 3. Regulatory limits for waste acceptance at landfills in EU (Council Decision 2003/33/EC), and Almagrera sludge concentration after EN 12457-2 leaching test. Data in mg/kg.

Table 4. Regulatory limits for hazardousness classification and universal treatment standard from US EPA (TCLP and UTS limits), and Almagrera sludge concentration after TCLP leaching test. Data in mg/L.