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Environmental assessment and management of metal-rich wastes generated in acid mine drainage passive remediation systems

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Abstract

As acid mine drainage (AMD) remediation is increasingly faced by governments and mining industries worldwide, the generation of metal-rich solid residues from the treatments plants is concomitantly raising. A proper environmental management of these metal-rich wastes requires a detailed characterization of the metal mobility as well as an assessment of this new residues stability. The European standard leaching test EN 12457-2, the US EPA TCLP test and the BCR sequential extraction procedure were selected to address the environmental assessment of Dispersed Alkaline Substrate (DAS) residues generated in AMD passive treatment systems. Significant discrepancies were observed in the hazardousness classification of the residues according to the TCLP or EN 12457-2 test. Furthermore, the absence of some important metals (like Fe or Al) in the regulatory limits employed in both leaching tests severely restricts their applicability for metal-rich wastes. The results obtained in the BCR sequential extraction suggest an important influence of the landfill environmental conditions on the metals released from the wastes. To ensure a complete stability of the pollutants in the studied DAS-wastes the contact with water or any other leaching solutions must be avoided and a dry environment needs to be provided in the landfill disposal selected.

Keywords:

Mine wastes, EN 12457-2 leaching test, TCLP leaching test, BCR sequential extraction

1. Introduction

Acid mine drainage (AMD) involves the formation and movement of highly acidic waters rich in heavy metals. These acidic waters are highly toxic and, when mixed with groundwaters, surface waters and/or soils, may have harmful effects on humans, animals and plants [1].

The Iberian Pyrite Belt (IPB) in the southwest of the Iberian Peninsula is one of the most outstanding massive sulfide provinces in the world, with about 1700 Mt of estimated original reserves [2]. The IPB is also known as a world-class example of ancient AMD pollution resulting in one of the most extreme and unique environments on the Earth (e.g., Rio Tinto River).

In many abandoned mine districts around the world, the AMD pollution is generally remediated by the use of passive technologies [3], and different treatments have been successfully used in coal districts to this end (e.g., Anoxic Limestone Drains and Anaerobic Wetlands) [4]. However, the metal mine drainage typically found in sulfide mining areas cannot be remediated using these conventional technologies, mainly due to the high metal content displayed.

So far, one of the few passive treatments that has shown good results facing high metal polluted AMD is based on the Dispersed Alkaline Substrate (DAS) technology. The DAS-based system relies on the use of fine-grained alkaline reagents (limestone sand or MgO powder), providing high reactivity and neutralizing capacity, mixed with a coarse inert matrix (pine wood shavings) to supply a high porosity to the reactive mixture. Limestone-DAS has been tested in laboratory, pilot and full scale experiments in the IPB, showing excellent results regarding Fe, Al, As, Cu and Pb removal [5, 6, 7]; whereas MgO-DAS was checked in laboratory and pilot scale plants with promising results for Zn, Mn, Cd, Co and Ni removal [6, 8, 9]. The mineralogy and geochemistry of the newly formed precipitates inside the limestone and MgO-DAS treatments have been widely analyzed [10, 11].

In DAS remediation systems, metals are accumulated in the substrate and it therefore needs to be replaced once the first symptoms of reactivity losing appear. The transition of metals from aqueous species to solid precipitates in the passive treatment implies the generation of a new metal-rich solid waste.

As mining environmental legislation is becoming more restrictive and higher efforts are being placed by governments to ensure its compliance, the remediation of AMD affected waters is turning into a top topic in the environmental agenda in many countries around the world [9, 12, 13, 14]. A good example of this worldwide situation is the current scene in the Odiel river basin at the IPB where the compliance of European Water Framework Directive (WFD) [15] and the future construction of the Alcolea reservoir (receiving AMD waters) [16], urges the widespread implementation of passive remediation technologies in a large number of AMD generation sources [17]. The DAS-based remediation technology is proposed to be adopted in the IPB [17] and the remediation processes employed in this technology could also be included in the remediation strategies to be developed in many other mine districts in the world. A proper management of the expected metal-rich wastes generated during the remediation of AMD waters is essential to control the possible release of metals from these solid residues.

Taking into account these considerations, it was decided to study the stability and environmental risk of the solid wastes generated after the use of different DAS-based passive treatments in the IPB. To this end, it was decided to employ the leaching tests proposed by the current European and US environmental regulations for these kinds of mine residues, namely EN 12457-2 [18] and TCLP [19, 20], respectively. These tests not only classify the wastes as hazardous or non-hazardous to the environment on the basis of the regulated concentration of several metals in the leachates but are also used to identify whether a treatment of the waste is necessary or not prior deposit in a landfill disposal (TCLP test) and to discern the type of landfill disposal that better hosts the studied wastes (EN 12457-2 test). Additionally, an estimation of metal mobility and environmental availability can also be obtained comparing the concentration of some selected metals in the leachates with the limits established for metals in natural waters.

Sequential extraction procedures are the most extensively employed techniques to assess the potential mobilization of contaminants under variable environmental conditions. Of the many existing schemes, the most widely accepted standardized method was proposed by the European Community Bureau of References (BCR sequential extraction procedure) [21] and improved in subsequent works [22, 23]. The BCR sequential procedure has been applied to assess metal mobility in sediments, soils, sludges and waste materials with different origins [24], including mining wastes [25, 26]. It is a simple method that involves the extraction of elements from the solid residue according to four fractions: acid extractable, reducible, oxidizable and residual.

The main objective of this research is to assess the potential environmental risk of the metallic wastes generated in DAS-based passive systems and propose management strategies for their secure disposal. The results obtained, due to the variety of characterization approaches and international environmental regulations covered, should be taken into account in the management of similar solid mine wastes coming from the alkaline treatment of AMD affected waters around the world.

2. Materials and methods

2.1 Origin and sampling of DAS-wastes

The limestone-DAS full-scale plant implemented at Mina Esperanza [7] (Fig. 1A) was developed to treat Fe and Al-rich AMD. Both metals, in addition to SO_4^{2-}, are typically the major components of the vast majority of the AMDs in the IPB (and in many other mining sites in the world), and therefore the wastes generated in this plant may be considered as representative of the solid residues potentially obtained after the remediation of AMD using alkaline-based processes. To characterize a divalent metal-rich residue, the MgO-DAS pilot plant implemented at Monte Romero was selected [10, 27] (Fig. 1A). This treatment is focused on the retention of divalent metals, mainly Zn, which is the major component of the Monte Romero AMD.

From the Mina Esperanza treatment [7], two different DAS-wastes were recovered: Fe-rich and Al-rich (Fig. 1B). The former is characterized for the presence of Fe, S and As as the main components [7, 11]. These inorganic contaminants are hosted in two Fe mineral phases, schwertmannite, $Fe_8O_8(OH)_6(SO_4)\cdot nH_2O$, and goethite, FeO(OH), [11]. The later is composed of Al, S, Ca and Cu mainly; being hydrobasaluminite, $Al_4(SO_4)(OH)_{10}\cdot 12\text{-}36H_2O$, gypsum, $Ca(SO_4)\cdot 2(H_2O)$, and calcite, $CaCO_3$, the minerals phases detected [7, 11], although calcite is inherited from the original reactive substrate. In Monte Romero abandoned mine, several multi-step limestone and MgO-DAS pilot-scale plants have been implemented during the last years [6, 27]. From the last step of the treatment (MgO-DAS step), a Zn-rich waste was obtained (Fig. 1B), showing Zn, Mg, Ca and Mn as their main constituents with minor amounts of Cd, Co and Ni. The neoformed minerals responsible of divalent metals removal were observed to be hydrozincite, $Zn_5(CO_3)_2(OH)_6$, and loseyite, $(Mn,Zn)_7(CO_3)_2(OH)_{10}$ [10].

Depth profiles were dug after completion of the treatment lifetime in each DAS plant. Samples (1-2 kg) were collected using a polypropylene shovel and transferred to clean polypropylene bags. In the laboratory, the wastes were oven-dried (40ºC), grounded, sieved (<2 mm) and stored in polypropylene containers until analyzed.

2.2 TCLP leaching test

The test was performed as specified by the US Environmental Protection Agency (EPA) [19, 20]. The wastes were extracted for 18 h by agitation on a shaker with a liquid to solid ratio of 20:1. The extraction liquids employed was chosen on the basis of waste alkalinity, using fluid 1 (CH_3COOH, pH = 4.93 ±0.05) for samples with pH < 5 and fluid 2 (CH_3COOH, pH = 2.88 ±0.05) for samples with pH > 5. Al-rich and Zn-rich DAS-wastes were extracted with fluid 2 and Fe-rich with fluid 1. Following the extraction, samples were centrifuged, the supernatant filtered through 0.45 µm pore size filters, acidified with HNO_3 and refrigerated stored until analyzed.

2.3 EN 12457-2 leaching test

This standard test is a one-step leaching procedure, which is applied to assess if a waste material can be accepted for disposal in a landfill site. The experimental concentrations obtained in the test can be compared with the limit threshold values issued by the European Council (European Council Decision 2003/33/CE) [28] as criterion for the acceptance of wastes in three types of landfill sites: landfills for inert wastes, non hazardous wastes and hazardous wastes.

The test was conducted by mixing the waste with deionized water at a liquid to solid ratio of 10:1, followed by agitation of the mixture for 24 h, filtration of the supernatant and determination of dissolved elements or pollutants.

2.4 BCR sequential extraction procedure

The method is summarized below and full details can be found elsewhere [22, 23].

Step 1 (Exchangeable and weak acid soluble fraction): 40 mL of 0.11 mol L^{-1} acetic acid, CH_3COOH, was added in 60 mL centrifuge tubes containing 1 g of sample, and shaken for 16 h at room temperature. The extract was separated by centrifugation and kept at 4ºC until analysis. The remaining residue was washed with deionized water and the washings discarded.

Step 2 (Reducible fraction): 40 mL of 0.1 mol L^{-1} hydroxylamine hydrochloride, $NH_2OH{\cdot}HCl$ (pH adjusted to 2 by adding HNO_3) was added to the residue from Step 1 in the centrifuge tubes. The solution was separated and the remaining residue was washed as in the previous step.

Step 3 (Oxidizable fraction): 10 mL of 8.8 mol L^{-1} H_2O_2 (pH 2.0-3.0) was added carefully in small aliquots into the remaining residue from Step 2. The tubes were covered loosely with its cap in order to allow release of vapor and left for 1 h at room temperature and for 1 h at 85ºC in a water bath. Then, the tubes were heated uncovered to obtain volume reduction to less than 1.5

mL. This step was performed twice. After cooling, 50 mL of 1.0 mol L^{-1} ammonium acetate, CH_3COONH_4 (pH adjusted to 2.0 with HNO_3), was added to the residue, which was extracted as described in Step 1.

Step 4 (Residual fraction): the remaining residue from Step 3 was digested adding 10 mL of aqua regia (12 mol L^{-1} HCl and 15.8 mol L^{-1} HNO_3 in a ratio 3:1) into Teflon reactors. Reactors were allowed to stand for 20 h in a fume cupboard and then simmered on a hot plate for 1 h at 100ºC.

For the analyzed elements, an internal check of the results was performed by comparing the sum of the four steps from the BCR sequential extraction with the pseudo-total metal analysis obtained from an independent aqua regia digestion performed to each residue (following the same procedure employed in the fourth step of BCR sequential extraction). These data were used to validate the cumulative extractability of the BCR procedure. The percentage recovery of the sequential extraction procedure was calculated as follows (Eq. (1)):

$$\text{Recovery}\ (\%) = \frac{\text{Step 1}+\text{Step 2}+\text{Step 3}+\text{Step 4}}{\text{Pseudo-total digestion}} \times 100 \qquad (1)$$

2.5 Analytical determinations

Duplicate and/or triplicate samples of each DAS-waste were used for both leaching tests and for BCR sequential extraction. No significant differences were found in the results of these replicate samples. Several blank samples were carried through the complete procedures of leaching tests and BCR extraction, no detectable contamination was found in the blank samples.

The analyses were performed at the Central Research Services of the University of Huelva. Concentrations of dissolved Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, S, Ti, V and Zn were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES Jobin- Ybon Ultima2). Multielement standard solutions prepared from single certified standards supplied by SCP SCIENCE were used for calibration. They were run at the beginning and at the end of each analytical series. Certified Reference Material SRM-1640 NIST fresh-water-type and inter-laboratory standard IRMM-N3 wastewater test material, European Commission Institute for Reference Materials and Measurements, were also analyzed. Detection limits were calculated by average and standard deviations from 10 blanks for each experimental procedure. The specific detection limits obtained for each element in the different methodologies employed are listed under each element symbol in both appendix A and B.

2.6 Quality assurance

For all replicated samples, the relative coefficients of variation, CV (%), were calculated as follows (Eq. (2)):

$$\text{CV (\%)}=\frac{\text{Standard deviation}}{\text{Mean}}\times 100 \qquad (2)$$

The relative coefficients of variation obtained for TCLP and EN-12457-2 leaching tests are shown in Appendix A. As can be observed, despite the existing heterogeneity of the metal-rich precipitates distribution in the original samples, for the great majority of elements the variability between replicates is consistently lower than 15%. Some unexpectedly high values can be attributed to: 1) the structure of the variability equation employed and sensitivity of the analytical method, that induce anomalously high CV (%) in the minor elements; and 2) the higher heterogeneity that certain metals present in the precipitates (e.g., Cu distribution in the Al-rich waste as a result of different adsorption/co-precipitation rates in the treatment reactive material).

CV (%) and Recovery (%) were calculated as well for the BCR sequential extraction. Appendix B shows a complete disclosure of the results obtained in each step of the BCR and the calculated CV (%) for replicates. As can be observed, the differences observed were significantly <15% for more than 90% of replicates. Recovery (%) values obtained were consistently within a range of 100 ± 20% for more than 90% of the elements analyzed in the three DAS-type wastes (Table 1). Considering the slight but existing heterogeneity of the samples, and the accumulation of variations as a result of the sum of 4 sequential extraction steps, the sequential extraction procedure shows a great recovery and reproducibility. The Recovery values obtained in this study fit the variability ranges observed by previous studies dealing with mine wastes [26, 29].

3. Results and discussion

3.1 DAS-type waste characterization based on current legislation

As previously mentioned, the generation of a DAS-type waste is linked to the use of the DAS passive treatment technology to remediate AMD and subsequently it could potentially exhibit the same widespread distribution around the world as AMD does. Taking this fact into account, it was decided to study the DAS-type residue according to two well-defined and accepted international leaching tests for waste characterization and management: TCLP and EN-12457-2. The regulated limit values for US and Europe legislation are shown in appendix C.

The most widely used, the TCLP leaching test (U.S. EPA method 1311), was designed to simulate co-disposal with municipal (putrescible) waste [19, 20], so the leaching solution is an organic acid (acetic acid). This procedure is commonly employed to indicate if a waste is hazardous or not regarding to the regulated limits of certain organic and inorganic pollutants in USA [30, 31, 32], although from the inorganic pollutants covered by this procedure only As, Ba, Cd, Cr, Ni and Pb are expected to be found in the DAS-type wastes. According to the obtained concentrations for As, Ba, Cd, Cr, Ni and Pb after the TCLP leaching test (Fig. 2A), the three classes of DAS-type wastes tested (Fe-, Al- and Zn-rich) could be considered as non-hazardous.

The concentration of the former inorganic pollutants plus Zn concentration in TCLP leachates are also employed as numerical standards 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) [33]. A land disposal is defined by this regulation to be any placement onto the land including, but not be limited to, use constituting disposal or placement of hazardous waste into the following hazardous waste management units: landfills, surface impoundments, waste piles, injection wells, land treatment facilities, salt domes, underground mines or caves and concrete vaults or bunkers. The results offered in figure 2B are consistently under the regulatory limits for the elements employed in this study and therefore any DAS-type waste would need to be treated prior to their land disposal.

Table 2 shows the European regulatory levels for the acceptance of a waste at different landfill sites. Based on the concentration of certain inorganic pollutants (As, Ba, Cd, Cr, Cu, Ni, Pb, Zn and SO_4^{2-}) after EN 12457-2 leaching test, the studied residue could be sent to a landfill for: inert wastes, non-hazardous wastes or hazardous wastes.

As can be observed, the Fe-rich DAS-type waste must be disposed in landfills for hazardous wastes because the high leachability of Cu (78.8 mg kg^{-1}) and Zn (197.47 mg kg^{-1}), which clearly exceed the limit of 50 mg kg^{-1} for both metals established for non-hazardous wastes landfills. Al-rich DAS-type waste has a low pollutant mobility and almost any of them exceed the limit for the disposal in landfill for inert wastes. However, the moderate leachability of SO_4^{2-} (12256 mg kg^{-1}) placed this residue in non-hazardous waste landfills. Inorganic pollutants content in Zn-rich DAS-type residue are the less mobile and available of all the DAS-type wastes and therefore this waste could be disposed at landfills for inert wastes (Table 2).

3.2 Environmental availability of the inorganic pollutants in DAS-type wastes

The extracted concentrations of all the inorganic pollutants analyzed, Al, As, Ca, Cu, Fe, Mg, Mn, S and Zn expressed in g kg^{-1} and Ba, Cd, Cr, Co, Ni, Pb, Ti and V in mg kg^{-1}, for the DAS-wastes in each step of the BCR sequential extraction are detailed in Appendix B. All this information has been summarized and reorganized in figure 3 where the total concentration and relative distribution of the extracted major, minor and trace elements along the different steps of the BCR are shown. For the discussion in this section is important to point out that the first step of the BCR (F1) is designed to release the exchangeable cations and weak acid soluble phases and therefore the elements recovered in this step are considered the most labile fraction of the pollutants in the residues. The second and third steps of the BCR are designed to dissolve the reducible (F2) and oxidizable (F3) fraction of the residue and thus, the elements released in those two steps correspond to pollutants with a moderate lability and subordinated to the existence of an oxidizing or reducing environment. Finally, the fourth step (R) corresponds to the residual fraction and the elements released can be considered as the non-labile fraction.

As expected from previous mineralogical studies [6, 11], Fe and S are the main constituents of the Fe-rich waste (Fig. 3A) although their lability is restricted to 41% and 69%, respectively, of the total concentration of these elements in the residue and it is almost completely conditioned to the appearance of oxidizing or reducing environments. The release of pollutants in the most labile fraction (F1) is only noticeable for Mg (92%), Al (35%), Zn (83%), Cu (60%), Mn (71%) and Co (74%), although as can be observed in figure 3A, the concentration of these elements in the residue is one, two and even three orders of magnitude lower than the one for the main constituents.

Al, S and Ca, the main constituents of the Al-rich waste, show an almost complete redisolution after the third step of the BCR and subsequently the great majority of all other pollutants are also almost completely release from the waste after F3 (Fig. 3B). Al (24%), S (40%), Ca (87%), Cu (61%), Mg (60%), Zn (56%) and Mn (53%) are the main pollutants released in the most labile fraction (F1). On the view of these results the Al-rich waste could be considered highly hazardous for the environment and prone to higher pollutants lability under oxidizing environments.

With the exception of Fe, S and As, the metals comprising the Zn-rich waste are mostly released in F2 (Fig. 3C), with values as high as 77% Zn and 86% Mn. This observation implies a higher risk of pollutants release if the Zn-rich waste is submitted to a reducing environment.

The sum of the principal pollutants concentrations (excluding the less toxic Ca and Mg) in the most labile fraction (F1), allows to arrange the DAS-type wastes according to their environmental hazard: Al-rich > Zn-rich > Fe-rich. However, if the mobile fractions obtained in F2 and F3 are taking into account, the release of pollutants highly increases for all DAS-type wastes and subsequently their environmental hazard. So far as this is concerned, the potential environmental risk of DAS-type wastes directly depends on the environmental conditions.

3.3 DAS-type wastes environmental impact assessment

To assess possible negative environmental effects in the aquatic life of an uncontrolled leachate from inappropriate disposal of DAS-type wastes, it was decided to compare the values obtained in the different leaching test with the limit values for certain inorganic pollutants according to the Criterion Continuous Concentration (CCC) from the National Recommended Water Quality Criteria of the US EPA. CCC is described 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”, [34]. The different disposal hypotheses covered with this study account for: contact of the residue with rainwater (EN-12457-2, Fig. 4A) like in surface impoundments, waste piles or other uncovered disposal facilities not submitted to a very oxidizing environment; contact of the residue with weak organic acids (TCLP, Fig. 4B) to simulate co-disposal with municipal (putrescible) waste in urban landfills; interaction between weak acidic leachates with the residue in reducing environments (F1+F2, Fig. 4C) like in underground mines or caves and flooded concrete vaults or bunkers, and finally the effect of weak acids and oxidizing environments in the residue (F1+F3, Fig. 4D) to simulate disposal in surface impoundments or waste piles.

After the leaching test employing deionized water (Fig. 4A, EN12457-2) only Cd slightly exceeded the regulated limit value for this metal in both Al-rich and Zn-rich DAS-type residues whereas for the Fe-rich class the concentration of Fe, Al, Zn, Ni and Cd were significantly higher than the regulated limits. The important difference observed in the release of inorganic pollutants by these three residues is attributed to the higher pH buffer capacity of the Al-rich and Zn-rich wastes due to the presence of limestone and MgO, respectively, as remaining alkaline reagents from the passive treatment system; whereas no remaining limestone is left in the Fe-rich DAS-type waste. For further details in the mineralogy of the precipitates formed within the reactive materials originating the DAS-type residues and the hydrochemistry of the AMD passive treatment system the reader is referred to previous studies [6, 7, 10, 11].

The limited pH buffer capacity of the residues is exposed by the higher release of metals after the leaching test employing weak organic acids (Fig. 4B, TCLP). In this case, the Al-rich and Zn-rich residues showed Al-Zn-Cd and Zn-Cd redissolutions, respectively, higher than the CCC limits for those metals. On the other hand, the Fe-rich waste experimented a lower concentration in the pollutants release compared with the results for this residue after the EN-12457-2 leaching test. This difference can be attributed to the used of a 4.93 ± 0.05 pH buffered solution in the TCLP leaching test instead of deionized water. This buffered solution diminishes the redissolution of the Fe-precipitates because the forming mineral phases (mainly schwertmannite and goethite) were generated under a similar pH environment [6, 7].

If in addition to the effect of a weak organic acid (F1) the residues are submitted to a digestion step simulating an oxidizing (F2) or reducing (F3) environment, the concentration and number of inorganic pollutants released are noticeably increased (F1+F2 and F1+F3 in Fig. 4C and D). Although on the light of the results obtained the contaminant release of the three DAS-type residues is similar for both oxidizing and reducing environments, the values obtained after F3 are probably overestimated due to the heating process employed in this step of the sequential extraction. A good example of this overestimation is observed in the results obtained for the Fe-rich residue where the high Fe recovery can not be justify by the dissolution of any of the forming minerals (mainly Fe oxides and hydroxisulfates) in an oxidizing environment.

4. Conclusions

In this study two leaching tests and a sequential extraction procedure have been applied for the environmental characterization and management assessment of the wastes generated in a DAS-based passive treatment system.

Although both, European and US regulations, try to evaluate pollutants mobility regarding to different scenarios of landfill disposal; the use of different leaching agents, the inorganic pollutants studied and the regulatory levels employed, lead to significant discrepancies in the classification and management of the DAS-type wastes. It is also important to notice that the regulatory levels employed in both leaching tests does not take into account the concentrations of some other metals that are present in DAS-type residues, primarily Fe and Al that are the main constituents of Fe-rich and Al-rich DAS-type wastes, respectively. In accordance to that, both TCLP and EN-12457-2 leaching test appears to be inappropriate to characterize metal-rich residues and specifically unsuitable to properly classified the DAS-type residue without the addition of new regulatory levels for some important inorganic pollutants like Fe or Al or the coupled use of other characterization techniques.

The BCR sequential procedure was applied to assess the environmental availability of the inorganic pollutants in the DAS-type wastes. Attending to the concentration of the metals released during the first step of the BCR (corresponding to the most labile fraction), the residues can be classified according to their environmental hazard as follows: Al-rich > Zn-rich > Fe-rich. Moreover, the important recovery of metals observed in the second and third steps of the BCR reflect the control that a reducing or oxidizing environment can have on the release of contaminants from the DAS-type wastes. In accordance to that and to ensure a proper disposal of a DAS-type residue, the environmental conditions of the landfill have to be controlled.

On the light of the results obtained in this study the best disposal option tested for Al-rich and Zn-rich DAS-type residues would be surface impoundments or waste piles (covered if possible), whereas co-disposal with municipal (putrescible) wastes in urban landfills would be a better option for Fe-rich DAS-type wastes because it implies a smaller metal release. If the Al-rich and

Zn-rich DAS-type residues are leached with water, a scenario that could resemble the rain over a surface impoundment or waste pile, Cd would be the only metal slightly exceeding the threshold value for a continuous water concentration of a metal without having an unacceptable effect for the aquatic life. Albeit if Fe-rich DAS-type residue is leached (whatever landfill disposal option selected), between 4 and 5 metals would exceed the limit for continuous concentration of metals without having an unacceptable effect for the aquatic life.

To ensure a complete metals and metalloids stability in the Al-, Fe-, and Zn-rich DAS-wastes characterized in this study, the contact with water or any other leaching solutions must be avoided. The landfill disposal option selected has to provide a dry environment for the DAS-type wastes and the generation of any leachate must be prevented in order to elude the generation of a new metal pollution source.

The high concentration of metals and their selective distribution in the three DAS-type wastes (namely: Fe and As in the Fe-rich waste, Al and Cu in the Al-rich waste and Zn, Mn, Ni and Co in the Zn-rich waste), encourage to consider these residues as potential metal ores and subsequently future studies should be focused on developing selective recovery techniques to transform these residues into economically feasible metal resources.

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FIGURE CAPTIONS

Figure 1. Location of the studied area (A), schemes of the Mina Esperanza full-scale and Monte Romero pilot-scale plants and cross sections images of wastes developed in both plants (B). A.c. (aeration cascade), D.p. (Decantation pond).

Figure 2. Comparison between element concentrations in the TCLP leachates for Fe-, Al- and Zn-rich DAS wastes and regulated limits for hazardous wastes (A) and land disposal restrictions (B) according to EPA regulations. TCLP and UTS EPA limits are included for each element (horizontal dashed lines). The hollow markers indicate that the regulatory limit has been not exceeded.

Figure 3. Concentrations obtained for some selected inorganic pollutants leached after each step of the BCR sequential extraction for Fe-rich (A), Al-rich (B) and Zn-rich (C) DAS-type wastes. 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.

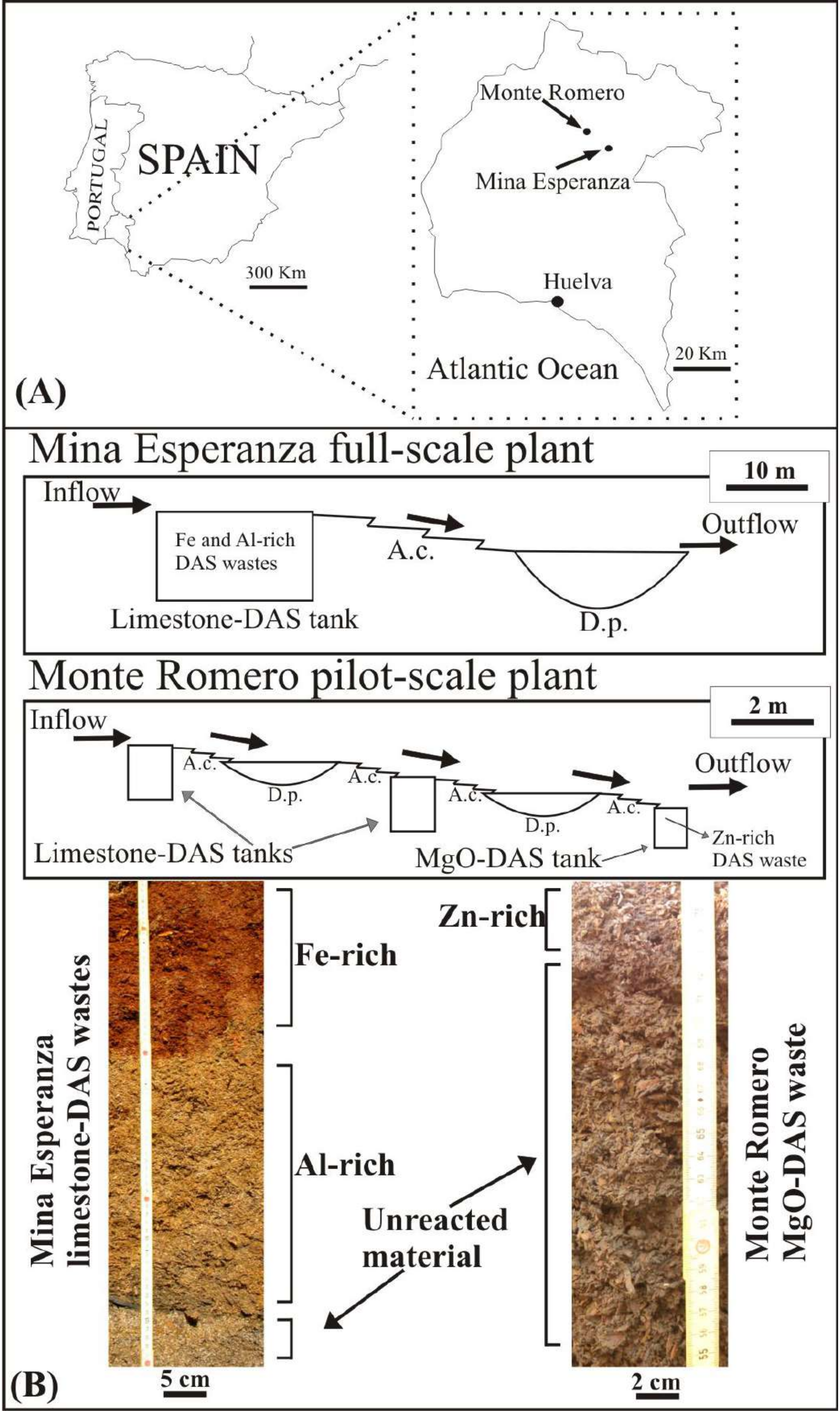
Figure 4. Al, As, Cd, Cr, Ni, Pb, Zn and Fe concentration obtained after EN 12457-2 test (A), TCLP test (B), F1+F2 BCR steps (C) and F1+F3 BCR steps (D). All data are presented in mg L^{-1}. EPA Continuous Concentration Criteria limits are included for each element (horizontal

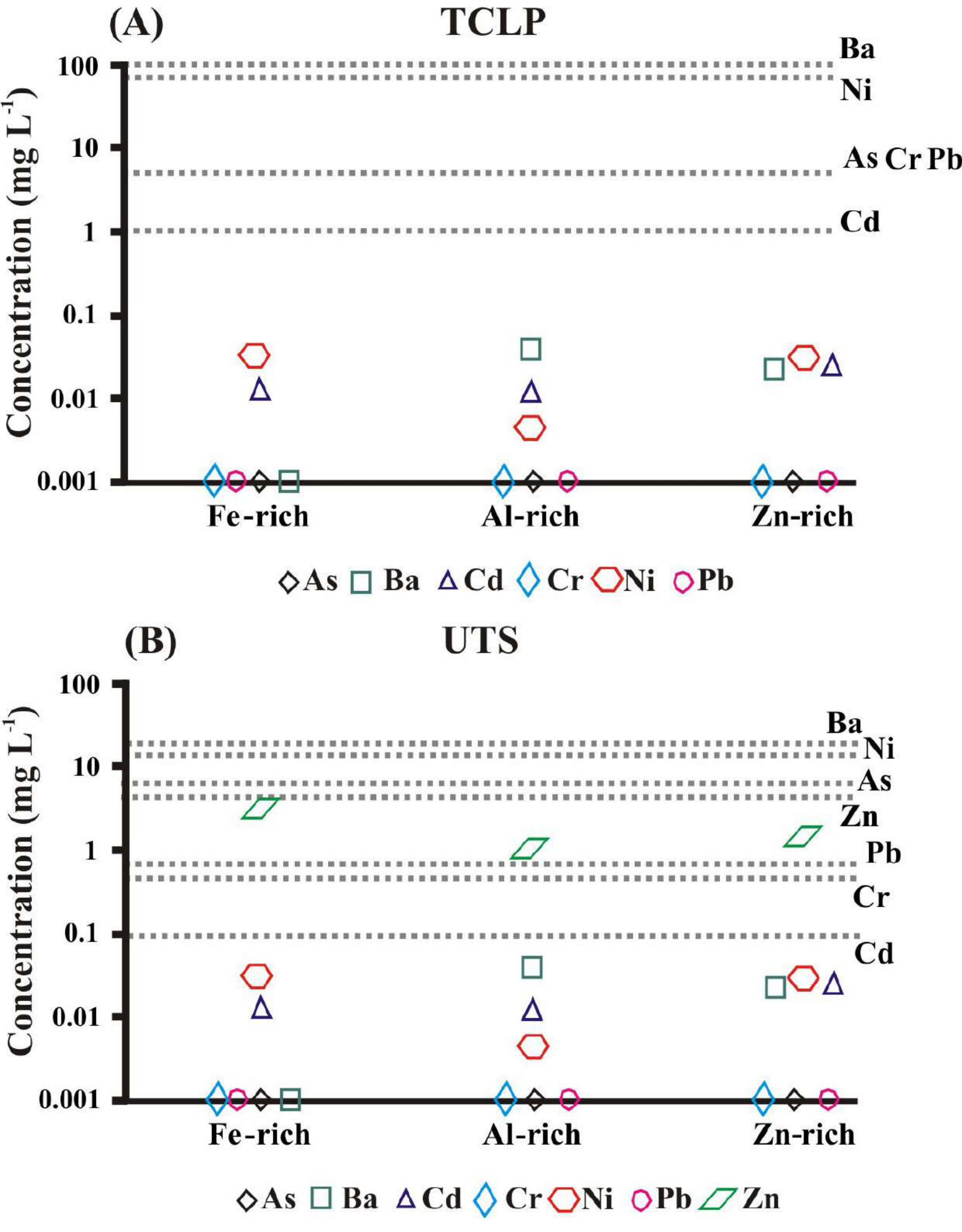
dashed lines). The solid markers indicate that the pollutant exceed the limit whereas the hollow markers indicate that the pollutant does not exceed the limit.

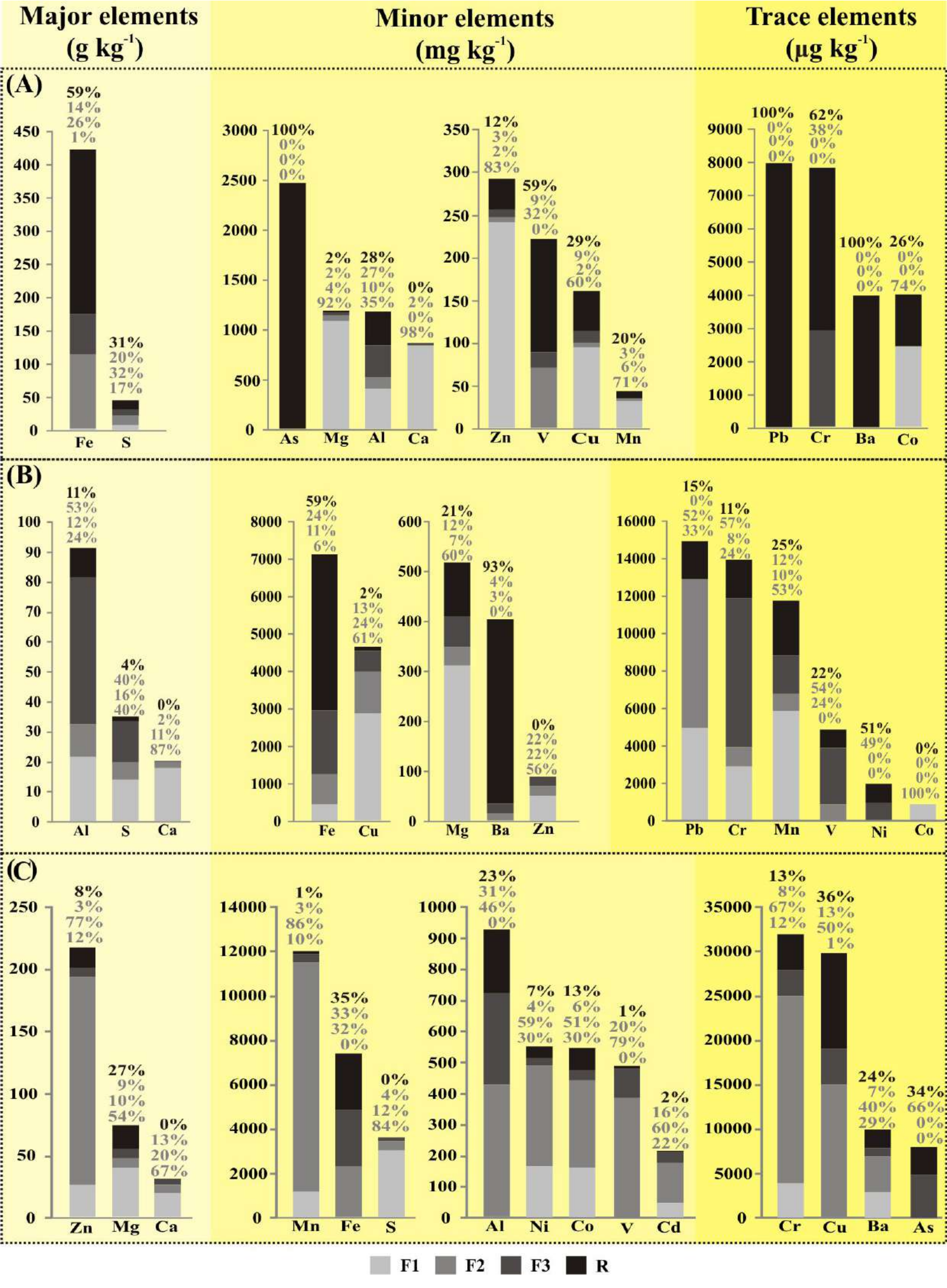
TABLES

Table 1. Comparative results of the BCR sequential extraction steps sum and the pseudo-total metal concentration obtained by an independent aqua regia digestion of the DAS-type wastes using the Recovery (%) parameter calculated according equation (1).

Table 2. Regulatory levels for waste acceptance at landfills (council decision 2003/33/EC), and leached metal concentration of DAS-type wastes after EN 12457-2 leaching test. Data in mg kg^{-1}.


(A)
SPAIN
PORTUGAL
300 Km
Monte Romero
Mina Esperanza
Huelva
Atlantic Ocean
20 Km
Mina Esperanza full-scale plant
10 m
Inflow
Fe and Al-rich DAS wastes
Limestone-DAS tank
A.c.
D.p.
Outflow
Monte Romero pilot-scale plant
2 m
Inflow
A.c.
D.p.
A.c.
A.c.
D.p.
A.c.
Outflow
Limestone-DAS tanks
MgO-DAS tank
Zn-rich DAS waste
Mina Esperanza limestone-DAS wastes
Fe-rich
Al-rich
Zn-rich
Unreacted material
Monte Romero MgO-DAS waste
(B)
5 cm
2 cm


(A)
TCLP
Ba
Ni
As Cr Pb
Cd
100
10
1
0.1
0.01
0.001
Concentration (mg L-1)
Fe-rich
Al-rich
Zn-rich
As
Ba
Cd
Cr
Ni
Pb
(B)
UTS
Ba
Ni
As
Zn
Pb
Cr
Cd
100
10
1
0.1
0.01
0.001
Concentration (mg L-1)
Fe-rich
Al-rich
Zn-rich
As
Ba
Cd
Cr
Ni
Pb
Zn


Major elements (g kg^{-1})
Minor elements (mg kg^{-1})
Trace elements (µg kg^{-1})
(A)
0
50
100
150
200
250
300
350
400
450
59%
14%
26%
1%
31%
20%
32%
17%
Fe
S
0
500
1000
1500
2000
2500
3000
100%
0%
0%
0%
2%
2%
4%
92%
28%
27%
10%
35%
0%
2%
0%
98%
As
Mg
Al
Ca
0
50
100
150
200
250
300
350
12%
3%
2%
83%
59%
9%
32%
0%
29%
9%
2%
60%
20%
3%
6%
71%
Zn
V
Cu
Mn
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
100%
0%
0%
0%
62%
38%
0%
0%
100%
0%
0%
0%
26%
0%
0%
74%
Pb
Cr
Ba
Co
(B)
0
10
20
30
40
50
60
70
80
90
100
11%
53%
12%
24%
4%
40%
16%
40%
0%
2%
11%
87%
Al
S
Ca
0
1000
2000
3000
4000
5000
6000
7000
8000
59%
24%
11%
6%
2%
13%
24%
61%
Fe
Cu
0
100
200
300
400
500
600
21%
12%
7%
60%
93%
4%
3%
0%
0%
22%
22%
56%
Mg
Ba
Zn
0
2000
4000
6000
8000
10000
12000
14000
16000
15%
0%
52%
33%
11%
57%
8%
24%
25%
12%
10%
53%
22%
54%
24%
0%
51%
49%
0%
0%
0%
0%
0%
100%
Pb
Cr
Mn
V
Ni
Co
(C)
0
50
100
150
200
250
8%
3%
77%
12%
27%
9%
10%
54%
0%
13%
20%
67%
Zn
Mg
Ca
0
2000
4000
6000
8000
10000
12000
14000
1%
3%
86%
10%
35%
33%
32%
0%
0%
4%
12%
84%
Mn
Fe
S
0
100
200
300
400
500
600
700
800
900
1000
23%
31%
46%
0%
7%
4%
59%
30%
13%
6%
51%
30%
1%
20%
79%
0%
2%
16%
60%
22%
Al
Ni
Co
V
Cd
0
5000
10000
15000
20000
25000
30000
35000
13%
8%
67%
12%
36%
13%
50%
1%
24%
7%
40%
29%
34%
66%
0%
0%
Cr
Cu
Ba
As
F1
F2
F3
R

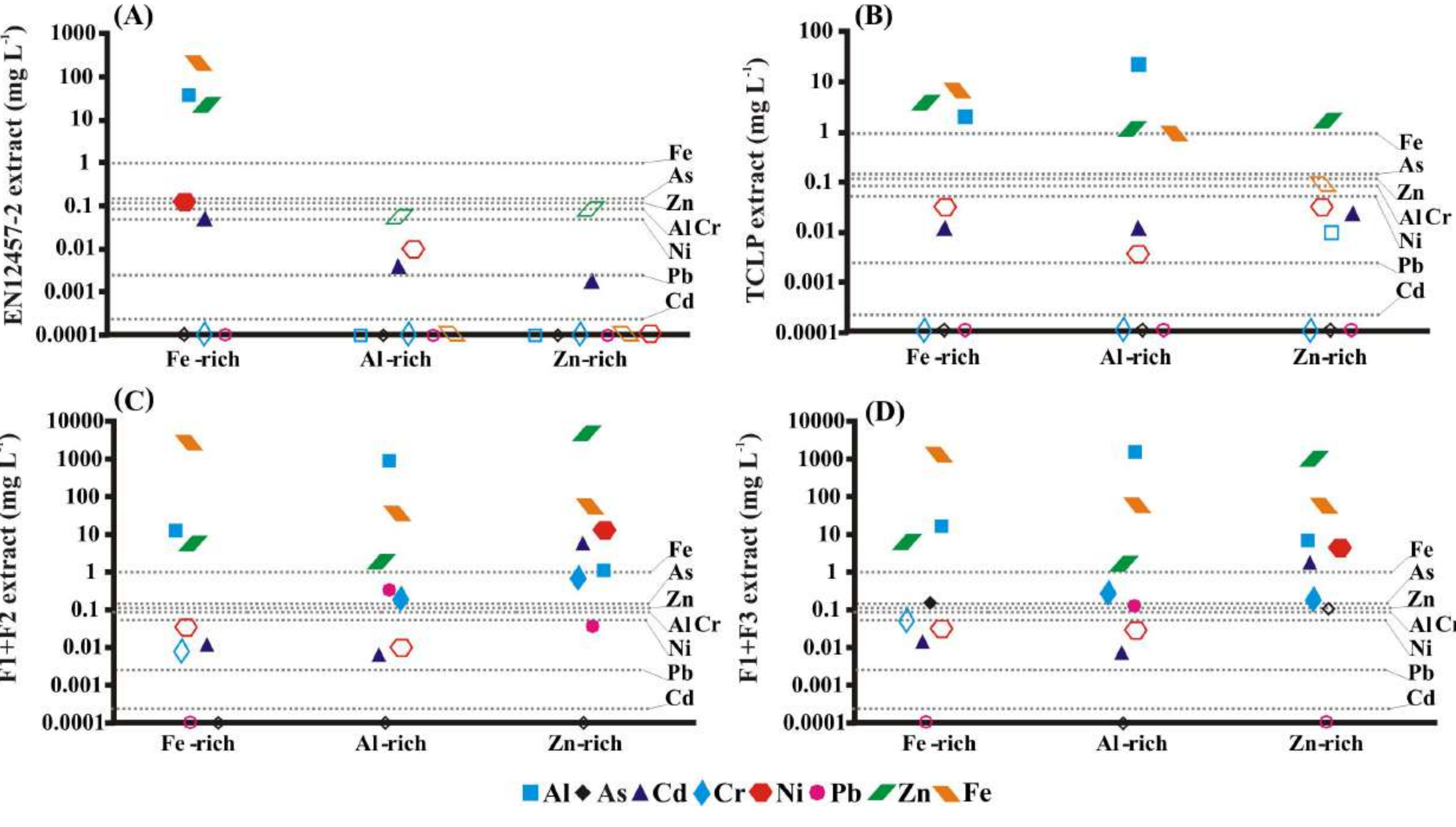

(A)
EN12457-2 extract (mg L^{-1})
1000
100
10
1
0.1
0.01
0.001
0.0001
Fe -rich
Al -rich
Zn-rich
Fe
As
Zn
Al Cr
Ni
Pb
Cd
(B)
TCLP extract (mg L^{-1})
100
10
1
0.1
0.01
0.001
0.0001
Fe -rich
Al -rich
Zn-rich
Fe
As
Zn
Al Cr
Ni
Pb
Cd
(C)
F1+F2 extract (mg L^{-1})
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
Fe -rich
Al -rich
Zn-rich
Fe
As
Zn
Al Cr
Ni
Pb
Cd
(D)
F1+F3 extract (mg L^{-1})
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
Fe -rich
Al -rich
Zn-rich
Fe
As
Zn
Al Cr
Ni
Pb
Cd
Al
As
Cd
Cr
Ni
Pb
Zn
Fe

Table 1. Comparative results of the BCR sequential extraction steps sum and the pseudo-total metal concentration obtained by an independent aqua regia digestion of the DAS-type wastes using the Recovery (%) parameter calculated according equation (1)

DAS waste	**% Recovery**															
	Al	**As**	**Ca**	**Cu**	**Fe**	**Mg**	**Mn**	**S**	**Zn**	**Ba**	**Cd**	**Cr**	**Co**	**Ni**	**Pb**	**V**
Fe-rich	87	94	114	89	90	104	102	82	112	96	-	87	105	-	114	84
Al-rich	80±1	-	94±2	87±1	87±4	81±1	87±0	91±1	84±3	102±2	-	80±3	58±2	107±5	129±23	71±3
Zn-rich	90±1	83±8	87±0	82±0	91±1	78±4	90±4	86±2	97±1	81±23	82±1	85±2	90±1	90±0	-	83±2

In samples with replicates the recovery value is presented as the mean value followed by the standard deviation

Table 2. Regulatory levels for waste acceptance at landfills (council decision 2003/33/EC), and leached metal concentration of DAS-type wastes after EN 12457-2 leaching test. Data in mg kg^{-1}

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
DAS waste									
Fe-rich	0	1.13	0.49	0	75.8	2.7	0	197.5	14544
Al-rich	0	0.23	0.04	0	0.3	0.1	0.1	0.6	12256
Zn-rich	0	0.13	0.017	0	0	0	0.2	1	3906