



Feasibility study on the use of soil washing to remediate the As–Hg contamination at an ancient mining and metallurgy area

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ARTICLE INFO

Article history:

Received 14 March 2011

Received in revised form 15 July 2011

Accepted 31 August 2011

Available online 6 September 2011

Keywords:

Soil pollution

Mercury

Arsenic

Ore processing

Soil washing

ABSTRACT

Soils in abandoned mining sites generally present high concentrations of trace elements, such as As and Hg. Here we assessed the feasibility of washing procedures to physically separate these toxic elements from soils affected by a considerable amount of mining and metallurgical waste ("La Soterraña", Asturias, NW Spain). After exhaustive soil sampling and subsequent particle-size separation via wet sieving, chemical and mineralogical analysis revealed that the finer fractions held very high concentrations of As (up to 32,500 ppm) and Hg (up to 1600 ppm). These elements were both associated mainly with Fe/Mn oxides and hydroxides. Textural and geochemical data were correlated with the geological substrate by means of a multivariate statistical analysis. In addition, the Hg liberation size (below 200 μm) was determined to be main factor conditioning the selection of suitable soil washing strategies. These studies were finally complemented with a specific-gravity study performed with a C800 Mozley separator together with a grindability test, both novel approaches in soil washing feasibility studies. The results highlighted the difficulties in treating "La Soterraña" soils. These difficulties are attributed to the presence of contaminants embedded in the soil and spoil heap aggregates, caused by the meteorization of gangue and ore minerals. As a result of these two characteristics, high concentrations of the contaminants accumulate in all grain-size fractions. Therefore, the soil washing approach proposed here includes the grinding of particles above 125 μm .

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1. Introduction

Abandoned mining-metallurgy sites are sources of environmental pollution. This contamination is a result of mine drainage, waste disposal, subsidence and other phenomena [1,2]. Specifically, Hg mining and processing are frequent causes of environmental concern because of the abundance of Hg and other toxic trace elements, such as As, in the ores exploited [3]. Hg participates in a number of complex environmental cycles. Geochemical studies have shown that, once in the environment, ionic Hg can be converted into organomercury compounds, which are highly toxic to most organisms [4]. Furthermore, As toxicity – specifically As (III) – has triggered severe environmental alarms throughout the world, in particular in relation to groundwater [5].

In this context, soil washing by means of physical and/or chemical procedures is a suitable technique to reduce the concentration of heavy metal contaminants in this matrix [6]. Physical processing technology in particular has been frequently used to remediate

heavy metal and semi-metal pollution, including Hg and As [7–11]. These techniques remove contaminants from soil by concentrating them into a minor volume by means of comminution, particle size separation, specific-gravity separation, attrition scrubbing, froth flotation or magnetic separators. Thus, physical processing concentrates contaminants by exploiting differences between the characteristics of metal-bearing particles and soil particles (size, density, hydrophobic surface properties, magnetism), in much the same way as mineral ores can be treated. Given that these technologies are versatile and cost-effective when high amounts of soil are to be treated, they may be highly appropriate for the remediation of former industrial sites and old mine dumps [12]. In contrast, chemical processing usually comprises procedures such as acid or base treatment for solubilisation, or the use of specific solvents, to release pollutants into the liquid fraction [6].

The information reported in feasibility studies usually allows consideration of a range of alternatives for soil washing treatments, the final objective of which is a noteworthy reduction in the volume of contaminated soil (ideally, in a soil washing process the goal pursued for a given contaminant is to achieve a high concentration in a small fraction [6]). This broad view requires a detailed characterisation of the edaphology, mineralogy and geochemical

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behaviour of the grain-size soil fractions. Here we applied this work-plan to soil highly contaminated with As and Hg as a result of the physico-chemical alteration of mining-metallurgic waste [13]. In addition, specific-gravity and liberation degree studies facilitated the evaluation of the viability of applying gravimetric and/or granulometric concentrators. Concretely, the particle-size fractions obtained were used for a specific-gravity study to examine the relationship between particle size, density and contaminant content of the fractions. Milling was also considered by means of a complementary approach consisting of Bond tests to evaluate the grindability of coarse fractions in order to obtain a finer grain-size that is more appropriate for physical separation.

Following all of the preceding considerations, the main aims of the current study were as follows:

- To integrate grain size distribution, specific-gravity separation and a liberation degree study with edaphological, geochemical and mineralogical information of the study site.
- To introduce the “C800 Mozley laboratory mineral separator” and the “Bond Ball Mill Standard test” as effective tools to improve the abovementioned feasibility studies.

2. Materials and methods

2.1. Site description and soil sampling

Until the end of the 1970, extensive Hg deposits in the central zone of Asturias (northern Spain) were exploited [14–18]. One of the main sites was known as “La Soterraña”. There, together with mining activity, ore processing and metallurgy were carried out intermittently from the middle of the XIX century in order to obtain Hg. Regarding ore geology, mining was performed through a low-temperature hydrothermal ore, which is hosted by highly fractured limestones with dispersion in the flanking sandstones and lutites of Carboniferous age. The paragenesis of this mineral deposit is constituted by cinnabar (HgS), orpiment (As₂S₃), realgar and pararealgar (AsS), As-enriched pyrite and marcasite (FeS₂), and arsenopyrite (FeAsS), in a gangue of quartz and calcite [14,19]. These sulphides were treated at “La Soterraña” mining-metallurgic plant, where the mineral was milled and roasted to obtain Hg vapour, which was then condensed. The emissions of polluting steams and particles and the dumping of mining and smelting waste greatly affected around 80,000 m² of the surrounding area [14]. Currently, the distribution of the pollutants throughout the site is caused mainly by the mechanical dispersion of the spoil heap waste, together with the oxidation and lixiviation of As–Hg-rich materials, and also the processes of complexation and immobilisation related to soil particles.

In order to conduct a soil washing feasibility study, three composite and representative soil samples (labelled S1, S2 and S3, 50 kg each) were collected from the tilled depth (0–35 cm) by means of a stainless steel hand-auger and a shovel. The soil was passed through a 2-cm mesh screen *in situ* to remove rock fragments, vegetation and other large material; finally, samples were homogenised and stored in inert plastic bags.

2.2. Sample preparation

In the laboratory, the three samples were gently dried at room temperature, thoroughly disaggregated, mixed, and subsequently sieved through a 4-mm screen. Materials with a grain size greater than 4 mm were washed and rubbed off to recover fine particles adhered to gravels and pebbles. Once these gravels and pebbles had been cleaned up, they were excluded from the study. Each sample below a grain size of 4 mm was quartered by means of a channel

separator to obtain representative 4-kg batches. These were then oven-dried for 48 h at 45 °C to prevent Hg loss.

2.3. Soil characterisation

Regarding pedology, the pH was measured with a glass electrode in a suspension of soil and water (1: 2.5) in H₂O and electrical conductivity was measured in the same extract (diluted 1:5). Organic matter was determined by the ignition method (weight loss at 450 °C). Exchangeable cations (Ca, Mg, K and Na) extracted with 1 M NH₄Cl, and exchangeable Al extracted with 1 M KCl were determined by atomic absorption/emission spectrophotometry [20] in an AA200 Perkin Elmer analyzer; the effective cation exchange capacity (ECEC) was calculated as the sum of the values of the latter two measurements (sum of exchangeable cations and exchangeable Al).

2.4. Wet sieving

The representative batches of each sample (S1, S2, S3) were slurried in water and then sieved (cycles of 100 g) into particle-size fractions of <63, 63–125, 125–250, 250–500, 500–1000, 1000–2000 and 2000–4000 μm batches were passed through normalised sieves positioned in a shaker (Restch) for 5 min with a water flow of 0.3 l/min (ASTM D-422-63, Standard Test Method for Particle-Size Analysis of Soils). The fractions were recovered with the help of a spray nozzle, and then dried at 50 °C and weighed. To complete the grain size distribution, the silt–clay fraction (<63 μm) was studied using a Laser Diffraction Particle Analyser (Beckman Coulter Inc.).

Representative samples of the grain size fractions were subjected to chemical analyses by means of ICP-OES (Section 2.5). However, some of these fractions were subdivided to obtain further samples for the mineralogical and specific gravity studies (see Sections 2.7 and 2.8). In order to standardise the conditions used for chemical attack, samples with a grain size over 125 μm were ground at 400 rpm for 40 s using a vibratory disc mill (RS 100 Retsch).

2.5. Chemical analyses

For chemical analyses, 1-g representative sub-samples of the diverse origins (soils, grain size fractions, light or dense specific gravity fractions, etc.) were leached by means of an ‘Aqua regia’ digestion (HCl+HNO₃). The digested material was analysed for total concentrations of 19 major and trace elements (Ca, Mg, K, Na, Al, Fe, S, Cu, Pb, Zn, Cd, Ni, Mn, As, Sr, Sb, La, Cr and Hg) by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) in the accredited (ISO 9002) laboratories Actlabs Int., Ancaster (Ontario, Canada).

2.6. Multivariate statistics

Cluster Analysis was undertaken following the Ward-algorithmic method, which maximises the variance between groups and minimises it between members of the same group [21]. A dendrogram obtained with the statistical software SPSS v18.0 was used to show the clustering of results. Groups of elements with a similar geochemical behaviour were identified on the basis of the statistical distance between them (squared-Euclidean distance was selected).

2.7. Mineralogy and liberation degree study

The mineralogical composition of the soil was estimated by means of an X-ray diffractometer (DRX, Philips X Pert Pro, incorporating databases of the International Centre for Diffraction Data). In

Table 1

Parameters used in the specific gravity study performed with a C800 Mozley laboratory separator (recommendations by the manufacturer were adapted to soil properties).

Grain-size fractions (μm)	Tray	Shake speed (r.p.m.)	Amplitude (mm)	Washwater (l/min)	Feed (g)	Time (min)
<63	'V'profile	70	2.5	3	50	3
125–63 250–125 500–250	Flat	90	3.5	3	150	3

addition, representative samples of each wet-sieving fraction were used to prepare polished sections to be studied by an Eclipse LV 100 POL Nikon petrographic microscope.

The morphology and composition of specific minerals were studied using a SEM-EDX system: Scanning Electron Microscope (Jeol JSM-6100) coupled with Energy Dispersive X-ray analyser (INCA Energy 200).

2.8. Specific gravity study

The particle-size fractions obtained were used for a specific-gravity study to examine the relationship between particle size, density and contaminant content of the fractions. A C800 Mozley laboratory mineral separator was used for this purpose. This separator, which operates using gravimetric classification, is commonly used to assess mineral processing equipment [22], although in our case it was tested for site remediation purposes.

In brief (see [22] for details), this separator comprises a riffleless shaking table; two types of table deck (trays) are available, a "V" profile for materials finer than 1000 μm and coarser than 63 μm , and a "Flat" profile for the separation of material below 63 μm .

Physical separation is governed by the flowing film principle [23], in addition to a perpendicular movement to the tray axis, thus favouring the advance of the solids on the tray. Therefore, the separation in this equipment is only partially conditioned by Stokes force (correlated with grain-size); conversely, mass forces related to an asymmetric acceleration are enhanced (specific-gravity separation effect).

In our case, 100-g samples of the particle-size fractions of <63, 63–125, 125–250, 250–500 μm were shaken under several controlled parameters (shaking speed and amplitude, water flow, and time, Table 1), in order to obtain dense and light fractions in every experiment.

However, for fractions above 63 μm , the effect of silt/clay particles physically adhered to the coarser ones should be considered; in our case, this adherence was directly linked to the efficiency of the previous wet-sieving performed. To determine the relevance of this effect, we carried out an experiment in which three representative 50-g samples from the 63 to 125 μm fraction were directly treated in the C800 separator, while another three samples were pre-treated for 30 min in a solution of dispersing agents (3 g of sodium hexametaphosphate and 0.5 g of anhydrous sodium carbonate dissolved in 250 ml of distilled water) at 400 rpm in a Heidolph RZR 2020 shaker.

2.9. Grindability characterisation

In soil washing approaches, milling could be required to free contaminants from the matrix aggregates in which they are embed-

ded, in order to facilitate the ulterior operation in concentrators. Therefore, we estimated the resistance of the soil samples to ball milling in terms of specific power consumption for grinding. This was done by means of the Bond Ball Mill Standard test [24–26].

In brief, with the aim to simulate closed circuit continuous operation with a recirculating load of 250%, the test [27] is carried out in a 12" \times 12" lab ball mill, in consecutive cycles of batch operations of grinding and sieving. In our case, the sieves selected to study the variation of the Bond Work index with the milling product size were 250, 180, 125 and 80 μm . The test is useful to obtain the internal parameter named "grindability index", Gbp, in an iterative procedure. The final value of "work index" is calculated using the following equation:

$$w_i = \frac{44.5}{P_i^{0.23} \cdot Gbp^{0.82} \left(\frac{10}{\sqrt{P_{80}}} - \frac{10}{\sqrt{F_{80}}} \right)}$$

where P_i (in μm): screen size at which the test is performed. Gbp is the Bond's standard ball mill grindability; net weight of ball mill product passing sieve size P_i produced per mill revolution (g/rev), once the end of the test is reached. F_{80} and P_{80} (in μm) are the 80% sieve opening through which 80% of the product passes (for Feed and Product respectively). w_i is the Bond Work index (in kWh/sht). Once obtained the work index, the specific power consumption W [kWh/t] can be calculated using the Bond Formula:

$$W = 10 \cdot w_i \left(\frac{1}{\sqrt{P_{80}}} - \frac{1}{\sqrt{F_{80}}} \right)$$

3. Results and discussion

3.1. Pedology, grain size study and soil geochemistry

The pedological characterisation (average of three determinations over the initial bulk samples S1, S2, S3, with a standard error below 5%) revealed a slightly acid pH (6.3), low electrical conductivity ($EC = 0.19 \text{ dS m}^{-1}$), low content of exchangeable base cations (5.42; 0.31; 0.28 and 0.47 $\text{cmol}_c \text{ kg}^{-1}$ for Ca, Mg, K and Na respectively), low ECEC (sum of exchangeable cations and exchangeable Al = 7.38 $\text{cmol}_c \text{ kg}^{-1}$), and a low organic matter content in the upper horizon (0.75%). All of these data are consistent with the geological origin of the soil and its development under particular geochemical conditions as a result of the influence of waste derived from mining activities and the metallurgy industry.

Furthermore, ICP-OES analyses (Table 2) revealed very high concentrations of As and Hg, and a lower presence of other contaminants such as Pb. These findings are also consistent with the

Table 2

Element concentration of representative subsamples of the three initial bulk samples (results correspond to the average of three determinations with a standard error <5%).

Sample	Trace elements (mg kg^{-1})					Major elements (%)		
	Hg	As	Pb	Zn	Sb	Al	Ca	Fe
S1	805	32,500	98	98	211	2.86	2.52	3.19
S2	1600	17,100	49	71	111	2.08	5.6	3.09
S3	132	6350	28	46	23	2.8	5.9	2.81

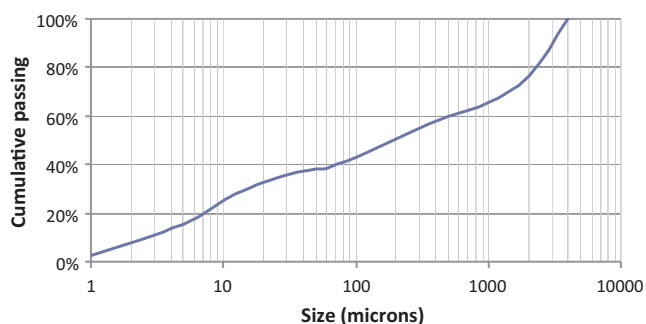


Fig. 1. Particle-size distribution of sample S2, obtained by compositing wet-sieving (4000–63 μm), and laser dispersion (<63 μm) data.

mineralisation-type of the ores treated at “La Soterraña”. In contrast, the high concentrations of Ca, Al and Fe point to a soil matrix composed of carbonates, clay minerals and iron oxides.

Regarding the grain-size analysis, the results for the three samples were very similar. For instance, the cumulative passing curve of sample S2 (Fig. 1) indicates that the coarsest (500–4000 μm : 39.9%) and finest fractions (<63 μm : 38.1%) were predominant, whereas intermediate fractions (250–500 μm : 1.8%; 125–250 μm : 15.7%; 63–125 μm : 4.5%) were less abundant. These data are particularly relevant given that the fineness of the material is one of the main factors impeding acceptable performance of soil washing for remediation purposes [7].

To facilitate the study of the relationship between contaminant contents and grain-size fractions, we then measured the total content of major and trace elements in the abovementioned grain-size fractions. Hg and other trace elements showed higher contents in the fine fraction, while As showed a slightly more homogeneous distribution in all the grain-size fractions (Table 3). Of the major elements, only Fe showed a similar pattern to that observed for the previously mentioned trace elements, especially Hg. Therefore we hypothesised that most of the trace elements remain geochemically associated with former iron-rich sulphur minerals, which are probably oxidised in the present soil conditions. In contrast, a different profile was observed for Al and Ca, thereby suggesting a distinct behaviour of these elements to that of Hg and As. This notion was confirmed by a multivariate approach in which a hierarchical cluster analysis and also a Principal Components Analysis (data not shown) revealed two main groups of elements, as shown in the dendrogram (Fig. 2). This outcome is congruent and complementary to the mineralogical and edaphological studies, thus suggesting the following about the geochemical behaviour of As and Hg:

Group AB: comprising mainly chalcophile trace elements and some major elements such as Fe, Al and K. This group is subdivided into two subgroups:

‘A’ contains a clear association between Fe, Mn, Hg, As and other trace elements of concern (Sb, Ni). Consequently, and given the high contents of ultrafine materials in the soil and the low amount

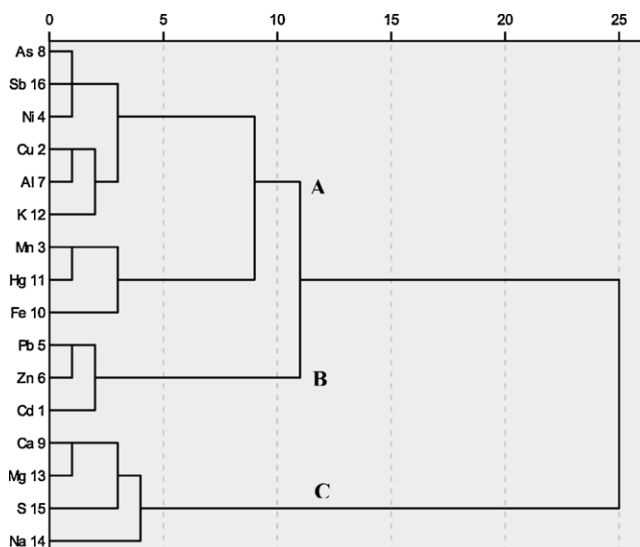


Fig. 2. Dendrogram showing the clustering of elements associated by their geochemical affinity within the samples (irrespective of the original sample and grain-size fraction). Main groups are indicated based on statistical distance between them.

of organic matter, Hg and As behaviour appears to be controlled mostly by their ion binding to iron/manganese oxides-hydroxides. The presence of Al and K in this subgroup suggests a main role of argillaceous minerals; however, the DRX data (see below) and the low ECEC suggest that phyllosilicates have little relevance.

‘B’ includes the well-known Pb–Zn–Cd association, which probably originated from the weathering of sphalerite (ZnS, slightly enriched in Cd) and galena (PbS), both accessory minerals in La Soterraña ore.

Group C: comprising elements linked to the alteration of the gangue rocks (for instance Ca from limestone). In addition, the presence of S in this group is linked to secondary minerals, such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and others that can be observed in the local paragenesis of the weathered ores. According to the statistical treatment, the elements included in C are distant from the Group AB (negative correlation).

3.2. Mineralogy and liberation degree study

DRX data showed that the predominant components in the samples were quartz and secondarily, calcite, hematite, ferrihydrite, goethite and maghemite. In contrast, clay minerals were clearly minority. Mineralogical analyses, particularly microscopy observations, revealed that some of the former sulphides from the ore were undamaged in the coarse fractions, and were usually covered by gangue minerals, which shielded them from the effects of weathering (Fig. 3a and b). Although scarce, free grains of arsenopyrite, (Fig. 3c), pyrite and chalcopyrite were also found. Cinnabar was the

Table 3
Total content in grain-size fractions for major and trace elements of sample S2 (results correspond to the average of three determinations with a standard error <5%).

Grain-size fraction (μm)	Trace elements (mg kg^{-1})					Major elements (%)		
	Hg	As	Pb	Zn	Sb	Al	Ca	Fe
4000–2000	495	15,800	36	60	87	2.9	3.31	3.87
2000–1000	720	18,400	44	70	101	3.25	3.42	3.74
1000–500	1000	21,900	54	80	144	3.1	3.71	3.75
500–250	1920	24,500	65	125	165	2.47	3.62	3.80
250–125	2030	27,900	67	125	195	2.95	4.51	3.84
125–63	2520	24,300	68	133	158	3.29	3.77	3.97
<63	4810	26,350	76	155	212	3.31	3.42	4.39

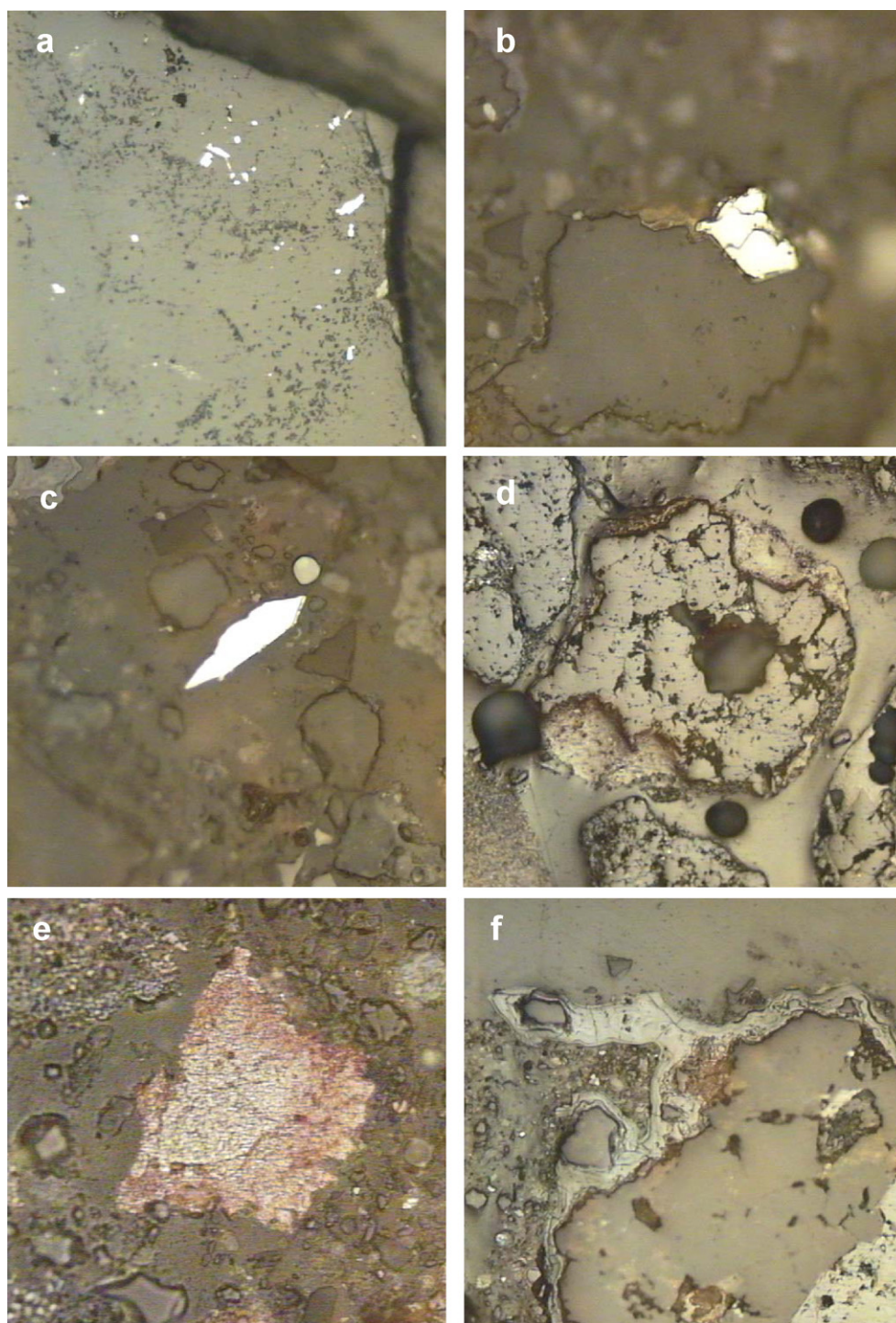


Fig. 3. (a) Arsenopyrite crystals within a quartz grain. (b) Pyrite inclusion in a quartz grain. (c) Unaltered free idiomorphic grain of arsenopyrite. (d) Quartz grain partially reemplaced by cinnabar (soft component). (e) Free altered cinnabar. (f) Hematite coating surrounding quartz grains. (Horizontal frame is 650 μm for Fig. 3a, 260 μm for b, c and e and 1.3 mm for d and f.)

most common sulphide and also appeared as inclusions in gangue minerals (Fig. 3d) and as free altered small grains (Fig. 3e and g). The texture is typical of a calcine material, the fractions below 250 μm being richer in metallic oxides and oxy-hydroxides, especially hematite (usually combined with gangue materials, Fig. 3f) and, to a lesser extent, goethite. These textures and morphologies can be attributed to the roasting process during ore treatment and also weathering. However, the most aggressive oxidising process was the former as it has the capacity to destroy As and Hg sulphides.

Nevertheless, the temperature range used in the ovens (much lower than 700 $^{\circ}\text{C}$) was not enough to destroy As-rich pyrite, arsenopyrite and chalcopyrite, irrespective of their original grain size (Fig. 4). In this regard, the presence and texture of cinnabar, and other mineral phases containing Hg denotes a deficient roasting procedure.

Therefore, the mineralogy of Hg (mainly as cinnabar) and As (mainly linked to Fe sulphides and oxides), which both show an irregular distribution within the grain-size fractions, hinders the design of an effective soil washing treatment. In fact, in the case

Table 4
Major and trace elements concentrations measured in the dense fractions after experiments carried out with a C800 separator (125–63 μm fraction). Results are an average of those obtained with three samples and show a standard error <5%.

Samples	Trace elements (mg kg^{-1})					Major elements (%)		
	Hg	As	Pb	Zn	Sb	Al	Ca	Fe
Feed material	785	29,433	96	152	180	2.38	3.19	4.17
Dense fraction with dispersant pretreatment	925	17,100	70	176	90	1.56	2.31	3.76
Dense fraction without pretreatment	897	15,733	76	165	82	1.47	2.26	3.81
% variation	2.99	7.99	9.05	6.06	8.18	5.98	2.16	-1.51

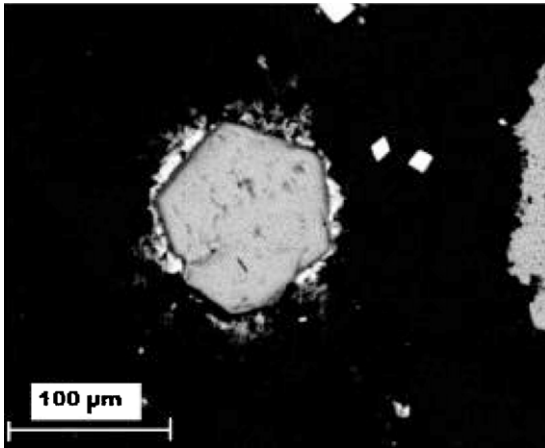


Fig. 4. Scanning electron micrograph of a hexagonal goethite grain that preserves the original morphology of pyrite. The surrounding area contains 22% of Hg. Smaller and more reflecting grains correspond to arsenopyrite.

of cinnabar (HgS), the liberation size calculated under the optical microscope (grain size for which the cinnabar grains are not mineral inclusions in other mineral phases) was below 200 μm , thus clearly limiting any physical separation equipment for fractions above this grain size. To obtain these data, we performed a complex liberation size study composed of dozens of microphotographs with the accompanying measurements of grain sizes.

3.3. Specific-gravity study

The use of dispersants did not imply a clear improvement in the classification obtained in the C800 system (none of the chemical elements notably changed in the dense fraction concentration, Table 4). Thus it can be concluded that the quality of the wet-sieving was sufficient to prevent distortions in the data described below.

Although the liberation degree was below 200 μm for Hg, a considerable amount of contaminants might be recovered by gravity separation procedures in the grain-size interval between 500 and 125 μm . Initially, for the grain-size interval between 500 and 250 μm , the C800 separator was not effective as the sizes with which this equipment operates are clearly above the liberation size (Table 5). Alternatively, for all the fractions below 250 μm , the results indicate that the dense fraction obtained in the C800

Table 5
Element content (percentage by weight) measured in the dense fraction for the indicated grain-size fractions. The separation between dense and light fractions was achieved in a C800 separator working as specified in Table 1. Results are an average of those obtained with three samples and show a standard error <5%.

Grain-size fraction (μm)	Textural classification	% in dense fraction		
		Hg	As	Fe
500–250	Medium sands	50.06	42.17	65.47
250–125	Fine	39.33	33.42	55.04
125–63	sands	19.73	14.09	29.72
$x < 63$	Silt-clay	15.65	6.82	14.06

Table 6
Results of Bond ball mill grindability test, corresponding to the average of three determinations with a standard error <10%. F_{80} and P_{80} are the 80% sieve opening through which 80% of the product passes (for Feed and Product respectively); P_i is the screen size at which the test is performed; Gbp is the Bond's standard ball mill grindability, w_i is the Bond index ('work index'), and W is the specific power consumption.

F_{80} (μm)	P_i (μm)	Gbp (g/rev)	P_{80} (μm)	w_i (kWh/sht)	w_i (kWh/t)	W (kWh/t)
2957	80	1.1032	72	15.01	16.54	16.45
2973	125	1.8917	109	11.22	12.37	9.69
2917	180	2.2967	154	10.97	12.09	7.50
2951	250	2.8523	194	9.90	10.91	5.82

was poorer in As and Hg than the light fraction (Table 5). In this context, the differences in density between the two fractions were quite low (e.g., 2.5 g/cm^3 for the lighter particles and 2.8 g/cm^3 for the heavier ones in the case of the 63–125 μm fraction, both measured with a water pycnometer). This is an unexpected effect, given that the presence of 'free' As and Hg dense minerals, for instance cinnabar and arsenopyrite, arises when grain size decreases. Consequently, the concentrations in the dense fraction should be higher than those indicated in Table 5. The most probable explanation for this observation is that the size ranges used in this study were not narrow enough, and therefore a granulometric separation overlies the densimetric separation, as generally occurs with other types of gravimetric separators [23]. In practical terms, these results imply that physical separation of this soil by means of gravity concentrators (spirals, shaking tables, etc.) would be very difficult.

3.4. Grindability characterisation

The results described in the previous section indicate that the use of grain size separators or gravity concentrators is strongly hindered in fractions coarser than 200 μm ; therefore milling is required to improve the liberation degree of Hg and As. This process, which normally accounts for 30% of the total costs in ore processing [23], can be significant enough to make the process unworkable. Thus, the cost of milling must also be taken into consideration in soil remediation procedures. In addition, milling would be an interesting option to address in future research into the immobilisation of trace elements [28].

Following the previous considerations, Bond tests were performed and the main results are presented in Table 6. The specific power consumption ranged from 16.45 kWh/t to 5.82 kWh/t, confirming that the finer the sieve, the greater the energy consumption.

Depending on the liberation size, the power consumption in comminution operations can double from one size fraction to another. This issue should be considered when addressing the operating costs of the process. In our case, 125 μm can be considered a safe cut-off point in accordance to the results of the mineralogical study; hence the specific power consumption to take into account is 9.69 kWh/t. This value reflects a medium-high level, similar to that required for grinding an average limestone [29]. Along with the previous statements, appropriate selection of the milling machine will yield a well balanced power efficiency process [30].

3.5. Consequences for soil washing design

The feasibility study carried out in this work should be completed by a cost analysis, highly conditioned by the huge amount of soil to be treated (80,000 m^2) and by other important questions such as cost of milling (as described above) and treatment of washing effluents. At any case, it is possible to propose a first approach to define soil washing stages, in brief:

- The grain-size fractions below 125 μm containing “free” As and Hg minerals could be treated with hydrocycloning because of the demonstrated increasing concentration of the contaminants with increasing fineness. A factorial design would be required to define optimum conditions (see for example a successful application in [10]).
- The design of the strategy for the fractions coarser than 125 μm is clearly conditioned by the results of the mineralogical and specific-gravity studies. Therefore in order to improve the Hg and As liberation degree, a milling process should be required. The ground material would be below 125 μm , thereby allowing hydrocycloning.

Some other supplementary technologies might be helpful. For instance, a considerable amount of minerals such as pyrite, goethite and hematite (enriched/bound to As and Hg) could be separated prior to hydrocycloning by means of magnetic field technologies [31,32]. Furthermore, given that cinnabar is highly hydrophobic [33,34], froth flotation may be an appropriate option to obtain satisfactory Hg recovery yields [35,36].

4. Conclusions

Hg and As are primary soil pollutants, particularly in areas formerly devoted to mining activities and the metallurgy industry. In these circumstances, a proper remediation approach to reduce the volume of contamination is soil washing. This approach has been reported to be a cost-effective physical separation technique. The feasibility study at the site of “La Soterraña” shows soils with very high As and Hg content. From geochemical, edaphological and mineralogical data, we have demonstrated that Hg is concentrated mainly in fine grain fractions (below 200 μm), where it is present in the original sulphide form and bound to Fe–Mn oxyhydroxides. In contrast, As is abundant in fine–medium (below 500 μm) fractions and predominantly linked to Fe mineral phases as well.

In the context of the feasibility study, the C800 separator proved effective to study narrow grain-size intervals whenever significant differences in specific-gravity within the particles of the soil were detected. However, in our case, the results obtained were not conclusive. In fact, the mineralogical data reflected the low liberation degree of As and Hg in sandy fractions, and thus the yields of gravimetric or grain-size separation of these fractions would be unsatisfactory. Accordingly, an interesting alternative, though possibly expensive, would consist of previous milling of the medium and coarse fractions in order to allow treatment. In this context,

the grindability test is a novel approach carried out to indicate the extent of power consumption and its influence on the energy efficiency and potential recovery of pollutants. This approach complemented the information from the feasibility study, and showed that in this case physical soil washing would be clearly conditioned by milling costs.

Acknowledgements

This research was funded by the CDTI (“Centro para el Desarrollo Tecnológico e Industrial”), part of the Spanish Council for Industry, within the research programme named “CLEAM CENT”. The corporations involved in this project are the final holders of the results presented here.

We thank Dr. Rodrigo Álvarez for his help with the mineralogical study. Carlos Sierra obtained a grant of the “Severo Ochoa” programme (Ficyt, Asturias, Spain).

References

- [1] J.E. Gray, J.G. Crock, D.L. Fey, Environmental geochemistry of abandoned mercury mines in West-Central Nevada, USA, *Appl. Geochem.* 17 (2002) 1069–1079.
- [2] J. Martínez, J. Llamas, E. de Miguel, J. Rey, M.C. Hidalgo, A.J. Sáez, Multivariate analysis of contamination in the mining district of Linares (Jaén, Spain), *Appl. Geochem.* 23 (2008) 2324–2336.
- [3] P. Higuera, R. Oyarzun, J. Lillo, J.C. Sánchez Hernández, J.A. Molina, J.M. Esbrí, S. Lorenzo, The Almadén district (Spain): anatomy of one of the world’s largest Hg-contaminated sites, *Sci. Total Environ.* 356 (2005) 112–124.
- [4] A. Davis, N.S. Bloom, S.S. Que Hee, The environmental geochemistry and bioaccessibility of mercury in soils and sediments: a review, *Risk Anal.* 17 (1997) 557–569.
- [5] A.A. Duker, E.J. Carranza, M. Hale, Arsenic geochemistry and health, *Environ. Int.* 31 (2005) 631–641.
- [6] G. Dermont, M. Bergeron, G. Mercier, M. Richer-Lafleche, Soil washing for metal removal: a review of physical/chemical technologies and field applications, *J. Hazard. Mater.* 152 (2008) 1–31.
- [7] R. Anderson, E. Rasor, Particle size separation via soil washing to obtain volume reduction, *J. Hazard. Mater.* 6 (1998) 89–98.
- [8] R. Griffiths, Soil washing technology and practice, *J. Hazard. Mater.* 40 (1994) 175–189.
- [9] M.J. Mann, Full scale and pilot scale soil washing, *J. Hazard. Mater.* 66 (1998) 119–136.
- [10] C. Sierra, J.R. Gallego, E. Afif, J.M. Menéndez-Aguado, F. González-Coto, Analysis of soil washing effectiveness to remediate a brownfield polluted with pyrite ashes, *J. Hazard. Mater.* 180 (2010) 602–608.
- [11] G. Dermont, M. Bergeron, G. Mercier, M. Richer-Lafleche, Metal-contaminated soils: remediation practices and treatment technologies, practice periodical of hazardous, toxic, an, Radioact. Waste Manage. 12 (2008) 188–209.
- [12] M. Pearl, M. Pruijn, J. Bovendeur, The application of soil washing to the remediation of contaminated soils, *Land Contam. Reclam.* 14 (2006) 713–726.
- [13] J. Loredó, A. Ordóñez, R. Álvarez, Environmental impact of toxic metals and metalloids from the Muñón Cintero mercury-mining area (Asturias, Spain), *J. Hazard. Mater.* 136 (2006) 455–467.
- [14] C. Luque, Las mineralizaciones de Hg de la Cordillera Cantábrica, *Doct. Thesis, Universidad de Oviedo* (unpublished), 1985.
- [15] C. Luque, El mercurio en la Cordillera Cantábrica, in: García Guinea, Martínez Frías (Eds.), *Recursos minerales de España, C.S.I.C. Textos universitarios No. 15*, Madrid, 1992, pp. 803–826.
- [16] C. Baldo, J. Loredó, A. Ordóñez, J.R. Gallego, J. García-Iglesias, Geochemical characterization of wastes from a mercury mine in Asturias (northern Spain), *J. Geochem. Explor.* 67 (1999) 377–390.
- [17] J. Loredó, R. Álvarez, A. Ordóñez, Release of toxic metals and metalloids from Los Ruedos mercury mine (Asturias, Spain), *Sci. Total Environ.* 340 (2005) 247–260.
- [18] R. Fernández-Martínez, J. Loredó, A. Ordóñez, M.J. Rucandio, Physicochemical characterization and mercury speciation of particle-size soil fractions from an abandoned mining area in Mieres, Asturias (Spain), *Environ. Pollut.* 142 (2006) 217–226.
- [19] J. Loredó, C. Luque, J. García-Iglesias, Conditions of formation of Hg deposits from the Cantabrian zone (Spain), *Bull. Mineral.* 111 (1998) 393–400.
- [20] M. Pansu, J. Gautheryou, *Handbook of Soil Analysis: Mineralogical, Organic and Inorganic Methods*, Springer, Berlin, 2006.
- [21] J.R. Gallego, A. Ordóñez, J. Loredó, Investigation of trace element sources from an industrialized area (Avilés, northern Spain) using multivariate statistical methods, *Environ. Int.* 27 (2002) 589–596.
- [22] M.G. Cordingley, M.P. Hallewell, J.W. Turner, Release analysis and its use in the optimisation of the comminution and gravity circuits at the Wheal Jane Tin concentrator, *Miner. Eng.* 7 (1994) 1517–1526.

- [23] B.A. Wills, T.J. Napier-Munn, *Mineral Processing Technology: An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery*, 7th ed., Butterworth-Heinemann, Burlington, MA, 2006.
- [24] F.C. Bond, Third theory of comminution, *Miner. Eng. Trans. AIME* 193 (1952) 484–494.
- [25] N. Magdalinovic, A procedure for rapid determination of the Bond work index, *Int. J. Miner. Process.* 27 (1989) 125–132.
- [26] J.M. Menéndez-Aguado, B.R. Dzioba, A.L. Coello-Valazquez, Determination of work index in a common laboratory mill, *Miner. Metall. Process.* 22 (2005) 173–176.
- [27] R.J. Deister, How to determine the Bond work index using lab ball mill grindability tests, *Eng. Miner. J.* 188 (1997) 42–45.
- [28] S. Montinaro, A. Concas, M. Pisu, G. Cao, Remediation of heavy metals contaminated soils by ball milling, *Chemosphere* 67 (2007) 631–639.
- [29] V. Deniz, H. Ozdag, A new approach to Bond grindability and work index: dynamic elastic parameters, *Miner. Eng.* 16 (2003) 211–217.
- [30] H.T. Ozkahraman, A meaningful expression between bond work index, grindability index and friability value, *Miner. Eng.* 18 (2005) 1057–1059.
- [31] C.W. Williford, R.M. Bricka, Physical separation of metal-contaminated soils, in: I.K. Iskandar (Ed.), *Environmental Restoration of Metals-Contaminated Soils*, 1st ed., CRC Press, Boca Raton, FL, 2000.
- [32] R.A. Rikers, P. Rem, W.L. Dalmijn, Improved method for prediction of heavy metal recoveries from soil using high intensity magnetic separation (HIMS), *Int. J. Miner. Process.* 54 (1998) 165–182.
- [33] E.G. Erspamer, R.R. Wells, Selective extraction of mercury and antimony from cinnabar-stibnite ore. Bureau of Mines Report of Investigations 5243, United States Department of the Interior, 1956.
- [34] P. Cauwenberg, F. Verdonck, A. Maes, Flotation as a remediation technique for heavily polluted dredged material. A feasibility study, *Sci. Total Environ.* 209 (1999) 113–119.
- [35] M. Vanthuyne, A. Maes, P. Cauwenberg, The use of flotation techniques in the remediation of heavy metal contaminated sediments and soils: an overview of controlling factors, *Miner. Eng.* 16 (2003) 1131–1141.
- [36] G. Dermont, M. Bergeron, M. Richer-Lafleche, G. Mercier, Remediation of metal-contaminated urban soil using flotation technique, *Sci. Total Environ.* 408 (2010) 1199–1211.