



Analysis of soil washing effectiveness to remediate a brownfield polluted with pyrite ashes

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ABSTRACT

Soil in a brownfield contaminated by pyrite ashes showed remarkably high concentrations of several toxic elements (Hg, Pb, Zn, Cu, Cd, and As). Initially, we assessed various physical, chemical and mineralogical properties of this soil. The data obtained, and particularly multivariate statistics of geochemical results, were useful to establish the predominant role of the soil organic matter fraction (6%) and iron oxyhydroxides in the binding of heavy metals and arsenic. In addition, we studied the viability of soil washing techniques to reduce the volume of contaminated soil. Therefore, to concentrate most of the contaminants in a smaller volume of soil, the grain-size fraction below 125 μm was treated by hydrocycloning techniques. The operational parameters were optimized by means of a factorial design, and the results were evaluated by attributive analysis. This novel approach is practical for the global simultaneous evaluation of washing effectiveness for several contaminants. A concentration factor higher than 2.2 was achieved in a separated fraction that contained less than 20% of the initial weight. These good yields were obtained for all the contaminants and with only one cycle of hydrocycloning. Hence full-scale soil washing is a plausible remediation technique for the study site.

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1. Introduction

During recent decades, the closure of heavy industry across Europe has left large extensions of contaminated land [1,2]. As a result of the accumulation of pollutants derived from industrial activity over many years this land is currently not suitable for use. The recovery of these affected areas, especially when they have multi-component contamination and are situated in urban or peri-urban zones – ‘brownfields’ – is of particular interest to economic and city-planning authorities [3].

In this context, a suitable remediation technique to reduce the initial volume of contaminated soil is the soil washing approach [4]. This technique involves concentrating polluting agents in a reduced volume fraction of the initial affected soil what generally results in the decontamination of the rest of the soil [5]. With this aim, particle-size separation, gravity separation, attrition scrubbing and other processes are used, with or without chemical additives [6]. In the case of heavy metals, most approaches are based on the isolation of the finest fractions of the soil, due to – among other phenomena – the greater specific surface of argillaceous particles, the organic matter, and the oxyhydroxide gels, all

of which bind heavy metals and other trace elements [7]. These effects are related to the mobility of the metals, which is generally controlled by precipitation, diffusion, volatilization and dissolution of unstable minerals, in addition to other surface complexation processes [8]. Also, bioavailability and toxicity may vary according to pH, redox conditions (Eh) and changes in the land use pattern; however, given that soil washing requires excavation, all of these environmental parameters are more controllable than in ‘in situ’ treatments.

Most effective soil washing technologies apply physical processes to concentrate contaminants by exploiting differences in characteristics between the metal-bearing particles and soil particles (size, density, magnetism, and hydrophobic surface properties) [6]. The general strategy is based on well known technologies commonly applied in the mineral processing industry to extract the desired particles from mineral ores [9]. This technology is relatively simple to operate, often inexpensive, and highly versatile as it can be used in mobile plants (on-site treatments) or large-scale facilities (ex situ treatments) [10].

The first step in the design of a full-scale washing treatment is a viability analysis, which involves several laboratory and analytical determinations to examine the main characteristics of the soil [7,11]. In the second step, experiments on a pilot-scale can be performed in similar equipment to full-scale ones. Here we applied this work-plan to soil highly contaminated over many years by

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the industrial activity of a fertilizer factory. The main aims of the current study were the following:

- To integrate grain-size distribution data with edaphological, geochemical and mineralogical information of the site in order to identify the soil fractions in which the contaminants were bound.
- To apply the information reported in the previous step to design and implement a physical separation study by means of hydrocycloning, thereby obtaining functional conclusions for the implementation of full-scale soil washing treatments.
- To develop and apply a theoretical formulation (attributive analysis) for the evaluation and selection of optimal parameters in the physical separation tests for our study site.

2. Experimental procedures

2.1. Site description and soil sampling

The study site is situated in the central zone of Asturias (Northern Spain), where a number of industrial and mining facilities have been closed in recent decades, thus generating several 'brown-fields'. In this area, the climate is Atlantic (European) with an annual average precipitation and evapotranspiration of 1,130 and 667 mm respectively, and an annual average temperature of 13 °C. The soil moisture regime is Udic, with adequate soil moisture for most of the growing season except for a one-month drought in the summer.

The soil samples analyzed were collected from the area surrounding a derelict fertilizer factory. Since its closure in 1997, this factory has been partially demolished and it is currently in an advanced state of abandonment. The total surface of the affected site is 70,000 m², more than half corresponding to landfills between 4 and 5 m deep comprised of pyrite ashes in addition to other iron and steel-type debris. The other plots of ground consist of natural soils however, these have been polluted as a result of decades of fertilizer manufacture, spills of waste and furnace emissions. Concretely, the pyrite ashes, comprising mainly oxides and hydroxides of iron and other metals, were produced as a by-product of roasting sulphur ores. These ores were industrially transformed to produce sulphuric acid and were subsequently used to manufacture ammonium sulphate fertilizer.

After initial "in situ" determinations and observations (data not shown), we identified several areas of natural soil distributed in the study site. We then carried out a double sampling campaign on these soils to perform a multi-element characterization to determine contamination. In the first case, samples were collected at 21 points randomly located in the natural soil areas, from a depth between 0 and 30 cm using a Dutch auger; formerly we ruled out deeper sampling following information of a previous campaign of exploratory core sampling. Three subsamples of 0.5 kg were obtained and then mixed to obtain composite samples, which were packaged in inert plastic bags. In the second case, a "macrosample" of about 50 kg (from one of the 'hot points' found in the first sampling, see Section 3) was taken from superficial soil with a shovel. In all the cases, the soil 'in situ' was passed through a 2-cm mesh screen to remove rocks, gravel and other large material.

2.2. Geochemical characterization

The soil samples taken in the first campaign were dried at room temperature. The soil was then disaggregated by a roller and subsequently sieved through a 4-mm screen. Materials with a grain-size greater than 4 mm were vigorously washed and rubbed off to recover fine particles adhered to the gravels and pebbles, which, once cleaned up, were excluded from the study. Given that fine-grained fractions are the most interesting in environmental

geochemistry, and especially in toxicology (see [12] and references therein), grain-size particles below 4 mm were then quartered by means of a channel separator to obtain about 20 g of representative fractions, which were passed through a sieve of 125 µm. For chemical analysis, representative 1-g subsamples were leached by means of an 'Aqua regia' digestion (HCl + HNO₃). The digested material was analyzed in duplicate for total concentrations of 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) at the accredited laboratory Actlabs int., Ancaster (Ontario, Canada).

Descriptive statistics and cluster analysis were used to study the geochemical association of elements in the samples. Concretely, clustering was undertaken following the Ward-algorithmic method, which maximizes the variance between groups and minimizes it between members of the same group [13]. To show clustering results, a dendrogram obtained with the statistical software SPSS v15.0 was used [14]. Groups of elements with a similar geochemical behaviour were identified using values of the statistical distance between them (squared-Euclidean distance was selected).

2.3. Grain, mineralogical and pedology soil study

The 50-kg sample was wet-sieved in 100-g batches by means of a standardized series of Restch screens, in agreement with the norm ASTM D-422-63. Two main fractions (0–125 µm, 125–4000 µm) were obtained and used for ICP-OES analyses (see above). Particularly, in order to homogenize conditions for chemical attack, samples with a grain-size higher than 125 µm were ground using a vibratory disc mill (RS 100 Retsch) operated at 400 rpm for 40 s to reduce grain-size to below 125 µm. Samples finer than 125 µm did not require grinding and their grain-size distribution was examined in depth using a Laser Dispersion Particle Analyser (Beckman Inc. Coulter). Finally, several batches of this fine fraction were used for the hydrocycloning tests.

Texture was determined by the pipette method after a disaggregating treatment with two dispersants: sodium hexametaphosphate and sodium carbonate [15]. Regarding mineralogical and pedological characterization, the composition of the silicate clay minerals (<2 µm particle-size fraction) was estimated by means of a diffractometer (Philips X Pert Pro, incorporating databases of the International Centre for Diffraction Data). The pH was measured in a suspension of soil and water (1:2.5) in H₂O with a glass electrode and the electrical conductivity was measured in the same extract (diluted 1:5). Organic matter was determined by the ignition method (400 °C). Exchangeable cations (Ca, Mg, K and Na) extracted with 1 M NH₄Cl, and exchangeable aluminium extracted with 1 M KCl were determined by atomic absorption/emission spectrophotometry [16] in a AA200 PerkinElmer 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. Experiments of physical separation

2.4.1. Experimental design

There are several approaches available to study the soil washing of the separated fine fraction (<125 µm). However, taking in consideration the most habitual equipment at soil remediation plants [6,10], we used a hydrocycloning lab-scale plant (C700 Mozley) with capacity to operate hydrocyclones from 10 to 50 mm in diameter. In this apparatus, an in-flow slurry (feed) is tangentially pumped inside the cyclone where the centrifugal forces merge with the thickness and density of the particles. This system determines whether an individual particle flows through by the apex (under-

flow) or the upper part (overflow) of the hydrocyclone. The lighter and finer particles generally flow through the overflow.

The solid concentration of the feeding slurry used in our experiments was constant (20% per weight) whereas the underflow diameters and different working pressures were combined in a factorial test (see Section 3). In all cases, after reaching a stationary regime, samples from the underflow and overflow were taken in borosilicate flasks. They were then weighed and later dried in an oven at low temperature (45 °C to minimize loss of Hg and As via volatilization) to obtain dry weight and representative subsamples for ICP-OES analyses.

Having completed the multi-element analyses, for each test and for each element we defined recovery as the percentage of the total element contained in the overflow or in the underflow with respect to the total concentration in the feed slurry (a recovery of 90% of a given element in the overflow implies that 90% of the initial concentration was recovered in the overflow and 10% is 'lost' in the underflow). In addition, the ratio of concentration for each test was defined as the ratio of the weight of the feed to the weight of the concentrates in the overflow or in the underflow.

2.4.2. Attributive analysis

Ideally, in a soil washing procedure the aim is to concentrate a given contaminant in a smaller volume of soil than the initial one, i.e., to maximize its recovery and to reduce the ratio of concentration of that fraction. However, here we simultaneously addressed several contaminants and therefore required a method to adjust the selection of recoveries and ratios of concentration in order to achieve good results for a group of contaminants rather than a single one. Therefore, we chose a methodology based on attributive analysis [17]. In our case, a merit index was obtained, which facilitates the classification of the quality of the results of the distinct tests. This approach offers the advantage that it takes into account all the results obtained and allows the selection of the optimal test. Considering a number 'n' of tests with distinct operational conditions, the procedure was as follows.

- First, we defined R^i (%) as the ratio of concentration in the test 'i'. In the 'n' tests performed, i.e., within the R^i , the test with the minimum ratio of concentration was identified and this parameter was labelled R_{min} (%).
- For a given element, e.g. Hg, conditions for concentration (i.e., recovery greater than ratio of concentration) were identified in each test. These conditions can occur in the overflow or in the underflow. For both cases, we labelled each recovery as Rec_{Hg}^i (recovery of Hg in test 'i'). One test showed maximum recovery of Hg and this value was labelled Rec_{maxHg} (%).
- Taking into account the set of values and parameters defined, the index of merit Q_{Hg}^i for Hg was defined for each test 'i' following the expression:

$$Q_{Hg}^i = \frac{R_{min}}{R^i} + \frac{Rec_{Hg}^i}{Rec_{maxHg}} \quad (1)$$

The expression (1) can be generalized for multi-element contamination as the sum of Q^i for diverse elements (in this particular case we considered Hg, As, Cu, Cd, Pb and Zn, based on the results of the sampling characterization). However, all the polluting agents do not have the same relevance in the washing process as they are not present in equal concentrations in the initial soil, nor the objective to achieve for each one of them in the remediation project is the same. Thus, we defined a weighting factor 'A' for each contaminant, e.g. Hg:

$$A_{Hg} = \frac{Co_{Hg}(ppm)}{RV_{Hg}(ppm)} \quad (2)$$

where Co_{Hg} it is the concentration in the initial soil, and RV_{Hg} is the value of environmental reference for Hg (it can be defined by clean-up standards, or geochemical backgrounds, or as a result taken from risk management). A weighting factor for each of the remaining elements can be defined in a similar way. Furthermore, these coefficients must be corrected to reflect the relative importance of each element in the washing process. Therefore, in our case, for Hg the corrected weighting factor A' was defined as follows:

$$A'_{Hg} = \frac{A_{Hg}}{A_{Hg} + A_{As} + A_{Cu} + A_{Cd} + A_{Pb} + A_{Zn}} \quad (3)$$

From (1)–(3) and the homologue equations for As, Cu, Cd, Pb and Zn, we obtained the index of global merit (Q_T^i), for test 'i':

$$Q_T^i = Q_{Hg}^i \cdot A'_{Hg} + Q_{As}^i \cdot A'_{As} + Q_{Cu}^i \cdot A'_{Cu} + Q_{Cd}^i \cdot A'_{Cd} + Q_{Pb}^i \cdot A'_{Pb} + Q_{Zn}^i \cdot A'_{Zn} \quad (4)$$

3. Results and discussion

3.1. Multielemental characterization

Raw data of the multi-element analyses of the samples taken in the initial sampling campaign were processed with SPSS v15.0. Table 1 shows the most representative statistical descriptors obtained. These data indicate significant contamination of several elements, such as As, Pb and Hg. The heterogeneous distributions of these elements (elevated coefficient of variation) probably follow a lognormal distribution typical of polluted areas [13]. In contrast, the descriptive measures for elements usually considered "natural" (Ca and Na) indicate a normal distribution [18].

Regarding the multi-variant statistical analysis, a dendrogram was introduced to show results of "clustering" (Fig. 1). The dendrogram shows three main groups of elements:

- Group 'a': formed mainly by chalcophilic elements (Cu, Zn, Sb, Ag, etc.), probably associated with the sulphides toasted in the factory. The result of the furnace emissions, including waste dumping and inappropriate storage practices for sulphides and oxidized residues (pyrite ashes, etc.), affected natural soils. In addition, this group of pollutants was concerned by rapid weathering in the superior horizons of the soil, which also explains the absence of S in this group of elements. Remarkably, Fe was the only major element included in this group which results redundant in the probable origin of all of these elements (Fe-rich minerals as pyrites and maybe other sulphides). It also appears a weak correlation with Ca suggesting also a certain association of the contaminants with carbonates (the content of Ca is high, as shown in Table 1).
- Group 'b': could be considered a sub-group of the group 'a', formed by other pollutant elements, such as Pb and Hg, mixed with other minority ones in pyrite ashes. S is included in this group and presented a good correlation with Hg. This observation may be attributed to the lower susceptibility of cinnabar (HgS) to weathering than other metallic sulphides [19].
- Group 'c': regarding with the statistical treatment is distant from the preceding ones. Most of the elements included in this group are probably related to the geochemical background of the natural soil before its contamination. It comprises mainly clay aggregates, including major elements such as Al and K.

We conclude that the soil presents evident although not elevated levels of contamination. The pollutants involved are mainly in the form of oxides as a result of the industrial processing of pyrites and other sulphides. There is no clear evidence of adsorption of

Table 1
Statistical descriptive corresponding to the ICP-OES analysis of 21 soil samples taken in the study site.

Element	Unit	Minimum	Maximum	Average	Std. deviation	Coefficient of variation
Ag	ppm	0.1	1.20	0.41	0.36	0.88
Al	%	0.95	2.67	1.77	0.50	0.28
As	ppm	45.00	181.00	98.90	40.09	0.41
B	ppm	5.00	17.00	7.85	4.39	0.56
Ba	ppm	31.00	268.00	135.81	73.64	0.54
Bi	ppm	1.00	11.00	2.81	3.43	1.22
Ca	%	1.71	4.26	2.66	0.75	0.28
Cd	ppm	0.5	3.5	1.57	0.87	0.55
Co	ppm	7.00	33.00	13.76	6.42	0.47
Cr	ppm	19.00	436.00	96.33	116.43	1.21
Cu	ppm	62.00	266.00	121.90	61.91	0.51
Fe	%	2.35	5.66	3.83	0.92	0.24
Hg	ppm	3.00	62.00	20.67	16.16	0.78
K	%	0.13	0.53	0.24	0.11	0.46
Mg	%	0.29	0.75	0.37	0.09	0.24
Mn	ppm	207.00	1100.00	416.14	222.55	0.53
Mo	ppm	0.5	26.00	5.74	7.16	1.25
Na	%	0.03	0.07	0.05	0.01	0.20
Ni	ppm	24.00	130.00	45.00	23.08	0.51
Pb	ppm	126.00	1130.00	427.14	271.26	0.64
S	%	0.22	0.79	0.39	0.14	0.36
Sb	ppm	5.00	26.00	12.19	6.38	0.52
Zn	ppm	196.00	1.270.00	417.00	284.04	0.68

the contaminants in clays or carbonates. Rather these contaminants are associated with Mn and Fe oxides and with the soil organic matter (see below). Finally, on the basis of the elementary concentrations and their potential toxicity, we took six elements as references for the rest of the study: As, Cd, Cu, Hg, Pb and Zn.

3.2. Pedologic and mineralogic characterization

A subsequent study was carried out with a 50-kg sample of soil from one of the zones most affected by contaminants. The representative subsamples of this area showed neutral pH (6.6), high organic matter content in the upper horizon (6%), low electri-

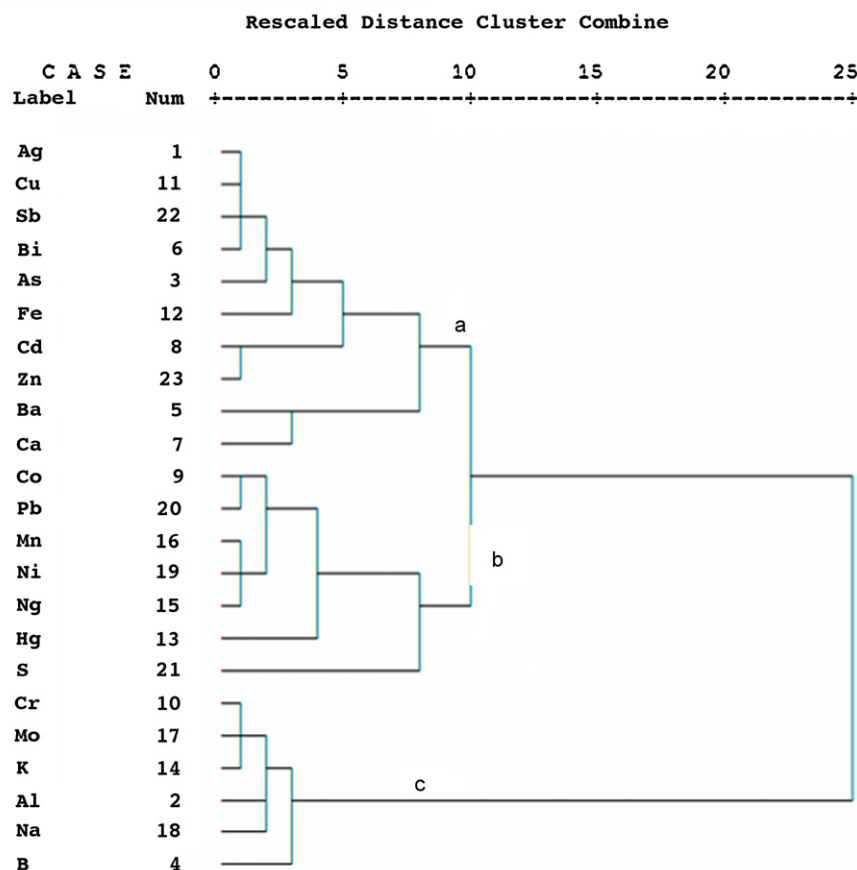


Fig. 1. Dendrogram showing the clustering of elements associated by their geochemical affinity within the samples. Main groups are indicated based on the statistical distance between them.

Table 2

Concentration of elements in the two grain-size fractions (the results correspond to the average of three determinations with standard error <5%).

Grain-size (μm)	Weight (%)	Trace elements of concern (ppm)					
		As	Cd	Cu	Hg	Pb	Zn
+125 to 4.000	9.5	48	1.0	69	10	181	162
–125	90.5	79	1.4	106	16	359	347

cal conductivity ($\text{EC} = 0.196 \text{ dS m}^{-1}$), low contents of exchangeable base cations (7.13; 0.37; 0.32 and $0.59 \text{ cmol}_c \text{ kg}^{-1}$ for Ca, Mg, K and Na respectively), and low ECEC ($8.42 \text{ cmol}_c \text{ kg}^{-1}$). These features are consistent with the properties displayed by neutral soils in cold humid areas.

We classified the soil as a silt loam on the basis that the particle-size distribution revealed a high percentage of silt fractions (77%). In contrast, the clay fractions (13%) were dominated by illites (2:1 clay mineralogy) and kaolinites (1:1 clay mineralogy). The specific surface area of illites and kaolinites range from 65 to $100 \text{ m}^2 \text{ g}^{-1}$ (including the interlayer surface) and from 10 to $20 \text{ m}^2 \text{ g}^{-1}$ respectively, and the cation exchange capacity (CEC), depending on soil pH, range from 10 to $40 \text{ cmol}_c \text{ kg}^{-1}$ and from 1 to $10 \text{ cmol}_c \text{ kg}^{-1}$ respectively [20]. The structures of these two clays have been extensively described [21]. Furthermore, mineralogical analyses by X-ray diffraction revealed the presence of a considerable proportion of ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$) – as representative of amorphous iron oxyhydroxides. With its high surface area per volume, Ferrihydrite is a highly reactive mineral and is known to be a precursor of crystalline minerals, such as hematite and goethite [22]. Ferrihydrite interacts, either by surface adsorption or by co-precipitation, with a number of chemical species with environmental relevance, including As and heavy metals like Pb and Hg [23].

The presence of two types of low specific surface clays, together with the large amount of organic matter in the soil (6%), and the abundance of Ferrihydrite indicates that the contaminants in the study site are, to a great extent, bound to the organic matter, Fe oxyhydroxides, and secondarily carbonates [24]. This finding verifies the results of the multivariate analysis.

3.3. Grain-size characterization

Table 2 summarizes the result of the grain-size study for the two main fractions obtained, as well as the contaminants of interest and the concentrations of elements found. As expected, concentrations were greater in the finer fraction ($-125 \mu\text{m}$). However, in the case of coarse particles ($+125 \mu\text{m}$), concentrations of contaminants were also elevated. This observation indicates that it might be pertinent to undertake a physical separation treatment, which is beyond the scope of the present study (see possibilities such as MGS – multigravity separators – in [11,25]).

We applied laser dispersion to focus on particle distribution in the fine fraction. Almost 40% of the material was below $10 \mu\text{m}$ and more than 10% comprised argillaceous matter (smaller than $2 \mu\text{m}$) (Fig. 2). These findings are consistent with the previous results on soil texture reported in Section 3.2. Given the composition of the finest materials, we propose that it is formed by a mixture of clays, organic matter and Fe oxide gels.

3.4. Hydrocycloning experiments

We completed a factorial test combining two apex diameters of the hydrocyclone (9.5 and 6.4 mm) and three levels of pressure (100, 200 and 300 kPa) for representative batches of the fraction of grain-size below $125 \mu\text{m}$. With this starting point, the calculation of weighting factors is presented in Table 3. In Table 4 the results

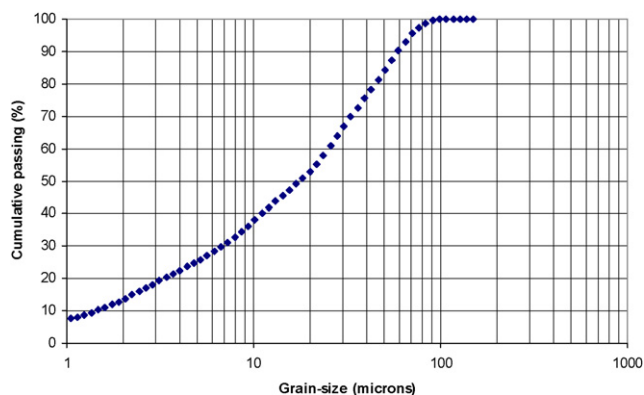


Fig. 2. Particle-size distribution obtained by laser dispersion corresponding to a representative sample of the fraction below $125 \mu\text{m}$.

of the attributive analysis are shown according the definitions and parameters previously described in Section 2.4.2.

It can be concluded that higher pressures are favourable only with the smaller apex diameter, i.e., there is no related general tendency with an increase in pressure. Overall, the best Q_T was obtained in test no. 6. We therefore studied the underflow and overflow samples of this test in further detail. First (Fig. 3), we performed a partition curve for hydrocyclones [28] from the particle-size distribution of both the underflow and overflow after laser dispersion of samples taken in stationary regime. This curve was used to evaluate the effectiveness of hydrocycloning, as well as to determine some characteristic parameters of the separation, such as the cut point (denoted d_{50}) defined as the size for which 50% of the particles in the feed report to the underflow, i.e., particles of this size have an equal chance of going either with the overflow or underflow.

In our case the cut point was $9.5 \mu\text{m}$. In addition, the curve demonstrates the presence of a “fish-hook” effect [29], thereby indicating that fine particles are not likely to move towards the heavy fraction, which is usually bound to the object of agglomeration. This effect could be due to the presence of organic matter that gave hydrophobic characteristics to the fine particles. Furthermore, the low slope of the curve indicates low efficiency in the separation; however, this efficiency did not impair decontamination (Table 5). Consequently, in spite of obtaining a deficient grain-size separation, the classification obtained appeared to be related to specific-gravity effects. Therefore a large amount of the contaminants was recovered in the overflow fraction, which was smaller in weight than the underflow. In fact, given that organometallic aggregates [30] can reach an average density of 1.4 g/cm^3 (approximately half of the mineral components of the soil), the influence of the organic matter is crucial in the separation [31].

Successive cycles of soil washing, commonly applied in full-scale processes [32], are effective in reducing metal contamination in sig-

Table 3

Data required for attributive analysis of hydrocycloning tests: initial concentrations (Co) of the soil fraction below $125 \mu\text{m}$, reference values used as clean-up targets (RV); the weighting factors (A) and the corrected ones (A') obtained as described in Section 2.4.2. RV parameters were selected following an international standard [1]. Given the high Hg geochemical background in this area [26,27], the only exception was Hg, for which 2 ppm was taken instead of 0.5 ppm.

Element	Co (ppm)	RV (ppm)	Weighting factor (A)	Corrected weighting factor (A')
As	71	20	3.55	0.16
Cd	1.3	1	1.30	0.06
Cu	104	50	2.08	0.09
Hg	14	2	7.00	0.31
Pb	359	50	7.18	0.31
Zn	358	200	1.79	0.08

Table 4

Summary of the calculations conducted by means of attributive analysis. For all the tests and elements, the concentration effect occurred in the overflows in which a combination of fine and light fractions accumulated. The optimal conditions were found in test no. 6.

Test number ('i')	Apex diameter (mm)	P (kPa)	Q_{As}^i	Q_{Cd}^i	Q_{Cu}^i	Q_{Hg}^i	Q_{Pb}^i	Q_{Zn}^i	Q_T^i
1	9.5	100	146.81	153.77	153.77	151.77	153.77	153.77	1.41
2	9.5	200	146.29	156.53	148.93	151.87	153.40	150.08	1.41
3	9.5	300	144.10	147.27	142.38	143.08	148.29	144.37	1.35
4	6.4	100	160.28	158.73	155.21	160.28	157.15	154.19	1.48
5	6.4	200	164.51	162.54	159.61	161.00	162.80	159.54	1.51
6	6.4	300	172.75	174.55	168.49	166.59	172.91	169.42	1.58

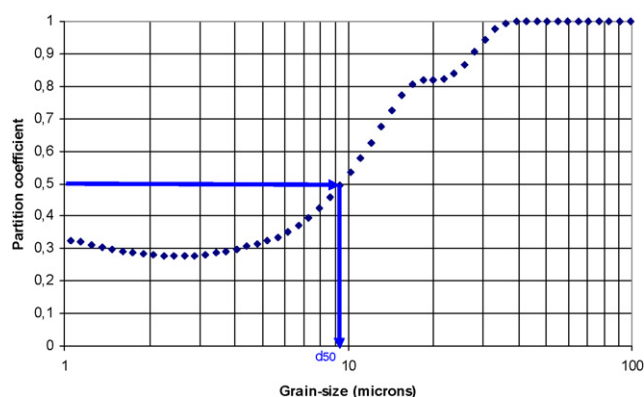


Fig. 3. Hydrocyclone partition curve obtained in test no. 6 (diameter of end 6.4 mm and 300 kPa pressure). This curve plots at each grain-size the corresponding partition coefficient, which represents the fraction of total particles of a given size which reports to the underflow.

Table 5

Element concentrations in test no. 6 (results are average of three determinations). 'Concentration factor' was defined as the quotient between the concentration in the overflow and the feed.

	Trace elements of concern (ppm)					
	As	Cd	Cu	Hg	Pb	Zn
Reference value (RV)	20	1	50	2	50	200
Feed (original soil)	71	1.3	104	14	359	358
Underflow (81.5% weight)	48	0.9	72	10	247	249
Overflow (18.5% weight)	171	3.1	241	32	857	844
Concentration factor	2.40	2.38	2.32	2.29	2.39	2.36

nificant fractions to acceptable levels (below the reference values). Our results support this finding, as one cycle of washing achieved notable concentration factor, as previously shown in Table 5.

4. Conclusions

The pyrite ash, a by-product of the sulphuric acid production process during the roasting of pyrite ores, has contributed to introducing toxic elements, such as As, Pb, Cd, Ni, Cu and Hg, into the natural soils in the study site. The soil presented marked multi-component contamination. Most of the contaminants were bound to the soil organic matter and secondarily to Fe oxyhydroxides, while processes such as clay adsorption made a minor contribution.

Here we applied hydrocycloning, a physical washing procedure, to clean the fine fractions of a soil contaminated with heavy metals. Instead of the extended premise of hydrocyclones achieving separation by sizes, the separation of the contaminants by specific-gravity effects was favoured. Therefore, under these conditions, it is more appropriate to refer to cut densities rather than cut-off sizes for hydrocycloning. Furthermore, we have demonstrated attributive analysis to be an effective tool for the quantitative determination of the quality of separations, and also to establish weighting factors based on the diverse elements to be removed.

Finally, optimum conditions allowed us to obtain concentration factors higher than 2.2 for all the contaminants in less than 20% of the weight of the original soil. This achievement implies that full-scale treatment with successive rewashing cycles is viable. This treatment should be considered in soil remediation programmes.

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