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ORIGINAL PAPER

Viability of adding gypsum and calcite for remediation of metal-contaminated soil: laboratory and pilot plant scales

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Abstract The effect of adding waste materials (gypsum and calcite) for the remediation of a soil contaminated by pyritic minerals was examined. Materials were characterised in terms of their acid neutralisation capacity (ANC), sorption capacity and structural components. Their effect on the contaminant leaching in soil + material mixtures over a wide range of pH was also evaluated. Results at laboratory and pilot plant scales were compared to account for the potential variability in the material efficiency when applied at larger scale. The use of gypsum permitted its valorisation, although calcite was a more effective amendment because its addition led to a greater increase in the pH and acid neutralisation capacity, and thus in the sorption capacity in the resulting soil + material mixture. In the same way, when the combination of gypsum + calcite was added to the soil, it led to an increase in the pH from 2.5 to 6.9 and in the ANC from −86 to 1,513 meq/kg. As a result, the concentration of extractable heavy metals and As was reduced, and they were successfully immobilised both at laboratory and at pilot plant scales. Thus, the use of these materials induced a significant reduction in the contaminant mobility and permitted the valorisation of waste materials.

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Introduction

The mining industry is a significant source of trace elements contamination in soils (Kumpiene et al. 2007). Besides the use of bioremediation techniques (Mani and Kumar 2013), the in situ remediation of contaminated soils by the addition of materials, focused on reducing the mobility of metals, is increasingly being applied because it is an inexpensive and more environmentally friendly approach compared to other ex situ engineering strategies. This remediation strategy is based on increasing the soil pH (and thus decreasing the metal leachability) and/or increasing metal sorption by increasing the number of specific sorption sites (Dijkstra et al. 2004; Kumpiene et al. 2008; Marqués et al. 2011). Materials such as organic matter, lime and phosphates have traditionally been used as amendments for the remediation of contaminated soils (Hamon et al. 2002; Illera et al. 2004), and the choice of amendments has recently been extended to industrial by-products or wastes (Brown et al. 2005; Rodríguez-Jordá et al. 2010) because their use also achieves the reduction of waste disposal through the revalorisation of industrial wastes into soil recuperation actions (Lombi et al. 2002). A number of soil amendments have been investigated for the immobilisation of trace metals, including liming materials (Garrido et al. 2005), phosphorus-, iron- or manganese-rich materials, zeolites and silicates (Hamon et al. 2002; Shi et al. 2009). Other by-products rich in gypsum, such as phosphogypsum and red gypsum (Illera et al. 2004; Garrido et al. 2006), or rich in calcium carbonate (Moraza et al. 2006;

Chang et al. 2013; Moon et al. 2013), have also been investigated. However, the efficiency of these treatments has only been evaluated at the laboratory level, solely from their specific chemical and mineralogical composition and from the observed effect in decreasing metal leaching (Lombi et al. 2002; Garrido et al. 2005; Rodríguez-Jordá et al. 2010). Conclusions drawn from tests with some materials (e.g. gypsum) are not fully consistent because their characterisation is not complete and/or results appear to be site specific. Thus, there is a general lack of data on metal sorption and acid neutralisation capacity of the materials although this type of information is essential to decide the suitability of a material for soil remediation previous to the application at field scale, and for the extrapolation of results to other soil–material combinations. Moreover, no projection of the material suitability has been performed on a larger scale, such as at the pilot plant or at the field level. In a few cases, the materials were not fully characterised; therefore, their usefulness could only be investigated for a specific soil, which makes extrapolating the results to other scenarios or elucidating the mechanisms responsible for the changes in leachability difficult. Therefore, to assess the performance of a material when it is added to any contaminated soil, information about its structural composition, acid–base neutralisation capacity and sorption capacity is required.

Here, we have evaluated and compared the potential of two industrial by-products, gypsum and calcite, at both laboratory and pilot plant scales, for the remediation of a soil contaminated by pyritic minerals. Whereas it is expected that calcite will be the main responsible for arising soil pH, the use of gypsum has the advantage of its valorisation as the waste disposal will be reduced due to its use in soil remediation. First, we conducted a systematic characterisation of gypsum and calcite that included structural analyses, the evaluation of the sorption capacity and the determination of the acid neutralisation capacity (ANC) of the materials (González-Núñez et al. 2011). Subsequently, a $\mathrm{pH_{stat}}$ leaching test (Dijkstra et al. 2004; Rigol et al. 2009) was performed to obtain the leaching curves of the major (Ca, Mg, Fe and Al) and trace (Cd, Zn, Ni, Cu, Pb and As) elements in the soil and the soil + material mixtures over a wide range of pH conditions, including the pH that results after the addition of the materials. After the experiments were performed at laboratory scale at the facilities of the Universitat de Barcelona, the proposed material mixture was also investigated at the pilot plant, at the facilities of Befesa at Huelva (Spain), to validate the results obtained and to account for the potential variability due to material and soil heterogeneity when used at a larger scale. Experiments were conducted during the period 2010–2011.

Materials and methods

Samples

A contaminated soil from the southwest of Spain and two materials were used in this study. The contaminated soil originated from Aljaraque (Huelva) (ALJ2), and it had been affected by mining and industrial activities and contained pyritic minerals. This soil was situated in a pyritic-rich formation, the Iberic Pyrite Belt, and it was exposed to mining activities and acidic drainages for decades. Materials, which were supplied by HC Energía, were as follows:

- Gypsum (G), which is a by-product of the desulphurisation of combustion gases from a thermal power station.
- Calcite (C), which is an alkaline material used to buffer solutions from the desulphurisation process.

All samples were air-dried, sieved through a 2-mm mesh sieve and homogenised in a roller table before the experiments.

Primary sample parameters

The methods used to obtain the primary sample parameters and to conduct the structural analyses are described in the Supplementary Material. In addition to these methods, and in order to have a good estimation of the readily soluble metals, which is an information required in waste management, the water-soluble metal content in the soil was quantified by obtaining soil water extracts after equilibrating a known amount of the soil or material with Milli-Q water for 16 h, using a liquid–solid ratio of $10\ \mathrm{mL\ g^{-1}}$ (DIN 1984), and thus expressing the metal concentration in the extracts in $\mathrm{mg\ kg^{-1}}$.

pH titration test

The neutralisation capacity of the soil and materials was examined using the CEN/TS pH titration test within a pH range of 2–12 (Kosson et al. 2002; CEN/TS 2006a). Details are given in the Supplementary Material. This test also permits the ANC value to be determined, which is the amount of acid or base, in meq/kg, required to shift the pH of a given sample to 4.

Trace element sorption–desorption experiments in materials

Determination of the solid–liquid distribution coefficients

Batch sorption experiments were conducted to determine the K_d of the target metals in gypsum and calcite separately, using the soil water extract as a contact solution. Two grams of each material (gypsum or calcite) was equilibrated with 20 mL of the soil water extract. The suspensions were shaken at 30 rpm for 16 h at room temperature, centrifuged (Beckman, $9{,}630\times g$), and then, the supernatants were filtered (0.45 µm) and stored at 4 °C until the analyses.

The K_d values were calculated from the quantification of the trace element concentration in the initial and final contact solutions, according to the following equation:

$$K_d = \frac{(C_i - C_f)\cdot V/m}{C_f} \tag{1}$$

where m is de mass of material, V is the volume of the soil water extract, and C_i and C_f are the trace element concentrations in the initial and final contact solutions, respectively.

Estimation of the reversibly sorbed metal fraction

The trace element sorption reversibility in materials was estimated from the application of extraction tests, conducted by adding 20 mL of a solution that simulated the composition of the major species in the soil water extract [Ca (550 mg/L) and SO_4^{2-} (2,830 mg/L)], to the sorption solid residues. The resulting suspension was shaken for 16 h at room temperature and then centrifuged. The supernatants were filtered and stored at 4 °C until the analyses.

Preparation of soil + material mixtures at laboratory scale

The mixtures of soil and materials [soil + gypsum (ALJ2 + G) and soil + calcite (ALJ2 + C)] were prepared at laboratory scale at 10 % doses (90 g soil/10 g material), as a commitment between the amount used and efficiency of the materials, as suggested by previous studies (unpublished results). Additionally, mixtures with the two materials were also prepared (80 g soil/10 g calcite/10 g gypsum; ALJ2 + GC). To simulate the field conditions, the mixtures were subjected to three drying–wetting cycles, which consisted of rewetting the mixtures at field capacity, maintaining them in closed vessels at 40 °C for 24 h and then drying them in open vessels at 40 °C for 48 h (Roig et al. 2007). These mixtures were homogenised in a rotary shaker for 24 h before collecting subsamples for the structural analyses and leaching experiments.

Application of the pH_{stat} leaching test to soil and soil + material mixtures originated at laboratory scale

The pH_{stat} test is based on the CEN/TS 14429 test (Kosson et al. 2002; CEN/TS 2006b) and examines the element release as a function of the pH. From the information provided by the pH titration test, the approximate amount of HNO_3 or NaOH required to obtain a given pH value, usually between 2 and 12, in the final suspension was calculated for a minimum of seven extracts. A suitable amount of acid or base was added to 6 g of sample that was suspended in a given volume of deionised water to yield a liquid–solid ratio of 10 mL/g. The sample suspensions were shaken with a rotary mixer for 7 days. Following the separation of the liquid phase through centrifugation and filtration (0.45 µm), the final pH of the leachates was measured and the major and trace elements in the extracts were determined.

Experiments at pilot plant scale

The pilot plant was located in Nerva (Huelva, Spain), within the facilities of Befesa. The pilot plant consisted of two pits, one containing the contaminated soil (non-remediated soil), ALJ2_PP, whereas the other pit contained a mixture of the contaminated soil with gypsum (10 %) and calcite (10 %) as amendments (remediated soil), ALJ2 + GC_PP. Each pit was 20 m^3, and the depth was 0.7 m. One of the challenges to scale-up this kind of remediation strategies from laboratory to pilot plant is to control the heterogeneity and maintain the representativeness of the amendment, soil and their mixture at the pilot plant, especially considering their intrinsic constitutional heterogeneity. To prepare the mixture, scales with a 1 m^2 of dimension and 3,000 kg of maximum weight were used and the soil sample and the soil + materials mixture were blended before applied to the respective pit using a biconical mixer of 1 m^3 volume with an estimated production of 5 t h^{-1}. After filling one pit with the contaminated soil (non-remediated soil) and the other pit with the soil + materials mixture (remediated soil), samples were allowed to stabilise for a few days and sampling was conducted subsequently following a systematic strategy. Each pit area was divided into a grid of nine squares. From each square, a randomly placed increment within each square was taken down to a 15-cm depth with a 3-cm diameter gauge auger. Three composite samples were then prepared from three individual increments, which defined the analytical samples. The samples were subsequently submitted to various tests to elucidate the role of the amendments in decreasing the leaching of the contaminants in the remediated soil. Therefore, both pH titration and pH leaching tests were also applied to samples originated from the pilot plant.

Determination of major and trace elements in the solutions

The major and trace elements were determined using a Perkin-Elmer Model OPTIMA 3200RL ICP-OES equipped with a Perkin-Elmer AS-90 Plus autosampler. The following emission lines were used for each element determined (nm) Cd: 214.440 and 228.802; Cu: 324.752 and 327.393; Pb: 220.353; Zn: 206.200 and 213.857; Ca: 315.887 and 317.933; Fe: 259.939 and 239.562; Al: 308.215; Mg: 279.077 and 285.213; As: 188.979 and 193.696; and Ni: 231.604. The detection limits of the inductively coupled plasma optical emission spectroscopy (ICP-OES) were 0.01 mg L^{-1} for Cd and Cu; 0.025 mg L^{-1} for Zn; 0.02 mg L^{-1} for Fe, 0.1 mg L^{-1} for Ca, Mg and Ni; 0.2 mg L^{-1} for Pb; 0.5 mg L^{-1} for As and Al.

A Perkin-Elmer ELAN 6000 inductively coupled plasma mass spectrometer (ICP-MS), equipped with a Perkin-Elmer AS-91 autosampler, was used for the lowest trace element concentrations. Several element isotopes (^{111}Cd, ^{112}Cd and ^{114}Cd; ^{63}Cu and ^{65}Cu; ^{208}Pb; ^{66}Zn, ^{67}Zn and ^{68}Zn; ^{75}As; and ^{60}Ni and ^{62}Ni) were measured to detect and control for possible isobaric or polyatomic interferences. Hydride generation was used in the solutions containing high chloride concentration prior to As determination. To correct for instabilities in the ICP-MS measurements, ^{103}Rh was used as an internal standard with a concentration of 200 μg L^{-1} in all of the samples. The detection limits of the ICP-MS measurements were 0.02 μg L^{-1} for Cd, 0.05 μg L^{-1} for Pb, 0.1 μg L^{-1} for Cu and 0.2 μg L^{-1} for As, Ni and Zn.

Results and discussion

Characterisation of soil and materials

Basic characterisation and major and trace elements

The ALJ2 soil had an extraordinary low pH (2.4, obtained at the 1:2.5 ratio), which was consistent with the exposure to the mining activity of the zone (Grimalt et al. 1999), a loam texture (34 % sand and 18 % clay with respect to the mineral matter content) and a high soluble sulphate content (28,300 mg/kg soil). Gypsum and calcite had basic pH values quantified at the 1:2.5 ratio (7.8 and 9.3, respectively).

Table 1 summarises the total major and trace element contents in the soil and materials as well as the concen-

Table 1 Total content (TC) of major and trace elements in soil and materials, as well as water-soluble (WS) content in soil (mg kg^{-1}, mean values; $n = 3$)

Sample	ALJ2				Gypsum (G)	Calcite (C)	ALJ2 + G	ALJ2 + C	ALJ2 + GC
	TC	JA	WS	EC	TC	TC	TC	TC	TC
Fe	187,200	–	6,400	–	4,804	2,480	168,900	168,700	150,500
Ca	10,800	–	5,500	–	294,040	397,700	39,200	49,500	77,900
Al	10,230	–	420	–	8,413	753	10,050	9,280	9,100
Mg	410	–	250	–	1,106	893	480	460	530
Cd	30	30	0.4	1	< lq	2	25	25	22
Zn	3,200	3,000	175	50	14	7	2,920	2,920	2,590
Cu	1,300	1,000	160	50	6	5	1,140	1,140	1,020
Pb	10,300	2,000	20	10	6	3	9,230	9,230	8,200
As	1,000	300	4	2	5	1	865	865	770
Ni	30	750	5	10	4	1	27	27	25

lq: limit of quantification; RSD < 5 %

JA: Intervention limits for soils with industrial use established by the Junta de Andalucía, Spain (Junta de Andalucía 1999)

EC: European Commission decision thresholds for waste management. Disposal of non-hazardous waste (European Council 2003) trations of water-soluble elements in the soil. The total trace element contents in soil, with the exception of Ni and Cd, were greater than the intervention limits established by the Junta de Andalucía, Spain (Junta de Andalucía 1999), for soils aiming at industrial use. The contents of water-soluble trace elements were compared with the criteria for acceptable waste limits at landfills for non-hazardous waste established by the European Council decision 2003/33/CE (European Council 2003). The comparison indicated that the soil could be considered as a hazardous waste in the case of excavation due to the high water-soluble concentrations of several metals, especially Cu, Pb and Zn, because their concentrations (160, 20 and 175 mg/kg, respectively) were greater than their threshold limits (50, 10 and 50 mg/kg, respectively).

The results also revealed that the concentrations of As and heavy metals in the materials were several orders of magnitude lower than in the soil. Therefore, the addition of materials could lead to a dilution of the total concentration of the contaminants according to the dosage used.

Structural and specific surface area characterisation

The mineralogy of the ALJ2 soil was dominated by pyrite ($FeS_{1.96}$) with the presence of quartz, gypsum and anglesite (Fig. S1a in supplementary material). The SEM–EDX analysis revealed the presence of particles compatible with pyrite, enriched in Si, Ca, Fe and S (Fig. S1b and S1c in supplementary material).

The XRD pattern of gypsum was compatible with a single phase of gypsum and was in good agreement with the SEM micrograph, which revealed a particle with block morphology (Fig. S2 in supplementary material). The XRD pattern of calcite confirmed that this material was not a pure calcite phase, as small reflections from another polymorph of $CaCO_3$, veterite, and a calcium silicate phase, plombierite (Fig. S3 in supplementary material) were present. The SEM micrograph revealed a platelet particle morphology with small sponge particles on the surface. The presence of spherical particles in the EDX spectra was also remarkable (not shown), which were compatible with a calcium silicate phase.

The textural analysis of the amended soil showed an increase of the surface area with respect to the untreated ALJ2 soil as a consequence of the addition of gypsum and calcite, since these materials exhibited a much higher surface area that the untreated soil (Table 2). Therefore, the added materials will help to the heavy metal immobilisation because they can play a role not only as pH regulator but also providing a higher sorption surface.

Table 2 BET surface of the untreated soil (ALJ2), the soil amended with gypsum (10 % w/w) and calcite (10 % w/w) (ALJ2 + GC) and the materials gypsum (G) and calcite (C)

	ALJ2	ALJ2 + GC	G	C
Surface area (m^2/g)	0.55	6.39	10.81	5.79

Table 3 Solid–liquid distribution coefficient values, K_d (L kg^{-1}; mean values (SD); $n = 3$) and desorption yields (%, mean values (SD); $n = 3$) of trace elements in the materials

		Gypsum	Calcite
As	K_d	8,000 (2,000)	10,000 (600)
	% desorption	<0.5	<0.5
Cd	K_d	5.4 (0.1)	44,000 (-)
	% desorption	4.6 (0.1)	<0.5
Cu	K_d	250 (30)	1,450 (70)
	% desorption	<0.5	<0.5
Ni	K_d	2.3 (-)	3.5 (0.8)
	% desorption	10 (-)	7.1 (0.2)
Pb	K_d	2,000 (-)	$>10^5$
	% desorption	<0.5	<0.5
Zn	K_d	5 (2)	45 (1)
	% desorption	2.1 (0.6)	0.70 (0.03)

Trace element sorption–desorption capacity of the materials

Table 3 summarises the K_d values obtained for As and metals in all the materials. Whereas the trace element K_d values for calcite were greater than for gypsum (especially in the case of Cd), there was a larger effect of the metal because the K_d values varied within three orders of magnitude for the same element, especially Cd and Pb. The reason for this result may be due to the higher pH of the sorption with the calcite and the precipitation caused by the high carbonate content of the materials. In fact, the sequence of the trace element K_d values in calcite and gypsum followed the sequence of their solubility product constants (K_{sp}) with carbonates and sulphates, respectively (Buscarons et al. 1986). For example, the high K_d(Pb) in the gypsum can be explained by its low K_{sp} values with sulphates ($10^{-7.8}$), whereas the trace elements with the highest K_d values in calcite, such as Cd and Pb, were those with the lowest K_{sp} values with carbonates ($10^{-11.8}$ and $10^{-13.5}$, respectively). Nickel had the lowest K_d, which was consistent with its highest carbonate K_{sp} ($10^{-8.2}$) among the trace elements examined (Buscarons et al. 1986).

Whereas the K_d differed among the investigated scenarios, the sorption reversibility was similar and low for all the considered element + material combinations because the extraction yields were <10 % (Table 3). Therefore, the K_d alone is a good parameter for predicting the suitability of the material in terms of the increase in the sorption capacity of the resulting soil + material mixtures because the reversibility of the process was low and similar among all the investigated cases.

The K_d values for calcite and gypsum cannot be compared with reported data for similar materials, as these data are not available to our knowledge in the open literature. Considering the low doses at which the materials are applied to the contaminated soils, a material may significantly increase the retention of the contaminants if its K_d exceeds that of the soils by at least two orders of magnitude. Materials with a K_d less than or similar to that of the soil should not be a candidate for soil remediation. Two different approaches can be used here to estimate the K_d values in the ALJ2 soil to allow comparison with the K_d in the materials. One approach is based on the equations proposed by Sauvé (Sauvé et al. 2000), which accounts for the pH, total metal content and the soil organic matter (SOM). In our case, this model was not fully applicable because the ALJ2 soil had soluble and particulate contamination. However, a simpler equation based solely on the pH of the soil can be used. The second approach is based on calculating the in situ K_d as the ratio of the total element content versus the soil water extract element contents. The resulting in situ K_d values for the ALJ2 soil were as follows (L kg^{-1}): As, 2500; Cd, 740; Cu, 70; Ni, 50; Zn, 180; and Pb, 5140. These values were generally greater than those determined using the soil pH equation; thus, they represent a considerably more conservative prediction. Therefore, calcite could be a promising material for certain elements, such as Cd and Pb, even when considering the most demanding scenario defined by the use of the in situ K_d, whereas the use of gypsum would not lead to a significant increase in the metal sorption capacity in soil + gypsum mixtures.

Application of titration and $\mathrm{pH_{stat}}$ leaching tests to soil, materials and soil + material mixtures originated at laboratory scale

Evaluation of the neutralisation capacity by the application of the titration test

The changes in pH after the addition of acid (positive scale) or base (negative scale) to the soil and materials suspensions, as well as the ANC values, were evaluated (Fig. S4 in supplementary material). The ANC values were positive or negative depending on the initial pH of the samples. The negative value observed for the ALJ2 soil, −86 meq/kg, was consistent with the initial soil pH being <4. The materials had a considerably greater ANC than the soil, which suggest that these materials would be appropriate for increasing the soil pH and improving the soil buffering capacity. Calcite had the highest ANC value 16,870 meq/kg, whereas the gypsum ANC was 1,155 meq/kg, which was among the highest values that have been previously reported (Cappuyns et al. 2004; González-Núñez et al. 2011).

Regarding soil + material mixtures, gypsum did not significantly improve the ANC in the resulting mixture, as it increased only up to −62 meq/kg. This result suggests that the effect of adding gypsum is virtually negligible when the pH of the soil is highly acidic. The addition of calcite increased the pH of the mixture and significantly increased the ANC value (1,054 meq/kg). The results improved when the two materials were added simultaneously, with a resulting ANC value of 1,513 meq/kg in the ALJ2 + GC mixture. These results suggest that the addition of gypsum has a potentially beneficial effect when added to an already neutralised soil.

Application of the pH_{stat} leaching test to soil and soil + material mixtures

Extraction of major elements Figure 1 plots the extraction curves of Ca, Mg, Al and Fe in the soil and soil + material mixtures. Table 4 lists several extraction yields for significant acidic and basic pH values.

The leaching curves of Ca and Mg were similar for the ALJ2 soil, with increased leaching when the pH decreased. The Ca and Mg concentrations in the extract at the more acidic pH level approached the total content, with extraction yields of approximately 70 %. The addition of calcite modified the Mg and the Ca leaching curves in the mixtures because calcite phases were solubilised at pH values <6, especially for Mg, which had extraction yields close to 100 %. The addition of gypsum did not induce a change in the pattern of the Ca leaching curve, although it led to a decrease in the Ca extraction yields to 20 % because the addition of gypsum induced a considerably greater total Ca concentration in the mixtures and gypsum was less soluble than calcite under acidic pH conditions. This behaviour was also observed in the ALJ2 + GC mixture.

The aluminium leachability in the ALJ2 soil increased under acidic pH conditions and was lower under basic pH

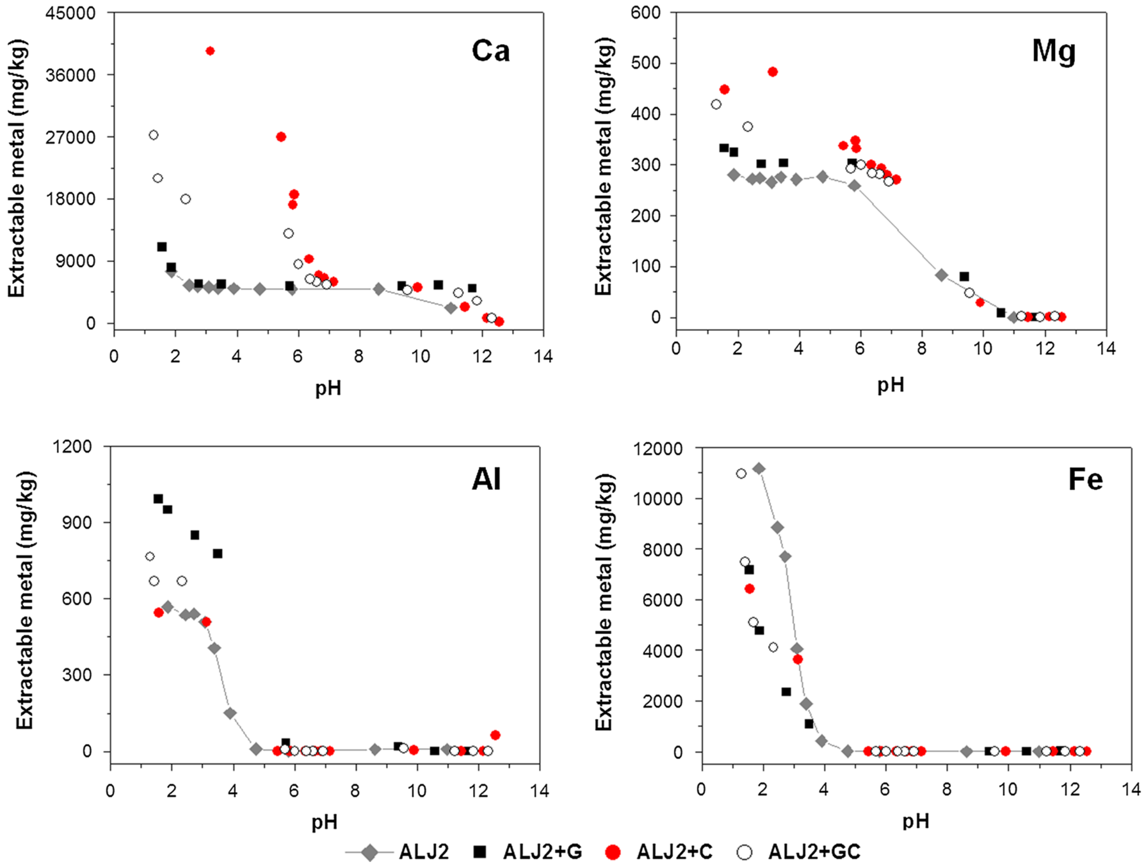

Fig. 1 pH_{stat} leaching curves for major elements at laboratory scale

conditions, as expected by the presence of amorphous hydroxide and hydroxysilicate phases (Meima and Comans 1997). For the mixtures, the Al leaching was similar to that of the initial soil, although slightly greater under the acidic pH conditions in the mixtures where gypsum was present, with extraction yields close to 10 %.

The pH_{stat} curves for Fe in the ALJ2 soil revealed that the Fe leachability was only significant at pH values <4, which was consistent with the solubility of Fe hydroxides, such as ferrihydrite (Dijkstra et al. 2006). The presence of insoluble, pyritic materials did not affect the Fe leaching curve. The addition of materials did not substantially modify the Fe leaching curves.

The results obtained from the application of the pH_{stat} leaching test were compared with the XRD analyses of selected samples of the soil and soil + material mixtures, before and after leaching (Fig. S5 in supplementary material). No new crystalline phases were formed as a consequence of the preparation of the mixtures. The examination of the soil + gypsum mixture residues after leaching (Figs. S5b–S5d in supplementary material) revealed that gypsum was unstable at both extreme pH levels, which was confirmed by the absence of diffraction peaks and/or a decrease in their intensities. The remainder of the phases were stable over the entire pH range. Regarding the soil + calcite mixture, it was difficult to analyse its pH stability using XRD analyses due to the strong overlapping of the primary reflection of calcite (29.4°) with the other phases of gypsum.

Extraction of trace elements Figure 2 presents the pH_{stat} leaching curves for Cd, Zn, Cu, Pb, As and Ni, and Table 4 lists several extraction yields at specific pH values. In the untreated ALJ2 soil, the leached concentrations of the trace elements exhibited strong pH dependence. The pattern of the leaching curves was similar for all trace elements. The maximum leachability was observed under the most acidic pH condition investigated; the extraction yields were the highest (19 %) for Cu, whereas Pb had the lowest extract yield

Table 4 Extraction yields under acidic, basic and medium pH conditions obtained from the application of pH_{stat} leaching tests at laboratory scale (%; mean values (SD); $n = 3–6$)

Sample	ALJ2			ALJ2 + G			ALJ2 + C			ALJ2 + GC		
pH	11	4.8	1.9	11.7	5.7	1.9	11.4	5.5	1.6	11.2	5.7	1.7
Ca	20 (-)	43 (2)	70 (1)	12.8 (0.2)	13.8 (0.1)	21 (1)	4.7 (0.3)	55 (19)	73 (7)	5.7 (0.1)	17 (2)	31 (1)
Mg	<0.5	63 (4)	67 (1)	<0.5	63 (1)	68 (4)	<0.5	74 (24)	98 (3)	<0.5	56 (7)	78 (1)
Al	<0.5	<0.5	5.3 (0.2)	<0.5	<0.5	9.5 (0.7)	<0.5	<0.5	5.9 (0.1)	<0.5	<0.5	8.0 (0.3)
Fe	<0.5	<0.5	5.7 (0.2)	<0.5	<0.5	2.8 (0.1)	<0.5	<0.5	3.8 (0.6)	<0.5	<0.5	3.4 (0.4)
Cd	<0.5	0.9 (-)	2.2 (-)	<0.5	1.1 (0.1)	1.6 (0.1)	<0.5	0.8 (0.3)	3 (1)	<0.5	0.88 (0.08)	1.9 (0.5)
Zn	<0.5	4.4 (0.5)	7 (1)	<0.5	3.7 (0.3)	7.6 (0.3)	<0.5	4.7 (1.8)	7.6 (0.1)	<0.5	5.0 (0.9)	8.4 (0.4)
Cu	<0.5	1.7 (0.6)	19 (1)	<0.5	<0.5	15 (1)	<0.5	<0.5	15 (1)	<0.5	<0.5	17 (1)
Pb	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	2.1 (0.2)	<0.5	<0.5	1.4 (0.1)
As	0.7 (-)	<0.5	1.8 (-)	<0.5	<0.5	0.9 (0.1)	<0.5	<0.5	1 (1)	<0.5	<0.5	<0.5
Ni	<0.5	15 (-)	18 (4)	<0.5	19 (1)	32 (2)	<0.5	19 (7)	27 (1)	<0.5	24 (2)	32 (1)

(<0.5 %). This behaviour is consistent with a decrease in pH and the related increase in the competition with protons for negative sorption sites, the decrease in the total amount of negative sorption sites and the increase in solubility of several solid phases (Tack 2010).

However, the extractability generally decreased to almost negligible values under neutral and basic pH conditions, with the exception of As, which exhibited a slight increase in leachability under basic pH conditions due to the anionic character of the As species in oxidised soils (Cappuyns et al. 2002), although in terms of extraction yields, it was <1 %.

The concentrations of Cd and Ni in the extracts were less than their corresponding threshold limits in all ranges of pH. In contrast, for the others metals, a pH > 6 was required to be under the threshold limit, except for As, which required a pH between two and ten.

The addition of materials did not significantly modify the pattern of the leachability curves, and only minor changes were observed, especially in the acidic pH range. This result was most likely due to the solubility of the materials at extremely low pH values, although these differences in the trace element concentrations were negligible when the comparison was made on the basis of the extraction yields (Table 4), as in the case of Pb, whose maximum extraction yield at the lowest pH assayed was always <2 %, whereas at the highest pH assayed, the yields were <0.5 % for all samples. Therefore, this soil presents a greater environmental risk under lower pH conditions. Due to the varying ANC values of the soil and soil + material mixtures, achieving acidic pH conditions in the soil was easier than in the mixtures, which is an additional beneficial effect of the addition of the materials. For example, in the case of the ALJ2 soil, it was necessary to add 350 meq/kg of acid to decrease the pH of the soils to 1.9, whereas for the ALJ2 + C mixture, it was necessary to add a considerably greater amount of acid, 2,760 meq/kg, to reach the same pH level.

In addition to considering the beneficial effect of the materials in front of the response of the contaminated soil to an acid or a basic stress, the detailed examination of the initial situation of the resulting mixtures is required to better assess the efficiency of adding the materials. Table 5 presents the leaching data for trace elements in the initial situation of the soil and the soil + material mixtures and the threshold limits established by the European Council decision (European Council 2003). The As concentration in the extracts was always less than the quantification limit. The addition of gypsum to the ALJ2 soil did not lead to a significant change in the pH, and thus, it only produced slight changes in the trace element concentrations in the

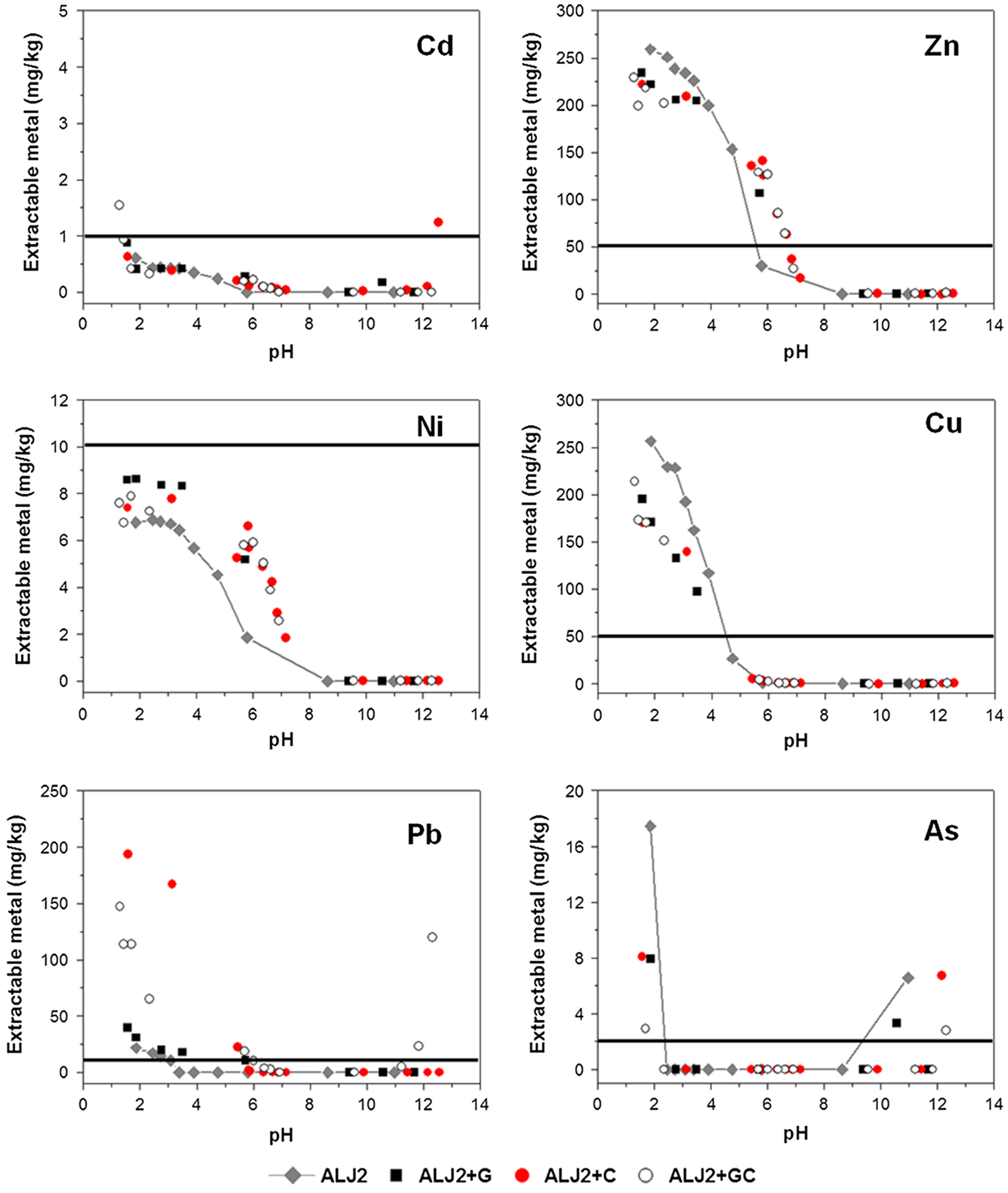

Fig. 2 $\mathrm{pH_{stat}}$ leaching curves for trace elements at laboratory scale. The *horizontal line* indicates the threshold limits for non-hazardous waste

extracts, which were still greater than the threshold limits. The changes could primarily be attributed to the dilution effect of the soil, especially for Cu and Zn, and to the minor increase in the soil pH and the low K_d values obtained for the trace elements in the gypsum. Conversely, the addition of calcite increased the pH to a neutral value, which caused a significant decrease in the trace element concentration in the extracts that was considerably greater than that due to the 10 % dilution effect caused by the addition of the material. Similar effects were observed by other authors, for some of the metals studied here, when adding $CaCO_3$-rich by-products to metal-contaminated soils (Chang et al. 2013; Moon et al. 2013). The increase in the soil pH led to a higher metal sorption and consequently to a decrease in the trace element leachability. This finding is consistent with the high K_d values obtained for Pb and Cd in the calcite. The combination of both materials also produced a decrease in the trace elements leaching due to the higher pH of mixture, with a slightly higher efficiency than that when using calcite alone. Therefore, it should be noted that the trace element concentration in the extracts obtained from ALJ2 + C and ALJ2 + GC mixtures decreased under the threshold limits, with the exception of Zn when using only calcite. From the obtained results, it was observed that although the addition of gypsum to the contaminated soil was a good strategy from the waste valorisation standpoint, its use alone could not sufficiently decrease the trace element leachability in the amended soil. Thus, calcite was required to be used because of the increase in the soil pH and the corresponding increase in the soil sorption capacity. Therefore, it was decided to use a mixture of calcite + gypsum for the experiments performed at the pilot plant scale.

Experiments with samples originated at pilot plant scale

Basic characterisation and major and trace elements in the contaminated soil

The contents of major and trace elements and pH values of the soil sample used in the pilot plant (Table S1 in supplementary material) differed from those of the soil sample used previously in laboratory experiments, but differences were of the same order of magnitude to the expected intrinsic variability of a contaminated soil. The soluble sulphate content was also slightly lower (16,800 mg/kg) than in the soil used for the previous laboratory experiments.

Acid neutralisation capacity of the non-remediated and remediated soils

The changes in the pH values after the addition of an acid (positive scale) or a base (negative scale) and the ANC values of the samples from the pilot plant were evaluated (Fig. S6 in supplementary material). The ANC of the non-remediated soil was extremely low (−2,035 meq/kg), whereas the remediated soil had a considerably higher ANC value (1,200 meq/kg), as expected from the addition of the gypsum and calcite materials. Therefore, the changes in the pH and ANC in the remediated soil were as predicted from the mixtures originated at laboratory.

Application of the pH_{stat} leaching test to non-remediated and remediated soils

Figure 3 presents the leaching curves of Ca, Mg, Al and Fe in the non-remediated and remediated soils, and Table S2 in supplementary material presents the extraction yields for significant acidic and basic pH values.

The behaviour observed with the samples from the pilot plant was consistent with that observed with the samples originated at laboratory scale. On the one hand, the leaching curves of the major elements in the non-remediated soil increased when the pH value decreased, and these curves decreased to almost negligible values under basic pH conditions. The addition of gypsum and calcite caused an increase in the leached concentrations of Ca and Mg due to the composition of the materials. However, when normalising the curves to the total content and comparing the extraction yields (Table S2 in supplementary material), it was observed that the leaching of Mg was similar between the non-remediated and remediated soils, whereas the leaching of Ca under the lowest pH condition assayed considerably decreased (from 100 to 31 %). This decrease was also observed with the samples prepared at laboratory scale. A similar behaviour to that of Ca was also observed for Al and Fe.

Figure 3 also presents the leaching curves for Cd, Zn, Cu, Pb and As in the pilot plant samples. The Ni leaching curves could not be obtained because the concentrations of Ni in the extracts were always less than the quantification limit. The pattern of the leaching curves was the same as that observed with the mixtures prepared at laboratory scale. The element concentration in the extracts of the non-remediated soils increased when the pH decreased, and they reached negligible values under basic pH conditions. The general variation of the leaching curves in the remediated soil with respect to the pH followed the same pattern to that of the non-remediated soil, except for Pb whose leaching increased under extremely basic pH conditions (4.6 %). The addition of gypsum and calcite produced a decrease in the concentration of trace elements in the extracts under acidic pH conditions with respect to the non-remediated soil. This decrease was greater than that due to only the dilution effect, as shown by the comparison of the extraction yields; for instance, the Cd extraction yields decreased from 26 to <0.5 % (Table S2 in supplementary material). In some cases, the concentrations

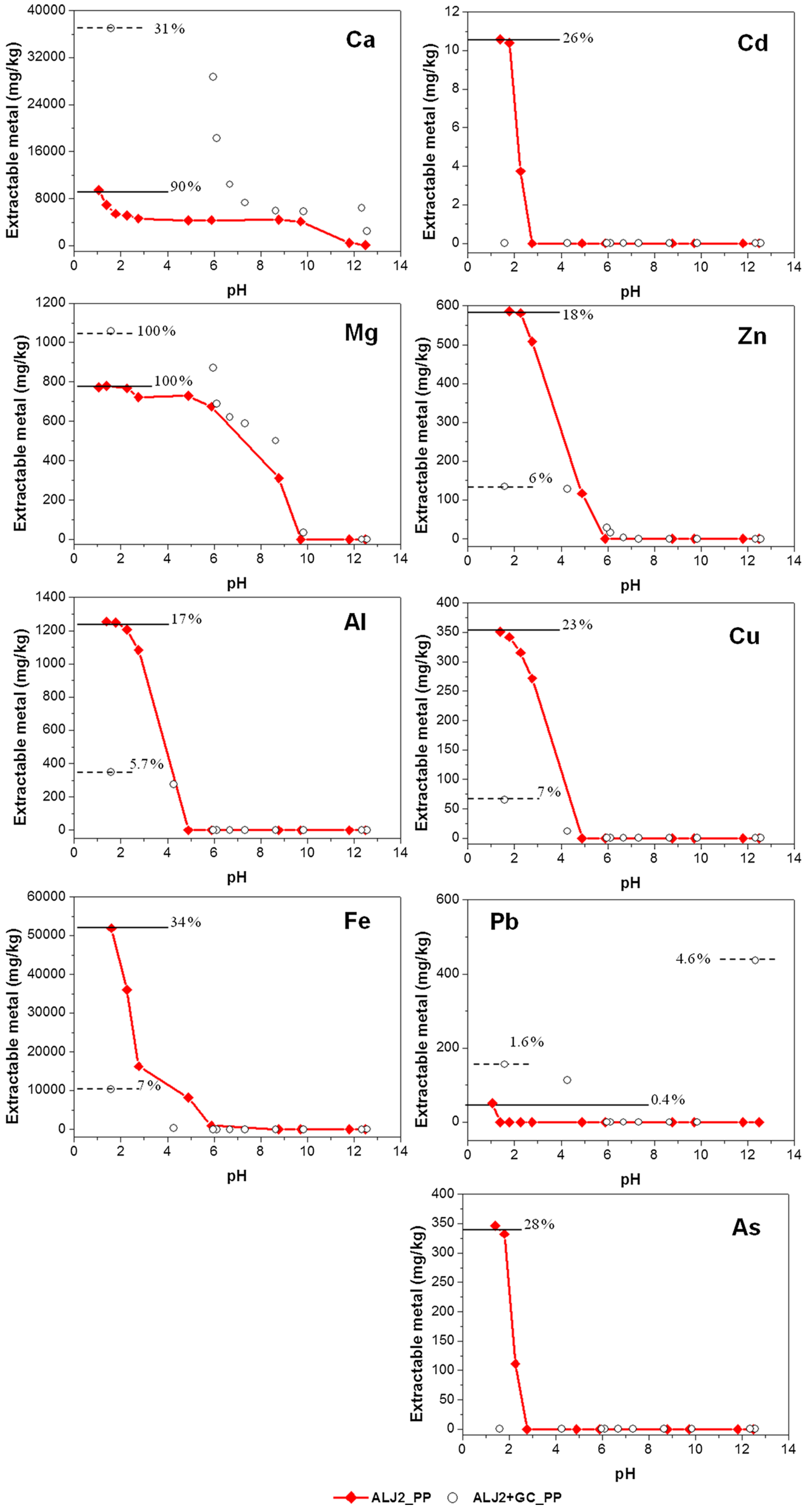

Fig. 3 pH$_{stat}$ leaching curves for major and trace elements at pilot plant scale. The *horizontal line* indicates the maximum extraction yield at acidic or basic pH (*solid line*, non-remediated soil; *dotted line*, remediated soil)

Table 5 Trace element leaching in the laboratory samples at their initial pH (mg/kg and %; mean values (SD); $n = 3–6$)

	ALJ2	ALJ2 + G	ALJ2 + C	ALJ2 + GC	EC*
pH	2.5	2.8	6.7	6.9	–
Cd					
mg/kg	0.38 (0.03)	0.42 (0.03)	0.09 (0.03)	<lq	1
%	1.6	1.7	0.3	<lq	–
Cu					
mg/kg	214 (5)	133 (7)	0.7 (0.1)	0.45 (0.01)	50
%	18	12	0.1	0.04	–
Ni					
mg/kg	6.4 (0.1)	8.4 (0.2)	4.2 (0.1)	2.6 (0.4)	10
%	22	31	16	11	–
Pb					
mg/kg	23.8 (0.2)	19.8 (0.4)	<lq	<lq	10
%	0.2	0.2	<lq	<lq	–
Zn					
mg/kg	240 (13)	205 (10)	63 (5)	27 (6)	50
%	7.8	7	2	1	–

lq: limit of quantification

* European Commission decision thresholds for waste management. Disposal of non-hazardous waste (European Council 2003)

decreased to less than the quantification limit, such as for As.

As observed previously with the mixtures prepared at laboratory scale, it would be extremely difficult for the remediated soil to decrease its pH level to the pH range in which the trace element leachability is maximum due to its higher ANC value. In fact, it was necessary to add more than 2,200 meq/kg of acid to achieve the same pH as the initial pH of the non-remediated soil (2.6). Furthermore, the detailed examination of the initial situation of the non-remediated and remediated soils allowed us to assess the efficiency of the addition of the materials without considering the prediction of the responses of the non-remediated and remediated soils to potential acidic stresses. The addition of materials led to a significant increase in the soil pH (7.3) compared to the non-remediated soil (1.8) measured in the pH_{stat} experimental conditions. Whereas the trace element concentration in the extracts from the non-remediated soil (As: 333 mg/kg; Cd: 10 mg/kg; Cu: 342 mg/kg and Zn: 587 mg/kg) was greater than the threshold limits, the concentration of all the trace metals was less than the quantification limit in the extracts obtained from the remediated soil at the initial pH and, consequently, under the threshold limits. Therefore, the decrease in trace element leaching was primarily due to the increase in pH in the resulting remediated soil, which led to an increase in the soil sorption capacity, although the soil dilution caused by the addition of both materials also contributed to the decrease in leaching.

Conclusion

From the results obtained with samples created at the laboratory scale and subsequently corroborated with the samples from pilot plant, we conclude that a mixture formed by gypsum and calcite, which are industrial by-products, is an excellent option for remediating metal-contaminated soils because the material mixture led to an increase in the soil pH and in its sorption capacity. We have confirmed the need of fully characterising candidate materials before being used in soil remediation, as the tested gypsum alone is not a suitable material for the remediation of contaminated soils, although it improved the efficiency of calcite when mixing both materials. The use of these materials allowed the concentration of trace elements in soil water extracts to decrease to values lower than the threshold limits associated with the management of hazardous waste. Besides, the remediation strategy proposed does not generate residues that require additional management and permits the valorisation of industrial wastes, these materials being more available and their application less expensive than the use of other adsorbents.

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