Remediation of metal-contaminated soils with the addition of materials. Part II: Leaching tests to evaluate the efficiency of materials in the remediation of contaminated soils

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Abstract

The effect of the addition of materials on the leaching pattern of As and metals (Cu, Zn, Ni, Pb and Cd) in two contaminated soils was investigated. The examined materials included bentonites, silicates and industrial wastes, such as sugar foam, fly ashes and a material originated from the zeolitization of fly ash. Soil + material mixtures were prepared at 10% doses. Changes in the acid neutralization capacity, crystalline phases and contaminant leaching over a wide range of pHs were examined by using pH_{stat} leaching tests. Sugar foam, the zeolitic material and MX-80 bentonite produced the greatest decrease in the leaching of pollutants due to an increase in the pH and/or the sorption capacity in the resulting mixture. This finding suggests that soil remediation may be a feasible option for the reuse of non-hazardous wastes.

Keywords: metal-contaminated soils, immobilization, sugar foam, fly ashes, bentonites, pH_{stat} leaching test.

1. Introduction

Chemical immobilization through the use of soil amendments is considered to be a valuable approach for the remediation of contaminated soils because it may reduce the mobility of metals (Querol et al., 2006; Malandrino et al., 2011) and may eventually allow for the recovery of the contaminated soil for agricultural or industrial use. Two mechanisms are responsible for the efficiency of this remediation action: 1) the increase in the metal sorption of the resulting soil + material mixture and 2) the dilution of the contaminant concentration when large material doses are used. Another indirect benefit from this remediation strategy is that it may allow the reuse of non-hazardous wastes generated by industrial processes.

After the candidate materials have been fully characterized at the laboratory level, the materials must be tested in the soil + material mixtures before being used at the field level. Soils contaminated by heavy metals and metalloids, aside from the modification of the content of certain soil phases in the resulting mixtures (e.g., clay mineral or organic matter), may lead to a significant variation in the sorption properties of the soil (Herwijnen et al., 2007). The modification of the soil pH is considered to be a key factor in reducing metal mobility (Dijkstra et al., 2004). This fact suggests examining the acid neutralization capacity of the mixtures and obtaining the leaching curves of the contaminants in a pH range of environmental interest as a better approach to assess the environmental impact. This approach is better than a simple analysis of the total concentration because it is also useful to develop end points for the remediation of contaminated soils (Kosson et al., 2002).

Here, we investigated soil and material mixtures created from the samples characterized in Part I of this work. Two contaminated soils of contrasting characteristics and materials, including sugar foam, silicates, bentonites, fly ashes and a zeolitic material derived from a zeolitization of the fly ashes (González-Núñez et al., 2011), were studied. The acid neutralization capacity of the mixtures was compared with that of the individual samples, and a pH_{stat} leaching test was applied to obtain the leaching curves of major (Ca, Mg, Fe, Mn and Al) and trace (Cd, Zn, Ni, Cu, Pb and As) elements as well as the dissolved organic carbon (DOC). A structural characterization of the samples was performed to examine the appearance of new solid phases in the mixtures and to evaluate which phases were removed after the pH_{stat} leaching test.

2. Materials and methods

2.1. Samples

Two contaminated soils from the south of Spain and seven materials were used in this study. The contaminated soils were HUE soil, which is a mineral soil, and a soil from Aljaraque (Huelva) (ALJ), which has been affected by mining and industrial activities. The materials tested were wastes and silicates: sugar foam (SF), wollastonite (Wolla), FEBEX, MX-80 and Zamora (ZamBent) bentonites, a waste material produced by the zeolitization of fly ash (Zeo) and fly ashes (FA).

All of the samples were air-dried, sieved through 2-mm mesh and homogenized in a roller table before the experiments and the analyses. A detailed description of the samples has been provided in González-Núñez et al. 2011.

2.2. Soil+material mixtures

The mixtures of soil and material were prepared at 10% doses (90 g soil/10 g material). The soil samples (270 g) were placed into plastic containers and mixed with 30 g of material. For the HUE soil, the materials tested were MX-80, FEBEX, Wolla, ZamBent, SF and Zeo. For the ALJ soil, the materials tested were MX-80, Wolla, FA, Zeo and SF. To simulate the field conditions in the short term, the mixtures were submitted to three drying-wetting cycles, which consisted of rewetting the mixtures at field capacity, maintaining them in closed vessels at 40 ºC for 24 h and then drying them in open vessels at 40ºC for 48 h. These mixtures were rotated end-over-end for 24 h to ensure homogeneity before taking subsamples for the X-ray diffraction (XRD) structural analyses and leaching experiments. A description of the XRD analyses is given in the Supplementary material.

2.3. pH_{stat} leaching test

The pH_{stat} test is based on the CEN/TS 14429 test (CEN/TS, 2006) and examines metal release as a function of pH. From the information provided by the pH titration test (González-Núñez et al., 2011), the amount of HNO_3 or NaOH required to obtain pH values between 2 and 12 in the final suspension was calculated for a minimum of 7 extracts (with two replicates for each extract). A suitable amount of acid or base was added to 6 g of sample suspended in a given volume of deionized water to give a liquid–solid ratio of 10 mL/g. Soil and soil + material mixtures were end-over-end extracted for seven days, which is the contact time proposed for the characterization of samples with a particle size of less than 2mm (Kosson et al., 2002). Following the liquid phase separation by centrifugation and filtration (0.45-µm), the final pH of the leachates was measured. The DOC and major and trace element contents were determined in the supernatants as described in the Supplementary material.

3. Results and discussion

3.1. Neutralization capacity of the mixtures

Fig. 1 shows the changes in pH after the addition of acid (positive scale) or base (negative scale) for all of the mixtures and the amount of acid required to decrease the pH of the soil + material mixture to 4 (acid neutralization capacity, ANC; meq/kg). Bentonites and the fly ash (Fig. 1a) did not improve the ANC of the soil satisfactorily. The ANCs of the mixtures with MX-80, FEBEX and Zamora bentonites with the HUE soil were lower than that of the initial soil, which had a neutral initial pH (6.7) in these experimental conditions. The ANC of the ALJ SOIL was extremely low (in the negative scale because the initial soil pH was 2.4). MX-80 and the fly ashes slightly improved the ANC in the resulting mixtures, although it was still in the negative scale (Fig. 1c). This result is consistent with the individual ANCs of the bentonites (González-Núñez et al., 2011), which were lower ANC values (within the 100 - 300 meq/kg) with respect to the other materials (Paschke et al., 1999). Conversely, the mixtures with zeolitic material, wollastonite silicate and sugar foam had higher ANCs than those of the soils (Figs. 1b and 1d). This finding is consistent with the behaviours of the individual materials with respect to their ANCs (González-Núñez et al., 2011). When the zeolitic material, the wollastonite silicate and sugar foam are used at an economical feasible dose, such as 10%, they are able to increase the soil pH in the resulting mixtures, which leads to lower trace element leaching due to the increase in the soil pH, and increase the buffer capacity of the soil against potential acid or basic stresses.

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

3.2.1. Structural characterization of soil+material mixtures

Figs. 2 - 4 show examples of the XRD patterns in soil + material mixtures before and after leaching. The XRD diagrams of the initial mixtures before leaching (Figs. 2a, 3a and 4a and Figs. 2e, 3e and 4e) are characterized by the main constituents of the soils, (quartz in the HUE soil and pyrite in the ALJ soil) along with other minor soil phases, such as illite, vermiculite, brushite ($CaHPO_4$) and anglesite ($PbSO_4$). The main phases representing the materials were also observed: calcite ($CaCO_3$) in the mixtures with sugar foam (Figs. 2a and 2e), montmorillonite in the mixtures with MX-80 (Figs. 3a and 3e) and zeolite (sodium aluminosilicate hydrate) in the mixtures with the zeolitic material (Figs. 4a and 4e). As could be expected no new crystalline phases were formed as a consequence of the preparation of the mixtures, and the XRD spectra of the mixtures were consistent with the pure XRD spectra of the materials at the doses assayed (González-Núñez et al., 2011).

The examination of the soil + sugar foam mixture residues after leaching (Figs. 2b - d and 2f - h) revealed that a few soil crystalline phases, especially calcite, vermiculite and illite, diminished after leaching at extremely acidic pH levels. It is well known that 2:1 phyllosilicates (such as illite or vermiculite) and calcite are rapidly and fully dissolved under acid conditions (Galan et al., 1999) . Anglesite disminished at basic pH, and brushite diminished at both extreme pH levels, as observed by the absence of the peaks and/or the decrease in their intensities. It is well know that brushite at pH> 8 is transformed to secondary phases, however, at pH acid showed to be quite stable (Larsen and Jensen, 1989). Therefore the observed diminishing of the XRD intensity can be ony explained by an amorphization of the phase. The rest of the phases, including the pyrite phase in the ALJ soil mixtures, were constantat the pH treatments. Regarding the soil + MX-80 mixtures (Fig. 3), the crystalline phase of the bentonite (montmorillonite) was affected by both increases and decreases in the pH, and it disappeared after leaching. It has been observed that montmorillonites are rapidly and fully dissolved under acid conditions (Galan et al., 1999) and in basic conditions the montmorillonite are dissolved and precipitate as secondary products (Huertas et al., 2009). However, a small peak could be observed at a basic pH for the HUE mixture. As in the previous mixtures, brushite diminished at extreme pH levels. With respect to the mixtures with the zeolitic material, the XRD patterns showed that the sodium aluminum silicate phase (Zeolite P-1), related to the zeolitic material and brushite, diminished in pH conditions more basic and more acidic than the initial condition. Brushite and zeolitic are not stable at basic and acid conditions, respectively (Larsen and Jensen, 1989 and Savage et al., 2007) and it is the reason of the observed diminishing of their XRD peaks. However, in the other extremes conditions such diminishing can be caused by an amorphization of these phases.

3.2.2. Extraction of major elements and organic matter

The leaching curves of major elements and DOC provide information on the phases that may be solubilized after changing the pH of the suspensions. To illustrate this effect, Fig. 5 plots the extraction curves of Ca, Mg, Al, Fe and Mn in all of mixtures as well as the DOC quantified in all of the soil extracts (expressed as mg C/L). Table S1 lists several extraction yields for significant acid and basic pH values.

The leaching of metals from soils may be affected by the DOC content, which includes soluble organic acids (Cappuyns and Swennen, 2008). The two soils showed a low DOC concentration (lower than 20 mg C/L) in the pH range tested with a DOC curve having the common U-shaped pattern, which was consistent with their low organic carbon content. At pH levels higher than 8, the DOC values were within the 6 - 12 and 8 - 17 mgC/L ranges for the HUE and ALJ soils, respectively. These values are lower than those reported in the literature for mineral soils (100-1000 mgC/L) (Rigol et al., 2009).

The leaching curves of Ca and Mg were similar for both soils, with increased leaching when decreasing the pH. The Mg extraction yields were lower than those of Ca, especially in the HUE soil. This leaching pattern agrees with the observed decrease in Ca-bearing crystalline phases, such as brushite, vermiculite, montmorillonite and illite, at acidic pH levels. The steeper increase in Ca and Mg leaching from pH 5 downwards in the HUE SOIL than in the ALJ soil was consistent with its larger carbonate content. For the ALJ soil, the Ca concentration in the extract at the more acidic pH level (1.9) approached the Ca total content with an extraction yield close to 70[UB5]%. The addition of certain materials, such as wollastonite and sugar foam, modified the Mg and the Ca leaching curves because these materials had a higher Ca and Mg content than the soil (González-Núñez et al., 2011) and they were associated with phases that were soluble at acidic pH levels. However, as indicated by the XRD analyses, these samples were not quantitatively solubilized at the more acidic pH level because the Ca extraction yields remained in the 60 - 70% range in the mixtures with wollastonite and sugar foam.

Aluminum solubility, which increased at acidic pH levels and was lower at basic pH levels, was explained by the presence of amorphous hydroxide and hydroxysilicate phases (Meima and Comans, 1997). The Al extraction yields were much higher in the HUE soil than in the ALJ soil. Only the addition of zeolitic material caused a marked change in the Al leaching curves, thus indicating its partial decomposition at an acidic pH (with Al extraction yields up to 36% in the HUE_Zeo mixture), as shown in Figs. 4c, 4f and 4g by the XRD analyses. For the other mixtures, including bentonites, the Al leaching was lower or similar to that of the initial soil, with the exception of the ALJ _FA mixture.

The pH_{stat} curves for Fe in both soils were similar, with higher extraction yields obtained at pH levels lower than 4. The extraction yields decreased to almost negligible values at basic pH, which was characteristic for the solubility of Fe hydroxides, such as ferrihydrite (Dijkstra et al., 2006). The total concentration of Fe in the ALJ soil was higher than in the HUE soil because the ALJ soil was affected by contamination with pyritic minerals (González-Núñez et al., 2011); however, the Fe leaching rates were lower in the ALJ soil due to the lower solubility of the pyritic phase. The addition of materials did not modify substantially the pattern of the Fe leaching curves.

Manganese solubility was also highly dependent on pH and similar to that of Fe. Its behavior was quite similar in all of the samples, with higher extraction yields at an acidic pH and almost negligible remobilization at a basic pH. The overall Mn solubility was lower in the ALJ soil than in the HUE soil. The addition of wollastonite, the material with the highest Mn content (González-Núñez et al., 2011), modified the leaching curve of Mn in the related mixtures, as observed in the ALJ soil, because the Mn that originated from the wollastonite was more soluble than that from the soil.

3.2.3. Extraction of trace elements

Fig. 6 shows the pH_{stat} leaching curves for Cd, Zn, Cu, Pb, As and Ni, and table S1 lists several extraction yields for given pH values.

The leached concentrations of the trace elements were generally much lower than the total concentrations and showed strong pH dependence. The leaching of Cd, Zn, Cu and

Ni in the soils increased with decreasing pH, especially in the HUE soil. A much lower amount of these elements was leached in the neutral and alkaline pH ranges. This finding was consistent with the fact that the number of negative sites for cation sorption decrease with pH. Zn, Ni, Cu and Cd extraction yields in the acidic pH levels (3.2) were high in the HUE soil, especially for the latter element, with values of approximately 70% of total element. The extraction yields were much lower in the ALJ soil (a maximum of 18% for Cu). For Zn, the reported potential formation of soluble anionic hydroxyl complexes or the likely associations of Cu with carbonate DOC were not observed in these mineral soils with such a low organic matter and carbonate content, thus their leaching rates at a high pH was negligible and only observed in a few cases (Van der Sloot et al., 1996).

The leaching curves for As and Pb differed from those of the other heavy metals, especially in the HUE soil, in which the maximum leachability for these elements was observed at pH values above 12, although with a low extraction yield for Pb (3.9%). This finding was consistent with the observed instability of the anglesite at the extreme basic pH levels. In addition to the solubilization of this mineral phase, an additional explanation for the release of Pb at alkaline pH values is its affinity to soluble organic compounds (Dijkstra, et al., 2004). The high extraction yield of As at a basic pH in the HUE soil was related to the anionic character of the As species because arsenate is the predominant species in oxidized soils, and it showed a high leaching rate at a basic pH because the surfaces are negatively charged (Cappuyns et al., 2002; Dijkstra, et al., 2004: Rigol et al., 2009). In the ALJ soil, this pattern was much less significant due to the arsenopyritic nature of the contamination, although the maximum As concentration in the leachates was also quantified at basic pH.

In the HUE soil, a few materials (MX-80 and FEBEX bentonites, wollastonite and sugar foam) produced a decrease in the leaching of Cd, Zn, Ni and Cu at acidic pH values in addition to the dilution effect, which was confirmed by a small decrease in the extraction yields, especially for Cd and Ni. These results were consistent with the sorption properties of these materials (González-Núñez et al., 2011). Although the zeolitic material exhibited a promising sorption capacity, it was partially dissolved at an acidic pH and was only partially efficient for Cd and Zn. In the ALJ soil that was affected by a particulate, pyritic source of contamination, the materials were much less efficient, and only decreases in the leaching aside from the dilution effect were observed for Cu and Zn (except for MX-80). Regarding As and Pb, practically all of the materials succeeded in decreasing their leaching at basic pH levels in the HUE soil. At acidic pH levels, the leaching rates were almost negligible, and the beneficial effect of the materials was difficult to be observed.

In addition to comparing and analyzing changes in the pattern of the leaching curves of the trace elements across the entire pH range, a detailed examination of the initial situation of the resulting mixtures without acid or base additions is required to assess the best materials to be used at field level. Table 1 shows the lixiviation data for trace elements at the initial situation of the soils and their mixtures. For HUE SOIL, which already had a neutral pH, the addition of materials did not lead to a significant change in the pH with the exception of the sugar foam, which increased the pH more than one unit at the 10% dose. This observation was fully consistent with the ANC previously calculated. Therefore, changes in leaching should be explained on the basis of the dilution effect and changes in the sorption capacity in the mixture, with the pH playing an additional role only in the mixture with sugar foam. From the results in Table 1, sugar foam, zeolitic materials and MX-80 produced the highest decreases in the trace element concentration in the extracts, as observed for Zn, Ni, Cu and Cd. This decrease was due to the increase in pH and the sorption capacity, respectively, because the zeolitic material was stable at this neutral pH. Therefore, for contaminated soils having a slightly acidic pH, a mixture of sugar foam with the zeolitic material (or a bentonite like MX-80) could be an efficient remediation strategy.

The effect on the pH by changes in the trace element concentrations in the extracts was more significant in the ALJ soil because the initial pH of many mixtures was still very acidic, The exceptions were the mixtures with wollastonite and sugar foam, which raised the pH to basic or neutral values, as predicted by the ANC sequence. The potential beneficial effect of MX-80 could not be observed due to the low pH of its mixture. Therefore, the decrease in trace element leaching was basically due to the increase in pH. Sugar foam and wollastonite led to the highest decreases in the amount of metal leached, which was more than two orders of magnitude for a few metals (e.g., Cu and Zn).

4. Conclusions

A remediation strategy based on the addition of materials to contaminated soils is a feasible approach because these materials could increase the metal retention and decrease metal leaching at economically acceptable doses. The most promising materials tested here in the remediation of soils of contrasting properties are sugar foam and wollastonite silicate, which increased the soil pH, and the zeolitic material, which increased the sorption capacity. When considering a remediation strategy that may make use of mixtures of materials, combinations of sugar foam with zeolitic materials and with bentonites (such as MX-80) should be considered. The decrease in the metal leaching would allow for the reuse of the soils at least for industrial purposes and/or their reclassification in waste categories with a lower management cost. The use of sugar foam and zeolitic material, alone or combined, would also permit the valorization of waste materials.

Moreover, the combined use of X-ray diffraction and analytical techniques has allowed not only controlling the leaching of element but also to determine the mechanism responsible of such leaching, such as dissolution of the phases or transformation in secondary phases or amorphization.

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