

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

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11 **Abstract**

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

22

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

25 **1. Introduction**

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

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

47 Here, we investigated soil and material mixtures created from the samples characterized
48 in Part I of this work. Two contaminated soils of contrasting characteristics and

49 materials, including sugar foam, silicates, bentonites, fly ashes and a zeolitic material
50 derived from a zeolitization of the fly ashes (González-Núñez et al., 2011), were
51 studied. The acid neutralization capacity of the mixtures was compared with that of the
52 individual samples, and a pH_{stat} leaching test was applied to obtain the leaching curves
53 of major (Ca, Mg, Fe, Mn and Al) and trace (Cd, Zn, Ni, Cu, Pb and As) elements as
54 well as the dissolved organic carbon (DOC). A structural characterization of the
55 samples was performed to examine the appearance of new solid phases in the mixtures
56 and to evaluate which phases were removed after the pH_{stat} leaching test.

57

58 **2. Materials and methods**

59 *2.1. Samples*

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

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

69 *2.2. Soil+material mixtures*

70 The mixtures of soil and material were prepared at 10% doses (90 g soil/10 g material).
71 The soil samples (270 g) were placed into plastic containers and mixed with 30 g of

72 material. For the HUE soil, the materials tested were MX-80, FEBEX, Wolla, ZamBent,
73 SF and Zeo. For the ALJ soil, the materials tested were MX-80, Wolla, FA, Zeo and SF.
74 To simulate the field conditions in the short term, the mixtures were submitted to three
75 drying-wetting cycles, which consisted of rewetting the mixtures at field capacity,
76 maintaining them in closed vessels at 40 °C for 24 h and then drying them in open
77 vessels at 40°C for 48 h. These mixtures were rotated end-over-end for 24 h to ensure
78 homogeneity before taking subsamples for the X-ray diffraction (XRD) structural
79 analyses and leaching experiments. A description of the XRD analyses is given in the
80 Supplementary material.

81

82 2.3. pH_{stat} leaching test

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

95

96

97 **3. Results and discussion**

98 *3.1. Neutralization capacity of the mixtures*

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

118

119 *3.2. Application of the pH_{stat} leaching test to soil and soil+material mixtures*

120 3.2.1. Structural characterization of soil+material mixtures

121 Figs. 2 - 4 show examples of the XRD patterns in soil + material mixtures before and
122 after leaching. The XRD diagrams of the initial mixtures before leaching (Figs. 2a, 3a
123 and 4a and Figs. 2e, 3e and 4e) are characterized by the main constituents of the soils,
124 (quartz in the HUE soil and pyrite in the ALJ soil) along with other minor soil phases,
125 such as illite, vermiculite, brushite (CaHPO_4) and anglesite (PbSO_4). The main phases
126 representing the materials were also observed: calcite (CaCO_3) in the mixtures with
127 sugar foam (Figs. 2a and 2e), montmorillonite in the mixtures with MX-80 (Figs. 3a and
128 3e) and zeolite (sodium aluminosilicate hydrate) in the mixtures with the zeolitic
129 material (Figs. 4a and 4e). As could be expected no new crystalline phases were formed
130 as a consequence of the preparation of the mixtures, and the XRD spectra of the
131 mixtures were consistent with the pure XRD spectra of the materials at the doses
132 assayed (González-Núñez et al., 2011).

133 The examination of the soil + sugar foam mixture residues after leaching (Figs. 2b - d
134 and 2f - h) revealed that a few soil crystalline phases, especially calcite, vermiculite and
135 illite, diminished after leaching at extremely acidic pH levels. It is well known that 2:1
136 phyllosilicates (such as illite or vermiculite) and calcite are rapidly and fully dissolved
137 under acid conditions (Galan et al., 1999). Anglesite diminished at basic pH, and
138 brushite diminished at both extreme pH levels, as observed by the absence of the peaks
139 and/or the decrease in their intensities. It is well known that brushite at $\text{pH} > 8$ is
140 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
141 be only explained by an amorphization of the phase. The rest of the phases, including the
142 pyrite phase in the ALJ soil mixtures, were constant at the pH treatments. Regarding the
143 soil + MX-80 mixtures (Fig. 3), the crystalline phase of the bentonite (montmorillonite)

145 was affected by both increases and decreases in the pH, and it disappeared after
146 leaching. It has been observed that montmorillonites are rapidly and fully dissolved
147 under acid conditions (Galan et al., 1999) and in basic conditions the montmorillonite
148 are dissolved and precipitate as secondary products (Huertas et al., 2009). However, a
149 small peak could be observed at a basic pH for the HUE mixture. As in the previous
150 mixtures, brushite diminished at extreme pH levels. With respect to the mixtures with
151 the zeolitic material, the XRD patterns showed that the sodium aluminum silicate phase
152 (Zeolite P-1), related to the zeolitic material and brushite, diminished in pH conditions
153 more basic and more acidic than the initial condition. Brushite and zeolitic are not stable
154 at basic and acid conditions, respectively (Larsen and Jensen, 1989 and Savage et al.,
155 2007) and it is the reason of the observed diminishing of their XRD peaks. However, in
156 the other extremes conditions such diminishing can be caused by an amorphization of
157 these phases.

158

159 3.2.2. Extraction of major elements and organic matter

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

165 The leaching of metals from soils may be affected by the DOC content, which includes
166 soluble organic acids (Cappuyns and Swennen, 2008). The two soils showed a low
167 DOC concentration (lower than 20 mg C/L) in the pH range tested with a DOC curve
168 having the common U-shaped pattern, which was consistent with their low organic

169 carbon content. At pH levels higher than 8, the DOC values were within the 6 - 12 and 8
170 - 17 mgC/L ranges for the HUE and ALJ soils, respectively. These values are lower
171 than those reported in the literature for mineral soils (100-1000 mgC/L) (Rigol et al.,
172 2009).

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

187 Aluminum solubility, which increased at acidic pH levels and was lower at basic pH
188 levels, was explained by the presence of amorphous hydroxide and hydroxysilicate
189 phases (Meima and Comans, 1997). The Al extraction yields were much higher in the
190 HUE soil than in the ALJ soil. Only the addition of zeolitic material caused a marked
191 change in the Al leaching curves, thus indicating its partial decomposition at an acidic
192 pH (with Al extraction yields up to 36% in the HUE_Zeo mixture), as shown in Figs.
193 4c, 4f and 4g by the XRD analyses. For the other mixtures, including bentonites, the Al

194 leaching was lower or similar to that of the initial soil, with the exception of the ALJ
195 _FA mixture.

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

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

211

212 3.2.3. *Extraction of trace elements*

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

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

217 Ni in the soils increased with decreasing pH, especially in the HUE soil. A much lower
218 amount of these elements was leached in the neutral and alkaline pH ranges. This
219 finding was consistent with the fact that the number of negative sites for cation sorption
220 decrease with pH. Zn, Ni, Cu and Cd extraction yields in the acidic pH levels (3.2) were
221 high in the HUE soil, especially for the latter element, with values of approximately
222 70% of total element. The extraction yields were much lower in the ALJ soil (a
223 maximum of 18% for Cu). For Zn, the reported potential formation of soluble anionic
224 hydroxyl complexes or the likely associations of Cu with carbonate DOC were not
225 observed in these mineral soils with such a low organic matter and carbonate content,
226 thus their leaching rates at a high pH was negligible and only observed in a few cases
227 (Van der Sloot et al., 1996).

228 The leaching curves for As and Pb differed from those of the other heavy metals,
229 especially in the HUE soil, in which the maximum leachability for these elements was
230 observed at pH values above 12, although with a low extraction yield for Pb (3.9%).
231 This finding was consistent with the observed instability of the anglesite at the extreme
232 basic pH levels. In addition to the solubilization of this mineral phase, an additional
233 explanation for the release of Pb at alkaline pH values is its affinity to soluble organic
234 compounds (Dijkstra, et al., 2004). The high extraction yield of As at a basic pH in the
235 HUE soil was related to the anionic character of the As species because arsenate is the
236 predominant species in oxidized soils, and it showed a high leaching rate at a basic pH
237 because the surfaces are negatively charged (Cappuyns et al., 2002; Dijkstra, et al.,
238 2004; Rigol et al., 2009). In the ALJ soil, this pattern was much less significant due to
239 the arsenopyritic nature of the contamination, although the maximum As concentration
240 in the leachates was also quantified at basic pH.

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

254 In addition to comparing and analyzing changes in the pattern of the leaching curves of
255 the trace elements across the entire pH range, a detailed examination of the initial
256 situation of the resulting mixtures without acid or base additions is required to assess
257 the best materials to be used at field level. Table 1 shows the lixiviation data for trace
258 elements at the initial situation of the soils and their mixtures. For HUE SOIL, which
259 already had a neutral pH, the addition of materials did not lead to a significant change in
260 the pH with the exception of the sugar foam, which increased the pH more than one unit
261 at the 10% dose. This observation was fully consistent with the ANC previously
262 calculated. Therefore, changes in leaching should be explained on the basis of the
263 dilution effect and changes in the sorption capacity in the mixture, with the pH playing
264 an additional role only in the mixture with sugar foam. From the results in Table 1,
265 sugar foam, zeolitic materials and MX-80 produced the highest decreases in the trace

266 element concentration in the extracts, as observed for Zn, Ni, Cu and Cd. This decrease
267 was due to the increase in pH and the sorption capacity, respectively, because the
268 zeolitic material was stable at this neutral pH. Therefore, for contaminated soils having
269 a slightly acidic pH, a mixture of sugar foam with the zeolitic material (or a bentonite
270 like MX-80) could be an efficient remediation strategy.

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

280 **4. Conclusions**

281 A remediation strategy based on the addition of materials to contaminated soils is a
282 feasible approach because these materials could increase the metal retention and
283 decrease metal leaching at economically acceptable doses. The most promising
284 materials tested here in the remediation of soils of contrasting properties are sugar foam
285 and wollastonite silicate, which increased the soil pH, and the zeolitic material, which
286 increased the sorption capacity. When considering a remediation strategy that may make
287 use of mixtures of materials, combinations of sugar foam with zeolitic materials and
288 with bentonites (such as MX-80) should be considered. The decrease in the metal
289 leaching would allow for the reuse of the soils at least for industrial purposes and/or

290 their reclassification in waste categories with a lower management cost. The use of
291 sugar foam and zeolitic material, alone or combined, would also permit the valorization
292 of waste materials.

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

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