

Immobilization of heavy metals in polluted soils by the addition of zeolitic material synthesized from coal fly ash

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ABSTRACT

The use of zeolitic material synthesized from coal fly ash for the immobilization of pollutants in contaminated soils was investigated in experimental fields at Doñana toxic spill (South of Spain). This area was flooded with a high heavy metal pyrite slurry in April 1998. Although reclamation activities were carried out very fast, a residual pyrite slurry mixed with soil accounted for relatively high leachable levels of potentially toxic elements such as Zn, Pb, As, Cu, Sb, Co, Tl and Cd. Phyto-remediation strategies are adopted for the final recovery of the polluted soils, and the immobilization of metals was necessary to avoid leaching processes and the consequent ground water pollution.

To this end, 3.5 tonnes of high NaP1 zeolitic material was synthesized from the Teruel and Narcea coal fly ashes in a 10 m³ reactor at CLARIANT SA facilities. This zeolitic material was applied using different doses (from 15 to 54 tonnes per hectare) to 8 different experimental fields. The zeolitic material was manually applied by mixing the powder with the soil. One of the fields were maintained without zeolite addition to compare the reduction of the metal leaching with the other fields. Sampling was carried out one and two years after the zeolite addition. The preliminary results show that the application of the zeolitic material considerably decreases the leaching of elements such as Cd, Co, Cu, Ni, and Zn. Although the reduction of the leachable proportion is mainly due to the ion exchange, the precipitation of insoluble phases (as a consequence of the pH rise from 3.3 to 7.6 due to the zeolite addition) also contribute to immobilize the pollutants.

INTRODUCTION

A pyrite slurry spill occurred in the Guadiamar river (a tributary river of the Guadalquivir river, Southwestern Spain) on the 25th of April 1998 as a result of the collapse of a dam

in a pond containing pyrite slurry and waste water with high contents of potentially toxic elements. This pond is located at Aznalcóllar (Sevilla), where Boliden-Apirsa extracted sulfide ore deposits. An area 40 km long and 0.5 km wide (following the Agrio and Guadiamar valleys) was covered by a 3 to 30 cm thick layer of pyrite slurry. The volume of the slurry flooding this area (located in the north of the Doñana Natural Park) was estimated¹ at about $2 \cdot 10^6 \text{ m}^3$.

Immediately after spill, the Ministry of the Environment in Spain and the Autonomous Council of Andalucía began soil-reclamation activities in order to: a) reduce to a minimum the potential impact due to leaching of the quickly weathered heavy metal sulfide compounds and b) to avoid spreading of the potentially toxic mud by autumn rains. These activities, which were carried out mainly during the dry season (June-September), involved the removal of the pyrite slurry by means of a large number of mechanical diggers, lorries and trucks.

After soil reclamation, a persistent soil pollution was detected in reduced areas due to the presence of an small fraction of pyrite mud mixed with soil. Weathering of the pyrite slurry plays a central role in soil contamination due to the high soil acidity and to the high mobile heavy metal contents. Phyto-remediation strategies are adopted for the final recovery of these polluted soils, and the immobilization of metals was necessary to avoid leaching processes and the consequent ground water pollution.

This study focuses on the application of NaP1 zeolitic material synthesized from the Teruel and Narcea coal fly ashes to the polluted soils to diminish the leachable contents of heavy metals while phyto-remediation strategies are applied. The alkalinity of the zeolitic product may also contribute to the buffering of the acidity of the soil, and consequently may also favor the plant growth.

EXPERIMENTAL

Synthesis of Zeolitic Products

Two different zeolitic products were obtained at a pilot plant scale from the Teruel and Narcea fly ashes^{2,3}. The Teruel and Narcea fly ashes were selected to reproduce the laboratory tests at a pilot plant scale by using low- and high-glass fly ashes, respectively. The synthesis conditions were selected from prior studies^{4,5} to obtain high NaP1 products. The experiments were carried out in a 10 m^3 R-410-A reactor made of 304 stainless steel. Two runs of 1.1 and 2.2 tonnes were carried out with the Teruel and the Narcea fly ashes, respectively. Table 1 summarizes the experimental parameters used for the synthesis of zeolitic materials.

The zeolitic material obtained from the different experiments was filtered and washed with water, dried at room temperature and analyzed by means of XRD with $\text{Cu K}\alpha$ radiation. A semi-quantitative estimation of the zeolite contents was obtained for by comparing their cation exchange capacity (CEC) with the CEC value of a pure NaP1 commercial product (produced by Industrias Químicas del Ebro, IQE). The cation

exchange capacity (CEC) of the zeolitic materials was obtained using ammonium solutions following the methodology of the International Soil Reference and Information Centre⁶.

Table 1. Experimental parameters used for the pilot plant zeolite synthesis using the Teruel and Narcea fly ashes.

| | | | |
|------------------|--|-----------------|---|
| Reactor: | R-410-A, 10m ³ stainless steel 304 | P | water vapor pressure |
| Teruel FA | 1100 kg | Cooling: | 2 h |
| Narcea FA | 2200 kg | Filtration: | 55 pneumatic press filters, 90 °C, 1 h |
| water / fly ash: | 2 l kg ⁻¹ | Washing: | 85, °C, 40 min |
| t | 24 h (Teruel) 8 h (Narcea) | Products | |
| T | 150°C (Teruel) 125°C (Narcea) | Moisture | 48 % |
| C | 2 M NaOH (Teruel) 3 M NaOH (Narcea) | Zeolite content | Teruel, 45 % Narcea, 65 % |

Zeolite application

Although most of the pyrite slurry was extracted from the flooded area, high levels of heavy metals were still persistent in the soils due to the high degradability of the small proportions of the pyrite mud remaining in the soil. With the aim of testing the immobilization potential of the direct conversion products for the leachable heavy metals, the zeolitic product was dosed in different proportions and manually mixed in 8 experimental fields around the Vicario farm (San Lúcar la Mayor village, Figure 1). A blank field was kept as a reference. The main purpose of this task was to immobilize heavy metals, while phyto-remediation strategies are applied, to avoid the contamination of the underground water table.

The zeolitic products were manually mixed with the 25 cm top soil by applying different doses (Figure 2 and 3). The zeolites were applied in two different periods:

- NaP1 from Teruel fly ash (henceforth NaP1-TE): April 1999 in three experimental fields (Table 2 and Figure 2 and 3). One of them, was mixed with natural FeOOH to induce As precipitation.
- NaP1 from Narcea fly ash (henceforth NaP1-NA): December 1999 in four experimental fields (Table 2 and Figure 2).

Sampling of treated and reference soils was carried out in the following four different dates:

- 17/05/1999: Sampling fields 1 to 4.
- 25/06/1999: Sampling fields 1 to 4.
- 30/09/1999: Sampling fields 1 to 4.
- 27/04/2000 Sampling fields 1 to 4 and 5 to 8, and a blank field (9).

The samples from the different experimental fields and the reference field were sieved (to pass 260 µm) and acid digested following the a two step dissolution procedure⁷.

Furthermore, a fraction of each sample was leached following the DIN 38-414 procedure to determine the levels of extractable elements in water (100 g of sample in 1 l MilliQ grade water, stirring under room temperature, 24 h in a PVC container). The contents of major and trace elements in the solutions obtained from sample digestions and leaching experiments were determined by: a) Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) for major and selected trace elements (Ca, Al, S, Fe, Mg, Na, Mn, Ba, Cu, Ni, and Zn) and b) Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for most of the trace elements (As, Ba, Cd, Co, Cu, Ni, and Zn). In addition pH and the conductivity were measured in the leachates.

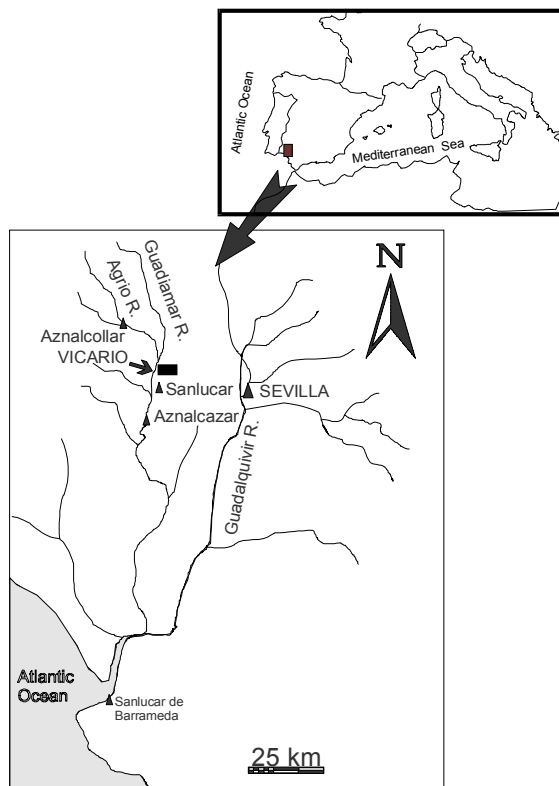


Figure 1. Location of experimental fields of Vicario.

Table 2. Doses of zeolitic products added to the selected fields.

| NaP1-TE zeolite: April 1999 | | | | |
|---------------------------------------|-------------------|------------|----------|-----------------|
| Field | Area | kg zeolite | kg FeOOH | Tm/ha |
| 1. | 20 m ² | 30 | | 15 |
| 2. | 20 m ² | 50 | | 25 |
| 3. | 20 m ² | - | 20 | 10 |
| 4. | 20 m ² | 20 | 10 | 5 (Fe)+10 (zeo) |
| NaP1-NA zeolite: December 1999 | | | | |
| Field | Area | kg zeolite | | Tm/ha |
| 5. | 5 m ² | 27 | | 54 |
| 6. | 5 m ² | 18 | | 36 |
| 7. | 5 m ² | 9 | | 18 |
| 8. | 5 m ² | 13.5 | | 27 |

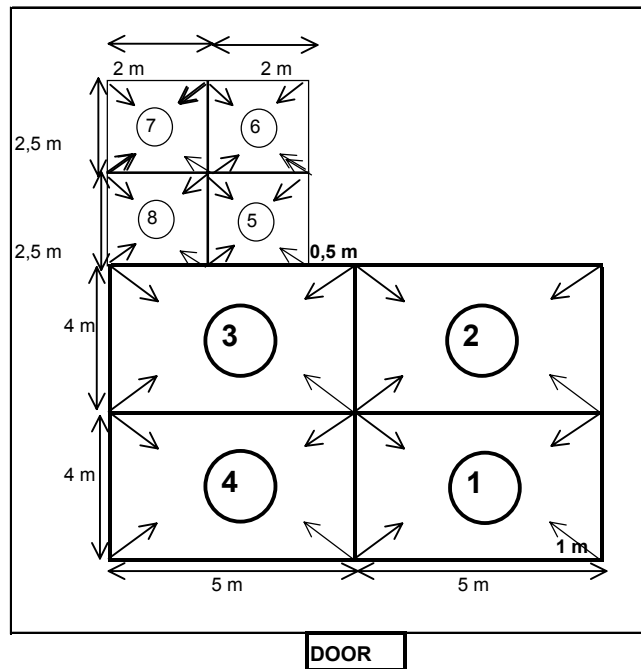


Figure 2. Distribution of the experimental fields.



Figure 3. Experimental fields during the addition of zeolites in December 1999.

RESULTS

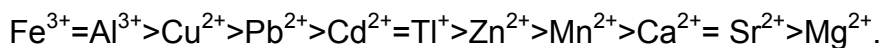
Table 3 shows the results on the conductivity, pH and bulk and leachable concentrations (mg/kg) of major and trace elements of the samples obtained in the last sampling period (27/04/2000, one year after the NaP1-NA addition and two years after the addition of NaP1-TE). Figure 4 shows the percentage of extractable concentrations (% of element leachable in water with respect to the bulk content) for the elements studied, as a function of the type and doses of the zeolitic product.

The results evidenced that two years after the flood, elements occurring in the pyrite slurry, such as, Cd, Co, Cu, Ni, and Zn are leached in a very high proportion. Thus, in the reference soil (field #9) the leachable contents of these elements reached: 45% Cd, 34% Co, 9% Cu, 11% Ni, and 58% Zn (Figure 4). The zeolite addition drastically decreased the mobility of these elements down to <1% after two years of the NaP1-TE zeolite addition with relatively low doses (15 and 25 tonnes per hectare). Similar results were obtained for NaP1-NA zeolite, but when high doses were applied (54 tonnes per hectare) probably due to the shorter reaction time (one year after the addition).

Table 3. Conductivity, pH, bulk content and leachable content in mg/kg of major and trace elements of the samples obtained in the last sampling (27/04/2000): Doses in tonnes of zeolite added per hectare of soil.

| | BLK | | NaP1-TE | | | | | | NaP1-NA | | | | | | | |
|----------------------------|-------|------|--------------|-------|-------|-------------------|------|------|--------------|-------|-------|-------|-------------------|------|------|------|
| | Bulk | Lea. | Bulk content | | | Leachable content | | | Bulk content | | | | Leachable content | | | |
| Tm/ha | 0 | 0 | 10 | 15 | 25 | 10 | 15 | 25 | 18 | 27 | 36 | 54 | 18 | 27 | 36 | 54 |
| Cond. ($\mu\text{S/cm}$) | | 2000 | | | | 2200 | 1360 | 870 | | | | | 2650 | 3100 | 3400 | 2650 |
| pH | | 3.5 | | | | 3.9 | 7.4 | 7.5 | | | | | 3.3 | 3.8 | 3.9 | 7.2 |
| Al | 60179 | 110 | 60969 | 61716 | 65657 | 33 | 7 | 7 | 65148 | 62863 | 66287 | 70296 | 601 | 82 | 119 | 1 |
| Ca | 12331 | 3133 | 13442 | 13250 | 15170 | 3920 | 2396 | 1154 | 13107 | 14583 | 14911 | 15562 | 3703 | 4683 | 4371 | 2255 |
| Fe | 39702 | 38 | 43907 | 34349 | 36485 | 2 | 7 | 5 | 47919 | 43191 | 45980 | 44053 | 18 | 5 | 6 | 4 |
| Mg | 5409 | 231 | 5392 | 5246 | 6162 | 179 | 119 | 89 | 6114 | 6176 | 6553 | 6866 | 346 | 370 | 330 | 229 |
| Mn | 635 | 154 | 707 | 666 | 827 | 145 | 12 | 2 | 620 | 756 | 707 | 873 | 131 | 211 | 148 | 37 |
| Na | 15188 | 80 | 15203 | 15873 | 15949 | 79 | 202 | 291 | 15947 | 16292 | 17287 | 17949 | 309 | 1295 | 2463 | 2417 |
| P | 341 | 1 | 421 | 343 | 388 | 1 | 1 | 2 | 397 | 427 | 441 | 474 | 1 | 1 | 1 | 1 |
| S | 10625 | 3560 | 9456 | 4406 | 3559 | 4041 | 2146 | 1126 | 14566 | 12515 | 13248 | 9002 | 5374 | 6178 | 6735 | 4030 |
| As | 107 | 0.2 | 104 | 51 | 46 | 0.1 | 0.1 | 0.2 | 152 | 114 | 118 | 96 | 0.1 | 0.1 | 0.1 | 0.1 |
| Ba | 276 | 0.3 | 328 | 306 | 320 | 0.2 | 0.2 | 0.1 | 348 | 340 | 357 | 387 | 0.1 | 0.1 | 0.1 | <0.1 |
| Cr | 51 | <0.1 | 57 | 55 | 60 | <0.1 | <0.1 | <0.1 | 65 | 60 | 65 | 71 | 0.1 | <0.1 | <0.1 | <0.1 |
| Pb | 261 | 0.1 | 311 | 181 | 165 | <0.1 | 0.1 | <0.1 | 422 | 400 | 372 | 328 | <0.1 | <0.1 | <0.1 | <0.1 |
| Sr | 99 | 1.8 | 115 | 111 | 125 | 3.3 | 2.1 | 1.7 | 113 | 111 | 116 | 127 | 0.9 | 2.9 | 3.0 | 2.0 |
| V | 68 | <0.1 | 86 | 58 | 73 | <0.1 | <0.1 | <0.1 | 82 | 60 | 62 | 68 | <0.1 | <0.1 | <0.1 | <0.1 |
| Cd | 1 | 0.5 | 1 | 1 | 1 | 0.4 | <0.1 | <0.1 | 2 | 2 | 2 | 2 | 0.7 | 0.5 | 0.5 | <0.1 |
| Co | 10 | 3.3 | 11 | 11 | 13 | 2.2 | <0.1 | <0.1 | 11 | 12 | 13 | 16 | 3.3 | 4.2 | 3.5 | 0.1 |
| Cu | 97 | 8.8 | 103 | 64 | 72 | 2.7 | 0.4 | 0.2 | 144 | 117 | 125 | 114 | 11.0 | 3.2 | 2.3 | 0.3 |
| Ni | 18 | 1.9 | 21 | 20 | 23 | 1.6 | 0.2 | 0.1 | 21 | 22 | 23 | 25 | 2.7 | 2.6 | 2.3 | 0.1 |
| Zn | 260 | 151 | 283 | 197 | 241 | 110 | 0.5 | 0.3 | 302 | 400 | 366 | 387 | 107 | 139 | 98 | 1.1 |

As shown in Table 3 the reference field has a pH of 3.5 after two years of the remediation activities, whereas the treated soils may reach up to 7.5 pH. This buffering of the acidity of the soils may also result in the precipitation of some of the metals. Prior studies on the heavy metal uptake from acid mine waters^{8,9} using NaP1 and 4A zeolites synthesized from fly ash demonstrated that the combination of the precipitation and the ion exchange processes accounts for the following affinity of the elements with respect to the zeolite addition:



It is important to note that the zeolitic product can selectively uptake heavy metals in a high Ca and Mg media.

As shown by Figures 3 and 5, the experimental fields with the addition of the zeolitic product show a significant plant grow, with respect to the reference field. In addition of the heavy metal sorption, the buffering effect of the zeolitic material is also contributing to the development of a soil substratum able to allow plant grow.

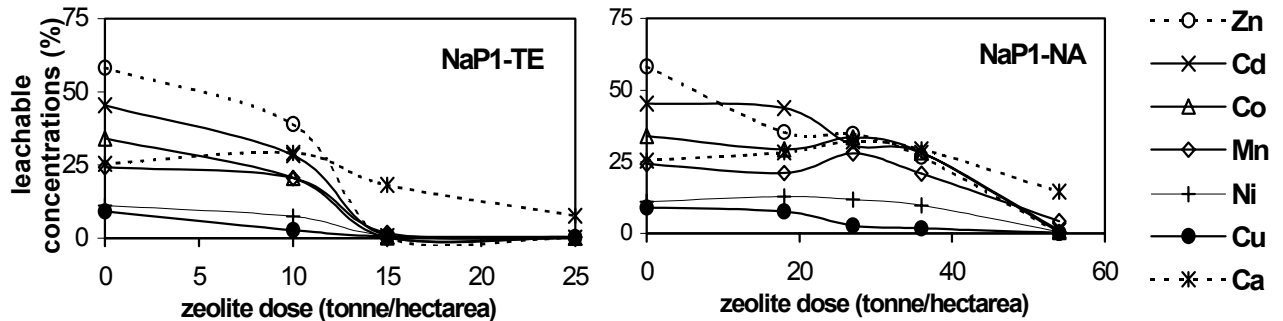


Figure 4. The % extractable (% of element leachable in water respect the bulk content) as a function of doses and type of zeolite added.



Figure 5. Experimental fields with the addition of the zeolitic product showing a significant plant grow, with respect to the reference field.

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REFERENCES

- [1] Grimalt, J.O., Ferrer, M. and Macpherson, E. *The science of the Total Environment*, 1999, 242, p.3.
- [2] Querol, X., Umaña, J.C., Plana, F., Alastuey, A., Lopez-Soler, A., Medinaceli, A., Valero, A., Domingo, M.J. and García-Rojo, E. *Fuel*, 2001, 80, p. 857.
- [3] Querol X., Moreno N., Umaña J.C., Medinaceli, A., Valero, A. International Workshop on Novel Products from Combustion Residues: Opportunities and Limitations. Morella (Spain) 7th June, 2001.
- [4] Querol, X., Plana, F. Alastuey, A. and López-Soler, A., *Fuel*, 1997, 76, p. 793.
- [5] Querol, X., Plana, F., Umaña, J., Alastuey A. Andrés, J.M., Juan, R. and López-Soler, A. Industrial applications of coal combustion wastes: zeolite synthesis and ceramic utilisation. European Coal and Steel Community Contract 7220/ED/079, Final report, 1999, 176 pp.
- [6] ISRIC, 1995. Procedures for soil analysis. Technical paper 9. International Soil Reference and Information Centre, FAO-UN, 9.1-9.13.
- [7] Querol, X., Alastuey, A., López Soler A., Mantilla, E. and Plana, F. *Atmospheric Environment*, 1996, 30, p. 3557.
- [8] Moreno, N., Querol, X. and Ayora, C. *Environmental Science and Technology*, 2001 (In press).
- [9] Moreno, N., Querol, X., Ayora, C., Alastuey, A., Fernández-Pereira, C. and Janssen, M. *Journal of Environmental Engineering*, 2001, (In press).