En este trabajo se ha estudiado el comportamiento como sorbente de la paligorskita en relación con el plomo, cobre, zinc y cadmio y de la sepiolita respecto del zinc y el cadmio. Ambos substratos minerales han sido considerados en la remediación de suelos contaminados por esos metales. Los experimentos muestran que las concentraciones de metal soluble así como las de metales lábiles disminuyen significativamente considerando cualquier concentración de los substratos estudiados (1, 2, 4%), aunque la máxima reducción se obtenía para dosis del orden del 4%. Los experimentos en columna también pusieron en evidencia una elevada reducción en la lixiviación de metales (50% para el plomo, 59% para el cobre, 52% para el zinc y 66% para el cadmio) cuando se aplicó una dosis del 4 % de paligorskita. La sepiolite también mostró una elevada reducción en la lixiviación de cadmio y zinc (69 y 52%, respectivamente). También se ha estudiado la capacidad de inmovilización de metales en suelos contaminados (del valle del Guadiamar, granja de El Vicario). Los resultados muestran que los materiales zeolíticos disminuyeron notablemente la lixiviación de Cd, Co, Cu, Ni y Zn. Esta inmovilización puede ser el resultado de la subida del pH desde 3.3 a 7.6 resultante de la alcalinidad de los materiales zeolíticos (trazas de cal libre en las cenizas o NaOH residual de la síntesis de las zeolitas). También se ha estudiado la adsorción de As(V) por parte de algunos oxihidróxidos de Fe naturales, por minerales de la arcilla y por $Al(OH)_3$ y FeOOH sintéticos. Los experimentos muestran una muy elevada capacidad de adsorción del As(V) tanto en el hidróxido de aluminio sintético (122 mg/g a pH 5) como en el oxihidróxido de Fe (76 mg/g a pH 5). Ambos adsorbentes fueron aplicados in situ para la remediación de dos emplazamientos con suelos contaminados por arsénico. Los mejores resultados se obtuvieron cuando se utilizaron el $Al(OH)_3$ y FeOOH sintéticos; Entre ambos redujeron entre un 55 y un 79 % de la fracción lixiviable (por agua) de uno de los suelos, y cerca del 100% en el otro, aunque en éste último el pH y el Eh eran más elevados.

The sorbent behaviour of palygorskite with respect to lead, copper, zinc and cadmium and that of sepiolite with respect to zinc and cadmium was studied in order to consider their application to remediate soils polluted with these metals. The soluble metal concentrations as well as the readily-extractable metal concentrations were substantially decreased at any concentration of minerals applied to soil (1, 2, 4%), although the highest decrease is obtained at the 4% dose. The column studies also showed a high reduction in the metal leaching (50% for lead, 59% for copper, 52% for zinc and 66% for cadmium) when a palygorskite dose of 4% was applied. Sepiolite also showed a high reduction in the leaching of cadmium and zinc (69 and 52%, respectively).The use of zeolitic material synthesized from coal fly ash for the immobilization of metals in contaminated soils in the Guadiamar valley (El Vicario farm) was also studied. The results showed that the zeolitic material considerably decreased the leaching of Cd, Co, Cu, Ni, and Zn. This immobilization could be a consequence of the rise in pH from 3.3 to 7.6 due to the alkalinity of the zeolitic material added (caused by traces of free lime in the fly ash, or residual NaOH from zeolite synthesis). The adsorption of As(V) by some natural Fe oxyhydroxides and clay minerals and synthetic $Al(OH)_3$ and FeOOH was also studied. The results showed a very high As(V) adsorption capacity on both synthetic Al hydroxide (122 mg/g at pH: 5) and Fe oxyhydroxide (76 mg/g at pH 5). The application of these adsorbents to arsenic immobilization in the remediation process of two polluted mining soils with some differences in their physicochemical characteristics was also studied. The best results were obtained when synthetic $Al(OH)_3$ and FeOOH were used; these materials decreased the water-extractable fraction of As by 55-79% for one soil and by nearly 100% for the other soil, the latter with higher pH and Eh values.

Soil Remediation in Mining Polluted Areas

/ ANTONIO GARCÍA SÁNCHEZ / ESTHER ALVAREZ AYUSO

Department of Environmental Geochemistry, IRNASA, CSIC, Apto 257, 37071 Salamanca, Spain.

INTRODUCTION

The main sources of metal pollutants in soils are mining and smelting activities, fossil fuel combustion, agricultural practices, industrial activities and waste disposal. The former stands out for its historical importance, for causing many severe pollution events in several countries and for being the source of all metals and metalloids considered most problematic in terms of environmental pollution and toxicity (Ross, 1994; Alloway, 1995). Among these toxic elements, Zn, Cd, Pb, Cu, and As (Sb) are usually present together in many ore minerals, and thus in the polluted surrounding environment of the mining sites.

The common total metal content in unpolluted-soils is below 1 mg/kg for Cd (Kabata-Pendias and Pendias, 1992), around 20–30 mg/kg for Cu (Alloway, 1995), below 20 mg/kg for Pb in remote or recently settled areas, but elsewhere, in soils with low-level pollution, between 30 and 100 mg/kg (Alloway, 1995), for zinc the common concentrations are ranged between 10 and 300 mg/kg, although its content is largely dependent on the composition of the parent rock materials (Lindsay, 1972; Kabata-Pendias and Pendias, 1992), for As is below 10 mg/kg (Adriano, 2001), and for Sb < 1 mg/kg (Bowen, 1979). These contents are greatly increased in soils polluted by mining activities, even reaching values which multiply by more than 100 times those present commonly in uncontaminated or low-contaminated soils. Once in the soil, the ore mine fragments disperse mechanically by wind or water or leach from tailing dams and undergo oxidation and other weathering reactions leading to metal ion distribution within the soil system in forms more mobile and also potentially more bioavailable than the original ones.

Lead is considered the least mobile heavy metal, especially under reducing or non-acid conditions. Complexation with organic matter, chemisorption on oxides and silicate clays and precipitation as carbonate, hydroxide or phosphate are the mechanisms responsible for lead immobilization, being all them favoured at higher pH, although, in alkaline soils its solubility may increase by formation of soluble Pb–organic and Pb–hydroxy complexes. The behaviour of copper is similar to that of lead, being also sorbed strongly on oxides, silicate clays and humus, and increasingly so as the pH is raised. Above pH 6 its precipitation as hydroxide, oxide or hydroxy-carbonates is also possible, nevertheless, under high pH conditions soluble hydroxy, carbonate and organic matter complexes are formed increasing significantly the low mobility shown by this element in near-neutral soils. Under acidic conditions, zinc, unlike

palabras clave: soil, trace toxic elements, low cost amendments, immobilization

key words: suelo, elementos traza tóxicos, enmiendas de bajo costo, inmobilización

*corresponding author: **antonio.gsanchez@irnasa.csic.es**

lead and copper, is one of the most soluble and mobile of the trace metal cations, being hold in exchangeable forms on clays and organic matter. At higher pH, however, chemisorption on oxides and aluminosilicates and complexation with humus lowers its solubility markedly. Cadmium is even more soluble than zinc in acidic conditions. This high mobility is attributed to the fact that cadmium sorbs rather weakly on organic matter, silicate clays and oxides unless the pH is higher than 6 (McBride, 1994).

Arsenate is the dominant form of available As in aerobic soils and is an analogous of phosphate (Meharg and Macnair 1992). Adsorption of arsenate on soil mineral surface is a very important process that affects its mobility and availability. The strong retention of arsenate by soil oxides and oxyhydroxides (Fe, Al, Mn) is caused by the formation of inner-sphere complexes (Fendorf et al., 1997), which is favoured to low pH, in consequence, soil amendments increasing the soil pH may results in As mobilization. Very little is known about the chemical behaviour of antimony in soils. Soluble fraction is probably present as Sb(V) species (antimonate), especially under oxidizing and basic conditions, and could be adsorbed by the same soil constituent that bind phosphate and arsenate (Adriano, 2001). In the supergene processes, antimony is considered relatively immobile under oxidizing conditions and/or with low available contents in soils (Boyle and Jonasson, 1984; Ainsworth et al., 1990, 1991; Hammel et al., 2000; Filella et al., 2002; Flynn et al., 2003). However, other recent studies, presented by Vink (1996) and Ashley et al. (2003), have pointed out the moderate mobility of the element.

In spite of the natural capacity of soils to reduce solubility and bioavailability of toxic metals by means of different mechanisms (precipitation, adsorption processes and redox reactions, at many of the most seriously polluted sites environmental risks persist, requiring immediate action. Because of the need of low-cost remediation methods and in situ inactivation techniques, such as chemical immobilization, soil amendments have been recently investigated, appearing as potential valuable alternative techniques for a wide range of polluted sites (Vangrosveld and Cunningham, 1998). Chemical immobilization limits the transport of pollutants into deeper soil layers and eventually into groundwater; moreover, revegetation of bare highly polluted sites might be possible after immobilization of phytotoxic trace elements (Vangronsveld et al., 1996). Many natural or synthetic materials have been tested, mainly in the last decade, in order to evaluate their ability to immobilize toxic trace metals.

Inactivation of lead in soils polluted from different sources has centred most of the attention. Most researches have studied the use of phosphate rocks *(Table 1)*. Phosphorus, independently of the source, lessens dramatically lead solubility by its precipitation as pyromorphite-like minerals, having, therefore, a great potential to cost-effectively treat Pb-polluted soils. Phosphate rocks have been also tested to remediate soils polluted with zinc, cadmium or copper *(Table 1)*. These treatments, although generally effective, do not attain the level of immobilization shown for lead. Other materials evaluated as soil amendments to stabilize Zn, Cd, Cu or Pb-polluted soils include zeolites, iron, manganese and aluminium oxides and oxyhydroxides and waste by-products rich in these oxides, alkaline agents such as lime, bauxite red-mud, beringite and fly ash, clay minerals and organic materials (compost, peat, manure, biosolids, leonardite, etc.) (Albasel and Cottenie, 1985; Vangronsveld et al., 1996; Berti and Cunningham, 1997; Narwal and Singh, 1998; Shuman, 1998; McBride and Martinez, 2000; Ciccu et al., 2002; Shuman et al., 2002; Farfel et al., 2005; Perez de Mora et al., 2007) *(Table 1)*. In general, these treatments lessen the risk of polluted soils limiting metal leaching and bioavailability. Nevertheless, some of them show an effect contrary to that pursued increasing metal solubility. This is the case of some amendments based on organic materials (Narwal and Singh, 1998; Shuman, 1998), those carried out with polynuclear Al-13 and Al-coated montmorillonite (Badora et al., 1998) and some of those performed with manganese oxides (McBride and Martinez, 2000).

Organic matter treatments to soils can have the effect of raising soil pH and adding to the exchange capacity both of which tend to decrease metal availability, however, these amendments also can add soluble organic ligands which have the effect of increasing the mobility of metals (Shuman, 1998). The effect of manganese oxide (k-birnessite) is attributed to the increase of soil pH which brings more metal into solution in organically complexed form (McBride and Martinez, 2000), and that of aluminium compounds to interactions between the applied aluminium and soil organic matter (Badora et al., 1998).

The main objectives of the present study were to determine the sorption capacity of some low cost materials with respect to lead, copper, zinc, cadmium, and arsenic, and to evaluate their effectiveness to reduce the mobility of these elements in polluted mining soils.

MATERIALS AND METHODS

Sorbents

The sorbent materials chosen for arsenic immobilization in polluted soils were synthetic Fe and Al hydroxides, limonitic minerals (mainly goethite with some impurities) of some ore deposits from Spain (Sierra de la Culebra (Zamora), Cerro del Hierro (Sevilla), Bufarreda (Asturias), Rio Tinto and Tharsis (Huelva)) and clay minerals (bentonite from Cabo de Gata (Almeria) and sepiolite from Orera (Zaragoza)). Synthetic Fe and Al hydroxides were prepared by precipitation in their chloride solutions following the method of Sims and Bingham (1968).

Sepiolite from Orera (Zaragoza, Spain) was tested for the immobilization of Cd and Zn in soils polluted with these elements.

Palygorskite from Bercimuel (Segovia, Spain) was tested for the immobilization of Pb, Zn, Cu and Cd in soils polluted with them.

The use of zeolitic products was investigated for the treatment of soils polluted with several trace elements (Co, Cd, Cu, Ni and Zn) after the Aznalcóllar mine spill. These products used were obtained at pilot plant scale by alkaline conversion of coal fly ash from the Teruel power plant (ENDESA) (Querol et al., 2001).

Polluted soils

The following polluted soils were chosen for this study:
A sandy soil (Cambisol) highly polluted with Cd and Zn as a result of the mining activity in the ZnS deposit of El Losar (Avila, Spain), which has been mined until recently. The Zn minerals are located in quartz veins within a granitic intrusion. The ore mainly contains wurtzite (α-ZnS) with minor sphalerite (β-ZnS) (contrary to that usual), which reveals an important presence of cadmium.

A soil highly Pb, Zn, Cu and Cd polluted as a result of the mining activity of

Material	Element	Sources	Reference
Lime	*Cd, Cu, Ni, Pb, Zn,Cr, Hg*	*Limestone processing*	*Li et al. (2000)* *Pyersinsky and Schwab (1993)* *Dermatas and Meng (1996)* *Bolan et al. (2003)*
Phosphate	*Pb, Zn, Cd, Cu* *Zn, Pb, Cu, Cd* *Pb, Zn, Cd*	*Phosphorite*	*Naidu et al.(1994)* *Mench et al.(1994 a,b)* *Chlopecka and Adriano (1996)* *Boisson et al. (1999a, b)* *Cao et al. (2003)* *Basta and McGowen (2004)* *Ma et al. (1993)* *Basta et al. (2001)*
Fly ash	*Cd, Pb, Cu, Zn, Cr*	*Coal thermal power plant*	*Carlson and Adriano (1993)* *Ciccu et al. (2001) (2003)* *Lau and Wong (2001)*
Activated slag *Montmorillonite* *Beringite* *Bauxite residue* *Cement*	*Cd, Pb, Zn, Cr* *Zn, Pb* *Zn, Cd* *Cd, Pb, Zn* *Cd, Pb, Zn* *Cd, Pb* *CR* *Cu,Zn, Pb*	*Blast furnace slag* *Mineral* *Coal Mine*	*Deja (2002)* *Auboiroux et al.(1996)* *Vangronsveld et al.(1995)* *Mench et al. (1994)* *Mench et al. (2000)* *Lombi et al. (1998)* *Li et al. (2001)*
Bentonite *Sludge* *Ettringite*	*Pb* *Zn, Cu, Cd* *Cd, Cu, Pb, Zn, Cr*	*Pozzolana* *Stone pulverization* *Bauxite*	*Geebelen et al. (2002)* *Krebs et al. (1999)* *Albino et al. (1996)* *Gougar et al. (1996)*
Zeolite	*Cd, Cu, Pb, Zn*	*Synthetic*	*Lin et al. (1998)* *Gworek (1992a, b)* *Chlopecka and Adriano (1996)* *Friels et al. (2003)* *Querol et al. (2006)*
Gypsum *Vermiculite* *Red-mud*	*Cd, Cu, Pb* *Cd, Cu, Pb, Zn* *Pb, Cd, Cu, Zn*	*Industrial by-products* *Mineral* *Industrial by-products*	*Illera et al. (2004)* *Abollino et al. (2007)* *Gray et al. (2006)* *Ciccu et al. (2003)* *Lombi et al. (2003)*
Oxides-hydroxides *(Fe, Al, Mn)(Fe, Al, Mn)*	*As, heavy metals*	*Mineral or* *Industrial by-products*	*Mench et al.(1994 a,b)* *Mench et al. (2000)* *Chlopecka and Adriano (1996, 1997)* *Berti and Cunningham (1997)* *Boisson et al. (1988, 1999a,b)* *McBride and Martínez (2000)* *Lombi et al. (2003)* *Garcia-Sanchez et al. (2002)*
$FeSO_4$	*As*	*Synthetic*	*Warren et al. (2003)* *Moore et al. (2000)*
Palygorskite *Sepiolite* *Vermiculite* *Al-smectite*	*Cd, Zn* *Cd, Zn, Pb, Cu* *Cu, Pb, Zn, Cr, Co* *As*	*Clay mineral* *Clay*	*Alvarez-Ayuso and Garcia-Sanchez (2003a, b)* *Abollino et al. (2007)* *Vangronsveld and Cunninghan (1998)*

Tabla 1. *Inorganic amendments for metal immobilization in polluted soils.*

sphalerite, galena and chalcopyrite deposits in Santibañez de Bejar (Salamanca, Spain).

Two As polluted soils at tungsten (arsenic) mines, Barruecopardo and Terrubias (Salamanca, Spain) were chosen. In this area waste rockdumps, with different barren rocks (mainly granites and shales), fine-grained ore minerals and ore weathering products are present (mainly scorodite, goethite, gypsum and other metal hydroxides; Antona et al., 1994).

Several soils of a plot at the Guadiamar valley (El Vicario farm, Sevilla, Spain) polluted by the Aznalcollar mine spill.

Soil treatment with additives

Except for the soils of the Guadiamar valley, studies were performed at lab-scale. Thus, the soil samples (200 g) were mixed thoroughly with the different additives (2 g or 10 g) by shaking (2 h) on a vertical rotary shaker (50 turns/min), after which the samples were transferred into adequate cultivation pots and were kept at 70 80% of their water-holding capacity and at a temperature of 25°C for 4 weeks.

In the Guadiamar valley zeolitic product was dosed in proportions of 10000, 15000 and 25 000 kg/ha and manually mixed with the 20 cm top soil in three experimental plots (20 m^2 each). Sampling of treated soils was done 1 year and 2 year after amendments.

Batch sorption tests

Sorption studies were carried out in centrifuge tubes by subjecting a given dose of sorbent to a shaking period of 6 h with 25 ml of metal solution on a vertical rotary shaker (50 turns/min) in a chamber set at 22 ºC. The sorbent was separated using a centrifugation step (4000 rpm) over 10 min. Metal concentrations in the supernatant were analysed by AAS. In the case of As its concentration was determined following the method of Jimenez et al. (1996) by HG-AAS. Its speciation (As^{+5} and As^{+3}) was determined following the method of Glaubig and Goldberg (1988).

Metal extractions

The soil soluble fraction was evaluated following the DIN 38414-S4 (1984) procedure. This method used a deionized water to solid ratio of 1 l:100 g and a shaking period of 24 h. The extractable fraction was evaluated following the DIN V 19730 (1993) procedure. In this method a soil/extractant ratio of 1:2.5 was stirred for 2 h using 1 M NH_4NO_3 solutions as extractant agent.

Soil column leaching

The mobility of metals was studied in glass columns packed with 100 g of soil. The columns (3x15 cm) were leached with 400-500 ml (560-750 mm annual rainfall) of deionized water under a saturated flow regime, collecting successive leach fractions of 25 ml using a fraction collector (Foxy Jr., ISCO).

RESULTS AND DISCUSSION

Sorption isotherms

The sorption isotherms of palygorskite are shown in *Fig. 1.* The sorption data were fitted to the Langmuir equation, X/M=(KbCe)/(1+KCe), where X/M is the amount of solute retained per unit weight of the sorbent, Ce is the equilibrium concentration of solute remaining in the solution, K is the equilibrium constant (affinity term) and b represents the maximum amount that can be sorbed. According to b parameter (mmol/g) sorption on palygorskite followed the order: Cu>Pb>Zn>Cd. This

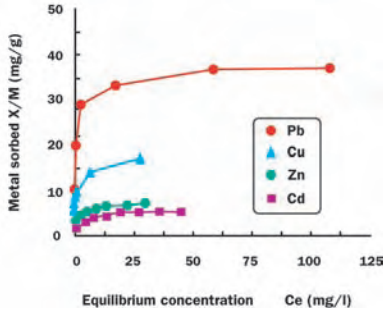

Fig 1. *Sorption isotherms of Pb, Cu, Zn and Cd on palygorskite.*

sequence follows quite accurately the facility of cations to hydrolyse (log KCu: 6.3; log K_{Pb}: 6.2; log K_{Zn}: 5.0; log K_{Cd}: 4.1; (K: first hydrolysis constant); Burriel et al., 1989), suggesting that sorption by reaction with silanol groups, really numerous on the surfaces of palygorskite, is the main mechanism responsible for metal cations retention.

The sorption capacities shown by palygorskite for these metals and specially the retention mechanism mainly involved in such sorption processes suggest that this mineral could be an effective amendment to remediate soil polluted with these toxic metals.

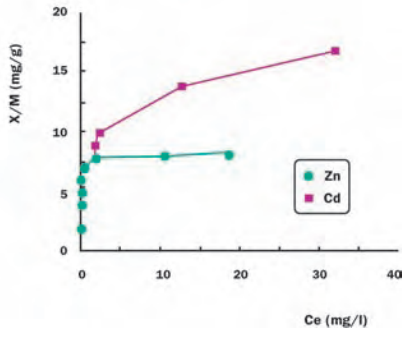

Fig 2. Sorption isotherms of Cd and Zn

The sorption isotherms of sepiolite are shown in *Fig. 2.* The Langmuir model also describes well the sorption processes. According to b parameter the sorption capacity of sepiolite for both metal cations surpasses clearly its low CEC (16.5 cmol(+)/kg). Therefore, a sorption mechanism different from the cation exchange process has to be involved in such retentions. The retention order (Cd > Zn) does not agree with the facility of cations to hydrolyse (log K_{Zn}: 5.0, log K_{Cd}: 4.1; (K: first hydrolysis constant); Burriel et al., 1989), suggesting that sorption by reaction with silanol groups, also numerous on the external surfaces of this mineral, is not the main mechanism responsible for their retention either. The hydrated radii (rh) of cadmium and zinc are very similar to that of magnesium (rh_{Cd}: 4.26 Å, rh_{Zn}: 4.30 Å, rh_{Mg}: 4.28 Å; Nightingale, 1959), making feasible the sorption of cadmium and zinc by replacement of magnesium located at the edges of the octahedral sheets in which its coordination sphere is completed with two H_2O molecules. The higher retention of cadmium with respect to zinc has to be related to their hydration energy values, ΔG_h, ($\Delta G_{h,Cd}$: -1755 kJ/mol, $\Delta G_{h,Zn}$: -1955 kJ/mol; Marcus, 1991). Cadmium requires less energy to break its coordination sphere of H_2O molecules, which results in favouring its sorption. The replacement of magnesium located at the edges of the octahedral sheets of sepiolite by metal cations was proved by Corma et al. (1985) studying a copper-exchanged sepiolite. Afterwards, Brigatti et al. (1996) also suggested this replacement when studing the sorption of zinc and lead on sepiolite, mainly in the case of zinc. The sorption capacity shown by sepiolite for both metals and mainly the retention mechanisms involved in such sorptions (replacement of structural cations at the edges of octahedral sheets and, in a lesser extent, reaction with silanol groups of mineral external surfaces) suggest that this mineral could be an effective amendment to remediate soil polluted with cadmium and/or zinc.

The adsorption capacity of As(V) by the different solids *(Fig. 3)* follows a sequence (as the isotherm parameter b decreases): synthetic $Al(OH)_3$ > synthetic FeO(OH) >>> goethite (Zamora) = goethite (Sevilla) >goethite (Huelva, Tharsis) > goethite (Huelva, Rio Tinto) >> goethite (Asturias) > bentonite (Almeria) > sepiolite (Zaragoza).

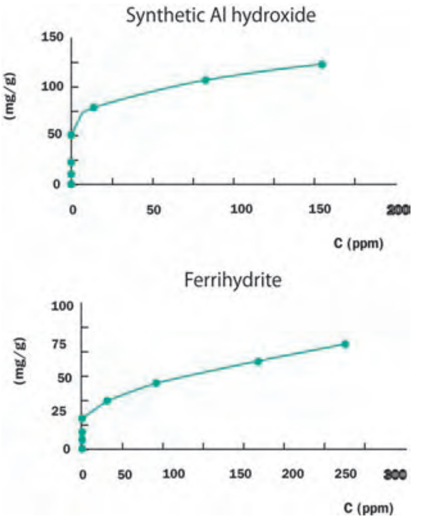

Fig 3. Sorption isotherms for synthetic Al hydroxide and ferrhydrite (pH 5); C: concentration in the equilibrium.

The great difference in the adsorption capacity between synthetic Al and Fe oxyhydroxides and the goethite samples studied must be due to the amorphous character of synthetic oxyhydroxides, and so to the larger number of reactive hydroxyl gropus. In addition, the adsorption capacity differences observed between the natural limonite samples could be a consequence of the presence of some impurities (mainly quartz and calcite) in the Huelva and Asturias samples, and their smaller specific surface areas. On the other hand, the lower As(V) adsorption capacity of the clays (bentonite and sepiolite) could be due their lesser number of reactive hydroxyl groups. These results agree well with the findings of previous works: amorphous Al hydroxide (Anderson and Malotky, 1979), adsorption maxima of ~110 mg/g at pH 5; amorphous FeOOH with adsorption capacity for arsenate of 112 mg/g at pH 4 (Pierce and Moore, 1982); synthetic ferrihydrite, which shows an arsenate adsorption capacity of 143 mg/g (Raven et al., 1998); freshly prepared FeOOH (Harrison and Berkheiser, 1982), where the arsenate anion demonstrated a very strong affinity for the oxide surface and the adsorption isotherm attained a plateau value of 160 mg/g; goethite (Manning and Goldberg, 1996, 1997; Hingston et al., 1971), having an As(V) adsorption range between 3 and 11 mg/g with a maximum at pH 3; and montmorillonite (Frost and Griffin, 1977), which adsorbed As(V) to a lesser extent, ~0.65 mg/g. The ferrihydrite isotherm shows less affinity for As(V) anions than the synthetic $Al(OH)_3$ isotherm. These different affinities for As(V) as well as the observed difference in their adsorption capacities, could be due to a smaller degree of crystallinity of the Al hydroxide with respect to the Fe oxyhydroxide (two-line ferrihydrite).

Soil treatments

The effect of soil treatment with palygorskite on the mobility of lead, copper, zinc and cadmium (evaluated by means of water and NH_4NO_3 batch extractions) is indicated in *Fig. 4.* Palygorskite showed an immobilizing effect for the four metal cations at any concentration applied to soil, independently of extract agent employed. At the highest palygorskite dose (4%) the soluble lead, copper and cadmium concentrations turn out to be almost completely immobilized while that of zinc decreased 60.4%. At this same palygorskite dose the readily-extractable concentrations decreased to 91.7% for Pb, 77.0% for Cu, 76.4% for Zn and 47.5% for Cd. Although the best results are obtained for the highest amendment dose, when lower doses are applied (1 and 2%) the soluble and the readily-extractable metal concentrations were also greatly reduced.

The effect of soil treatments with sepiolite on the mobility of cadmium and zinc (evaluated by means of water and NH_4NO_3 batch extractions) is indicated in *Fig. 5.* Sepiolite shows an immobilizing effect for both metal cations at any concentration applied to soil, independently of extractant agent employed. The soluble cadmium and zinc concen-

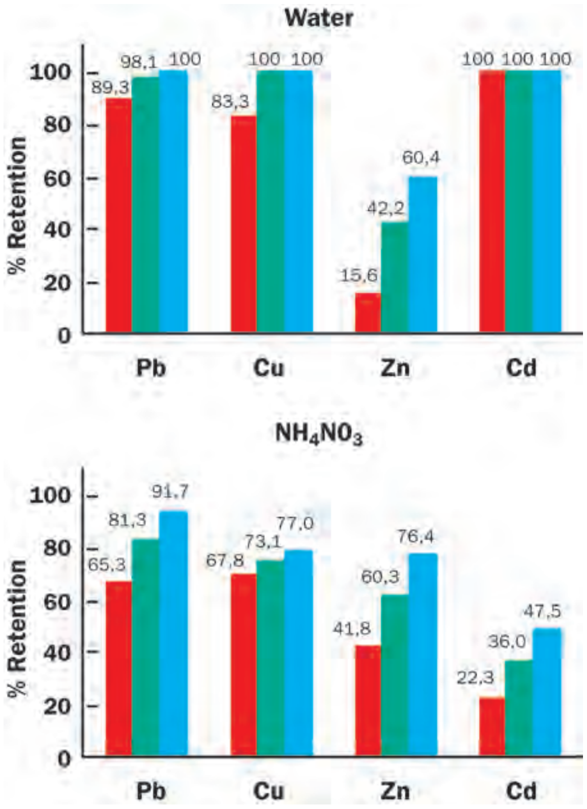

Fig 4. Effect on metal mobility of soil treatment with palygorskite

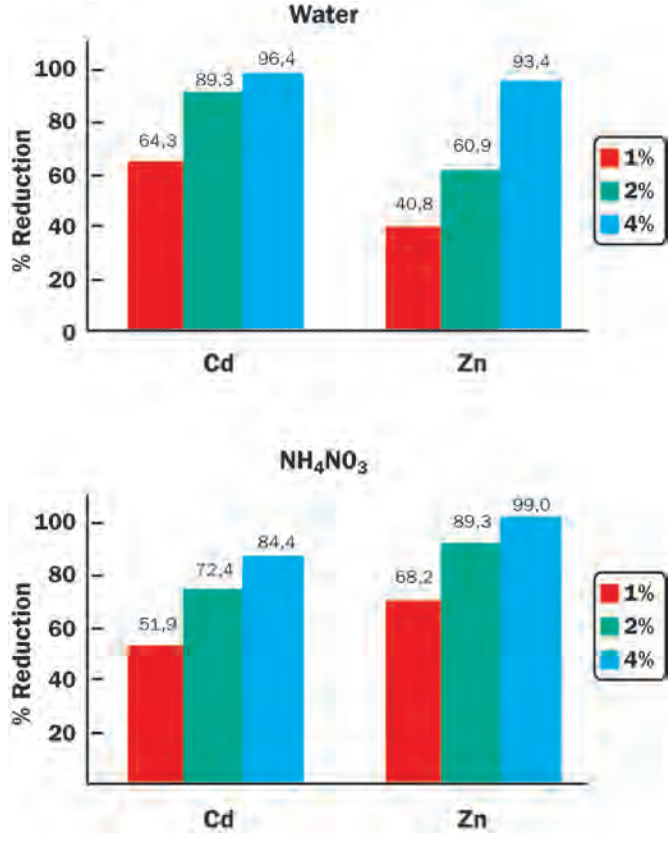

Fig 5. Effect on metal mobility of soil treatment with sepiolite.

trations decrease 96.4 and 93.4%, respectively, at the highest sepiolite dose applied (4%), while their extractable concentrations undergo a decrease of 84.4 and 99.0%. Although the best results are obtained for the highest sepiolite dose, when lower doses are applied (1 and 2%) the soluble and the extractable cadmium and zinc concentrations are also strongly reduced. The best ameliorative effect shown by sepiolite for extractable zinc with respect to extractable cadmium, despite its higher sorption capacity for cadmium has to be related to the concentration effect. The much greater zinc concentration with respect to cadmium (300 vs. 6.28 mg/kg) could act by displacing its sorption reaction resulting, therefore, as more favourable.

The effect of the various soil additives on the mobility of As (evaluated by means of water extraction) is presented in *Fig. 6*. The best results were obtained for the Barruecopardo soil with ferrihydrite and amorphous $Al(OH)_3$ as additives. In both cases the water-extractable fraction of As was decreased by 100%. In the other soil studied (Terrubias), only 55-79% of As was adsorbed on Fe and Al oxyhydroxides, in spite of its smaller water extractable content. This could be due to the greater arsenite content in this soil, which might be a consequence of the lower pH and Eh (Garrells and Christ, 1965). This form could be adsorbed to a lesser extent than As(V) by the soil additives (Bowell, 1994; Manning and Goldberg, 1997; Smith et al., 1999).

Fig. 7 shows the percentage of water extractable concentrations for six metals depending on the zeolite doses applied to polluted soils in the area of El Vicario. The results demonstrated that 2 years after the Aznalcollar spill, elements occurring in the pyrite slurry, such as Cd, Co, Cu, Ni, and Zn, were leached in a very high proportion. In the control soil the leachable contents reached 45% for Cd, 28% for Co, 7% for Cu and Ni, and 53% for Zn. The mobility of these elements drastically decreased down to 1% after 1 and 2 years of the zeolite addition with relatively low doses (15000 and 25000 kg/ha). Concentrations of metals in leachates of control samples for the two sampling periods reached values of 14692 and 16900 µg Zn/l, 805 and 1130 µg Cu/l, 282 and 280 µg Co/l, 4 and 60 µg Pb/l, 165 and 220 µg Ni/l, 56 and 80 µg Cd/l; and 20 and 40 µg As/l. In the field, with a zeolite dosage of 25000 kg/ha, the water extractable contents are reduced down to 37 and 10µg Zn/l, 28 and 20 µg Cu/l, 9 and 10 µg Ni/l, 15 and 20 µg As/l and <1 µg/l of Cd, Co and Pb. As shown in *Fig. 7*, the control field had a pH of 3.5 and 3.9 after 1 and 2 years of the clean-up activities, whereas the treated soils reached pH values of 7.5 and 8.0 as a consequence of the alkalinity of the zeolitic material. The buffering of the acidity of the soils may also result in the precipitation of some of the metals or in the adsorption of cations on clay surfaces.

Prior studies of heavy metal sorption from acid mine waters using NaP1 and 4A zeolites synthesized from fly ashes have demonstrated that the combination of the precipitation and ion exchange processes accounts for the following affinity of the elements with respect to the zeolite addition: $Fe^{+3} = Al^{+3} > Cu^{+2} > Pb^{+2} > Cd^{+2} = Tl^{+} > Zn^{+2} > Mn^{+2} > Ca^{+2} = Sr^{+2} > Mg^{+2}$ (Querol et al., 2006). It should therefore be pointed out that the zeolitic product can selectively uptake metals in a high Ca and Mg media. The experimental fields with the addition of the zeolitic product showed significant plant growth, with respect to the control field, probably as a consequence of the heavy metal sorption and the pH buffering effect of the zeolitic material. The following plant species were identified: *Lupinus angustifolious, Oxalis pes-caprae, Lamarckia aurea* and *Mentha piperita*.

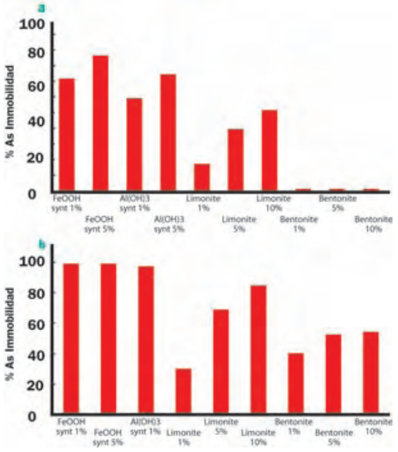

Fig 6. Effect on arsenic mobility in soils treated with different additives (a: Terrubias soil, and b: Barruecopardo soil).sepiolite.

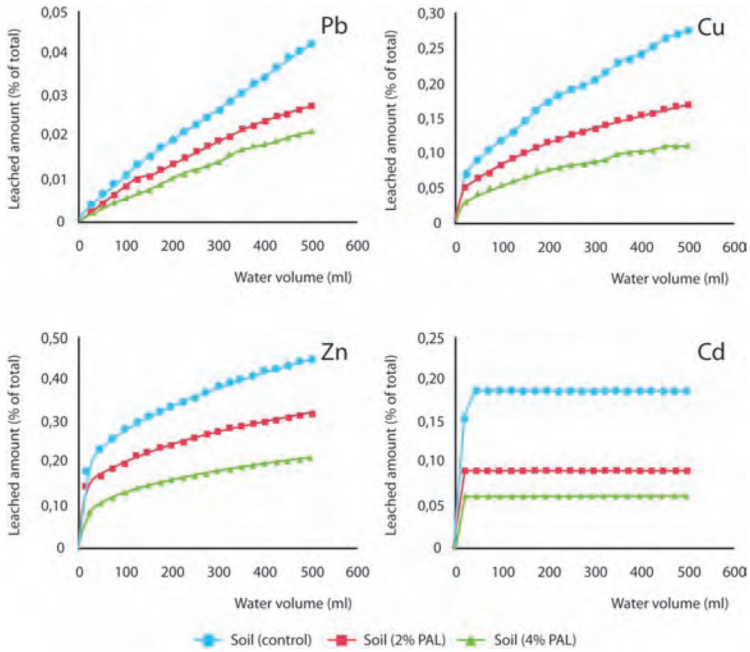

Fig 8. Cumulative curves of metal leaching for the soil treated with palygorskite.

The results obtained from these batch studies give a measure of metal potential mobility as an approximation to the potential risk of natural waters or plants pollution, allowing to determine the suitability or not of the soil treatment. Nevertheless, to evaluate a more real mobility (downward displacement), in order to establish the risk of groundwater pollution, leaching studies in soil columns should be performed (Tyler and McBride, 1982).

Soil column leaching studies

The percolation curves of lead, copper, zinc and cadmium (in the cumulative form) obtained from the untreated soil and from the soil amended with palygorskite are shown in *Fig. 8.* The total metal amounts leached from the untreated soil column along the percolated water volume, which is equivalent to the annual rainfall, represent 0.04% of the total content for lead, 0.27% for copper, 0.46% for zinc and 0.19% for cadmium. The shape of the percolation curves showed an increase in its concavity following the order Pb<Cu<Zn<Cd. This sequence, in agreement with the increasing mobility shown commonly by these metals, is indicative of metal leaching rate. Nearly all the percolated amount of cadmium is quickly leached, finishing its total elution long before the percolation of all water volume. Most of the eluated amount of zinc (about 60%) is leached in the three first fractions, after which there is a progressive decrease in the amount leached, but without finishing its elution at the percolated water volume, nevertheless, the shape of this concave cumulative curve, resulting from this slow and constant decrease in the metal amount leached, suggests that the end of leaching of zinc potentially leachable with water is relatively close. The leaching behaviour of copper, although quite similar to that of zinc, is slower and its total elution seems to be also further. The downward displacement of lead appears to be low; nevertheless, its cumulative curve shows a linear shape indicating a constant and slow leaching from the beginning which could be considerably extended increasing the percolated water volume. The total metal amounts leached from the column of soil amended with a palygorskite dose of 2% along

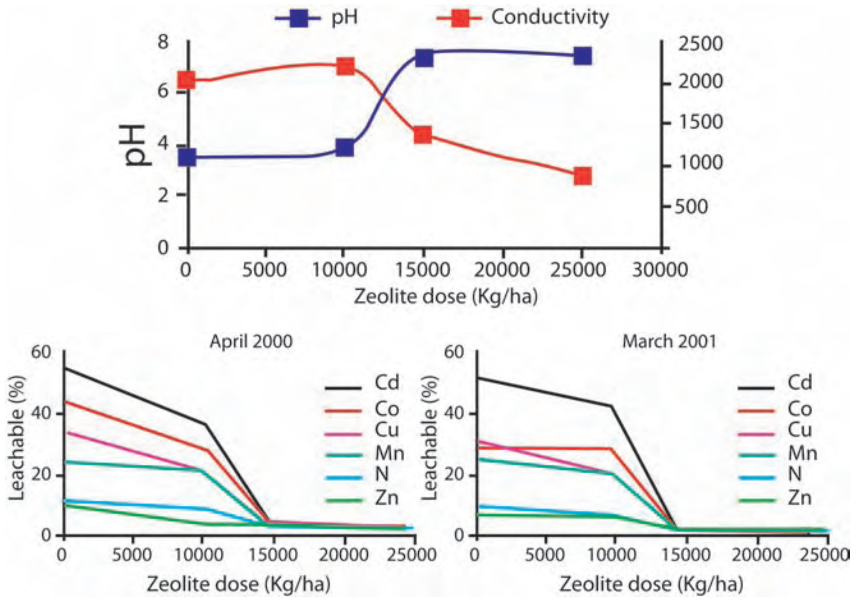

Fig 7. pH and conductivity (27/04/2000) (a) and water extractable proportions for metals (% of element leachable in water with respect to the total content) as a function of the zeolite dosing after 1 and 2 years (27/04/2000 (b) and 23/03/2001 (c), respectively).

the percolated water volume represent 0.03% for lead, 0.17% for copper, 0.33% for zinc and 0.09% for cadmium. At a palygorskite dose of 4% these amounts are reduced to 0.02% for lead, 0.11% for copper, 0.22% for zinc and 0.06% for cadmium, representing a metal leaching decrease with respect to the untreated soil of 50% for lead, 59% for copper, 52% for zinc and 66% for cadmium. In addition to this great reduction in the metal amounts leached, the cumulative curves (at any amendment dose) turn to a more concave form (even those of lead), which suggests a reduction of the extend of metal leaching with the increase of the percolated water volume.

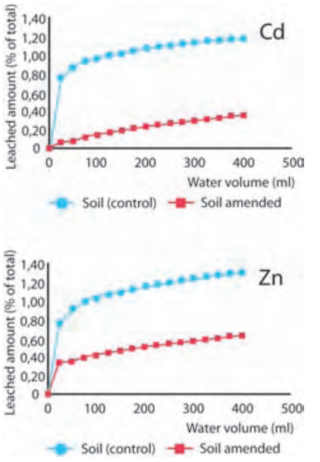

Fig 9. . *Cumulative curves of metal leaching for the soil treated with sepiolite.*

The percolation curves of cadmium and zinc in soil amended with sepiolite are shown in *Fig. 9.* The total cadmium amount leached from the untreated soil column along the percolated water volume, which is equivalent to the annual rainfall, represents 1.2% of the total content and that of zinc 0.56%. Most of the eluated amount of cadmium and zinc (approx. 60%) is leached in the two first fractions, mainly in the first one. After this very early stage the amounts leached decrease greatly undergoing a progressive decrease, but without finishing the amounts of cadmium and zinc potentially leachable at the percolated water volume. Nevertheless, the shape of the percolation curves reveals an increase in their concavities with a clear tendency to reach the plateau. This indicates that although the leaching of cadmium and zinc potentially leachable with water has not finished at the percolated water volume, it would tend to finish with a moderate increase in the amount of percolated water. The total cadmium amount leached from the column of soil amended with sepiolite along the percolated water volume represents 0.37% of the total content and that of zinc 0.27%. The amendment lessens greatly the amount of cadmium and zinc leached, 69.2 and 51.8%, respectively. The main decrease is produced in the first eluated fractions. For cadmium, in the two first fractions this decrease reaches values of 90–85% which diminish progressively to be cancelled out before the middle of the percolated water volume. For zinc, the leaching decrease experienced in the first fractions is lesser, but after a progressive diminution in its value it stands at approximately 20% all along the rest of percolated fractions.

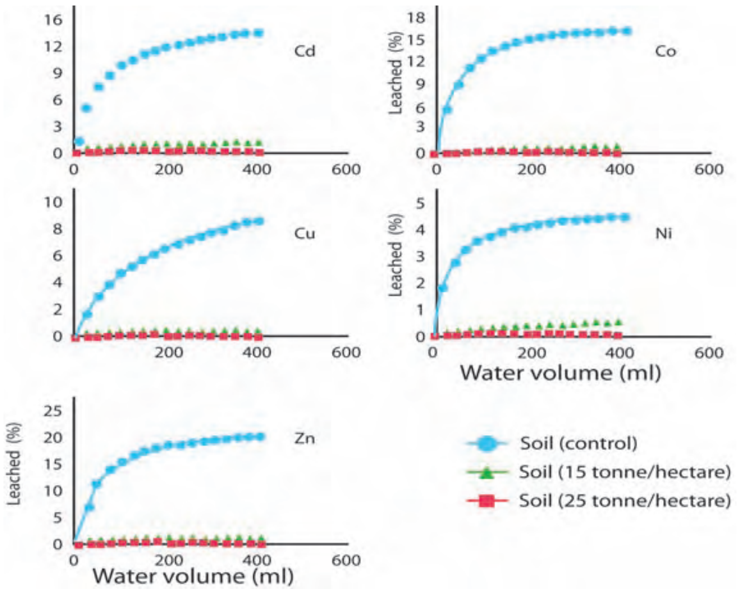

Fig 10. *Cumulative curves of metal leaching for the soil treated with zeolite.*

The results of the leaching tests performed with the control soil and with the soils amended with zeolite in plots of the El Vicario area (at doses of 15000 and 25000 kg/ha) are presented in *Fig. 10* for Cd, Co, Cu, Ni and Zn. In the case of the control soil, percentages of the metal leached with respect to the total metal content are 13% for Cd, 16% for Co, 9% for Cu, 4% for Ni and 19% for Zn. Most of the eluted amounts of Cd, Co, Ni and Zn (>50%) were leached in the first two fractions (50 ml). Subsequently, there was a progressive decrease in the leached amounts. The percolation curves tend to reach the plateau, indicating that the water leachable fraction of the metals was almost completely releaed (for the current stage of the weathering of sulphide phases). In the case of Cu, percolation curves suggest a less effective leaching, probably because of its lower mobility due to its strong sorption on clays when pH is increased (McBride, 1994). In the case of the soil amended with the zeolite dose of 15000 kg/ha, the leached fractions of metals account for 1.1% of the total content of Cd, 0.6% of Co, 0.1% of Cu, 0.6% of Ni and 0.9% of Zn. For the highest zeolite dose (25000 kg/ha) these proportions are reduced to 0.2% for Cd, Co, and Ni, and <0.03% for Co and Zn. Thus the amendment considerably reduced the leached metal amount, to about 1–10%, even at the lowest zeolite dose applied to soil. The leaching rate decreased along the percolated water volume. Moreover, the cumulative curves took on a more concave form, reaching even the plateau at the highest amendment dose indicating that, in this case, the leachable fraction of metal was completely extracted. In the light of these results it could be concluded that zeolite amendment decreases the leaching of metals, thereby eliminating or considerably minimizing the risk of groundwater pollution.

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