ZEOLITE SYNTHESIZED IN POLLUTED SOILS TREATED WITH FLY ASH. THE ROLE OF THE SYNTHETIC MINERAL IN HEAVY METAL MOBILIZATION

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INTRODUCTION

Over the last few years a great deal of research has been carried out in order to develop remediation methods for reducing environmental risks due to polluting metals. Some of these lean towards toxic element immobilization in natural and synthetic zeolite (Lin *et al.*, 1998; Moreno *et al.*, 2001a, 2001b; Castaldi *et al.*, 2004; Querol *et al.*, 2006). Zeolite can be synthesized from different source materials (Murat *et al.*, 1992; Ruiz *et al.*, 1997; Gualtieri, 2001) and fly ash is one of the most used (Shigemoto *et al.*, 1993; Berkgaut & Singer, 1996; Shih & Chang, 1996; Querol *et al.*, 2002). The synthetic mineral can be added to polluted soils (Lin *et al.*, 1998; Querol *et al.*, 2006; Rayalu *et al.*, 2006) or crystallized directly in those contaminated (Terzano *et al.*, 2006) in order to solve environmental problems. To determine the effective contribution of zeolite to soil remediation, the chemical extraction could be a useful method. This is based on a one-step extraction (Li *et al.*, 1995; Quevauviller *et al.*, 1996) and/or multi-step sequential extractions (Tessier *et al.*, 1979; Campanella *et al.*, 1995; Quevauviller *et al.*, 1997). Despite their rapidity and relative simplicity, the one-step techniques cannot easily find a single effective reagent to dissolve quantitatively the heavy metal non-residual forms without attacking detrital forms. On the contrary, the sequential extraction gives more detailed information on possible metal chemical forms in addition to the physico-chemical availability and the mobilization of toxic elements.

In this study a soil sample – treated with coal fly ash and artificially contaminated, in separate experiments, with a high concentration of Ni, Pb, Zn, Co and Cr^{6+} – was used for synthesizing zeolite at low temperatures. The role played by this mineral in the immobilization of heavy metals was investigated. The synthesis was carried out both in the laboratory and on a bench-scale for 1 year with the aim of developing a method for reducing the mobility and the availability of the toxic element in a natural and economical way, based on the direct formation of zeolites in contaminated soil by using fly ash under environmental conditions.

STARTING MATERIALS AND EXPERIMENTAL PROCEDURE

The experiments were carried out using coal fly ash obtained from the ENEL thermoelectric power plant of Brindisi (Italy) and a soil sample collected from an area near Potenza (Southern Italy).

A 1:1.2 weight ratio of fly ash and NaOH was grounded in a mechanical mortar for a few minutes, and then the well-mixed powder was fused at 550°C for 1 h in accordance with previous studies (Chang & Shih, 1998). The resultant fused mixture was cooled and milled again. The powder thus obtained was mixed with the soil contaminated artificially with Ni, Pb, Zn, Co and Cr^{6+}, in separate experiments, and stirred for 1 h. Finally, the mixture was incubated in a water bath at 27°C.

The procedure used in bench-scale experiments was the same in terms of soil contamination, relative amounts of fly ash and mode of incubation. In fact, a particular type of water bath was set up in order to carry out experiments using about 33 kg of artificially contaminated soil and 7.8 kg of pre-fused fly ash. The water content was kept constant. The temperature of incubation was around 30°C, ranging from 27 to 31°C. This temperature value was chosen in order to approximate environmental conditions as much as possible and speed up the reaction time a bit.

In both experiments samples were collected periodically up to 1 year of incubation.

The pellets were centrifuged at 4500 rpm for 15 min, washed twice with Milli-Q water, centrifuged and dried at 80°C overnight. The same amount of each pellet was finally used for mineralogical, morphological and chemical analyses.

The characterization of zeolites was performed by XRD using a Rigaku Rint 2200 diffractometer with Cu*K*α radiation and graphite monochromator. The morphology was observed by FE-SEM (Zeiss Supra 40).

Adsorbed and exchangeable of different toxic elements was determined by ammonium acetate extraction (single-step chemical extraction). The stability and speciation of Ni and Pb were determined by modified BCR three-step sequential extraction proposed by Quevauviller *et al.* (1997). The solid residues of a single-step chemical procedure were washed twice with Milli-Q distilled water, dried overnight and subjected to a sequential chemical extraction. The procedure was conducted in three steps, assuming that the forms of heavy metals extracted are: 1) exchangeable and/or weakly bonded with carbonate fractions; 2) correlated with reducible phases; 3) organically bonded and sulphide fractions. The reagents for trace metals analysis were the following: i) first step (exchangeable fractions and fractions bounded with carbonate): 0.11 M acetic acid solution (*p*H 2.86); ii) second step (reducible fraction): 0.1 M of hydroxylamine hydrochloride solution, acidified by the addition of HNO_3 (65%); iii) third step (oxidisable fraction): hydrogen peroxide (acid-stabilized at *p*H 2-3) and H_2O_2 at *p*H 2.0-3.0. The solid residues of each extraction step were also analysed by XRD.

RESULTS AND DISCUSSION

The results of contaminated soil incubated at 27°C in laboratory experiments indicate that the formation of zeolite X takes place in all the samples readily after 1 month, and the amount of the newly formed mineral generally increases during the entire incubation period. The data from bench-scale experiments using only Ni and Pb contaminated soil confirm the general trend of zeolite formation resulting from laboratory experiments. The presence of different toxic elements does not exert any influence on zeolite crystallization.

The toxic elements concentration determined after a single-step chemical extraction both in laboratory and bench-scale experiments shows that a smaller amount of heavy metals was extracted from the samples of soil containing zeolite. Starting with the 1-month-incubated soil samples, a reduction in the total metal content of the ammonium acetate fraction can be seen (Fig. 1). When applying the modified BCR procedure to the samples derived from bench-scale experiments, the average quantities of metal extracted (Ni and Pb) from the different three steps changes depending on the presence of synthetic zeolite.

The data obtained clearly show that zeolite X captures both Ni and Pb in its structure while forming, thus reducing the mobilization of the toxic elements. When the structure of the newly-formed mineral is destroyed by chemical extractions, the toxic element is mobilized through the action of the

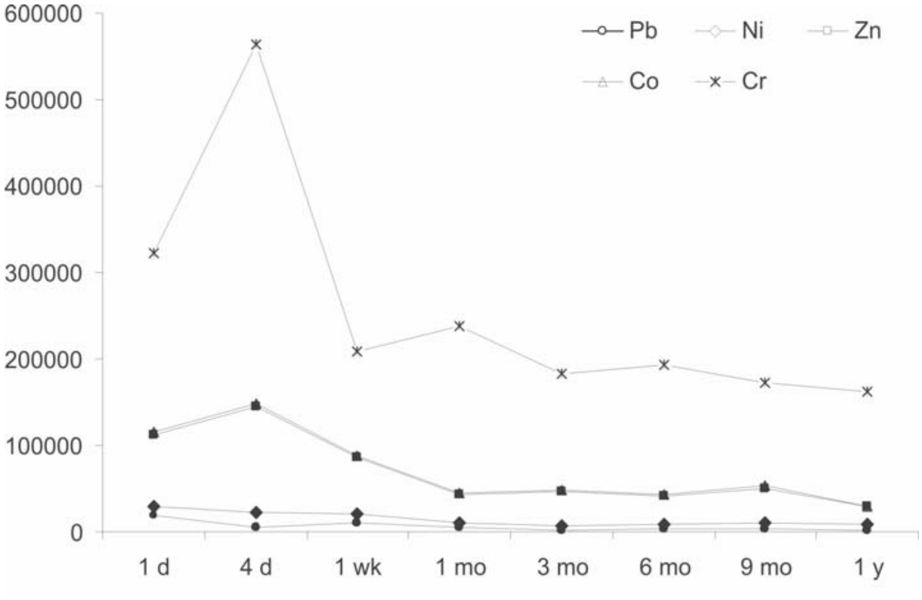

Fig. 1 - Heavy metal extraction with single-step procedure in experiments in laboratory.

different reagents depending on toxic elements speciation. Fig. 2 shows a lower mobilization of Ni in the samples characterized by the presence of zeolite (samples of soil incubated for more than 1 month) after an acid acetic attack. The similar trend of the second step shows that Ni cannot be found as oxide-idroxide in the zeolite structure. A higher concentration of Ni mobilized by peroxide + ammonium acetate solutions shows that the speciation of the metal, previously entrapped in the zeolite destroyed after the BCR first step, took place in the oxidable form. The higher Ni-content mobilized from the samples containing a higher amount of zeolite (samples aged more than 1 month) clearly suggests that organic matter and clay minerals have a negligible role in binding the element.

The behaviour of Pb seems to be different. The higher concentration of Pb mobilized with the second step shows that the speciation of the metal took place in the reducible form (Fig. 2). It does not exclude that Pb speciation might also take place as oxidable form in the zeolite structure such as indicated by the third step trend showing a mobilization of the toxic element by peroxide + ammonium acetate attack. Although further investigations are necessary, these data indicate a speciation of Pb as hydroxide phases inside the synthetic zeolite.

CONCLUSIONS

The results obtained show that the direct synthesis of zeolite X takes place at low temperatures in the contaminated soil treated with coal fly ash. The experiments carried out in the laboratory and on a bench-scale at 27 and about 30°C, respectively, show the formation of zeolite readily after a month and the amount of the newly-formed mineral increases during the entire incubation period.

The presence of Ni, Pb, Zn, Co and Cr^{6+} does not exert any influence on zeolite formation which, on the contrary, plays a leading role in the mechanism of the toxic element immobilization. In fact, a reduction in heavy metal availability characterizes the soil samples in which zeolite X was synthesized. In particular the sequential chemical extraction suggests that Ni and Pb mobilization takes place after zeolite

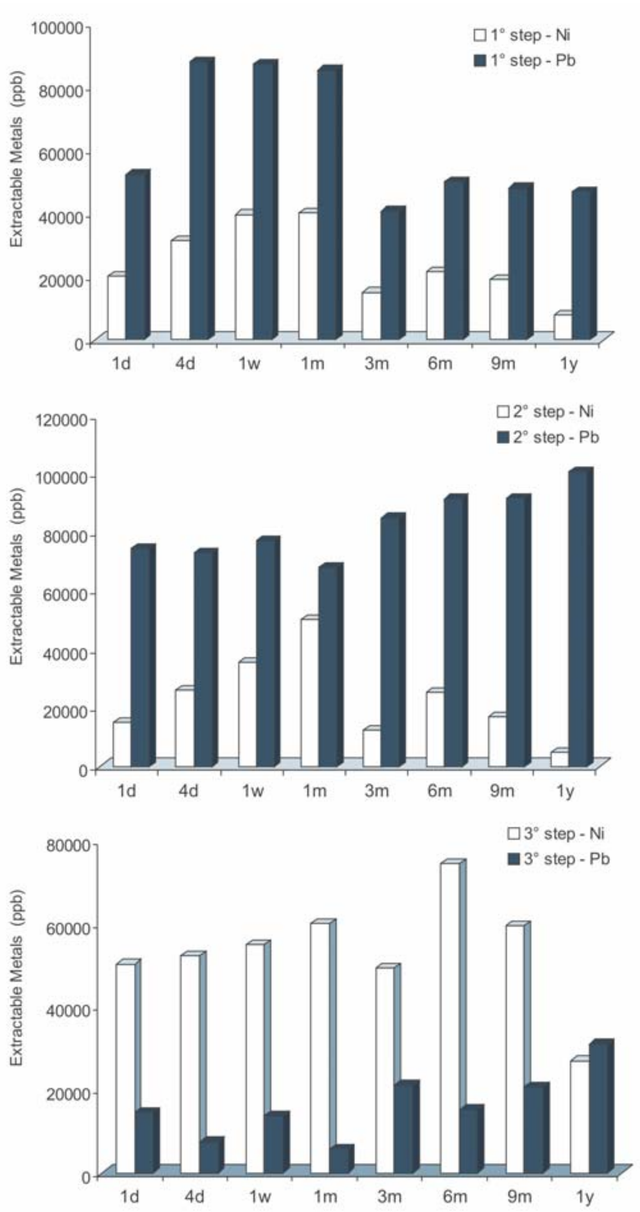

Fig. 2 - Results of three-step BCR procedure in experiments at bench-scale.

structure is destroyed. This causes the availability of the metals, previously trapped in the mineral and/or co-precipitated on its surfaces in the oxidable and hydroxide form respectively. In all cases synthetic zeolite forms complexes with the toxic metals which are broken by a strong chemical attack but are stable under normal environmental conditions.

The results of our research carried out a request of patent in USA.

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