Technical Note

Immobilization of Ni by synthesising zeolite at low temperatures in a polluted soil

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ABSTRACT

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. Zeolite formation in contaminated soils mixed with coal fly ash could be a useful method to reduce both the availability and the mobility of metals in contaminated areas. In this study a soil sample – treated with coal fly ash and artificially contaminated with a high concentration of Ni – was used for synthesizing zeolite at low temperatures. The role played by this mineral in the immobilization of heavy metal was investigated. The materials were analysed chemically (sequential extraction) and by XRD and SEM–EDS analyses. The synthesis was carried out both in the laboratory and on a bench-scale for 1 year. Zeolite crystallization readily occurred after a month. The presence of Ni does not exert any influence on zeolite formation. On the other hand newly-formed zeolites reduce the toxicity of the element in the polluted soil. A reduction in heavy metal availability was observed after ammonium acetate extraction. The use of the modified BCR three-step sequential extraction (sequential extraction protocol developed by Community Bureau of Reference of the Commission of the European Communities) suggests that Ni mobilization takes place when zeolite structure collapses after the BCR second step. The Ni thus available was mobilized in the third step.

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1. Introduction

It is well-known that high concentrations of heavy metals in soils can pose long-term health risks both to ecosystems and human beings. Over the last few years the amount of research on soils contaminated with heavy metals has shown that metals can occur in different fractions and chemical species in soils and sediments. The geochemical form of toxic elements influences their mobility, bioavailability and the risk of water pollution (Harrison, 1981; Xian, 1989).

Several remediation technologies have been developed in order to clean up contaminated soils. Some techniques lean towards heavy metal immobilization through the addition of reactive constituents that alter solid-phase partitioning of the metal contaminant in a manner that reduces bioavailability without dramatically disturbing natural soil function. As a matter of fact many studies describe the positive results obtained by adding natural and synthetic zeolites to polluted soils (Gworek, 1992; Shanableh and Kharabsheh, 1996; Lin et al., 1998; Moreno et al., 2001a,b; Fernandez-Pereira et al., 2002; Ponizovsky and Tsadilas, 2003; Castaldi et al., 2004; Penilla et al., 2006; Querol et al., 2006; Kocaoba et al., 2007; Stefanović et al., 2007). Other authors describe the role played by zeolite synthesized in soils contaminated with Cu, showing that the formation of these minerals can have the advantage of entrapping a toxic element in their structure (Terzano et al., 2005b, 2006).

In order to determine the effective contribution of zeolite or other minerals to soil remediation, different methods, which include chemical extraction, are widely used. Chemical extraction is for assessing operationally-defined toxic metal fractions, which can be related to chemical species as well as potentially mobile, bioavailable or ecotoxic phases. Various single step extractions are widely used because of their simplicity and rapidity (Li et al., 1995; Quevauviller et al., 1996; Ford et al., 1999; Alvarez et al., 2006). However, these techniques do not provide any information on heavy metal speciation. On the contrary, sequential extractions can provide information on the possible chemical forms of the metal in addition to the physicochemical availability and the mobilization of toxic elements providing a good indicator under what conditions sorbed/bound contaminants would likely to be mobilized.

There are many multi-step extraction procedures and the scheme proposed by Tessier et al. (1979) was one of the first. This procedure and the relative modifications (e.g. Campanella et al., 1995) were used for distinguishing trace metals in: exchangeable, bonded with carbonates, bonded with iron–manganese oxides or organic matter and residual metal in soils and sediments. The growing interest in sequential extraction aroused by the work of Tessier et al. (1979) has led to the use of several procedures with a different number of steps, reagents and extraction conditions. As a consequence, drawing comparisons between the results

obtained in different laboratories has become difficult. The Community Bureau of Reference of the Commission of the European Communities (BCR Measurement and Testing Programme) developed a three-step sediment sequential extraction protocol (Ure et al., 1993; Quevauviller et al., 1997), which could be considered as a standard method to be used in laboratories working in the field of trace elements in contaminated soils. According to this method metals are divided into acid-soluble/exchangeable, reducible and oxidizable fractions.

Our study involved 1-year-long experiments carried out both in the laboratory and on a bench-scale, 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. Zeolite formation is generally based on a complex mechanism. In the case of the synthesis of aluminium-rich zeolite such as zeolite X, the mechanism consists of a first step during which an alluminosilicate gel is formed by mixing alumina, silica and alkali metal hydroxide ions in water. Nucleation occurs in a following step. Our procedure concerns the synthesis of zeolite X, in a soil artificially polluted by a high amount of Ni (10 mg Ni g^{-1} of soil dry weight). The alumina and reactive silica sources were supplied by soil forming minerals and amorphous material of fly ash. In order to better evaluate the chemical process responsible for Ni immobilization during zeolite formation, and whether Ni can be trapped in the newly-formed zeolite, the BCR sequential extraction method was employed in addition to the ammonium acetate extraction step. The solid residues of each extraction step were analysed by XRD.

2. Materials and methods

2.1. Soil contamination and experiments in the laboratory and on a plant scale

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). Table 1 reports the chemical and mineralogical composition of both source materials.

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 and Shih, 1998). The resultant fused mixture was cooled and milled again. The powder thus obtained was mixed with the soil contaminated artificially with Ni (the final concentration of 10 mg Ni g^{-1} of the total dry solid matter). In particular, laboratory experiments were carried out by mixing 8 g of soil with 17 mL of Ni solution in polypropylene bottles. The mixture was stirred for 24 h at room temperature and atmospheric pressure, and then 1.8 g of fused fly ash were added and stirred again 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, soil and Ni solution 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. Experiments with non-contaminated soil were carried out by Terzano et al. (2005a) using source materials analogous to those used in these experiments.

Table 1
Chemical and mineralogical properties of soil and fly ash. Minerals and major elements as wt.%; trace elements as ppm.

Parameter	Fly ash	Soil
pH	13.20	7.88
Organic carbon	–	1.75
$\sum$ Phy	–	84
K-feld	–	2
Cal	–	4
Qtz	6	10
Mullite	17	–
Amorphous	77	–
SiO_2	46.80	49.3
Al_2O_3	28.21	16.7
Fe_2O_3	5.23	6.6
TiO_2	1.49	0.9
MnO	0.06	0.1
MgO	1.43	2.3
CaO	5.57	6.3
Na_2O	0.54	0.4
K_2O	1.26	1.8
P_2O_5	0.78	0.2
LOI	8.66	15.6
SiO_2/Al_2O_3	1.66	3.0
As	14.5	8.0
Cd	0.30	0.10
Co	48.3	16.2
Cr	138	105
Cs	3.41	5.47
Cu	68.3	42.8
Pb	74.6	23.0
Se	4.00	0.90
Zn	76.3	106

2.2. Investigation of solid phases

Soil samples from laboratory and bench-scale experiments were collected at the above mentioned regular intervals.

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 Kα radiation and graphite monochromator. The morphology was observed by FE-SEM (Zeiss Supra 40).

Adsorbed and exchangeable Ni was determined by ammonium acetate extraction. One gram (dry weight) of each pellet obtained after centrifugation was suspended in 8 mL of 1 M solution of NH_4–CH_3COOH (pH 7.0). The suspension was shaken for 2 h at room temperature and centrifuged at 4500 rpm for 45 min. The solution was filtered and analysed for Ni by inductively-coupled plasma spectrometry (ICP-MS). The solid residues were analysed by XRD.

The stability and speciation of toxic elements were determined by modified BCR three-step sequential extraction proposed by Quevauviller et al. (1997). This chemical method is the result of a ring test carried out by 18 EU laboratories.

The solid residues of a single-step chemical procedure were washed twice with 40 mL of 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 Ni extracted were: (1) exchangeable and/or weakly bonded with carbonate fractions; (2) correlated with reducible phases and (3) organically bonded and sulphide fractions. The reagents were for trace metals analysis and the analytical procedures utilized are the following: (i) first step (exchangeable fractions and fractions bounded with carbonate): the soil sample was extracted with 40 mL of 0.11 M acetic acid solution (pH 2.86) shaken for 16 h at