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Copper Stabilization by Zeolite Synthesis in Polluted Soils Treated with Coal Fly Ash

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This study deals with the process of zeolite formation in an agricultural soil artificially polluted by high amounts of Cu (15 mg of Cu/g of soil dry weight) and treated with fused coal fly ash at 30 and 60 °C and how this process affects the mobility and availability of the metal. As a consequence of the treatment, the amount of dissolved Cu, and thus its mobility, was strongly reduced, and the percentage of the metal stabilized in the solid phase increased over time, reaching values of 30% at 30 °C and 40% at 60 °C. The physicochemical phenomena responsible for Cu stabilization in the solid phase have been evaluated by EDTA sequential extractions and synchrotron radiation based X-ray microanalytical techniques. These techniques were used for the visualization of the spatial distribution and the speciation of Cu in and/or on the neo-formed zeolite particles. In particular, micro XRF (X-ray fluorescence) tomography showed direct evidence that Cu can be entrapped as clusters inside the porous zeolitic structures while μ-XANES (X-ray absorption near edge structure) spectroscopy determinations revealed Cu to be present mainly as Cu(II) hydroxide and Cu(II) oxide. The reported results could be useful as a basic knowledge for planning new technologies for the on site physicochemical stabilization of heavy metals in heavily polluted soils.

Introduction

Several soil remediation technologies based on physicochemical processes of solidification/stabilization (S/S) employ mixtures of inorganic compounds (cement, sodium silicates, oxides, coal fly ash, etc.) to reduce the environmental hazard posed both by organic and by inorganic xenobiotics in polluted soils (*1*). Alkalizing agents such as sodium hydroxide and/or lime are often added to these mixtures to enhance the stabilization of heavy metal pollutants. Among the constituents of certain mixtures employed in S/S technologies, coal fly ash is frequently present because it is inexpensive, it has good pozzolanic properties, and it solves the problem of its disposal in an economically advantageous way (*2*).

Coal fly ash is the most abundant coal combustion byproduct of thermoelectric power plants and mainly consists of amorphous glass phases, crystalline phases such as quartz and mullite, and other minor constituents such as hematite and magnetite (*3*). Van Jaarsveld et al. (*4*) have demonstrated that this waste material readily dissolves in alkaline media and promotes so-called geopolymerization reactions. Geopolymers can be viewed as the amorphous equivalent of certain synthetic zeolites and have more or less the same chemical composition, although the absence of the distinctive long-range zeolite structure makes them amorphous to X-ray diffraction (XRD) detection (*4*). It has been shown that geopolymerization reactions can lead to the immobilization of toxic metals such as Cu and Pb inside a solid phase. In this situation, heavy metal immobilization may occur through a combination of physical encapsulation and chemical bonding into the amorphous phase of the geopolymeric matrix (*5*).

Amorphous aluminosilicates can transform, over time, into crystalline compounds (*6*, *7*) in the same way as other Al or Fe amorphous phases do (*8*−*10*). Very often, these crystallization processes are long-term transformation reactions, so that they cannot be observed if the system under investigation is studied for a limited period of time. To simulate spontaneous long-term transformation of solid phases, a thermal treatment is usually adopted (*11*). Crystallization may be favorable from a thermodynamic point of view because it increases the stability of the solid phase (*8*, *10*). Moreover, when the fate of heavy metals during the process of crystallization is monitored, a decrease in the solubility of the metals with aging can be achieved due to changes in their structural location and chemical form (*8*). Nonetheless, Sorensen et al. (*10*) observed that the formation of closely packed minerals, such as hematite, is likely to result in a lower heavy metal binding capacity. Conversely, the formation of loosely packed crystalline phases could contribute to improved toxic metal stabilization by entrapping part of them inside stable minerals. In this context, the crystallization of amorphous aluminosilicates into minerals with highly porous structures such as zeolites and its environmental consequences deserve attention. Newton et al. (*12*) have observed that, following the application of a S/S mixture (Georemediation) to a soil polluted by hydrocarbons, a slightly detectable amount of zeolite crystals (mordenite) was formed. Similarly to what has been observed in some cements (*13*, *14*), the synthesis of zeolites in a soil polluted by heavy metals could play an important role in the stabilization processes of these toxic elements.

Zeolites are widely employed in environmental applications for the decontamination of soils polluted by heavy metals where they are usually added as cation exchangers (*15*−*18*). In previous research (*19*), it has been shown that significant amounts of zeolites (Zeolite X and Zeolite P) can be crystallized in agricultural soil treated with fused coal fly ash (about 5 and 12% of soil dry weight at 30 and 60 °C, respectively).

The present study is concerned with the process of zeolite formation in an agricultural soil artificially polluted by high amounts of Cu (15 mg of Cu/g of soil dry weight) and treated with fused coal fly ash and the influence of this process on the mobility and availability of the metal. To better evaluate whether Cu can be entrapped inside the neo-formed zeolitic structures and the physicochemical processes responsible for Cu stabilization in the solid phase, three synchrotron radiation X-ray based microanalytical techniques for the determination of the spatial distribution and the speciation of Cu in/on the neo-formed zeolites were employed in

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addition to bulk chemistry experiments using EDTA sequential extractions. Using a submicron hard X-ray beam from a third generation synchrotron radiation source, X-ray diffraction (μ-XRD) and X-ray fluorescence tomography (3-D μ-XRF) on microscopic Zeolite X particles were performed to identify the crystalline structure and to visualize the Cu distribution inside single particles of ca. 10−20 μm diameter. Moreover, micro-X-ray absorption near edge structure (μ-XANES) spectroscopy measurements on these particles were performed to obtain information on the chemical environment of Cu present in and/or on the zeolite.

Experimental Procedures

Coal Fly Ash. The coal fly ash used in this study was obtained from the ENEL thermoelectric power plant of Cerano (Brindisi, Italy). This material was fully characterized with particular attention to the average Cu concentration (2.1 ± 0.2 μg/g) and other trace element contents (*20*). To obtain a completely amorphous aluminosiliceous material, coal fly ash was pretreated in a fusion process by mixing it with NaOH powder (5:6 w/w) and heating the mixture for 1 h at 550 °C in a muffle furnace (*21*).

Soil Contamination and Treatment. Copper solutions (7.15 mg/mL) were prepared from analytical reagent grade copper acetate (J. T. Baker). Twenty grams of an agricultural soil sieved at 2 mm (organic carbon = 2.4%; $N_{\mathrm{Tot}} = 2.352$ g/kg; $\mathrm{pH_w} = 7.94$; and $\mathrm{pH_{KCl}} = 6.88$) was mixed with 42 mL of a Cu solution in a sealed polypropylene bottle to obtain a final concentration of 15 mg of Cu per gram of the total dry solid matter. Soil mineralogical and chemical compositions have been reported elsewhere (*19*). The mixture was stirred for 24 h at 20 °C and atmospheric pressure. After this artificial contamination step, 4.4 g of pretreated coal fly ash was mixed with the polluted soil by stirring for 1 h at room temperature. Mixtures were subsequently incubated in an electrical oven at 30 °C (FA30) or 60 °C (FA60) and atmospheric pressure. Control experiments in the absence of fly ash were also performed by adding 2.4 g of NaOH powder to the contaminated soil to achieve the same pH (about 13.0) in the soil suspensions as was obtained after the treatment with coal fly ash (NaOH30, NaOH60). The ability of the untreated soil to reduce the aqueous concentration of Cu after contamination (pH 5.5) was also investigated. Each experiment was conducted in triplicate. Samples were collected after incubation times of 1 h, 24 h, 1 week, 1 month, 3 months, 6 months, and 1 year.

Bulk Investigations. Each sample was centrifuged at 20 600*g* for 10 min, and the supernatant was recovered, filtered (0.2 μm polycarbonate filter), and analyzed to determine the Cu concentration by means of differential pulse voltammetry (DPV) or differential pulse anodic stripping voltammetry (DPASV) on a hanging dropping mercury electrode (HDME) using a Metrohm 757 VA Computrace voltammeter. The 0.1 M HNO_3 was used as a background electrolyte. K_d values were determined as the ratio of the mass of Cu in the solid-phase per unit mass of solid phase to the mass of Cu in solution per unit volume of the liquid phase.

Pellets were washed 3 times with deionized water followed by centrifugation and dried at 80 °C for 12 h. The dried pellets were saved for further investigations on the solid phase. The mineralogical phases in the dried solids were identified by XRD and scanning electron microscopy−energy dispersive X-ray analysis (SEM−EDX) (LEO Stereoscan 440). XRD patterns were collected using a Rigaku D-max Rapid micro-diffractometer operating at 40 kV and 30 mA with CuKα radiation and a flat graphite monochromator. Zeolite quantification was obtained by Rietveld refinement, using the EXPGUI software (*22*), after X-ray powder collection with a corundum NIST 676 internal standard.

The stabilization of Cu in the solid phase was assessed by sequential EDTA extractions. A total of 300 mg (dry weight) of each pellet obtained after centrifugation was suspended in 30 mL of a 5 mM EDTA (sodium salt, J. T. Baker) solution at pH 7.5 (0.2 M phosphate buffer solution) and shaken for 24 h at room temperature. Suspensions were centrifuged at 20 600*g* for 10 min, supernatants were separated, and fresh EDTA solutions were added to the remaining solids for a new extraction of trace metals for 24 h. The sequential extraction with EDTA was repeated 5 times. Dissolved Cu was determined by DPV or DPASV as described previously.

SR Based X-ray Microbeam Analyses of Zeolite X Particles. All the μ-SR based X-ray microbeam investigations were performed on samples of artificially contaminated soil treated with coal fly ash and collected after 6 months of incubation at 30 and 60 °C.

Single Zeolite X particles were isolated directly from the soil treated with coal fly ash by using a Nikon Diaphot 200 inverted microscope and were glued to the top of a 100 μm diameter quartz capillary (Hilgenberg, Germany) using a Nikon Narishige MN 188 NE micromanipulator. The capillaries on which the samples had been glued were placed on a motorized stage having one rotational and three translational degrees of freedom. To confirm that the soil particles mounted on the top of quartz capillaries were Zeolite X, they were analyzed by means of μ-XRD at the ID18F microbeam end-station of the European Synchrotron Radiation Facility (ESRF), Grenoble, France (*23*). A double-crystal Si (111) monochromator was used for defining the energy of the monochromatic excitation radiation with an energy resolution ($\Delta E/E$) of 10^{-4}. To generate the microbeam, a polymer compound refractive lens (CRL), consisting of 10 series of crossed refractive lenses suitable for focusing 10 X-ray energies in the 5 up to 30 keV range on one silicon wafer, was used. The beam size obtained was 0.8 (H) × 0.5 (V) μm at 28 keV with an intensity of about 5×10^9 photons/s. The diffracted X-rays were detected by a 2-D large area CCD (Mar, Evanston, IL) X-ray detection system. The data acquisition was performed by rotating the sample in the range $\phi = 0-360°$ with a 3° step size and 5 s exposure time. The Fit 2D V12.034 software package (*24*) was used for data handling and XRD pattern evaluation.

μ-XRF tomography was also performed at the ID18F microprobe of the ESRF. The microbeam used was the same as described previously for μ-XRD. The characteristic X-ray line intensities of the samples were detected by a Si(Li) detector (GRESHAM Scientific Instruments LTD) placed at 90° to the incoming X-ray beam. The AXIL software package (*25*) was used for the evaluation of the resulting energy-dispersive X-ray spectra. The sample was rotated around a horizontal axis and scanned vertically to make use of the smallest X-ray beam size. The sample was rotated in the range $\phi = 0-180°$ with a 3° step size, while the vertical scan was of a 0.4 μm step size with a collection time of 2 s per location.

μ-XANES spectra were collected at 298 K on Beamline L at the Hamburger Synchrotronstrahlungslabor (HASYLAB, Hamburg, Germany). A Si (111) double-crystal monochromator was used for the selection of energy with an energy resolution (ΔE) of ca. 0.8 eV at the CuK edge. The beam energy was calibrated by recording the absorption edge of Cu foil in the energy range of 8900−9500 eV. The beam was focused down to approximately 20 μm by means of an X-ray Optical System (Albany, NY) polycapillary lens. Samples were placed on a motor $x-y-z$ stage and set at an angle of 45° to the incident beam. μ-XANES spectra were collected in fluorescence-yield mode on single Zeolite X particles directly isolated from the treated soil and glued on the top of quartz capillaries, as previously described. Spectra were collected from 100 eV below to 200 eV above the CuK edge in step

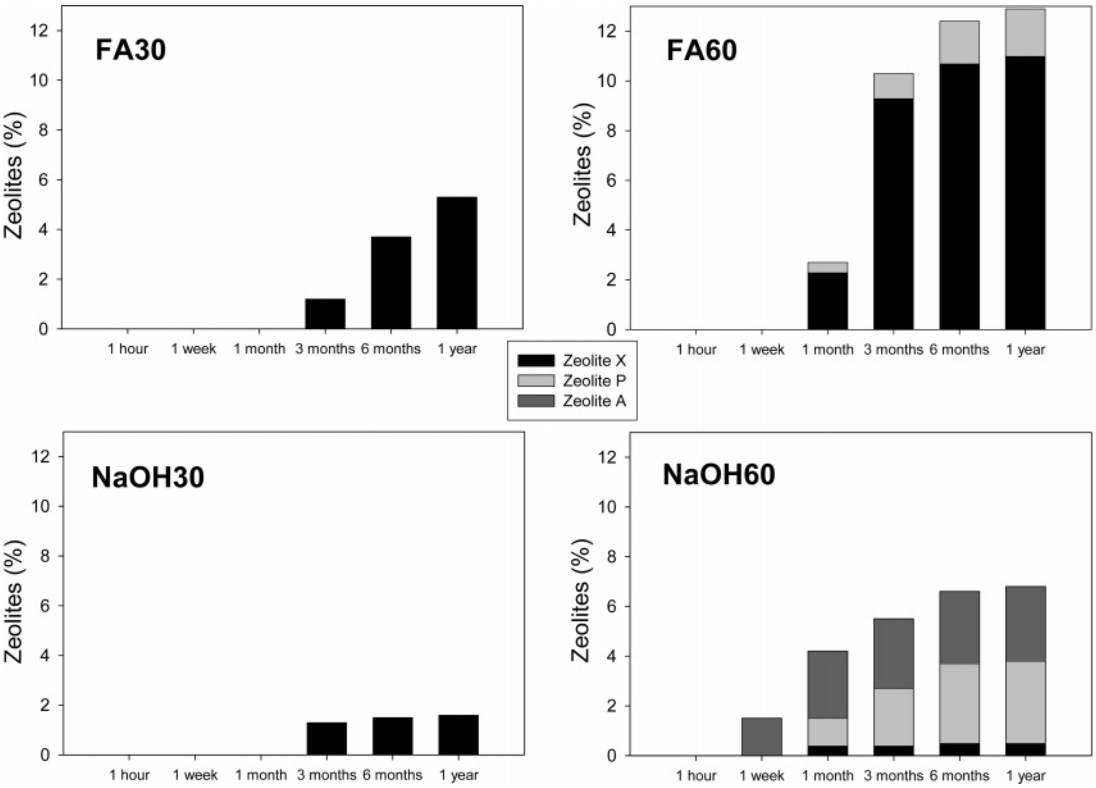

FIGURE 1. Amount of zeolites, as a percentage of the soil total dry weight, formed after curing the soil artificially polluted by Cu with fused coal fly ash or with NaOH, at 30 °C (FA30, NaOH30) and 60 °C (FA60, NaOH60) and at different incubation times.

increments of 0.5 eV. Typically, two to three scans were collected for model compounds, and about 10 scans were collected for Zeolite X samples. The resulting XANES profiles were evaluated using the WINXAS 3.1 software package (*26*). Semiquantitative analysis of the edge spectra was performed by least-squares fitting of linear combinations of standard spectra to the spectrum of the sample. XANES spectra of standard copper compounds such as $CuCl_2$, $Cu(OH)_2$, CuO, $CuSO_4$, Cu_2O, Cu(II)-Zeolite X (exchanged), Cu(II)-amorphous aluminosilicate, and Cu foil were also recorded.

Results and Discussion

Zeolite Synthesis. The total amount of zeolites formed by treating the Cu-polluted soil with fused coal fly ash or with NaOH alone (so as to reach the same pH as in the samples treated with fused fly ash) and incubating the mixtures at 30 °C (FA30, NaOH30) and 60 °C (FA60, NaOH60) is reported in Figure 1. After 1 month of incubation at 60 °C at atmospheric pressure, XRD analysis of the coal fly ash treated soil (FA60) revealed the formation of Zeolite X (zeolite belonging to the Faujasite series) and of a smaller amount of Zeolite P (zeolite belonging to the Gismondine series). The amount of the two synthesized zeolites increased with the incubation time, and in particular, the Zeolite X concentration (w/w) reached about 9% of the total sample dry weight after just 3 months of incubation at 60 °C. After 1 year, the total amount of zeolites synthesized amounted to about 13%, of which 11% could be attributed to Zeolite X. When compared with results obtained in the absence of copper contamination (*19*), these results suggest that high amounts of Cu(II) added to soil induce a delay in zeolite formation (previously noticed after just 1 week) and drive the synthesis toward Zeolite X. Zeolite P appeared to be only a minor product accounting for about 2% of soil dry weight after 1 year of incubation. However, at the end of the incubation period, the total amount of zeolites synthesized in the soil polluted with Cu and treated with fused fly ash at 60 °C was similar to that obtained in the absence of artificial Cu contamination (*19*). Zeolite synthesis was also obtained when the soil was treated only with NaOH and cured at 60 °C (NaOH60). However, in this case, XRD analysis revealed the synthesis of Zeolite A after 1 week and of Zeolite X and Zeolite P after 1 month. Zeolite X was only a minor product and detected at an almost constant quantity, 0.5% throughout the observation period, whereas the quantities of Zeolite P and Zeolite A gradually increased to maximum values of 3.3 and 3%, respectively, after 1 year of incubation. After 1 year of incubation at 60 °C, the total amount of zeolites obtained by simply treating the soil with NaOH was less than 7% and, therefore, slightly more than a half the amount obtained by treating the soil with fused coal fly ash at the same temperature. In the absence of coal fly ash, the Si and Al species necessary for zeolite synthesis were supplied by the partial dissolution of soil minerals in the alkaline medium (*19*).

XRD analysis also revealed appreciable zeolite formation in the soil treated with fused coal fly ash at 30 °C (FA30), after 3 months of incubation. Under these conditions, only Zeolite X could be detected by XRD. Zeolite synthesis appeared to have been hindered by the presence of a high amount of Cu(II) initially, but after 1 year of incubation, the total amount of zeolite formed was similar (more than 5%) to that obtained in the absence of copper artificial contamination (*19*). Under the same experimental conditions, zeolite synthesis was also observed after 3 months when the soil was mixed with NaOH alone and cured at 30 °C (NaOH30). As previously observed for FA30, only Zeolite X was formed, albeit at a much lower amount of just 1.6%, after 1 year of incubation.

In conclusion, the presence of high amounts of copper does not appear to interfere negatively with the process of zeolite synthesis in soil treated with fused coal fly ash, and it seems to favor the formation of Zeolite X over Zeolite P at 60 °C.

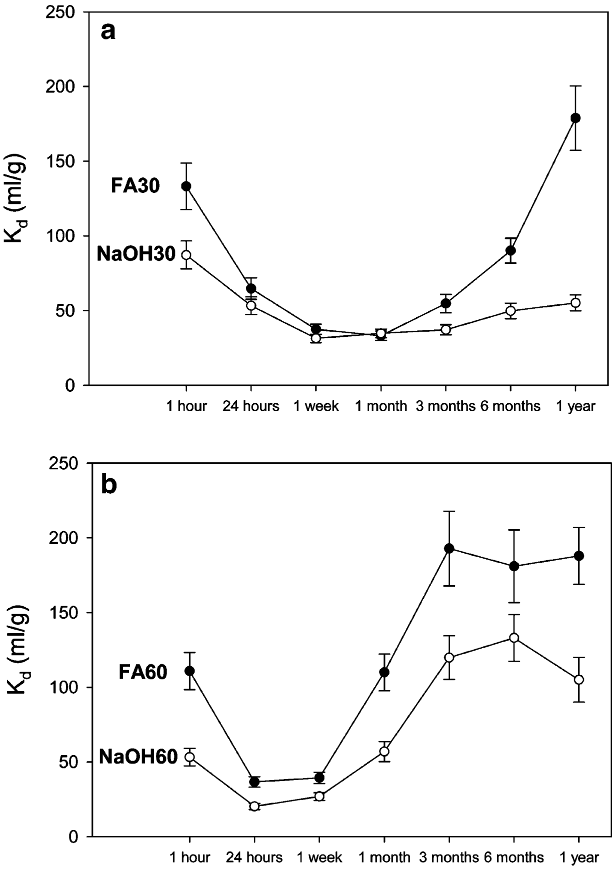

FIGURE 2. Variation over time in the distribution coefficient (K_d) of Cu, after the treatment of the artificially polluted soil with fused fly ash (FA30, FA60) or NaOH (NaOH30, NaOH60) at 30 °C (a) and 60 °C (b), determined for an initial Cu concentration of 7.15 mg/mL and a 15 mg of Cu per g of solid dry weight. A higher K_d value means a higher Cu distribution in the solid phase.

Copper Distribution. Simultaneously with the process of zeolite synthesis, the partitioning of Cu between the solid phase and the soil solution, in samples of the artificially polluted soil treated with fused coal fly ash or only with NaOH, was determined over a period of 1 year, at both 30 and 60 °C. The K_d values determined over time for the Cu load adopted in this research are shown in Figure 2. After the addition of pretreated coal fly ash to the contaminated soil, the determined K_d was 130 and 110 mL/g for the soil treated with fly ash at 30 and 60 °C, respectively (FA30 and FA60). These high K_d values were due to the high pH (about 13.0), which certainly generated a higher rate of sorption phenomena (precipitation, in particular). However, during the first month of incubation for the soil treated at 30 °C and the first week for the soil treated at 60 °C, the K_d value strongly decreased, thus indicating increased Cu redissolution. This process was favored by the high alkaline conditions caused by the addition of fused fly ash, which probably promoted the solubilization of soil organic matter in addition to Cu dissolution. In fact, it is well-known that soil soluble organic matter forms strong complexes with copper (*27*). The K_d values started to increase again, simultaneous with the beginning of zeolite synthesis: after 3 months and 1 month of incubation at 30 and 60 °C, respectively. From this point on, the K_d values gradually increased to 180−190 mL/g, after 1 year. This value was reached after 1 year of incubation at 30 °C and after just 3 months at 60 °C, after which it remained relatively constant to 1 year. K_d values calculated for the untreated soil (pH 5.5) were generally much lower, ranging from 2.5 mL/g at 24 h to 11.5 mL/g after 1 year for the soil incubated at 30 °C and from 7.5 to 16.5 mL/g for the soil treated at 60 °C (data not shown).

K_d values were also determined over a 1 year period of incubation for the polluted soil treated only with NaOH, so as to reach alkaline conditions (pH 13.0) similar to those of the samples treated with fly ash (Figure 2). After 1 year of incubation, the distribution coefficient determined for the soil treated with NaOH at 30 °C was more than 3 times lower than that determined for the soil treated with fused fly ash, whereas at 60 °C, it was about 60% lower. These results indicated that the addition of fused coal fly ash promoted a higher partitioning of Cu on the solid phase than the simple NaOH treatment. Therefore, such a treatment appeared to be highly effective in reducing the amount of dissolved copper and thus Cu mobility.

At the beginning of the incubation period, the pH value in all samples was very close to 13.0 and decreased, after 1 year of incubation, to 11.5 for the samples cured at 30 °C and to 10.5 for the samples cured at 60 °C (see Supporting Information). In general, the pH values were similar for both the samples treated with coal fly ash or with NaOH alone, throughout the period of observation. The only differences were related to the temperature at which the incubations were carried out.

Cu Availability. Figure 3 shows the residual copper (as mg of Cu/g of soil dry weight) remaining in/on the solid phase, plotted against the number of EDTA sequential extractions for the aging series of Cu polluted soil samples subjected to treatments with fused fly ash or NaOH, to assess the unavailable metal fraction. It is evident that, in all situations, Cu became increasingly resistant, over time, to extraction with EDTA, both at 30 and 60 °C. In the samples treated with fused coal fly ash, after 1 year of aging, 4.5 mg of Cu per gram of soil dry weight and 6.0 mg of Cu per gram of soil dry weight were stabilized in/on the solid phase at 30 and 60 °C, respectively, from soils initially loaded with 15 mg of Cu per gram soil dry weight.

The values relative to copper stabilization for the soil samples treated only with NaOH were generally lower than those observed after fused coal fly ash addition. For the soil sample treated with NaOH at 30 °C, the amount of Cu remaining in/on the solid phase following EDTA extraction amounted to 1.6 mg (30% of that obtained for FA30), whereas it was 4.5 mg (75% of that obtained for FA60) for the soil sample treated with NaOH at 60 °C.

Microscopic Investigations. To verify that zeolite synthesis in the contaminated soil treated with fused coal fly ash played an effective role in Cu stabilization processes, zeolite particles were analyzed by synchrotron X-ray microbeam based analytical techniques to determine the spatial distribution and speciation of Cu in and/or on the new formed minerals. To study these small particles (10−20 μm), an X-ray beam in the submicrometer range was employed. Only Zeolite X particles were investigated because they represented the majority of the zeolites synthesized in the treated soil and because Zeolite P particles were too small (ca. 5 μm diameter) to be properly analyzed using the reported microanalytical techniques.

Zeolite X particles analyzed by μ-XRF tomography were preliminarily identified by means of μ-XRD. From these particles (10−20 μm diameter), the characteristic *d* spacing pattern of Zeolite X was obtained (see Supporting Information). In addition to the μ-XRD measurements, the elemental distribution of Cu and other elements within the Zeolite X particles was recorded by means of XRF microtomography. With this technique, it was possible to directly investigate a given cross-section of the particles without any physical disruption or other modifications of the chemical and morphological characteristics of the particles themselves. As can be seen in the Cu-tomographic map shown in Figure

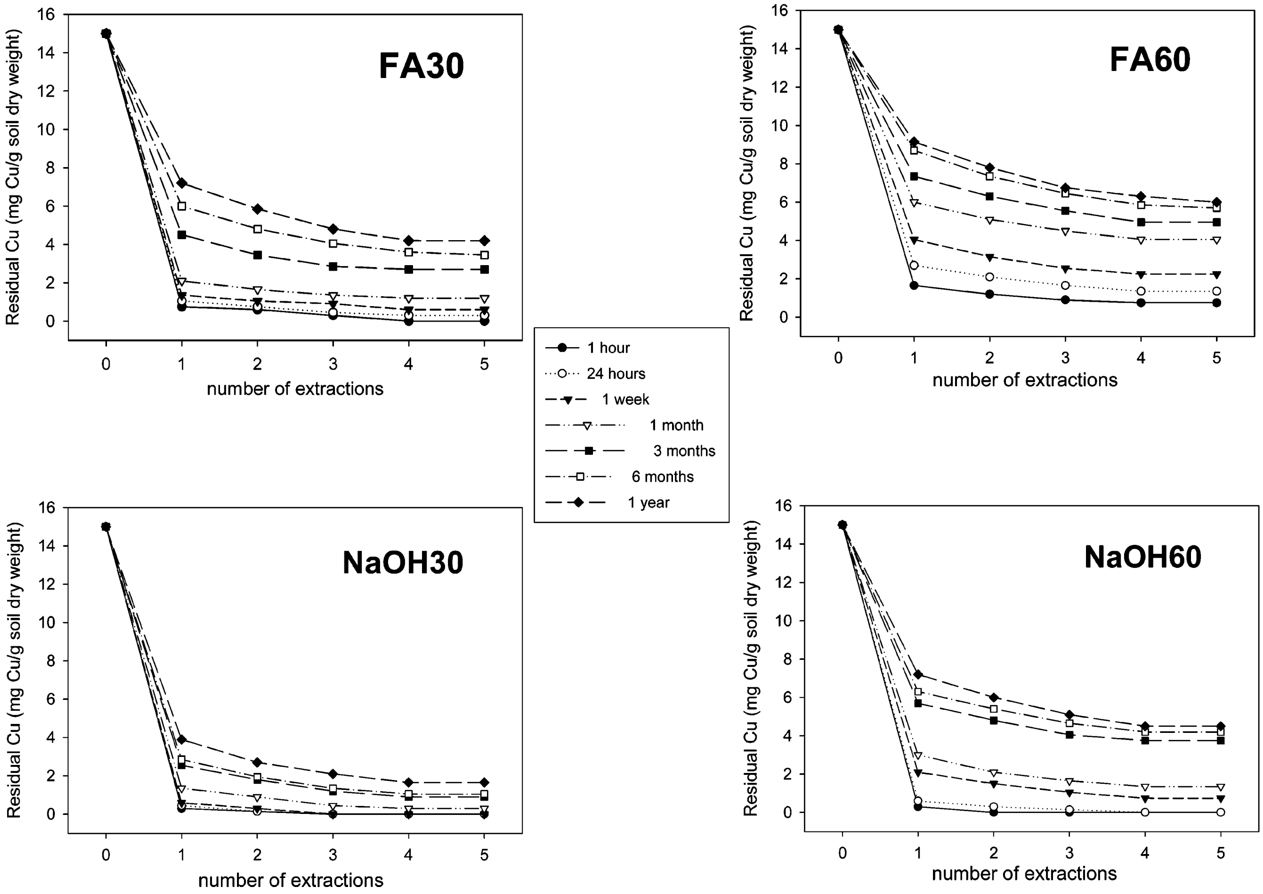

FIGURE 3. Copper contaminated soil treated at 30 and 60 °C with fused coal fly ash (FA30, FA60) or with NaOH (NaOH30, NaOH60): residual Cu remaining in/on the solid phase following EDTA extractions (EDTA 5 mM, pH 7.5) as a function of the number of extractions for a Cu-treated soil aging series.

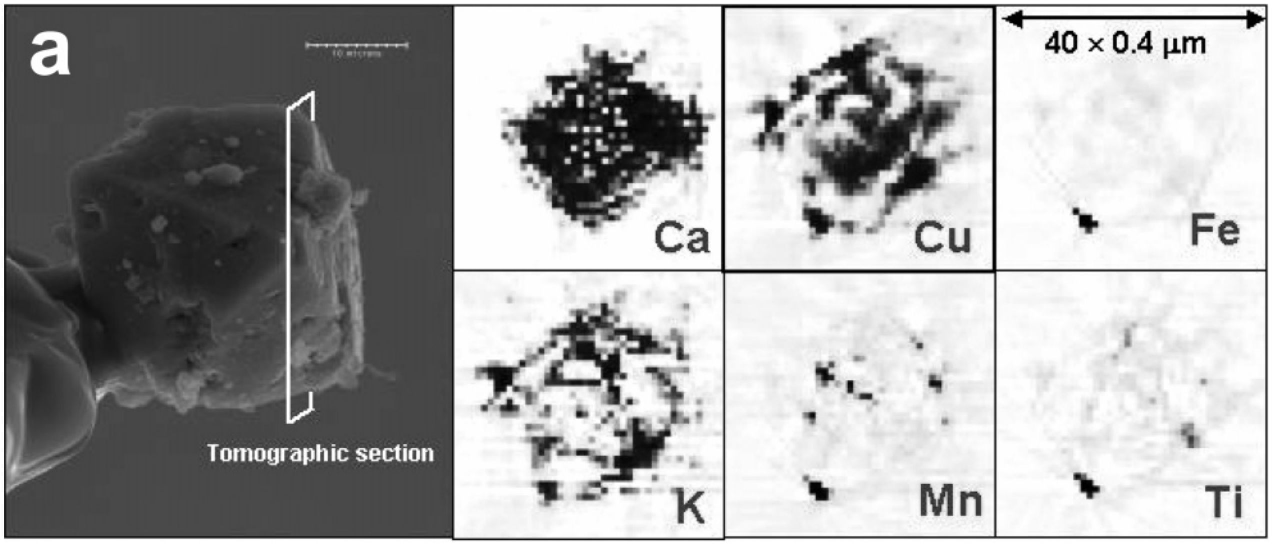

FIGURE 4. Reconstructed elemental maps from XRF microtomography on a single Zeolite X particle (a), directly isolated from a Cu artificially contaminated soil treated with fused coal fly ash at 30 °C and collected after 6 months of incubation.

4, Cu was heterogeneously distributed both inside and outside the zeolitic particle. The distribution of Ca was much more homogeneous and could be used to delineate the particles' outer perimeter in the plane of tomography. A condensed Cu rich nucleus was clearly visible at the center of the tomographic section, and other layered and clustered Cu-rich structures were located both inside and outside the zeolite particle. The heterogeneous distribution of K, when compared to the more homogeneous distribution of Ca, could be attributed to the presence of K-rich phases other than Zeolite X both inside and on the surface of the investigated particles. The submicrometer X-ray beam used to perform μ-XRF tomography was essential to visualize these subtle internal structures in the zeolite particles.

These results provided direct evidence that Cu could be entrapped inside the newly formed zeolitic minerals. However, it is reasonable to think that Cu is not located in the zeolite framework (*28*) but is most likely buried as micro- or

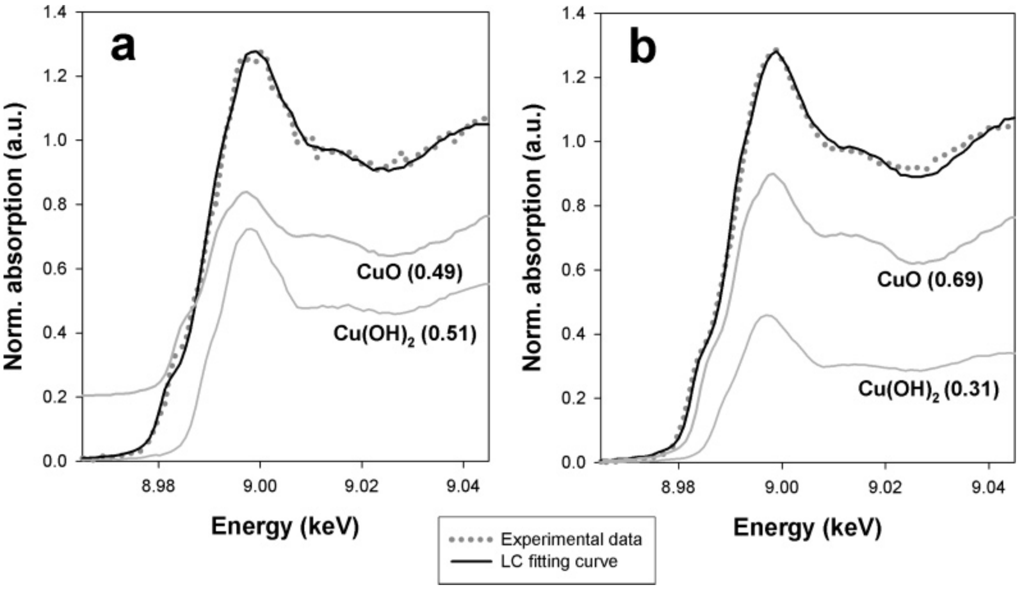

FIGURE 5. Experimental data and the least-squares fits for the CuK μ-XANES spectra of Zeolite X particles synthesized in Cu-polluted soil treated with fused coal fly ash at 30 °C (a) and at 60 °C (b). The fractional contribution of the two principal components making up the fitted spectra is also reported.

(nano-) clusters inside the newly formed minerals. This kind of distribution could be explained by considering that Zeolite X has been formed from an amorphous aluminosiliceous matrix in which Cu has been precipitated as a consequence of the addition of alkaline-fused coal fly ash to the soil.

The chemical state of Cu in and/or on the formed Zeolite X was investigated by means of μ-XANES spectroscopy. The comparison between the linear combinations of Cu standard spectra and the measured XAS spectra for the selected particles allowed for an estimation of the concentrations of the possible copper compounds in zeolite particles. In all the analyzed Zeolite X particles, Cu appeared to be mainly present as a mixture of $Cu(OH)_2$ (from 30 to 60%) and CuO (from 40 to 70%). In Figure 5, an example of the contributions of $Cu(OH)_2$ and CuO to describe the experimental XANES data obtained from two individual Zeolites X particles, synthesized at 30 and 60 °C, is reported. The set of standards that was used was by no means exhaustive, but these results are probably highly indicative of the major forms in which copper could be present in/on the selected zeolitic particles. The discrepancies observed in fitting the experimental data may be due to second neighbor interactions between Cu (outside the zeolite framework) and Si or Al belonging to the zeolite framework.

The results obtained both from the macroscopic and from the microscopic investigations performed yield enough information to formulate hypotheses about the concurrent physicochemical phenomena responsible for Cu stabilization in soil treated with fused coal fly ash. First of all, the precipitation of Cu hydroxides, due to the high increase in solution pH after the addition of pretreated coal fly ash, was certainly the main process responsible for the observed marked depletion of Cu from the liquid phase. However, by comparing these results with those obtained by simply adding NaOH to the contaminated soil to reach the same pH, it is evident that other phenomena contributed to the further increase in the amount of Cu sorbed in the solid phase observed with the addition of fly ash. Processes such as chemisorption and, especially, coprecipitation could also be involved. In particular, the latter could have been extremely effective since Cu could coprecipitate with the amorphous aluminosilicates coming from the dissolution of pretreated coal fly ash. It is well-known on a thermodynamic basis that coprecipitation is a process that could reduce heavy metal solubility below that of the least soluble pure heavy metal mineral phases likely to form under environmental conditions (*8*). These phenomena are probably also connected with the increased Cu stabilization in the solid phase, which was evaluated by means of sequential EDTA extractions. It is well-known that EDTA promotes desorption of heavy metals and the dissolution of poorly crystalline oxide and hydroxide phases from mineral surfaces (*29*). Therefore, the increasing residual fraction obtained after aging the artificially polluted soil treated with coal fly ash most likely represented the fraction of the metal that was immobilized into a newly formed solid phase. Very often, this residual fraction may be considered representative of the unavailable metal fraction (*30*). Cation exchange reactions could not be invoked because at the highly alkaline pH of the experiments, Cu was present in solution predominantly in anionic-hydroxy forms. Cu stabilization inside the solid phase could be partly ascribed to the formation of the zeolitic structures that originated from the added amorphous aluminosiliceous matrix of fused coal fly ash or from the partial dissolution of soil minerals. The hypothesis of the active role of zeolites in immobilizing Cu inside their structure was supported by the sudden increase in the K_d values observed just as zeolite synthesis started and, mainly, by the results obtained from synchrotron X-ray based microanalyses of the zeolitic particles, directly isolated from the treated soil. In fact, they showed clear evidence that Cu could be trapped inside the mesopores of the zeolitic structures as microscopic or nano-inclusions in the mineral (*31*), mainly as heterogeneously distributed clusters of Cu(II) hydroxide or Cu(II) oxide. As a consequence of this, Cu could be immobilized inside stable crystalline alluminosiliceous materials.

According to Cheah et al. (*32*), CuO is more stable than $Cu(OH)_2$ even if $Cu(OH)_2$ is the phase that is commonly precipitated from aqueous solutions. However, $Cu(OH)_2$ would become the more stable phase when the precipitating particle sizes are small enough that surface energy could make an important contribution to the $Cu(OH)_2$ free energy. Presumably, with time, the precipitated Cu^{2+} phases would grow, and $Cu(OH)_2$ would be converted to CuO. The formation of amorphous geopolymers, especially in the fraction of coal fly ash that has not been transformed into more crystalline minerals (at least as can be seen by XRD), should also be considered to exhaustively describe the physicochemical processes that could contribute to Cu stabilization. As evaluated by EDTA sequential extractions, soil treatment with fused coal fly ash allowed 30−40% of Cu initially present in soil to be immobilized in the solid phase. Nevertheless, when solidification/stabilization techniques are employed for field applications, consideration of the concurrent effects of other constituents of the mixtures (e.g., cement, sodium silicates, etc.), with which fly ash is usually mixed, is essential.

In conclusion, this research shows that the process of zeolite formation in soils polluted by heavy metals and treated with mixtures containing coal fly ash and alkalizing agents could play a significant role in reducing the mobility of these dangerous pollutants. However, as a first study ever carried out on this kind of specific process, some of the conditions adopted in this research, such as soil artificial contamination and incubation temperatures, have been set up to simplify the system under investigation and to enhance the yield of zeolite synthesis and metal immobilization. Conditions unlike those reported in this investigation (e.g., lower temperatures) could lead to different yields and times of zeolite synthesis and therefore to dissimilar rates of Cu stabilization. Nevertheless, these results could be useful as basic knowledge for planning new technologies for the on site physicochemical stabilization of heavy metals in heavily polluted soils. Moreover, this work demonstrates that together with macroscopic data obtained from bulk sequential extractions methods, the information obtained from microscopic and submicroscopic synchrotron X-ray based analytical techniques is extremely useful for better understanding and more correctly evaluating the processes responsible for the stabilization of heavy metals in polluted soils.

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Supporting Information Available

μ-XRD data used to characterize the Zeolite X particles prior to μ-XRF tomography analysis and a graph reporting the pH time history of the fly ash versus the NaOH treated soil. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Conner, J. R.; Hoeffner, S. L. A critical review of stabilization/solidification technology. *Crit. Rev. Environ. Sci. Technol.* **1998**, *28* (4), 397−462.

(2) Dermatas, D.; Meng, X. Utilization of fly ash for stabilization/solidification of heavy metal contaminated soils. *Eng. Geol.* **2003**, *70*, 377−394.

(3) Mohapatra, R.; Rao, J. R. Some aspects of characterization, utilization, and environmental effects of fly ash. *J. Chem. Technol. Biotechnol.* **2001**, *76*, 9−26.

(4) Van Jaarsveld, J. G. S.; Van Deventer, J. S. J.; Lorenzen, L. The potential use of geopolymeric materials to immobilize toxic metals: Part I. Theory and applications. *Miner. Eng.* **1997**, *10* (7), 659−669.

(5) Van Jaarsveld, J. G. S.; Van Deventer, J. S. J.; Schwartzman, A. The potential use of geopolymeric materials to immobilize toxic metals: Part II. Material and leaching characteristics. *Miner. Eng.* **1999**, *12* (1), 75−91.

(6) Farmer, V. C.; McHardy, W. J.; Palmieri, F.; Violante, A.; Violante, P. Synthetic allophanes formed in calcareous environments: nature, conditions of formation, and transformations. *Soil Sci. Soc. Am. J.* **1991**, *55*, 1162−1166.

(7) Kloprogge, J. T.; Komarneni, S.; Amonette, J. E. Synthesis of smectite clay minerals: a critical review. *Clay Clay Miner.* **1999**, *47*, 529−554.

(8) Martinez, C. E.; McBride, M. B. Aging of coprecipitated Cu in alumina: Changes in structural location, chemical form, and solubility. *Geochim. Cosmochim. Acta* **2000**, *64* (10), 1729−1736.

(9) Bigham, J. M.; Schwertmann, U.; Traina, S. J.; Winland, R. L.; Wolff, M. Schwertmannite and the chemical modeling of iron in acid sulfate waters. *Geochim. Cosmochim. Acta* **1996**, *60* (12), 2111−2121.

(10) Sorensen, M. A.; Stackpoole, M. M.; Frenkel, A. I.; Bordia, R. K.; Korshin, G. V.; Christensen, T. H. Aging of iron (hydr)oxides by heat treatment and effects on heavy metal binding. *Environ. Sci. Technol.* **2000**, *34*, 3991−4000.

(11) Martinez, C. E.; Jacobson, A.; McBride, M. B. Thermally induced changes in metal solubility of contaminated soils is linked to mineral recrystallization and organic matter transformations. *Environ. Sci. Technol.* **2001**, *35*, 908−916.

(12) Newton, J. P.; Baveye, P.; Spagnuolo, M. Reduction of the bioavailability of PAHs in heavily contaminated soils and sediments via a physicochemical process. In *Bioavailability of organic xenobiotics in the environment*; Baveye, P., Block, J.-C., Goncharuk, V. V., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1999; pp 451−461.

(13) Atkins, M.; Glasser, F. P.; Jack, J. J. Zeolite-P in cements—its potential for immobilizing toxic and radioactive waste species. *Waste Manage.* **1995**, *15* (2), 127−135.

(14) Fernandez-Pereira, C.; Galiano, Y. L.; Rodriguez-Pinero, M. A.; Vale, J.; Querol, X. Utilization of zeolitized coal fly ash as immobilizing agent of a metallurgical waste. *J. Chem. Technol. Biotechnol.* **2002**, *77*, 305−310.

(15) Lin, C.-F.; Lo, S.-S.; Lin, H.-Y.; Lee, Y. Stabilization of cadmium contaminated soils using synthesized zeolite. *J. Hazard. Mater.* **1998**, *60*, 217−226.

(16) Edwards, R.; Rebedea, I.; Lepp, N. W.; Lovell, A. J. An investigation into the mechanism by which synthetic zeolites reduce labile metal concentrations in soils. *Environ. Geochem. Health* **1999**, *21*, 157−173.

(17) Cama, J.; Querol, X.; Ganor, J.; Ayora, C. Properties of fly ash synthetic zeolite NaP1 for soil remediation. *Geochim. Cosmochim. Acta* **2002**, *66* (15A), A116−A116.

(18) Oste, L. A.; Lexmond, T. M.; Van Riemsdijk, W. H. Metal immobilization in soils using synthetic zeolites. *J. Environ. Qual.* **2002**, *31* (3), 813−821.

(19) Terzano, R.; Spagnuolo, M.; Medici, L.; Tateo, F.; Ruggiero, P. Zeolite synthesis from pretreated coal fly ash in the presence of soil as a tool for soil remediation. *Appl. Clay Sci.* **2005**, *29* (2), 99−110.

(20) Terzano, R.; Spagnuolo, M.; Medici, L.; Tateo, F.; Ruggiero, P. Characterization of different coal fly ashes for their application in the synthesis of zeolite X as cation exchanger for soil remediation. *Fresenius Environ. Bull.* **2005**, *14* (4), 263−267.

(21) Chang, H. C.; Shih, W. H. A general method for the conversion of fly ash into zeolites as ion exchangers for cesium. *Ind. Eng. Chem. Res.* **1998**, *37*, 71−78.

(22) Toby, B. H. EXPGUI, a graphical user interface for GSAS. *J. Appl. Crystallogr.* **2001**, *34*, 210−213.

(23) Somogyi, A.; Drakopoulos, M.; Vincze, L.; Vekemans, B.; Camerani, C.; Janssens, K.; Snigirev, A.; Adams, F. ID18F: a new micro-X-ray fluorescence end-station at the European Synchrotron Radiation Facility (ESRF): preliminary results. *X-ray Spectrom.* **2001**, *30*, 242−252.

(24) Hammersley, A. Fit2D V12.034 (ESRF); www.esrf.fr/computing/scientific/FIT2D/index.html; 2004.

(25) Vekemans, B.; Janssens, K.; Vincze, L.; Adams, F.; Van Espen, P. Analysis of X-ray spectra by iterative least squares (AXIL)—New developments. *X-ray Spectrom.* **1994**, *23*, 278−285.

(26) Ressler, T. WinXAS: A XAS Data Analysis Program under MS Windows. *J. Synchrotron Radiat.* **1998**, 5, 118−122.

(27) Xue, H.; Sigg, L. Comparison of the complexation of Cu and Cd by humic or fulvic acids and by ligands observed in lake waters. *Aquat. Geochem.* **1999**, *5*, 313−335.

(28) Terzano, R. Zeolite synthesis in polluted soils treated with coal fly ash: a tool for heavy metals stabilization. Ph.D. Thesis, University of Bari, Bari, Italy, 2005.

(29) Ford, R. G.; Scheinost, A. C.; Scheckel, K. G.; Sparks, D. L. The link between clay mineral weathering and the stabilization of Ni surface precipitates. *Environ. Sci. Technol.* **1999**, *33*, 3140−3144.

(30) Garrabrants, A. C.; Kosson, D. S. Use of chelating agent to determine the metal availability for leaching from soils and wastes. *Waste Manage.* **2000**, *20*, 155−165.

(31) Wark, M.; Kessler, H.; Schulz-Ekloff, G. Growth and reactivity of zinc and cadmium oxide nanoparticles in zeolites. *Microporous Mater.* **1997**, *8*, 241−253.

(32) Cheah, S. F.; Brown, G. E., Jr.; Parks, G. A. XAFS study of Cu model compounds and Cu^{2+} sorption products on amorphous SiO_2, γ-Al_2O_3, and anatase. *Am. Miner.* **2000**, *85*, 118−132.

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