

Submicroscopic XRF-tomography investigation at ESRF-ID18F of Cu inside zeolite particles synthesized in polluted soil treated with coal fly ash

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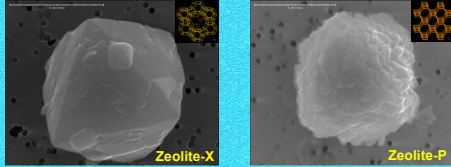
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INTRODUCTION

Many soil **solidification/stabilization (S/S)** technologies adopt **coal fly ash** and **alkalising agents** in order to reduce the mobility of **heavy metals** in polluted soils.

As a result of the application of such a treatment to a heavily polluted soil in highly alkaline conditions, the amorphous aluminosilicates constituting coal fly ash can, over time, undergo transformation into crystalline zeolitic minerals (**Zeolite-X** and **Zeolite-P**) [1].



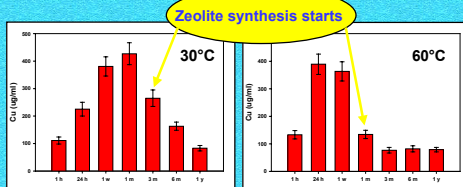
SEM micrographs of Zeolite-X and Zeolite-P isolated from a Cu polluted soil treated with fused fly ash.

During the crystallization process, the pollutant elements can be entrapped inside the new-formed minerals so that their threat to the environment is strongly reduced.

In this work, a **multiscale analytical approach** was used to evaluate the stabilization process of Cu over a long time period (**1 year**) in a highly artificially polluted (**15 mg Cu/g soil**) agricultural soil, where zeolites were getting synthesized as a consequence of the addition of **fused coal fly ash** [2] (fly ash/soil equal to 1/10 w/w). This process was studied at **30°C** and **60°C** and atmospheric pressure.

MACROSCOPIC investigation

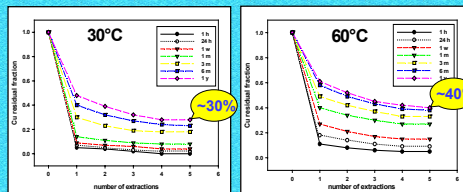
Cu solubility: the solubility of Cu over time was assessed by DPV or DPASV analysis of the soil solution.



Samples centrifuged at 20600 x g for 10 minutes, supernatants filtered (0.2 µm) and analysed on a HDME using a Metrohm 757 VA Computrace voltammeter. Background electrolyte: 0.1 M HNO₃.

Cu solubility observed after 1 year was more than **90% lower** than the one observed in the **untreated soil** after 1 year, both at 30°C and 60°C.

Cu availability: the availability of Cu over time was assessed by **sequential EDTA extractions** [3] (EDTA 5 mM, pH=7.5, 24h each) and DPV or DPASV analysis of the extracted fractions.



EDTA extractions data show that **Cu non-available fraction** increases over time and, after 1 year of incubation, it becomes about **30%** of the initial Cu amount at **30°C** and about **40%** at **60°C**.

MICROSCOPIC investigation

In order to verify that the observed data coming out from macroscopic bulk analysis were due to the stabilization of Cu inside the new-formed zeolites, several **X-ray based micro-analytical techniques** for the determination of the **spatial distribution** and the **speciation** of Cu in/on the new-formed zeolites were employed.

The zeolitic particles characterised in this study were isolated from the treated soil after 6 months of incubation both at 30°C and 60°C.

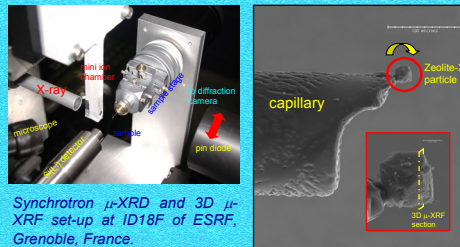
EPXMA

Zeolite-X and Zeolite-P were identified and characterized with respect to morphology and chemical composition by means of **Electron Probe X-ray Microanalysis (EPXMA)**. These zeolites were analyzed (E= 20 keV, I= 1 nA) after performing a dispersion of the treated soil with n-hexane over a 0.4 µm pore Nuclepore (Whatman) filter and covering it with carbon.

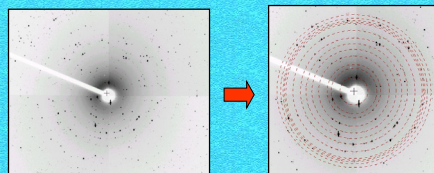
	Zeolite-X (30°C)	Zeolite-X (60 °C)	Zeolite-P (60 °C)
SiO ₂	53 ± 7 % w/w	53 ± 3 % w/w	62 ± 2 % w/w
Al ₂ O ₃	32 ± 4 %	33 ± 2 %	32 ± 2 %
Na ₂ O	1.3 ± 0.7 %	2.0 ± 0.9 %	3 ± 1 %
CaO	11 ± 3 %	7 ± 4 %	2 ± 1 %
Fe ₂ O ₃	1.7 ± 0.9 %	2 ± 1 %	1.1 ± 0.7 %
K ₂ O	1.9 ± 0.7 %	2 ± 1 %	2.3 ± 0.9 %
Si/Al	1.4 ± 0.2	1.4 ± 0.1	1.7 ± 0.1
Diam.	10 ± 2 µm	9 ± 5 µm	7 ± 2 µm

µ-XRD

The crystalline structure of single Zeolite-X particles was identified by means of **microscopic synchrotron X-ray diffraction (µ-XRD)**. These particles (**15-20 µm** diameter) were selected directly from the treated soil using an optical microscope and were mounted onto a quartz capillary (100 µm diameter) by means of a micromanipulator.



Synchrotron µ-XRD and 3D µ-XRF set-up at ID18F of ESRF, Grenoble, France.

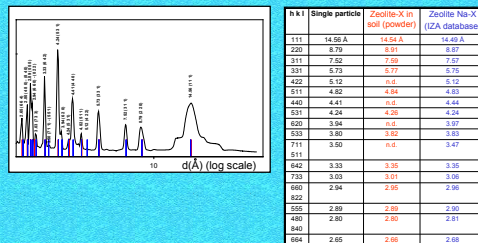


µ-XRD diffraction pattern resulting from the summation of diffractograms collected during a 360° rotation of the particle inside the X-ray beam.

The characteristic pattern of d-spacings (red circles) of Zeolite-X fits very well to the experimental data, as can be also seen in the integrated profile and in the table below.

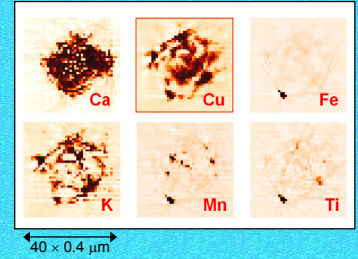
Beamsize: 0.5 µm (V) × 0.8 µm (H); E= 28 keV; I= 5×10⁹ ph/s.

Scan: φ= 0-360°, step size= 3°



3D µ-XRF

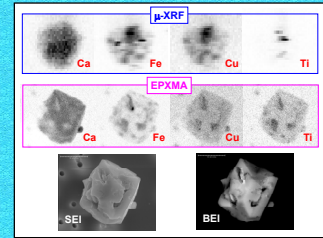
Simultaneously with µ-XRD data acquisition, also the **elemental distribution** of Cu and of other elements within the Zeolite-X particles were recorded by means of **microscopic synchrotron X-ray fluorescence tomography (3D µ-XRF)**. With this technique it was possible to directly look **inside a section** of the particles while none of the characteristic of the particle itself was altered.



Beamsize 0.5 µm (V) × 0.8 µm (H), E=28 keV; I= 5×10⁹ ph/s; Scan (V): 0.4 µm step size; Rotation: Φ=0-180°, 3° step size; Collection time: 2s per location.

2D µ-XRF

Cu distribution within individual Zeolite-X particles, together with that of other elements, was recorded by means of **microscopic synchrotron X-ray fluorescence mapping (2D µ-XRF)** and these data were compared with those coming from **EPXMA** superficial mapping on the same particle.

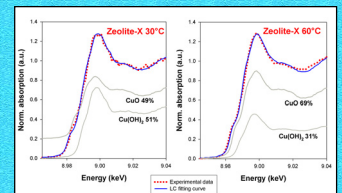


2D µ-XRF: beamsize 0.5 µm (V) × 0.8 µm (H), E=28 keV; I= 5×10⁹ ph/s; Scan: 1 µm² step size, 2 s collection time per location.

EPXMA: E= 15 keV, I= 15 nA, 2 h total collection time.

µ-XANES

The **chemical state** of Cu in/on the formed zeolite-X (both at 30 and 60°C) was investigated by means of **microscopic X-ray absorption near-edge structure (µ-XANES) spectroscopy** at HASYLAB, Beamline L, Hamburg, Germany. Preliminary results are reported. Further µ-EXAFS investigations are necessary in order to clarify in which forms Cu (II) is present in zeolites.



Polycapillary beamsizes: 20 µm. Scan: step size 1 eV each 5 s.

CONCLUSIONS

The results obtained from the multi-scale approach adopted in this research show that **Cu can be entrapped inside the mesopores of the newly-formed zeolitic structures as heterogeneously distributed clusters of microscopic or nano-inclusions of Cu(II) hydroxide/oxide**. In this way, Cu can be immobilized inside stable crystalline aluminosiliceous minerals.

In conclusion, this work demonstrates that, together with macroscopic data obtained from bulk sequential extractions methods, the information coming from the use of microscopic and sub-microscopic X-ray based analytical techniques is extremely valuable for a better understanding and a more correct evaluation of the processes that are responsible for the stabilization of heavy metals in polluted soils.

References:

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- Chang, H.C. and Shih, W.H. (1998). A general method for the conversion of fly ash into zeolites as ion exchangers for cesium. Industrial and Engineering Chemistry Research 37, 71-78.
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