

## THE ROLE OF CLAY MINERALS IN THE TRANSPORT OF INORGANIC CONTAMINANTS IN SEDIMENT

JESSICA BELLANOVA

Dipartimento Geomineralogico, Università di Bari "A. Moro", Via E. Orabona 4, 70125 Bari

### INTRODUCTION

In the framework of the activities related to the mitigation of natural and environmental hazards, the mineralogical and geochemical characterization of soil-subsoil plays a particularly significant role. In fact, the study of phenomena occurring in soils and sediments would provide useful information for the timely detection of the occurrence of environmental stress phenomena, and, therefore, for the development of innovative techniques for the monitoring and the remediation of polluted sites. In literature there are numerous studies on the phenomena of absorption and release of heavy metals by soils, sediments and their constituent components, such as clay minerals, oxides and hydroxides of iron and manganese, carbonates and organic matter (Elzahabi & Yong, 2001; Polcaro *et al.*, 2003; Manceau *et al.*, 2005). Numerous studies deal with the absorption of metals by clay, with the aim of assessing the feasibility of using these materials as a possible remedy in the case of deposition of contaminated waste, or where there is a high concentration of metals, as in the case of industrial areas. It is worth considering that almost all the experiments described in these studies were performed in laboratory, often with synthetic materials, and therefore they could hardly simulate all the natural conditions.

The aim of this work was to carry out the first experiment under controlled conditions at an intermediate stage between a laboratory scale and a field survey, in order to study the reactions of adsorption/release of some heavy metals (lead, copper, nickel, and zinc) by the two most common clay minerals (kaolinite and smectite), as well as their speciation and mechanisms of transport/release, by simulating a pollution event.

The experiment was performed at the "Hydrogeosite", a new testing ground realized by the Institute of Methodologies for Environmental Analysis (IMAA) of the National Research Council (CNR) of Marsico Nuovo (PZ); it consists of a covered structure, which occupies an area of 300 square meters, within which an underground pool, 12×7×3 m in size, was made. This testing ground allowed us to perform measurements close to the field scale and under controlled conditions. The pool was built in a particular armed cement, practically waterproof, and it was divided into two parts (Pool 1 and Pool 2) by an impermeable internal wall (Fig. 1).

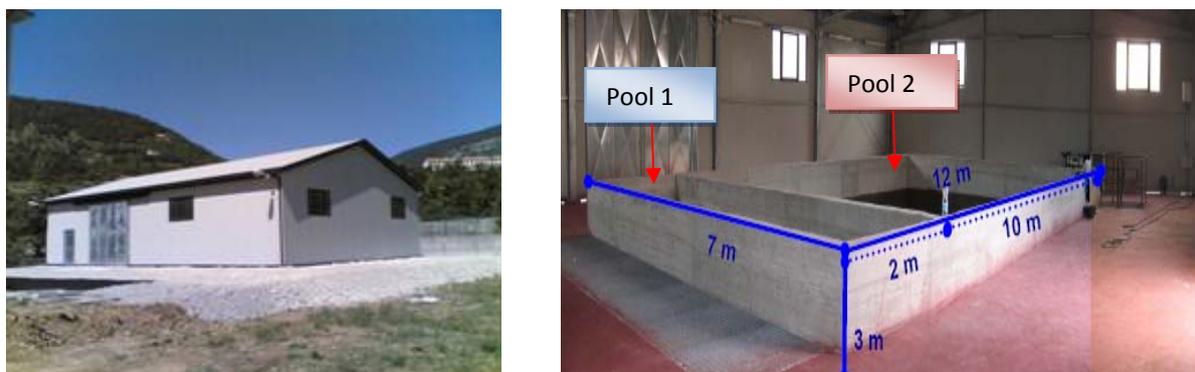


Fig. 1 - The large scale Hydrogeosite laboratory: external (left) and inside view (right).

The experiment was carried out in the Pool 1 (2×7×3 m) and consisted of the following steps: filling, pollution, and sampling.

### Filling

The first step was devoted to the research, the selection and the chemical- mineralogical characterization of sediments with the most suitable characteristics for carrying out the experiment. The sediments had two distinct mineralogical compositions: one was mainly composed of kaolinite and the other was nearly pure smectite. After this, the pool was divided into two areas ( $2 \times 3.35 \times 3$  m), hydraulically isolated using a bentonite septum (about 30 cm in thickness). The pool's floor was covered with a layer of gravel capped by a layer of sand, (both 20 cm in thickness), in order to control water discharge. On this two levels clay and silica sand layers, (25 cm in thickness), were alternately deposited. Therefore, each sector has a different alternating layers of sand, kaolin and bentonite, (Fig. 2).

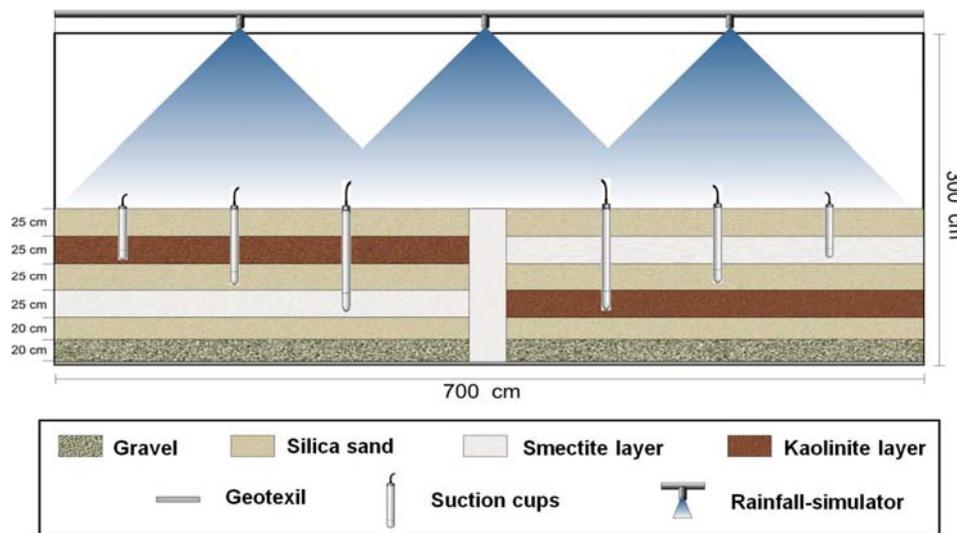


Fig. 2 - Stratification scheme of the Hydrogeosite.

### Pollution

Contaminated solutions were introduced through superficial sprinklers. The sediments were polluted with approximately  $3 \text{ m}^3$  of a solution containing Pb, Cu, Ni and Zn in the form of nitrate and having a concentration of  $10^{-4} \text{ N}$ , buffered at pH 5 with acetic acid (Bradbury & Baeyens, 1999). The solution was introduced through a rainfall-simulator constructed so that a simulated rain was distributed uniformly throughout the area and with a mean intensity corresponding to about 20 mm/hour.

### Sampling

During the experiment, both the interstitial solutions and the contaminated clays were sampled. Seven samples of the interstitial solutions were collected by a suction lysimeters in a period of 4 months between February and May 2010. On these samples the following analyses were performed: a) pH monitoring; b) concentration of silica, aluminium and heavy metals.

The sediment samples were collected using a micro-corer, after 1, 2, 3, and 6 months after the pollution event. The cores were taken in the first layer of sand and clay in both sectors.

### Chemical and mineralogical characterization

In order to carefully examine the mineralogical and chemical composition of the new phases formed and the chemical changes, which took place during adsorption and desorption processes, the adsorption of Zn, Co, Ni and Pb ions on kaolinite and smectite was investigated by PXRD, FESEM, XPS and ICP-MS. In particular:

- the mineralogical investigations were mainly aimed to the characterization of clayey sediments, sampled in the months following the pollution event, either to verify the possible formation of new phases or to have information on their structural variations, due to the absorption of heavy metals;

- the chemical analysis conducted on the two different clays and on the interstitial solutions were focused to evaluate the composition of clays and solutions before and after the pollution event, in order to follow the evolution of absorption of heavy metals;

- with the sequential selective extraction was possible to check the speciation of the contaminants in clays (Sahuquillo *et al.*, 1999);

- the X-ray induced Photoelectron Spectroscopy (XPS) was used to integrate the results obtained from the sequential extractions and, in particular, to have more details on the characteristics of metals on the surface of smectite and kaolinite;

- observations by Field Emission Scanning Electron Microscopy (FESEM) were carried out to identify the metal-containing phases in the samples taken before and after the pollution event.

Below are given briefly, for each type of sediment, the main results obtained from these investigations.

### *Bentonite*

The diffraction patterns of the polluted sediments have ruled out the formation of new phases containing heavy metals, or, at least, that their concentration was below the detection limits of the instrument. The diffractograms also showed a shift of the peak (001) of the smectite to higher angles with the increasing time of contact between the clay and the contaminated solution. The  $d_{001}$  value of the unpolluted bentonite is 15.22 Å, whereas 6 months after the pollution event the  $d_{001}$  shifted to 14.74 Å, thus showing a decrease of the basal spacing (Fig. 3).

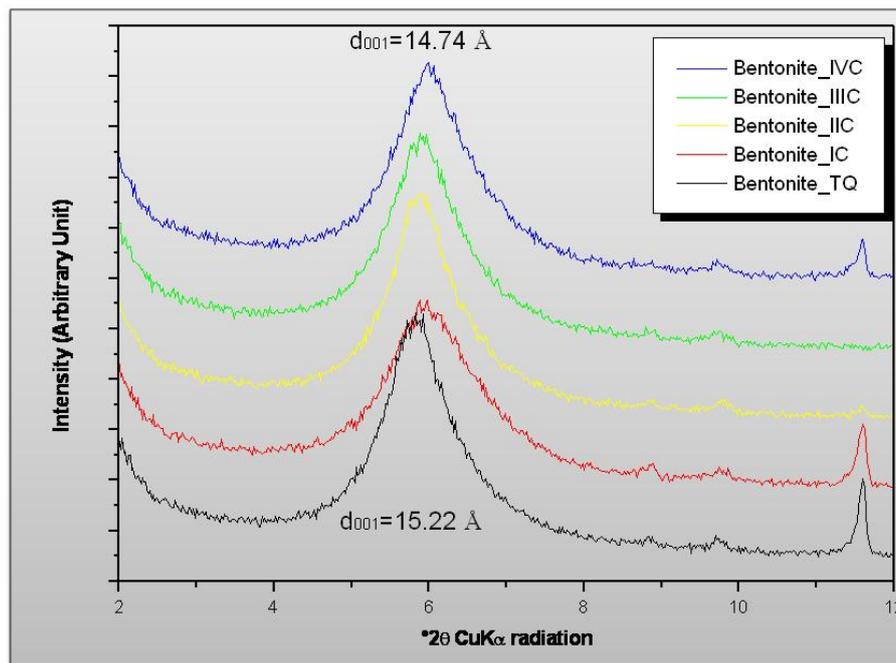


Fig. 3 - Diffractograms showing the shift of the smectite (001) peak.

The chemical analyses of the sediments showed that only the Pb concentration increases, whereas the others heavy metals remained roughly constant. The concentration of all metals decreases in the interstitial solutions. Nevertheless, the increase in Al, Ca, Mg, Na and K observed in the interstitial solutions could be explained by a partial replacement between these elements and lead. This increase could also be due to the

substitution, and subsequent dissolution, of Al in the structures of clay minerals by other elements such as Ni and Zn (Scheidegger *et al.*, 1997, 1998);

The chemical analyses of leachates, obtained from the attack of the exchangeable fraction, showed that concentrations of heavy metals did not increase. However, an increase of Ni, Cu and Zn in leachates, obtained from the fraction bounded to reducible phases, was observed. It could be assumed that Pb was absorbed in a non-exchangeable position, whereas the other metals surrounded predominantly the oxides that were present in the bentonite;

The XPS surveys did not show the presence of Pb in any of the spectra as well as in the narrow scans. Since XPS is a technique very sensitive to Pb, it was possible to conclude that it was not present on the first 7-8 nm of the smectite surface.

Finally, the FESEM investigations revealed the presence of precipitates containing lead.

Comparing the results obtained, it is possible to conclude that the increase in Pb found in bentonite was mainly due to the phenomenon of precipitation which led to the formation of small Pb-containing phases; they were observed by electron microscopy, but not detected by diffraction investigation, because of their low concentration. However, the observed decrease of the interlayer space in the smectite structure was probably due to the entry of Pb in its structure (Jozja *et al.*, 2006), but in concentrations not detectable by XPS.

#### *Kaolin*

The results of PXRD analysis ruled out the formation of new phases containing heavy metals. Moreover, the results showed only a small shift in the position of the 001 reflection of illite, whereas the 001 peak of kaolinite remained unchanged (Fig. 4).

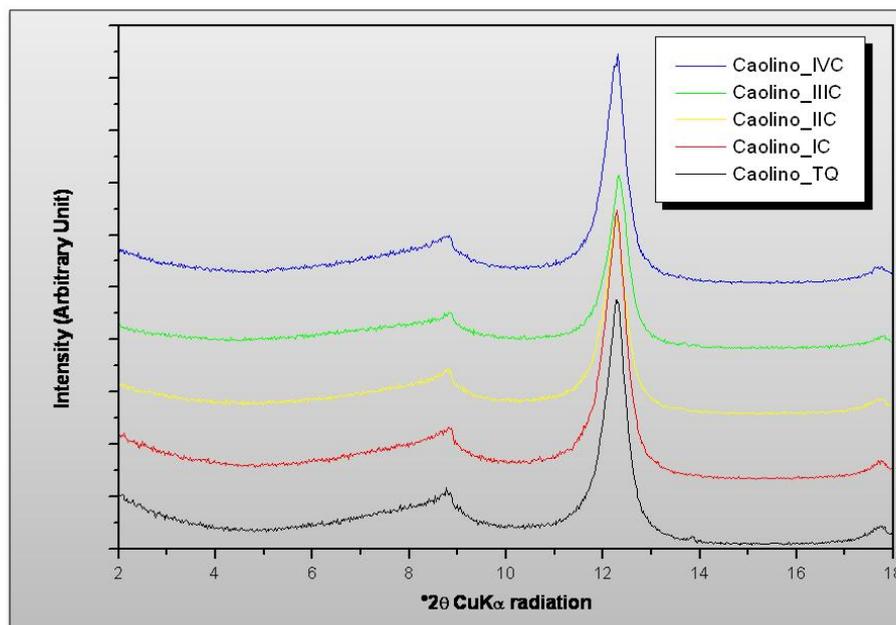


Fig. 4 - Diffractograms showing the (001) peaks of illite and kaolinite.

The chemical analyses of sediments suggested that the content of heavy metals was roughly constant; Al, Ca, Mg, and Na increased in the interstitial solutions, whereas the K content decreased.

The chemical analyses of leachates, obtained by the attack for exchangeable fraction and by fraction bound to the reducible phases, showed that the concentration of heavy metals increased in both fractions.

Finally, the FESEM observation showed the presence of Pb-bearing precipitates.

The joint analyses showed that kaolinite did not participate to the absorption reactions, due to its crystalline structure. In fact, this mineral is a 1:1 phyllosilicate with a structure that does not allow the entry of ions and/or molecules in the interlayer site. Hence, the variations in Na, Ca, Mg and K concentrations could be explained by a cation exchange reaction inside the illite structure. Heavy metals were precipitated as reducible phases, in agreement with the FESEM observations.

#### *Sand*

The silica sand was introduced in the experiment in order to act as drainage; moreover, it was chosen in a way that its composition does not affect the reactions between clay and heavy metals. Nevertheless, the data analysis documented that also the sand interacted with the polluted solution. In fact, the chemical analyses conducted on sand samples taken after the release of heavy metals evidenced an increase in their concentration. This increase may be due to the presence of Fe-, Cr-, Ni-, and Pb-bearing phases which acted as a sink for the metals contained in the polluted solution.

The preliminary results, obtained from the first mesoscale experiment in controlled conditions, led to the hypothesis that, in a simplified situation, the “scale factor” did not significantly affect the mechanisms of absorption/release of metals. On the other hand, however, it is necessary to extend the time of this experiment for a better understanding of the mechanisms leading to the increase of Si, Al, Ca, K, Mg, and Na in the interstitial solutions, combined with the decrease of heavy metals. Therefore, the study conducted in this PhD thesis, represents a first phase of future researches in the Hydrogeosite test site, whose future developments could be manifold.

#### REFERENCES

- Bradbury, M.H. & Baeyens, B. (1999): Modelling the sorption of Zn and Ni on Ca-Montmorillonite. *Geochim. Cosmochim. Acta*, **63**, 325-336.
- Elzahabi, M. & Yong, R.N. (2001): pH influence on sorption characteristics of heavy metal in the vadose zone. *Engin. Geol.*, **60**, 61-68.
- Jozja, N., Baillif, P., Touray, J., Muller, F., Clinard, C. (2006): Incidence of lead uptake of a (Mg, Ca)-Bentonite (Prrenjas, Albania). *Eur. J. Mineral.*, **18**, 361-368.
- Manceau, A., Tommaseo, C., Rihs, S., Geoffroy, N., Chanteigner, D., Schelegel, M., Tisserand, D., Marcus, M.A., Tamura, N., Chen, Z. (2005): Natural speciation of Mn, Ni and Zn at the micrometer scale in a clayey paddy soil using X-ray fluorescence, absorption and diffraction. *Geochim. Cosmochim. Acta*, **69**, 4007-4034.
- Polcaro, A.M., Mascia, M., Palmas, S., Vacca, A., Tola, G. (2003): Competitive sorption of heavy metal ions by soils. *Env. Engin. Sci.*, **20**, 607-616.
- Sahuquillo, A., López-Sánchez, J.F., Rubio, R., Rauret, G., Thomas, R.P., Davidson, C.M., Ure, A.M. (1999): Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. *Anal. Chim. Acta*, **382**, 317-327.
- Scheidegger, A.M., Lamble, G.M., Sparks, D.L. (1997): Spectroscopic evidence for the formation of mixed-cation, hydroxide phases upon metal sorption on clays and aluminum oxides. *J. Colloid Interface Sci.*, **186**, 118-128.
- Scheidegger, A.M., Strawn, D.G., Lamble, G.M., Sparks, D.L. (1998): The kinetics of mixed Ni-Al hydroxide formation on clay and aluminum oxide minerals: a time-resolved XAFS study. *Geochim. Cosmochim. Acta*, **62**, 2233-2245.