

# **Microspectroscopic study of the uptake of nickel by the host rock of Boda Siltstone Formation, Hungary**

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There is a general European consensus that high level nuclear waste will be disposed in deep geological formation. The type of suitable rock has to be selected by the individual countries, but many in Europe consider argillaceous rocks: Opalinus clay in Switzerland; Boom and Ypresian clays in Belgium, Callovo-Oxfordian and Toarcian clays in France and the Boda Siltstone Formation in Hungary. Clay minerals such as illite, smectite, illite/smectite mixed layers and kaolinite are important components in such rock types and can often make up 50 or more wt.% of the total mass. Transport in natural barriers depends strongly on retardation like chemical sorption or other physical processes. Consequently, an understanding of sorption processes, and of the physico-chemical parameters, which influences them, is becoming increasingly important. The present study focuses on the interaction of escaped radionuclides with the host-rock surrounding the planned high-level radioactive waste (HLW) repository in Hungary (Boda Siltstone Formation – BSF). The aim is to investigate the uptake mechanisms of key radionuclides on clay and other minerals of the host rock, by gaining information on the local environment of the element of interest using micro-EXAFS. Ni was selected for the present study as  $^{63}\text{Ni}$  is a key radionuclide representing corrosion products in HLW. Our previous micro-XRF/micro-XRD studies show that mainly illite is the responsible mineral phase for the Ni uptake of the rock [1].

The rocks investigated were prepared from geochemically characterized cores from drillings in BSF. Polished thin sections were prepared on 350- $\mu\text{m}$  thick high-purity silicon holders. The average thicknesses of the sections are 30-60  $\mu\text{m}$ . Two areas of interest were pre-selected from each sample. The samples were subjected to 72-hour sorption experiments with  $\text{Ni}^{2+}$  added at different concentrations (0.1 mM or 1 mM in 0.1 M NaCl solution, pH set to 7.0). The micro-distribution and the local environment of nickel in the argillaceous rock samples were investigated using micro-XRF and micro-EXAFS at the micro-fluorescence Beamline L of HASYLAB. The white beam of a bending magnet was monochromatized by a Si(111) double crystal monochromator. A polycapillary half-lens (X-ray Optical Systems) was employed for focusing a beam of  $3 \times 1.5 \text{ mm}^2$  down to a spot size of 15  $\mu\text{m}$  diameter. The absorption spectra were recorded in fluorescence mode, tuning the excitation energy near the K absorption edge of Ni by stepping the Si(111) monochromator, while recording the Ni-K $\alpha$  fluorescence yield using an energy-dispersive Radiant silicon drift detector. The energy step and the measurement time for each energy point was varied using the “EXAFS” scan utility, taking into account the necessary statistics for the EXAFS oscillations. A series of micro-EXAFS measurements were performed on the thin sections, at points of interest (POI) with different Ni content. Up to 16 scans were averaged in order to get a sufficient signal to noise ratio. Standard EXAFS data treatment was performed using the ATHENA software package [2]. Fe K-edge micro-EXAFS measurements were also performed as supporting information on the microscopic distribution of differently bound iron in the clayey matrix.

Micro-XRF elemental maps collected at an excitation energy of 8800 eV revealed that mostly K- and Fe-rich phases – clay minerals and iron oxides – are responsible for the Ni uptake of the rock (Fig. 1). The micro-EXAFS spectra can be divided into three categories: 1) The observation of Ni-Ni backscattering pairs indicate the formation of a Ni precipitate. Since the initial solution was undersaturated with respect to  $\text{Ni(OH)}_2$  this precipitation is either induced by the surface or the sample preparation method. 2) Several micro-EXAFS spectra could be fitted without adding Ni-Ni backscattering pairs, indicating the formation of inner-sphere surface complexes (Fig. 2). 3) A mixture of surface complexes and surface precipitates (Fig. 2). Since Ni-Fe backscattering pairs could not totally be excluded from the fit, the role of iron oxide nanocrystals embedded in the clayey matrix needs further investigation.

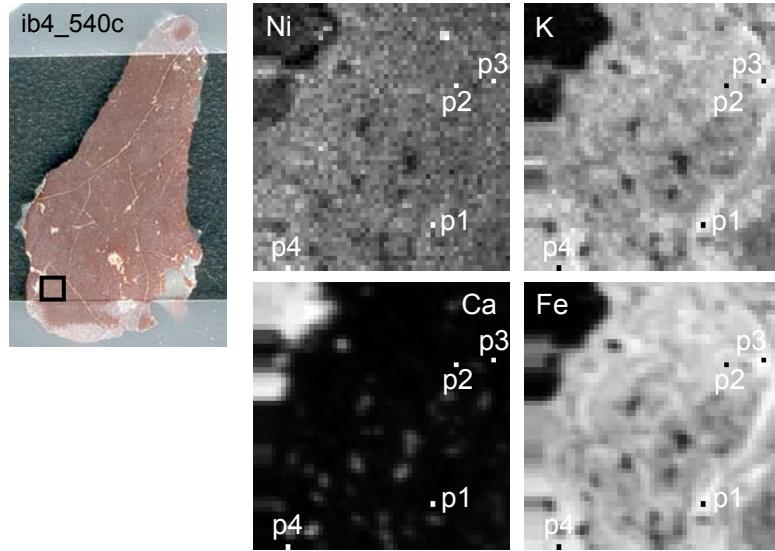


Figure 1: Microscopic image of sample ib4\_540c treated by solution containing 0.1 mM  $\text{Ni}^{2+}$ . Elemental maps of K, Ca, Fe and Ni correspond to the area marked by a rectangle in the microscopic image. Selected points of interest (POIs) of micro-EXAFS measurement are highlighted in white (Ni, Ca) or black (K, Fe).

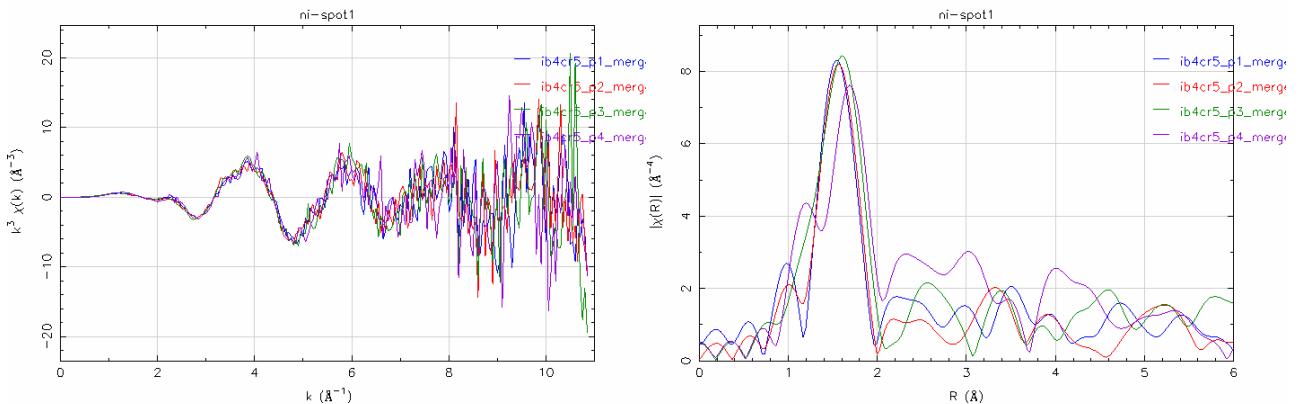


Figure 2:  $k^3$ -weighted Ni K-edge micro-EXAFS spectra of various POI, and the corresponding RSF's, obtained by Fourier Transforming the micro-EXAFS spectra in the range from 2 to  $10 \text{ Å}^{-1}$ .

The selected POIs were measured using Fe-K micro-EXAFS as well. The ratio between Fe in clay and Fe in hematite was obtained by fitting of linear combinations (LC) of a hematite ( $\text{Fe}_2\text{O}_3$ ) and an Fe-rich clay (IdP, Illite du Puy, 7 %  $\text{Fe}_2\text{O}_3$ ) standard (both samples were diluted with BN in order to obtain an edge jump of one). The LC fitting results indicate that 50( $\pm 5$ )% Fe is present as Fe in clay and 50( $\pm 5$ )% Fe is present as hematite, from which an illite–hematite ratio of 14:1 can be estimated for all POIs, indicating a homogeneous dispersion of hematite nanocrystals in the clayey matrix even within a  $20 \times 20 \mu\text{m}^2$  area of the samples.

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## References

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