

Micro-XRF and micro-EXAFS study of the uptake of nickel by argillaceous rocks

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One of the main aspects in evaluating the safety of a potential radioactive waste repository in a deep geological formation is to understand the geochemical and physical processes that influence the mobility of the radionuclides in the geochemical environment imposed by the host rock and to quantify these processes. This information is needed to make reliable predictions of the long-term safety. Once radionuclides are released from the waste packages and the surrounding engineered barriers, they can migrate by diffusion through the argillaceous host rock towards the biosphere. This transport occurs in the pore solution of the host rock and is function of the quantity of the dissolved radionuclides in the solution phase (= the mobile part). When radionuclides come in contact with a solid matrix (for instance the clay host rock), they will redistribute between the solid and the aqueous phases. The equilibrium distribution is determined essentially by sorption [1].

Argillaceous rocks are being viewed with continuing interest in many waste management programmes as suitable host formations for the deep geological disposal of radioactive waste: Opalinus clay, Switzerland; Boom and Ypresian clays, Belgium, Callovo-Oxfordian and Toarcian clays, France; Boda Siltstone Formation, 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. One of the most important characteristics of many clay minerals is their generally strong radionuclide retention properties.

The rocks investigated were prepared from geochemically characterized cores from drillings in Boda Siltstone Formation, Hungary. Polished thin sections were prepared on 1-mm thick high-purity quartz glass holders. The average thicknesses of the sections are 30-60 μm . Two areas of interest were pre-selected from each sample. The samples are albitic clay stones that represent the most significant constituent of Boda Siltstone Formation. Thin sections were placed for 72 hours into a synthetic ground water solution representative for Boda Siltstone Formation with 0.1 mM Ni^{2+} or 1 mM Ni^{2+} added. After the treating period the samples were dried up by high pressure Ar gas.

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 (Hamburg, Germany). The white beam of a bending magnet was monochromatized by a Si(111) double 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 μm diameter. The absorption spectra were recorded in fluorescent mode, tuning the excitation energy near the K absorption edge of Ni by stepping the Si(111) monochromator, while recording the Ni-K α fluorescent 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. Energy scans in the 8150–8800 eV range could be collected using MOSTAB without any problems, indicating the feasibility of micro-EXAFS at Beamline L. 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].

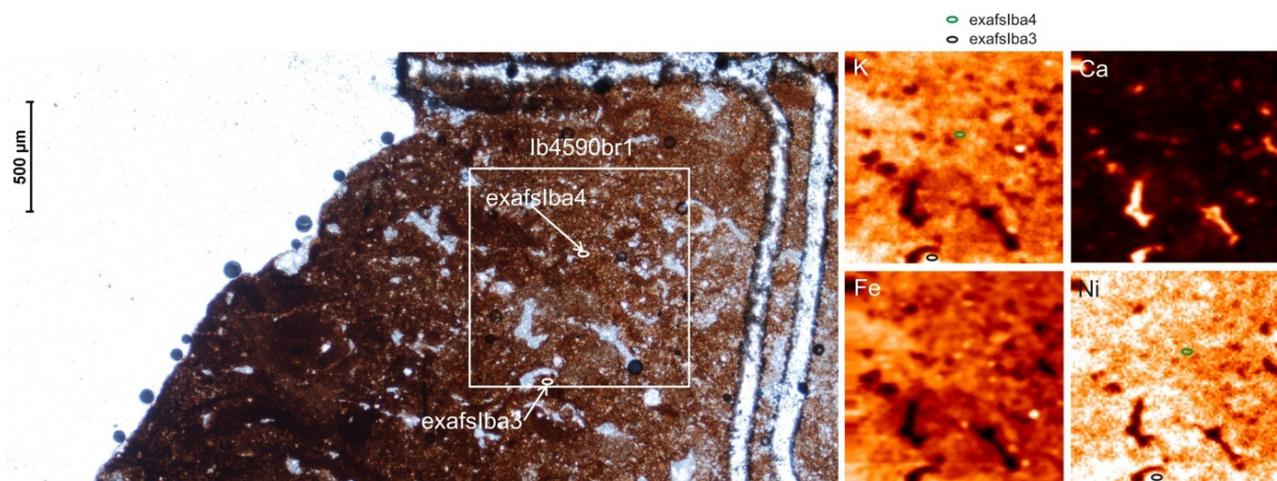


Figure 1: Microscopic image of sample Ib-4/590b treated by solution containing 0.1 mM Ni²⁺. Elemental maps of K, Ca, Fe and Ni correspond to the area marked by a rectangle in the microscopic image. Selected positions of micro-EXAFS measurement are marked with ellipses.

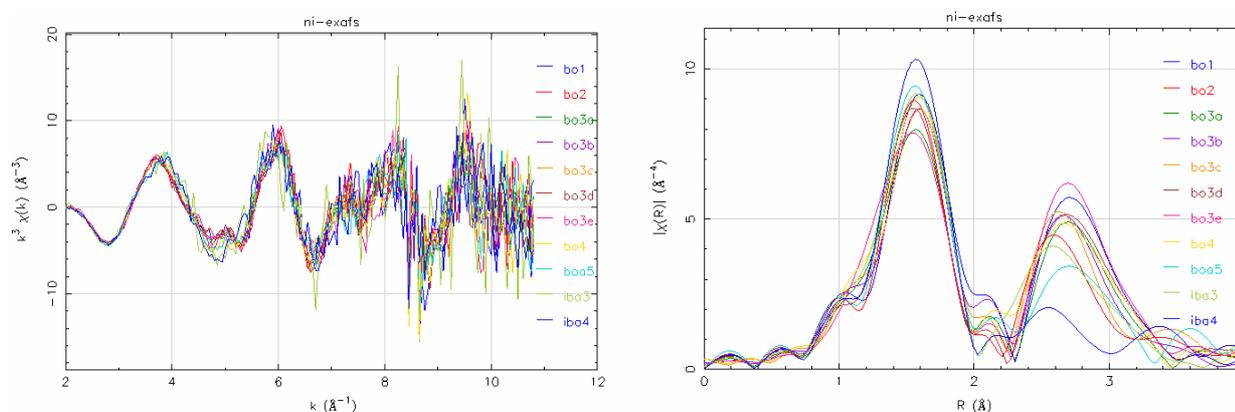


Figure 2. k^3 -weighted Ni K-edge micro-EXAFS spectra of various POI, and the corresponding RSF's, obtained by Fourier Transforming the micro-EXAFS spectra in the range from 2 to 10 Å⁻¹.

Micro-XRF elemental maps collected at an excitation energy of 17500 eV revealed that mostly K-rich phases – clay minerals – are responsible for the Ni uptake of the rock. The precise identification of the particular clay minerals responsible for the sorption would need additional micro-XRD investigations.

The strong second peak in the radial structure functions (RSF) at $R+\Delta R = 2.7$ Å indicates the formation of a precipitate from the Ni-containing synthetic ground water solution on the rock surface, and can mainly be attributed to Ni-Ni backscattering pairs (Fig. 2). The micro-EXAFS spectra of the POI Exafsiba4, however, can be fitted without any Ni-Ni backscattering pair, indicating the formation of a surface complex. The obtained fitted structural parameter (5.3 Ni-O at 2.05 Å, 1 Ni-Al at 3.03 Å, and 2.1 Ni-Si 3.3 Å) are consistent with Ni-uptake on “weak sites” of clay minerals.

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References

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