



Microscale analysis of metal uptake by argillaceous rocks using positive matrix factorization of microscopic X-ray fluorescence elemental maps



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ABSTRACT

Argillaceous rocks are considered in most European countries as suitable host rock formations for the deep geological disposal of high-level radioactive waste (HLW). The most important chemical characteristic in this respect is their generally strong radionuclide retention property due to the high sorption capacity. Consequently, the physico-chemical parameters of these processes have to be studied in great detail. Synchrotron radiation microscopic X-ray fluorescence (SR μ -XRF) has sufficient sensitivity to study these processes on the microscale without the necessity of the application of radioactive substances. The present study focuses on the interaction between the escaped ions and the host-rock surrounding the planned HLW repository. SR μ -XRF measurements were performed on thin sections subjected to sorption experiments using 5 μ m spatial resolution. Inactive Cs(I), Ni(II), Nd(III) and natural U(VI) were selected for the experiments chemically representing key radionuclides. The thin sections were prepared on high-purity silicon wafers from geochemically characterized cores of Boda Claystone Formation, Hungary. Samples were subjected to 72-hour sorption experiments with one ion of interest added. The μ -XRF elemental maps taken usually on several thousand pixels indicate a correlation of Cs and Ni with Fe- and K-rich regions suggesting that these elements are predominantly taken up by clay-rich phases. U and Nd was found to be bound not only to the clayey matrix, but the cavity filling minerals also played important role in the uptake. Multivariate methods were found to be efficient tools for extracting information from the elemental distribution maps even when the clayey matrix and fracture infilling regions were examined in the same measured area. By using positive matrix factorization as a new approach the factors with higher sorption capacity could be identified and with additional mineralogical information the uptake capacity of the different mineral phases could be quantified. The results were compared with cluster analysis when the regions dominated by different mineral phases are segmented. The multivariate approach based on μ -XRF to identify the minerals was validated using microscopic X-ray diffraction.

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1. Introduction

In most European countries, clay-rich rocks are considered as suitable host rock formations for isolation of the radionuclides generated by the nuclear industry from the biosphere for thousands of years. During this time period the radionuclides might migrate from the engineered barriers and the safety is determined by the retention capability of the host rock. Following water intrusion into the repository, radionuclide contaminants can be released. Clay rocks have very good retention capability due to their high sorption capacity. Sorption depends on the water/solid compositions, porewater properties such as pH and Eh, as well as the presence of complexing anions as they determine the radionuclide chemical speciation. The interaction of radioactive ions with clay minerals has been thoroughly studied in the

past [1–3]. Nowadays, most attempts to quantify the retention function are focused on the measurement of distribution ratios (K_d) between the mobile and stationary phase [4–6]. These experiments are necessary but will not give the final answer to the questions: which minerals retain the radionuclides and how reversible the processes are (type of chemical bonds involved). With the revolutionary development of X-ray sources (synchrotrons) and optics such questions can be answered by micro scale resolution spectroscopy and diffraction techniques [7–11]. A recent review emphasizes the relevance of versatile micro- and nanoanalytical techniques for actinide environmental research [12].

Microscopic X-ray fluorescence (μ -XRF) spectroscopy combined with microscopic X-ray diffraction (μ -XRD) is a unique possibility to study these highly heterogeneous rocks [10,13]. The samples and the sorption concentrations must be in the good analytical performance domain of the used techniques.

Geological samples are most often studied with microscopy techniques using petrographic thin sections prepared from the rocks

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of interest. Sorption experiments involving thin sections have to be designed in order to model the chemical conditions present at the depth of the planned repository. Also, the concentrations of the elements of interest in the solutions involved should be sufficiently low in order to avoid precipitation. For this reason, the element of interest after sorption experiment will be present in minor or trace concentration level heterogeneously distributed in the sample. Due to its high dynamic range, μ -XRF is a suitable tool to detect simultaneously the distribution of the sorbed elements of interest and elements corresponding to rock-forming minerals. Especially excitation using synchrotron radiation (SR) offers a lateral resolution of 5 μm or better, in the same dimension as heterogeneities in the studied rocks. It is also advantageous that the key radionuclides representing transuranium elements, fission and corrosion products that are not present in the rock can be substituted with inactive or natural analogues without requiring high activity radioisotopes for microscopic sorption studies.

Although SEM/EDX is well suited for determination of major elements in thin sections, the usually applied high vacuum can cause dehydration and collapse in clay mineral structure [14,15] hindering additional studies of the uptake mechanism on the same samples. The low-vacuum version of the method, however, suffers from limited quantitativeness. Powder μ -XRD has limitation as well in phase determination because oriented crystals comparable to the beam size can be present in the samples of interest. The presence of oriented crystals can yield erroneous crystalline composition by μ -XRD since some representative reflections can be missing from the diffractograms.

Two-dimensional scanning of a selected area using μ -XRF results in a large data matrix with dimensions $n_{el} \times n_x \times n_y$, where n_{el} is the number of analyzed elements, n_x and n_y are the number of scanned pixels horizontally and vertically, respectively. Even though μ -XRF performed in air is not capable of detecting major light elements (O, Na, Mg, Al), information on the mineral phases responsible for the uptake of the radionuclide of interest can be derived from the data set if suitable mathematical methods are applied for data treatment. The assumptions derived from μ -XRF can be verified using μ -XRD phase analysis at representative selected positions [10,13].

One possibility is to examine inter-elemental correlations through scatter plots of the X-ray intensities of two selected elements. The connection of the element of interest to a given mineral phase can be judged based on the similarity of the correlation between two elements representative for the mineral phase and the correlation between each of these elements and the element of interest. The single value of the correlation coefficient bears insufficient information since more mineral phases can be present in the scanned area. Due to differences in sample thickness and matrix composition, the position of the points in the scatter plot can deviate from the expected straight line, even if the concentration ratio of the two elements is constant, which has to be taken into account [16,17].

Other possibility is to apply multivariate methods such as principal component analysis (PCA) or factor analysis (FA). These methods are generally used for analysis of large data sets. However, the expression of factors in the original variables (factor loadings) can contain negative values expressing anticorrelation with original variables (chemical elements). This problem can be overcome by using positive matrix factorization (PMF), since the factor loadings (called as factor profiles in PMF) are forced to be positive. PMF is commonly used in air pollution studies where factors representing sources are derived from the time variation of pollutant concentrations [18–20]. PMF was successfully applied to process three-dimensional datasets, e.g. distribution maps from Raman imaging [21]. However, no applications of PMF to scanning μ -XRF datasets have been reported to date.

Segmentation of the data set can be performed using cluster analysis, based on the similarity (distance) of the pixels in the abstract space defined by elemental X-ray intensities. The most commonly used method is the non-hierarchical K-means clustering algorithm. Instead of using the original variables (elemental intensities), PCA

pretreatment can be useful, where clustering is performed in a space with reduced dimensions [22–24].

The aim of the present study was to evaluate the combination of μ -XRF and multivariate methods especially PMF as a new mathematical approach for application in sorption studies involving argillaceous rock thin sections in order to obtain quantitative information on the sorption capacity of the mineral phases responsible for the uptake. The presence of the phases predicted by μ -XRF was verified by μ -XRD. The performance of the combined method is discussed on thin clay rock sections subjected to sorption experiments, using inactive Cs(I), Ni(II), Nd(III) and natural U(VI), chemically representing fission and corrosion products as well as transuranium elements of interest.

2. Materials and methods

2.1. Samples

The rocks investigated were prepared from geochemically characterized cores from drillings in Boda Claystone Formation (BCF), considered as a possible formation for high-level radioactive waste (HLW) repository in Hungary. The Upper Permian sedimentary sequence of the BCF is located in West-Mecsek Mountains, SW Hungary. The sediments of the BCF are dominantly red and reddish brown in colour, reflecting the oxidizing nature of the depositional and early diagenetic environments. The BCF was deposited in a shallow-water salt lake environment surrounded by dry to saline mudflat, under semi-arid to arid climatic conditions [25–28]. Two distribution areas of BCF are known in West-Mecsek Mountains, the perianticline structure of the West-Mecsek Anticline (WMA) Block and the Gorica Block (GB) [28].

The main rock-forming minerals of the BCF are: clay minerals (mainly illite and chlorite), authigenic albite, analcime (GB only), detrital quartz, carbonate minerals (calcite and dolomite) and hematite [29,30]. The rocks are highly heterogeneous on the microscale, two major regions can be distinguished, the clayey matrix and the fracture infillings. High amount of clay minerals (around 50 m/m% phyllosilicates, mainly illite-muscovite, chlorite, kaolinite and mixed structure clay minerals) as well as albite cement (and analcime cement for GB) form the clayey matrix. The most important clay mineral is illite, containing potassium and iron. Nanoscale hematite flanks were detected between illite plates by transmission electron microscopy [31]. The fracture infillings contain mostly authigenic albite (or analcime for GB), carbonate minerals (calcite and dolomite) and authigenic potassium feldspar. The absolute dominant rock type of the formation is albitic claystone in the WMA Block and albite- and analcime-bearing claystone in the Gorica Block [32].

Representative core samples were selected from both blocks for preparation of thin sections. Small pieces of selected core samples from GB (sample Ib-4) and WMA (sample D-11) were grinded and mounted onto 350- μm thick high purity silicon wafers and polished by 0.25 μm diamond paste. The average thicknesses of the sections were 50 μm . Samples were subjected to 24–72 hour sorption experiments with one ion of interest added, using synthetic porewater for Cs and Ni, and a 0.1 M NaCl solution for Nd and U as background electrolyte. The NaCl solution was applied due to solubility constraints to ensure a sufficient loading of the element of interest to match the sensitivity of μ -XRF while avoiding precipitation in the solution itself.

2.2. Microscopic XRF/XRD measurements

The experiments were performed at the FLUO beamline of ANKA. The white beam of a bending magnet was monochromatized by a W/Si multilayer double monochromator. A silicon-drift detector was used to collect fluorescence spectra. The μ -XRF elemental mapping measurements were performed at a primary beam energy of 17.5 keV ($\Delta E/E = 10^{-2}$), using a compound refractive lens for focusing a beam down to a spot size of $2 \times 5 \mu\text{m}^2$. Elemental maps were recorded for

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