Interaction of Pu with Opalinus Clay Studied by μ-XRF, μ-XRD, and μ-XANES

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Abstract

A combination of spatially-resolved synchrotron based techniques (μ-XRF, μ-XRD, μ-XANES) was used to study the distribution and speciation of Pu on Opalinus Clay (OPA) after sorption and diffusion processes. μ-XRF maps showed Ca, Fe, and Pu hot spots on the OPA surface of all investigated thin sections. Pu L_{III}-edge μ-XANES spectra on Pu hot spots confirmed that Pu(IV) is the dominating species on OPA, i.e., the highly soluble Pu(VI) was retained by OPA in the reduced and less mobile tetravalent oxidation state of Pu. Preliminary μ-XRD results indicate that Pu is localized on or in the close vicinity of the Fe(II) mineral siderite and the clay mineral kaolinite.

Introduction

Plutonium will be a major contributor to the radiotoxicity of high-level nuclear waste after a storage time of more than 1,000 years due to the long half-lives of ^{239}Pu, ^{240}Pu, and ^{242}Pu. Argillaceous rocks are under consideration as potential host rock formation for the construction of high-level nuclear waste repositories in several European countries, i.e., Belgium, France, Germany, and Switzerland [1]. The aim of our study was to improve our understanding of the interaction of Pu with natural opalinus clay at a molecular level. Such studies are important in the context of save disposal and long-term storage of hazardous radioactive wastes.

Experimental

The speciation of ^{242}Pu(VI) sorbed on OPA has been investigated by μ-XANES, μ-XRF, and μ-XRD measurements. For this study three samples were prepared: two thin sections of OPA on glass object slides and one sample from an intact OPA drill core, which was contacted with 20 μM ^{242}Pu(VI) in OPA pore water (pH= 7.6) for more than one month. In one sample, (20 μM, pH=7.6) ^{242}Pu(VI) solution was deposited directly by pipetting on the thin section. For the second sample, (20 μM, pH=7.6) ^{242}Pu(VI) was sorbed using a deposition cell. A summary of the employed sample preparation methods as well as the chemical conditions are listed in Table 1.

Table 1. Summary of the measured samples

Samples	Preparation	pH	Sample area (mm^2)	Activity of ^{242}Pu (Bq)	Pu (ng/mm^2)
^{242}Pu(VI)	Sorption	7.6	19.6	917	311
^{242}Pu(VI)	Deposition	7.6	50.7	750	96
^{242}Pu(VI)	Diffusion	7.6	510.4	400	7

Pu L_{III}-edge µ-XANES spectra were collected on several Pu hot spots. Background and energy correction of these spectra were performed using the software package Athena [2]. By using an iterative transformation factor analysis program (ITFA) [3], the amounts of different Pu oxidation states (IV, V, VI) on the measured hot spots were determined. XRD data was analysed using the Area Diffraction Machine software program [4]. All data were recorded using the dedicated radioactive X-ray microprobe setup of the microXAS beamline facility at the Swiss Light Source.

Summary and Conclusions

For all samples fluorescence maps with good signal intensity were collected for Pu, Ca, and Fe. Figure 1 shows, for example, the µ-XRF maps of Pu, Fe, and Ca on the sorption sample. In this sample several hot spots of Pu, Fe, and Ca can be found. In the regions where Pu localizes, the correlation between Pu and Fe was analyzed using the program XY-MAP DISPLAY [5]. The resulting correlation plots (not shown) do not immediately point towards an unequivocally correlation between the local concentrations of Pu and Fe. However, in all cases where elevated levels of Pu were detected, a moderately enhanced Fe concentration could be established as well. Areas of highest Fe concentrations, however, turned out to be free of Pu. Similar correlated detection of Pu and Fe was observed also in the diffusion sample.

Pu L_{III}-edge µ-XANES spectra of Pu hot spots show a complete reduction of Pu(VI) to Pu(IV) in all samples. Pu(IV) is the dominating oxidation state after sorption and diffusion processes. Figure 1 shows the Pu L_{III}-edge µ-XANES spectrum and µ-XRD images of the hot spot in the sorption sample. Preliminary results of µ-XRD measurements indicate that Pu potentially localizes on siderite and kaolinite mineral phases contained in OPA (see Figure 2).
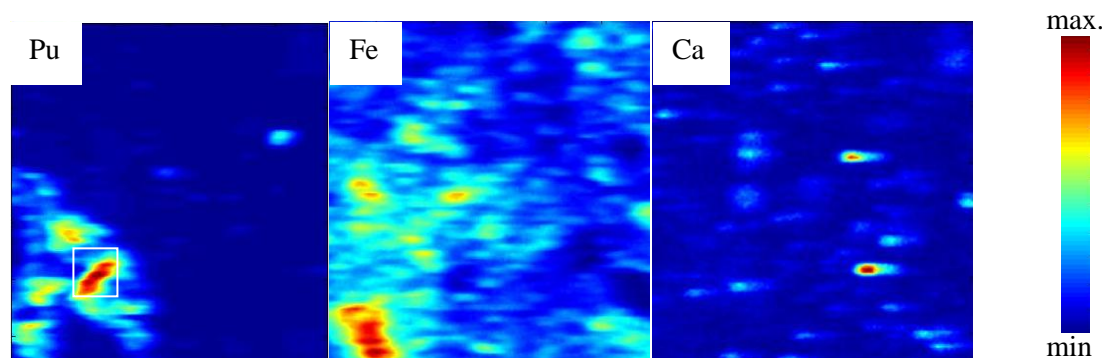

Figure 1. µ-XRF maps for Pu, Fe, and Ca of sorption sample (200µm X 200 µm). Square in the left figure indicates the selected location for recording µ-XANES.
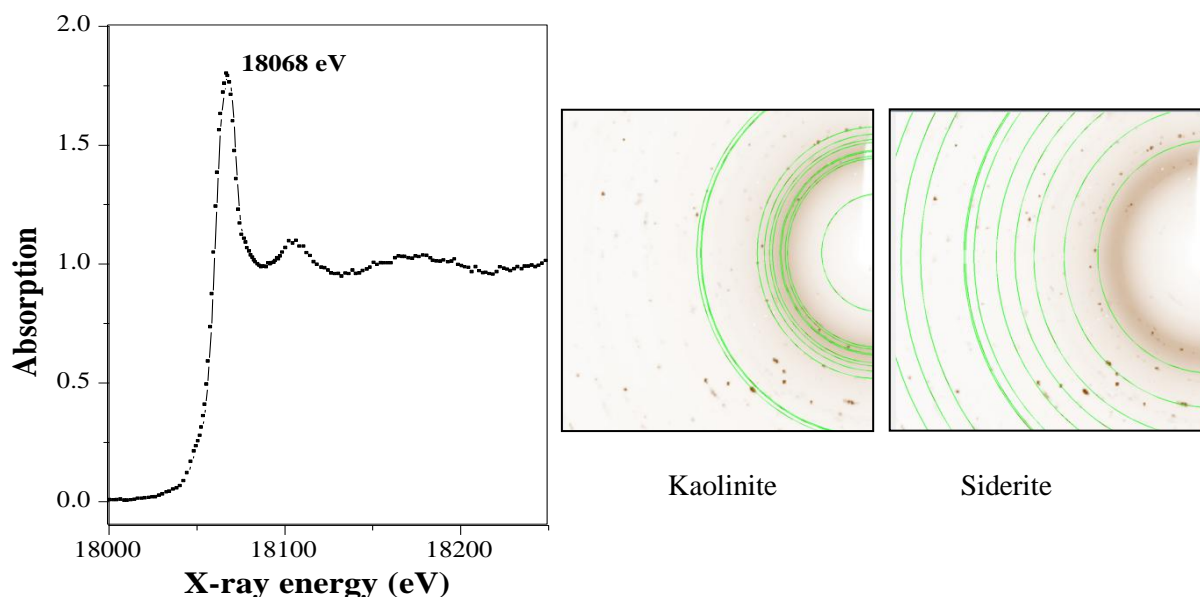
Figure 2. Normalized Pu L$_{III}$-edge μ-XANES spectrum and two dimensional μ-XRD image transmission mode of Pu hot spot in sorption sample. The Debye rings for kaolinite and siderite are shown in green.

References

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