

Micro-XRF and micro-XAFS study of Pu sorption on Opalinus Clay

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The aim of this study was to improve this understanding of the interaction of plutonium (Pu) with natural clay at a molecular level. Such studies are important in the context of the safe disposal and long-term storage of hazardous radioactive wastes. The transport and retardation of Pu in clays is mainly determined by sorption and diffusion processes. In the present work a combination of spatially-resolved synchrotron based techniques was used to determine Pu speciation after sorption and diffusion process of Pu in Opalinus Clay (OPA, Mont Terri, Switzerland). The elemental distributions of Pu and of several elements contained in OPA (e.g., Ca, Fe) were determined by μ -XRF measurements. Regions with high Pu concentrations were then analyzed by μ -XANES to determine the oxidation state of Pu. The distribution of crystalline mineral phases near Pu enrichments (hot spots) was investigated using μ -XRD. For our measurements at the micro-XAS beamline at the Swiss Light Source, two types of samples were prepared: thin sections from sorption or deposition experiments of Pu on OPA (on glass object slides) and one sample from an in-diffusion experiments. In one thin section $^{242}\text{Pu(VI)}$ solution was deposited directly by pipetting on OPA. For the second thin section sample $^{242}\text{Pu(VI)}$ was sorbed using a sorption cell. For the diffusion sample an intact OPA bore core was contacted with $^{242}\text{Pu(VI)}$ in OPA pore water for more than one month in a diffusion cell. After that the OPA was removed from the cell, dried, cut into small pieces, and one piece was measured. An overview of measured samples is shown in Tab. 1.

Table 1 : Summary of the measured Pu samples

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

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 [1]. Scatter plots (not shown) showed a significant correlation between Pu and Fe in some regions. Pu L_{III} -edge μ -XANES spectra were collected on several Pu hot spots. Figure 2 shows for example the Pu L_{III} -edge μ -XANES of the marked hot spot in the sorption sample (see Fig. 1). The Pu L_{III} -edge occurs at 18068 eV, which agrees well with

Pu L_{III} -edge energy of the Pu(IV) aquo ion [2]. By analysing the XANES spectra with an iterative transformation factor analysis program (ITFA) [3], the relative amounts of different Pu oxidation states in the measured hot spot were determined to be > 90% Pu (IV). Generally, in all measured samples a complete reduction of Pu(VI) to Pu(IV) was found. Therefore, Pu(IV) is the dominating oxidation state after sorption and diffusion processes.

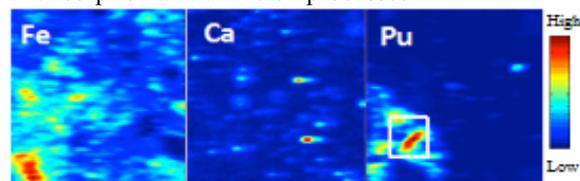


Figure 1: μ -XRF maps for Fe, Ca and Pu of sorption sample (120 μm X 120 μm , step size: 10 μm). Square in the Pu map indicates the selected location for recording μ -XANES.

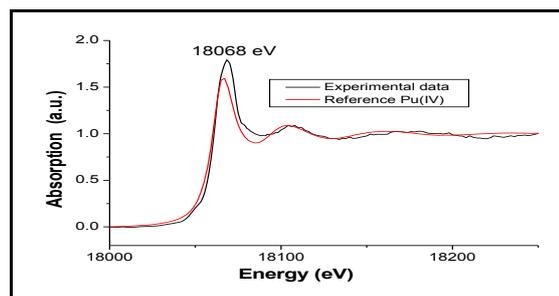


Figure 2: Normalized Pu L_{III} -edge μ -XANES spectrum of Pu hot spots (in Fig 1) in comparison to a reference spectrum of Pu(IV).

The collected XRD images (not shown) near Pu hot spots indicate that Pu potentially localizes on siderite and kaolinite mineral phases contained in OPA [4]. This preliminary result showed that siderite is one of the redox-active mineral phases in OPA, which determine the Pu speciation after sorption process.

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