

# Micro-XRF and micro-XANES studies of Pu diffusion in Opalinus Clay

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The aim of this study was to investigate the interaction of plutonium (Pu) with Opalinus Clay, a potential host rock for a geological repository for spent nuclear fuel, using a combination of synchrotron based techniques. The transport and retardation of Pu in clay formations is 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 diffusion process in Opalinus Clay (OPA, Mont Terri, Switzerland). The elemental distributions of Pu and other elements contained in OPA (e.g. Ca, Fe) were determined by micro X-ray fluorescence ( $\mu$ -XRF) measurements. Regions with high Pu concentrations were then analyzed by micro X-ray absorption near edge structure ( $\mu$ -XANES) spectroscopy to determine the oxidation state of Pu.

The setup and experimental procedure for the diffusion of Pu were the same as those used for the in-diffusion experiment of Np(V) and OPA by Wu et al. [1]. For the diffusion experiment an intact OPA bore core was contacted with 20  $\mu$ M <sup>242</sup>Pu(V) for about one month (26 days) under ambient air conditions using OPA pore water as mobile phase. The orientation of the clay cylinder in the diffusion cell was such that the direction of transport (diffusion) was parallel to the bedding of the clay. At the end of the diffusion experiment, the OPA core was removed from the cell, dried and cut into small pieces. One piece was prepared to study Pu speciation along its diffusion path (diffusion path) and another one to investigate Pu speciation on the OPA surface. This sample included a part of the surface that had been in contact with the solution (diffusion surface).

All spatially resolved investigations of these two samples were performed at the microXAS Beamline of the Swiss Light Source (SLS, Paul Scherrer Institut, Villigen, Switzerland) using a beam size (h  $\times$  w) of  $\approx 1.5 \times 3 - 1.5 \times 5 \mu\text{m}^2$ . Figure 1 shows the collected  $\mu$ -XRF mappings of elements of interest, i.e. Ca, Fe, and Pu in the diffusion surface sample. Good signal intensities of all measured elements with several hot spots of Pu and Fe were detected. The investigated surface shows diffuse areas with slightly increased Fe signals near the Pu enrichments. Pu L<sub>III</sub>-edge  $\mu$ -XANES spectra were collected on selected Pu hot spots (i.e. spot 1).

The amounts of different Pu oxidation states in the measured spots were determined using a linear combination fitting procedure that included reference spectra of Pu(III), Pu(IV), Pu(V) and

Pu(VI). For example at the OPA surface (spot 1 in Fig. 1) the distribution of Pu oxidation states equaled 28% Pu(III), 50% Pu(IV), and 22% Pu(V).

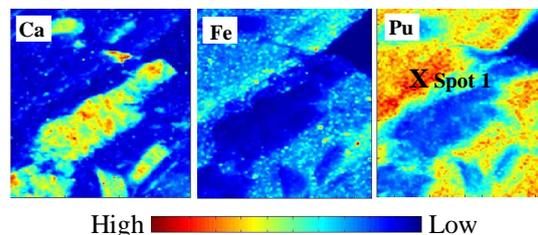


Figure 1:  $\mu$ -XRF elemental distribution maps of Ca, Fe, and Pu on the diffusion surface sample (1 $\times$ 1 mm; step size 10  $\mu\text{m}$ ; E = 18.07 keV). Pu L<sub>III</sub>-edge XANES spectra were recorded at spot 1.

In the diffusion profile sample (not shown), along the diffusion path of Pu in OPA, the reduction of Pu(V) to Pu(IV) became more pronounced. In comparison to the surface of the bore core, at a diffusion distance of 250  $\mu\text{m}$ , 32% Pu(III) and 68% Pu(IV) were detected. It can be concluded that Pu(V) was reduced progressively along its diffusion path to Pu(IV), so that Pu(IV) is the dominating Pu species after diffusion process in OPA.

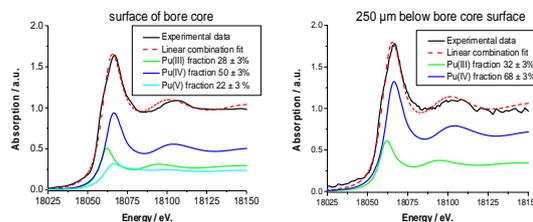


Figure 2: Left: Normalized Pu L<sub>III</sub>-edge XANES spectrum on the Pu spot marked in Fig. 1 of diffusion surface sample. Right: Normalized Pu L<sub>III</sub>-edge XANES spectrum of diffusion path sample measured on a Pu spot 250  $\mu\text{m}$  below the bore core surface. The experimental spectra are compared to linear combination fits using Pu(III), Pu(IV), and Pu(V) reference spectra.

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## References

1. Wu, T., Amayri, S., Drebert, J., Van Loon, L.R., Reich, T.: Neptunium(V) sorption and diffusion in Opalinus Clay. *Environ. Sci. Technol.* 43, 6567-6571 (2009).