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Speciation and distribution of plutonium after uptake by Opalinus Clay as measured by synchrotron microbeam techniques

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Due to its long half-life Pu has a significant contribution to the radiotoxicity of spent nuclear fuel in a repository after long periods of storage. Pu exhibits a complicated redox chemistry, where up to three oxidation states can coexist under environmentally relevant conditions [1]. In order to predict the migration behavior of Pu after its potential release from a repository of spent nuclear fuels into the environment, the interaction of Pu with the host rock formation has to be understood in detail. Argillaceous rocks are under consideration in several European countries as a potential host rock for high-level nuclear waste repositories. In clay formations diffusion and sorption are considered to be the main transport and retardation processes [2]. Accordingly, the interaction of $^{242}\text{Pu(VI)}$ with Opalinus Clay (OPA) from Mont Terri, Switzerland, in particular, the sorption and migration behaviors were studied by batch and diffusion experiments, respectively.

A combination of spatially-resolved synchrotron based techniques (micro X-ray absorption spectroscopy ($\mu\text{-XAS}$), micro X-ray fluorescence spectroscopy ($\mu\text{-XRF}$), and micro X-ray diffraction ($\mu\text{-XRD}$) was used to study the distribution and speciation of Pu on Opalinus Clay (OPA) after sorption and diffusion processes. Several thin sections of OPA were contacted with $20\text{ }\mu\text{M}$ $^{242}\text{Pu(VI)}$ in OPA pore water (pH 7.6, $I=0.4\text{ M}$) under aerobic conditions for at least three days. For comparison, a OPA bore core in a diffusion cell was contacted with $20\text{ }\mu\text{M}$ $^{242}\text{Pu(VI)}$ under the same conditions for more than one month. The sorption and diffusion samples were investigated at the microXAS beamline at the Swiss Light Source, Paul Scherrer Institut, Switzerland. $\mu\text{-XRF}$ based chemical imaging has been used to determine the elemental distribution of Pu and other elements contained in OPA, e.g., Fe and Ca. Regions of high Pu concentrations were subsequently investigated by $\mu\text{-XANES}$ to identify the oxidation state of Pu sorbed onto the OPA clay material. The results of Pu LIII-edge $\mu\text{-XANES}$ spectra on Pu hot spots showed that Pu(IV) is the dominating species within OPA, i.e., the highly soluble Pu(VI) was reduced within the clay rock material and Pu was retained by the Opalinus Clay rock in the reduced and less mobile tetravalent oxidation state. Simultaneously to chemical imaging and micro-spectroscopy, $\mu\text{-XRD}$ was employed to gain knowledge about reactive crystalline mineral phases in the vicinity of the observed Pu enrichments. $\mu\text{-XRD}$ results indicated that Pu is localized on or in close vicinity of the Fe(II)-bearing mineral siderite and the clay mineral illite. Siderite is one of the redox-active mineral phases of OPA. Our results point towards a decisive role of siderite regarding the speciation on Pu after migration into Opalinus Clay rock. The obtained results and inferred geochemical understanding indicate that OPA is a suitable host rock for a high-level nuclear waste repository.

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