Reactive transport of redox-sensitive Selenium in geological media: New insights from an inside view

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The environmentally safe disposal of radioactive waste is a major and pressing challenge for modern societies. Safety assessment calculations identified ^{79}Se in high level radioactive waste as a key radionuclide that could contribute to the release of radioactivity in the biosphere. Se(IV) was identified as the predominant form in vitrified high level waste. The oxyanionic character of ^{79}Se in combination with its long half-life of 3.27 10^5 years causes an enhanced risk potential for radiotoxic impairment of the biosphere.

The prevailing redox conditions in the spreading medium and corresponding speciation strongly influence the fate of Se. Reduced Se species [Se(0), Se(-II)] exhibit a low solubility in aqueous systems resulting in a limited mobility and bioavailability. Under oxidizing conditions, the Se speciation is dominated by the oxyanions $Se^{IV}O_3^{2-}$ and $Se^{VI}O_4^{2-}$, that have higher solubities. In addition to these higher solubities, clay based engineered and geological barrier systems are not very efficient in retaining oxyanions: the predominantely negatively charged mineral surfaces present in such reactive barrier systems preclude any significant chemical retention of anions. Thus anionic nuclides might eventually diffuse from the repository through the hostrock reaching the biosphere.

The present study visualizes *in-situ* micro-scale reactive transport of Se(IV) within undisturbed natural samples of two potential deep argillaceous hostrock formations (Opalinus and Upper Toarcian claystone). To characterize the transport and Se-mineral interactions in the micro-heterogenous clay rock matrix, we used a combination of synchrotron-based micro-imaging techniques – μXRF, μXRD, and μXAS – and created two-dimensional Se oxidation state images.

Spatially resolved chemical information from within the undisturbed porous medium turned out to be a necessity concerning the identification of the most relevant reactive transport processes.