Oxidation state and local structure of technetium reacted with siderite

K. SCHMEIDE[1], A.C. SCHEINOST[1,2], S. WEISS[1], V. BRENDLER[1]

[1] Helmholtz-Zentrum Dresden-Rossendorf e.V., Institute of Resource Ecology, Bautzner Landstr. 400, 01328 Dresden, Germany (k.schmeide@hzdr.de)
[2] The Rossendorf Beamline at ESRF, F-38043 Grenoble, France (scheinost@esrf.fr)

^{99}Tc is a long-lived ($t_{1/2} = 2.1 \times 10^5$ years) β-emitter formed during the fission of U and is of major concern for radioactive waste disposal. Its environmental mobility is primarily governed by the oxidation states VII and IV, with Tc^{VII} forming the highly mobile TcO_4^- aquo anion, whereas Tc^{IV} is rather immobile due to the low solubility of its hydrolysis products [1]. Redox processes, which are able to convert Tc^{VII} into Tc^{IV}, are hence of paramount importance for the safety of radioactive waste repositories. Fe^{II}-bearing minerals, ubiquitous in nature and also forming as corrosion products of the carbon steel canisters foreseen as a possible first enclosure of radioactive waste, play a vital role in these redox reactions due to their high redox reactivity and high sorption capacity, as has been shown not only for Tc, but also for Se, U, Np and Pu.

Here we focus on the retention of Tc^{VII} by a typical Fe^{II} mineral in carbonate-rich environments, siderite ($FeCO_3$), which we studied in the relevant pH range (7 – 12.6) under anoxic conditions by means of batch sorption experiments and by X-ray absorption spectroscopy. Sorption experiments showed that Tc retention by siderite is fast (within minutes) and efficient (log R_d ~5) across the investigated pH range and independent of ionic strength (0.1 – 1 M NaCl). Tc *K*-edge X-ray absorption near-edge structure (XANES) data confirmed that the Tc immobilization is due to the surface-mediated reduction of Tc^{VII} to Tc^{IV}. The local structure of Tc^{IV} as probed by extended X-ray absorption fine-structure (EXAFS) spectroscopy revealed two different species: in the pH range 7.8 to 11.5, TcO_2-dimers form inner-sphere sorption complexes at the surface of siderite or of an $Fe^{II,III}$ (hydr)oxide potentially formed during the redox reaction. At pH 11.8 to 12.6, the retention proceeds through the (near-surface) incorporation of Tc^{IV} by siderite.

In conclusion, siderite contributes effectively to the retention of Tc in the near-field of nuclear waste repositories.

[1] Eriksen, T.E., Ndalamba, P., Bruno, J., Caceci, M.: The solubility of $TcO_2 \times nH_2O$ in neutral to alkaline solutions under constant pCO_2. Radiochim. Acta 58-9, 67 (1992).