Tc(VII) immobilization on granitic rocks from Äspö HRL (Sweden) and Nizhnekansky massif (Russia)

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⁹⁹Tc is one of the most abundant long-lived components of SNF (half-life of $2.14 \times 10^5 a$ and a fission yield of ~6%), which possesses high mobility under oxidizing conditions as Tc(VII) and low solubility under reducing ones as Tc(IV). Tc mobility data under natural conditions is necessary for safety assessment of deep geological repositories.

This work focuses on the interaction of Tc(VII) with crystalline rock materials from the generic underground research laboratory in Sweden (Äspö Hard Rock Laboratory) and from a prospective site of nuclear waste and SNF disposal in Russia (Nizhnekansky massif; NK). Drilling of the Äspö cores were performed under anoxic conditions to preserve *in situ* conditions. Part of the Äspö diorite (ÄD) was artificially oxidized to compare with the original sample.

It was found, that Tc(VII) immobilization on the crystalline rocks is strongly dependent on sample preservation conditions, sorption values on ÄD are ~2 times higher for unoxidized material in comparison to oxidized one. These results can be explained by Tc(VII) reduction to the insoluble Tc(IV) oxide by the Fe²⁺ pool available in the ÄD. Tc(VII) reduction was proven by XPS and XANES analyses of granite surface after sorption. R_s values for the both oxidized ÄD and NK materials are almost similar. Formation of the colloidal phase was not detected under the groundwater conditions used (pH 8, 0.2 M ionic strenght). Tc desorption is insignificant under natural conditions, but after artificial oxidation technetium release is increased up to ~95%.

To investigate the Tc mobility under near-natural conditions an unoxidized ÄD core with a natural fracture was used for column migration studies. Injections of HTO and ³⁶Cl showed long tailings due to the complex fracture geometry without anion exclusion under the experimental conditions. Tc migration is investigated using ^{95m}Tc at a concentration of ~10⁻¹¹ M. Tc recovery is inversely dependent on residence time showing accelerated reduction kinetics as compared to batch sorption studies.