

# A Contribution from Fundamental and Applied Technetium Chemistry to the Nuclear Waste Disposal Safety Case

Yury Totksiy<sup>1</sup>, Ezgi Yalcintas<sup>1</sup>, Florian Huber<sup>1</sup>, Xavier Gaona<sup>1</sup>, Thorsten Schäfer<sup>1</sup>, Marcus Altmaier<sup>1</sup>, Stepan Kalmykov<sup>2</sup> & Horst Geckeis<sup>1</sup>

<sup>1</sup>Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Karlsruhe, Germany

<sup>2</sup>Lomonosov Moscow State University, Russia

Nuclear waste disposal in deep geological formations such as crystalline (granite), sedimentary (claystone) or rock salt, is the favoured option of the international nuclear waste disposal community. For the long term safety assessment of nuclear waste repositories, a reliable prediction of radionuclide migration behaviour is required. A potentially relevant mobilisation and migration mechanism is caused by water intrusion into the repository, leading to radionuclide release via transport pathways. In this case, detailed knowledge of key parameters controlling the retention and mobilization of radionuclides in solution, i.e. redox processes, solubility limits and sorption properties, is essential. Dedicated research is required in order to derive process understanding and develop accurate site-independent chemical and thermodynamic models, applicable for all considered host rock formations and scenarios.

Technetium-99 is a  $\beta$ -emitting fission product highly relevant for the safety assessment of nuclear waste repositories due to its significant content in radioactive waste (fission yield >6%), long half-life ( $t_{1/2} \approx 2.1 \cdot 10^5$  a) and redox sensitivity. The mobility of Tc in the environment strongly depends on its oxidation state. Tc(VII) exists as highly soluble and mobile  $\text{TcO}_4^-$  pertechnetate anion under sub-oxic and oxidizing conditions, whereas Tc(IV) forms sparingly soluble hydrous oxide ( $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ ) solid phases under reducing conditions.

In the first part of this study focusing on fundamental Tc chemistry, the redox behavior of Tc(VII)/Tc(IV) was investigated in dilute to concentrated solutions. The results are systematised according to *Pourbaix* diagrams calculated with the NEA–TDB data selection for Tc to assess the effect of homogeneous and

heterogeneous reducing systems and ionic strength on Tc redox behaviour. Investigations focussing on the solubility and speciation of  $\text{TcO}_2 \cdot x\text{H}_2\text{O}(s)$  were performed in dilute to concentrated solutions over the entire pH range. Complete and improved chemical, thermodynamic and activity (SIT, Pitzer) models were derived.

The second part of this work focuses on applied Tc chemistry in near-natural systems. Interaction of Tc(VII) with crystalline rock material from a prospective repository site (Nizhnekansky massif, Russia) and from an underground research laboratory (Äspö HRL, Sweden) were studied. Drilling of the Äspö cores were performed under anoxic conditions. Part of the material was artificially oxidized to test the importance of sample preservation. Batch sorption studies under variation of the Tc(VII) concentration were performed in synthetic groundwater simulate to estimate the retention kinetics and  $R_s$  values. For better understanding of the retention mechanisms, advanced surface sensitive analytics (XPS, XANES) were carried out and the data compared to reference systems. Tc migration behavior was further investigated by injections of Tc(VII)-containing groundwater simulant into the natural fracture in the unoxidized Äspö diorite core. The data obtained are compared with the results of batch sorption studies and will be used for subsequent geochemical reactive transport modelling.

This work highlights the importance of combining fundamental Tc chemistry and applied studies in order to derive a comprehensive assessment of Tc mobilisation and retention processes in support of the nuclear waste disposal Safety Case.