

Aquatic chemistry and thermodynamics of Tc in dilute to concentrated saline systems

E. Yalcintas¹⁾, X. Gaona¹⁾, A. C. Scheinost²⁾, M. Altmaier¹⁾, H. Geckeis¹⁾

¹⁾Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Germany

²⁾Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, Germany

ezgi.yalcintas@kit.edu

Technetium-99 is a β -emitting fission product highly relevant for the safety assessment of waste repositories for radioactive waste disposal due to its significant inventory in spent nuclear fuel, long half-life ($t_{1/2} \sim 211.000$ a) and redox sensitivity. Tc(VII) and Tc(IV) are the most stable redox states of Tc in the absence of any complexing ligands. Tc(VII) exists as highly soluble and mobile TcO_4^- pertechnetate anion under sub-oxic and oxidizing conditions, whereas Tc(IV) forms sparingly soluble hydrous oxide ($\text{TcO}_2 \cdot x\text{H}_2\text{O}$) under reducing conditions. For understanding Tc behaviour under repository relevant conditions, investigations focussing on redox state distribution, solubility and hydrolysis of Tc(IV) in dilute to concentrated NaCl, MgCl_2 and CaCl_2 solutions are required.

In the present study, the redox behavior of Tc(VII)/Tc(IV) was systematically investigated using various homogenous and heterogeneous reducing systems in dilute to concentrated NaCl and MgCl_2 solutions. Measured E_h and pH values were represented in *Pourbaix* diagrams calculated using thermodynamic data selected in the NEA-TDB [1] in order to assess Tc redox distribution in these systems. The thermodynamically calculated borderline for the Tc(VII)/Tc(IV) couple agrees well with the experimental data, indicating that E_h and pH are robust and reliable parameters for the prediction of Tc behavior in the absence of complexing ligands in the investigated aqueous systems. The study was complemented by advanced spectroscopy (EXAFS) to investigate the reduction/sorption mechanism of Tc on solid iron phases of special relevance for nuclear waste disposal.

Tc(IV) solubility was investigated in dilute to concentrated NaCl, MgCl_2 and CaCl_2 solutions in the presence of reducing chemicals. In the acidic pH range, a very significant increase in solubility (up to 4 orders of magnitude) is observed with increasing ionic strength for all considered salt systems. Thermodynamic analysis of this pH-region are on-going, taking into consideration hydrolysis species selected by NEA-TDB [1] but also polymeric $\text{Tc}_n\text{O}_p^{(4n-2p)+}$ and/or $\text{Tc}_n\text{O}_p\text{Cl}_m^{(4n-2p-m)-}$ species previously reported on the basis of spectroscopic observations [2]. In concentrated alkaline NaCl solutions, the same speciation as for diluted systems is retained (predominance of $\text{TcO}(\text{OH})_3^-$), although a decrease in solubility compared to dilute systems takes place due to ion interaction processes. Changes in the aqueous speciation are observed in concentrated alkaline MgCl_2 and CaCl_2 brines, where the formation of ternary $\text{Mg}_3[\text{TcO}(\text{OH})_5]^{3+}$ and $\text{Ca}_3[\text{TcO}(\text{OH})_5]^{3+}$ species is proposed based on the slope analysis and model (SIT/Pitzer) calculations. These ternary Tc(IV) species are similar to those previously reported for actinides in analogous brine systems. XRD, SEM-EDS and chemical analysis confirm that $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ is the solid phase controlling the solubility of Tc(IV) in the saline systems at $\text{pH}_m \leq 10.5$. Unreported sharp XRD reflections from the Tc solid phases in 4.5 M CaCl_2 at $\text{pH}_m \geq 10.5$ hint towards a possible solid phase transformation of $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ into a so far unknown Ca-Tc-OH solid. Chemical, thermodynamic and activity models (SIT, Pitzer) are derived for the system $\text{Tc}^{4+}-\text{H}^+-\text{Na}^+-\text{Mg}^{2+}-\text{Ca}^{2+}-\text{OH}^- - \text{Cl}^- - \text{H}_2\text{O}$ based upon the newly generated experimental solubility data and complement the current data selection of the OECD Nuclear Energy Agency (NEA-TDB) [1].

[1] Guillaumont, R., Fanghänel, T., Neck, V., Fuger, J., Palmer, D. A., Grenthe, I. and Rand, M. H., ed. OECD Nuclear Energy Agency. Vol. 5. North-Holland, Amsterdam, Elsevier, (2003).

[2] Vichot, L., Fattahi, M., Musikas, C. and Grambow, B., *Radiochimica Acta*, **91**, 263-271, (2003).