

Thermodynamic description of Tc(IV) solubility and hydrolysis in dilute to concentrated NaCl, MgCl₂ and CaCl₂ solutions

E. Yalcintas, X. Gaona, M. Altmaier, H. Geckeis

Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, P.O. Box 3640, 76021 Karlsruhe, Germany

ezgi.yalcintas@kit.edu

Technetium-99 is a β -emitting fission product highly relevant for the safety assessment of waste repositories for radioactive materials due to its significant inventory in spent nuclear fuel, long half-life ($t_{1/2} \sim 211.000$ a) and redox sensitivity. Under sub-oxic/oxidizing conditions, Tc(VII) is the most stable oxidation state of Tc and exists as highly soluble and mobile pertechnetate anion (TcO_4^-). In reducing environments, Tc(IV) prevails forming sparingly soluble hydrous oxides ($\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s})$). The later redox state is expected to dominate the aqueous chemistry of Tc in the reducing conditions predicted for deep geological repositories. In this framework, an appropriate understanding of the solubility and hydrolysis of Tc(IV) in dilute to concentrated saline systems is required for the performance assessment of repositories for radioactive waste disposal.

In the present study, the solubility of Tc(IV) was investigated from undersaturation conditions in 0.5–5.0 M NaCl, 0.25–4.5 M MgCl₂ and 0.25–4.5 M CaCl₂ solutions in the pH_c range 2–14.6. Experiments were performed at $22 \pm 2^\circ\text{C}$ in Ar gloveboxes with < 2 ppm O₂. Strongly reducing conditions ($\text{pH} + \text{pe} < 4$) were chemically set for each independent solubility sample with Na₂S₂O₄, SnCl₂ or Fe powder. Technetium concentration, pH_c and E_h values were monitored at regular time intervals. Thermodynamic equilibrium was assumed after repeated measurements with constant [Tc] and pH_c . After attaining equilibrium conditions, the redox speciation of technetium in the aqueous phase was quantified for selected samples using solvent extraction with TPPC and XANES analysis. Solid phases of selected batch experiments were also characterized by XRD, SEM–EDS and quantitative chemical analysis.

Solvent extraction and XANES analysis confirm the predominance of Tc(IV) in all the systems evaluated. Experimental solubility data determined in dilute NaCl and MgCl₂ solutions agree well with thermodynamic calculations considering the Tc(IV) chemical model and data selected by the NEA–TDB [1]. In the acidic pH range, a very significant increase in the solubility (up to 4 orders of magnitude) is observed with increasing ionic strength for all investigated salt systems. In concentrated alkaline NaCl solutions, the same speciation as for diluted systems is retained (e.g. 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 MgCl₂ and CaCl₂ brines, where the formation of $\text{Mg}_x[\text{TcO}(\text{OH})_y]^{2x-2y}$ and $\text{Ca}_x[\text{TcO}(\text{OH})_y]^{2x-2y}$ ternary species is proposed based on the slope analysis of the corresponding solubility curves and analogy with actinide chemistry. XRD, SEM–EDS and chemical analysis confirm that $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}(\text{s})$ is the solid phase controlling the solubility of Tc(IV) in all the saline systems evaluated. 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.

[1] Guillaumont, R., Fanghänel, T., Neck, V., Fuger, J., Palmer, D. A., Grenthe, I. and Rand, M. H., Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium, ed. OECD Nuclear Energy Agency. Vol. 5. North-Holland, Amsterdam, Elsevier, (2003).