Solubility and hydrolysis of Tc(IV) in KCl solutions

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

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

alexander.baumann@student.kit.edu

Technetium-99 is one of the main fission products of ^{235}U and ^{239}Pu in nuclear reactors. Due to its long half-life ($2.1 \cdot 10^5$ a) and redox-sensitive character, ^{99}Tc is a very relevant radionuclide in Performance Assessment exercises (PA) of repositories for radioactive waste. Tc(VII) is the prevailing oxidation state under oxidizing and redox-neutral conditions and exists as soluble and mobile TcO_4^-. On the contrary, Tc(IV) forms sparingly soluble hydrous oxides ($TcO_2 \cdot xH_2O(s)$) under reducing conditions as those expected in deep underground repositories. Potassium is an abundant cation in different types of natural groundwaters. It can also be found in high concentrations (up to 0.6 M) in cementitious environments as considered in concepts for the disposal of low and intermediate level (L/ILW) and high level waste (HLW). In this context, an appropriate understanding and thermodynamic description of Tc(IV) solubility and hydrolysis in dilute to concentrated KCl solutions is required.

In this work, the solubility of Tc(IV) oxyhydroxide phases in dilute to concentrated (0.1 M to 4.0 M) aqueous KCl solutions is investigated within $1.5 \leq pH_c \leq 14.5$. $Na_2S_2O_4$ and Sn(II) were used as reducing agents to ensure that ^{99}Tc is present in oxidation state +IV. [Tc], pH_c and E_h were monitored at regular time intervals up to several months. Solid phase characterization of selected batch experiments were performed by XRD, SEM–EDS and quantitative chemical analysis. Redox speciation of Tc in the aqueous phase was quantified for selected samples using solvent extraction with TPPC.

In all cases and pH regions, the increase of [KCl] significantly impacts the solubility of Tc(IV). Under acidic conditions and low [KCl], the solubility of Tc(IV) defines a slope of –2 indicating the predominance of TcO^{2+} in the aqueous phase in equilibrium with $TcO_2 \cdot 1.6H_2O(s)$. In this region, the increase of ionic strength up to 4.0 M KCl leads to a very significant increase in Tc(IV) concentration which cannot be explained by ion interaction processes but likely indicates the formation of a new species involving complexation with chloride. An unexpected increase in Tc(IV) solubility takes place with increasing [KCl] under near-neutral pH conditions where the formation of the neutral species $TcO(OH)_2(aq)$ is predicted by the NEA–TDB [1]. This new and surprising effect is further evidenced by experiments in KCl–NaCl mixtures of constant ionic strength but increasing KCl/NaCl ratios where a clear dependence on the K^+ concentration is observed. The effect can be properly explained by defining the aqueous species $KTcO(OH)_2^+$ according to the solubility reaction $TcO_2 \cdot 1.6H_2O(s) + K^+ \Leftrightarrow KTcO(OH)_2^+ + 0.6H_2O$. For each investigated KCl concentration, the solubility of Tc(IV) under hyper-alkaline pH conditions follows a well-defined slope of +1, indicating the expected formation of the anionic hydrolysis species $TcO(OH)_3^-$.

The present work provides comprehensive chemical, thermodynamic and activity (SIT) models of Tc(IV) solubility and hydrolysis in acidic to hyper-alkaline KCl media.

[1] J.A. Rard, M.H. Rand, G. Anderegg, H. Wanner, *Chemical Thermodynamics of Technetium*, Vol. 3 of Chemical Thermodynamics, Elsevier, Amsterdam, **1999**.