

Chemistry of technetium in cementitious environments:

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. Although several oxidation states of technetium have been reported in literature, only +VII and +IV are long-term stable in the absence of complexing ligands. 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 ($\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s})$) under reducing conditions as those expected in deep underground repositories. Potassium is an abundant cation in different types of groundwaters, but can also be found in high concentrations (up to 0.4 M) in cementitious environments as those considered in several concepts for the disposal of low and intermediate level (L/ILW) and high level waste (HLW). In this context, an appropriate understanding of the Tc(IV) solubility and hydrolysis in dilute to concentrated KCl solutions is required for assessing the behaviour of technetium in cement-bearing underground repositories for radioactive waste disposal.

In this work, the solubility of Tc(IV) in dilute to concentrated aqueous KCl solutions is investigated at ionic strengths ranging from 0.1 M KCl to 4.0 M KCl. The experiments were performed within $2 \leq \text{pH}_c \leq 14$, where the values of $\text{pH}_c = \text{pH}_{\text{exp}} + A_c$ were calculated from the operational “measured” pH_{exp} using empirical correction factors (A_c) derived for the KCl system in the present work. $\text{Na}_2\text{S}_2\text{O}_4$ and Sn(II) were used as reducing agents to ensure that ^{99}Tc both as solid and in solution remains in oxidation state +IV. About 3 mg of $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ were added to each independent batch experiment with the corresponding background electrolyte and reducing system. Technetium concentration, pH_c and E_h were monitored at regular time intervals. After reaching equilibrium conditions, solid phase characterization of selected batch experiments are performed by XRD, SEM-EDS and quantitative chemical analysis. Thermodynamic and activity models will be developed using both the SIT and the Pitzer approach over the entire pH range to complement the system $\text{Tc}^{4+}\text{-H}^+\text{-Na}^+\text{-Mg}^{2+}\text{-Ca}^{2+}\text{-K}^+\text{-OH}^-\text{-Cl}^-$ (see also poster by Yalcintas et al.).

My name is Alexander Baumann and I am currently in the course of completing my diploma studies in chemistry at the Karlsruhe Institute of Technology (KIT). My main interests and hence focus throughout my studies have been in radiochemistry and physical chemistry, which led me to the obvious conclusion to write my thesis at the Institute for Nuclear Waste Disposal (INE) under the supervision of Prof. Horst Geckeis.

I will complete my thesis by May 2014 and intend to continue research and work in the fascinating and broad field of radiochemistry.