Redox behavior of the Tc(VII)/Tc(IV) couple in dilute to concentrated NaCl and MgCl$_2$ solutions

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For the long-term performance assessment of nuclear waste repositories, reliable predictions of radionuclide mobility have utmost importance. ^{99}Tc is a β-emitting long-lived (T½ ~ 211.000 a) fission product highly relevant for nuclear waste disposal. Tc(VII) and Tc(IV) are the most stable and dominant redox states of technetium under environmental conditions. Heptavalent Tc exists under non-reducing conditions as the highly soluble TcO_4^- pertechnetate anion. Technetium present in the tetravalent oxidation state, however, forms hydrous oxides ($TcO_2 \cdot xH_2O(s)$) which drastically limit Tc solubility and mobility. Because of the significant impact on Tc chemistry, the redox behaviour of the Tc(VII)/Tc(IV) couple needs to be investigated in detail. In order to predict Tc behaviour for nuclear waste disposal in rock salt formations, dedicated studies under saline conditions are required.

In this study, the redox behaviour of the Tc(VII)/Tc(IV) couple was investigated in dilute to concentrated saline systems. Reduction experiments were performed under Ar atmosphere by using different homogenous and heterogeneous reducing systems in NaCl (0.5 M and 5.0 M) and MgCl$_2$ (0.25 M, 2.0 M and 4.5 M) solutions to provide for repository-relevant geochemical conditions. E_h and pH were measured after given aging times and the results systematised according to Pourbaix diagrams in order to assess the redox behaviour of technetium in highly saline systems. Technetium concentrations, redox state and aqueous speciation were analysed. The results show a clear effect of the specific reducing systems and ionic strength conditions on measured E_h values and Tc(VII)/Tc(IV) redox transformations. The experimental data are compared to thermodynamic calculations and geochemical model predictions.