

TECHNETIUM REDOX CHEMISTRY AND SOLUBILITY: APPLIED CHEMISTRY RELEVANT FOR NUCLEAR WASTE DISPOSAL

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A reliable prediction of the chemical behavior of technetium is necessary for the safety assessment of nuclear waste repositories. The knowledge of redox state distribution, complex formation and solubility limits provides the basis to assess the potential mobilization of Tc from a repository. Accurate chemical and thermodynamic models are required. In the case of nuclear waste repositories in salt rock formations, the chemical boundary conditions include highly concentrated salt brines which strongly impact the chemical behavior of radionuclides. This specific complexity is addressed within activity models (Pitzer, SIT) capable to accurately account for ionic strength effects on aqueous radionuclide chemistry.

⁹⁹Tc is a long-lived ($t_{1/2} \sim 211.000$ a) β -emitting fission product of ²³⁵U and ²³⁹Pu. Due to its relatively high abundance in nuclear waste (6% fission yield), technetium retention and mobilization processes are very important to understand and predict. The mobility of Tc in the environment strongly depends on its oxidation state. 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. Only heptavalent or tetravalent technetium species are stable in repository relevant aqueous solutions under absence of strongly complexing ligands. In view of the very different mobility of Tc(VII) and Tc(IV), investigating the redox behavior of Tc as well as Tc(IV) solubility and hydrolysis is of special relevance in the context of nuclear waste disposal.

In the present study, the redox behavior of Tc(VII)/Tc(IV) are systematically investigated using various homogenous and heterogeneous reducing systems in dilute to concentrated NaCl and MgCl₂ solutions. Measured E_h and pH values are analyzed in *Pourbaix* diagrams to assess Tc redox behavior 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. Thermodynamic data for Tc(IV) are derived from experimental solubility studies in dilute to concentrated NaCl, MgCl₂ and CaCl₂ solutions 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., Rand, M.H.: Chemical Thermodynamics Vol. 5. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. (OECD, NEA-TDB) Elsevier, North Holland, Amsterdam (2003).