Goldschmidt 2025 Abstract
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Thermodynamic Reference Database (THEREDA): Updated Pitzer activity model for Tc(IV) solubility and hydrolysis in the Tc(IV)–Na^+–K^+–Mg^{2+}–Ca^{2+}–H^+–Cl^-–OH^-–H_2O(l) system

CHRISTIAN KIEFER, DAVID FELLHAUER, MARCUS ALTMAIER AND XAVIER GAONA

Karlsruhe Institute of Technology

Technetium-99 ($t_{1/2}$ = 2.11·10^5 a) is a β-emitting radionuclide produced with high yield in nuclear reactors. Under the reducing conditions expected in deep underground repositories for radioactive waste, its oxidation state +IV should be dominant and hence the formation of sparingly soluble hydrous oxides $TcO_2{\cdot}xH_2O$(s) [1]. An accurate knowledge of the aquatic chemistry of technetium is required to assess properly its solubility and aqueous speciation, which represent relevant input parameters for estimations on source term and retention. The Thermodynamic Reference Database THEREDA [2] targets geochemical calculations in the context of nuclear waste disposal, with focus on solubility of radionuclides (actinides, fission and activation products), chemotoxic and waste matrix elements. THEREDA addresses high saline conditions (> 3.5 m), which may occur in repository concepts in rock salt and some clay rock formations, therefore using the Pitzer formalism for ionic strength corrections.

An updated thermodynamic and Pitzer activity model was derived for the system Tc(IV)–Na^+–K^+–Mg^{2+}–Ca^{2+}–H^+–Cl^-–OH^-–H_2O(l). It was based on available Tc(IV) solubility studies [3,4,5] in diluted to concentrated NaCl, KCl, $MgCl_2$ and $CaCl_2$ solutions, and thermodynamic data selected in the second update book of the Nuclear Energy Agency-Thermochemical Database (NEA-TDB) project [1] as anchoring point. In agreement with the previous THEREDA Tc release (2016), the updated chemical model selects the hydrolysis species $Tc_2O_3^{2+}$, $TcO(OH)_2$(aq), $TcO(OH)_3^-$, $Mg_3[TcO(OH)_5]^{3+}$ and $Ca_3[TcO(OH)_5]^{3+}$, whilst deriving a new hydrolysis constant for $TcO(OH)_3^-$ and new Pitzer activity coefficient for the interactions between $TcO(OH)_3^-$ and Na^+/K^+. The updated model describes well Tc(IV) solubility data in NaCl, KCl, $MgCl_2$ and $CaCl_2$ systems, as well as in selected mixed solutions (ternary, quaternary, quinary). The results of this work will be included in the THEREDA release 2025.

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References

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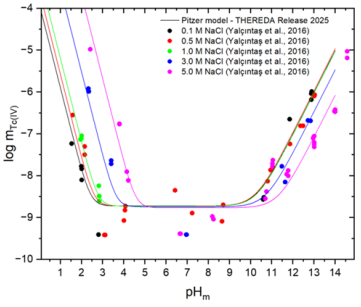

Figure 1. Comparison of experimental solubility data in 0.1, 0.5, 1.0, 3.0 and 5.0 M NaCl (m_{NaCl} = 0.10, 0.51, 1.02, 3.20, 5.61 mol kg^{-1}) by Yalçıntaş et al. (2016) with the updated model calculations from the present work.

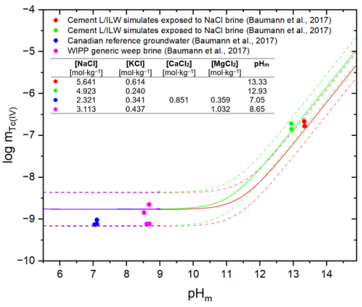

Figure 2. Comparison of experimental solubility data in simulated reference systems (ternary, quaternary, quinary mixed background electrolytes) by Baumann et al. (2017) with the updated model calculations from the present work.