REDOX CHEMISTRY, SOLUBILITY AND HYDROLYSIS OF TECHNETIUM IN DILUTE TO CONCENTRATED NaCl and $MgCl_2$ SOLUTIONS

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Technetium–99 is a β–emitting fission product highly relevant for the safety assessment of nuclear waste repositories due to its significant inventory in radioactive waste, long half-life ($t_{½}$ ~211.000 a) and redox sensitivity. Tc(VII) and Tc(IV) are the most stable redox states of Tc in the absence of any complexing ligands under sub-oxic/oxidizing or reducing aqueous environments. Tc(VII) exists as highly soluble and mobile TcO_4^- pertechnetate anion, whereas Tc(IV) forms sparingly soluble hydrous oxides ($TcO_2{\cdot}xH_2O(s)$). Due to the very different mobility of both redox states, the redox chemistry of Tc as well as Tc(IV) solubility and hydrolysis are of special relevance in the context of radioactive waste disposal. An appropriate understanding of the chemistry of Tc in concentrated NaCl and $MgCl_2$ solutions of extremely high ionic strength is required in the performance assessment of underground repositories in rock-salt formations.

The redox behaviour of Tc(VII)/Tc(IV) was investigated in 0.5–5.0 M NaCl and 0.25–4.5 M $MgCl_2$ solutions with $[Tc(VII)]_0 = 10^{-5}$ M in the presence of homogenous ($Na_2S_2O_4$, Sn(II), Fe(II)/Fe(III), Fe powder) and heterogeneous (magnetite, mackinawite, siderite) reducing systems. Samples were prepared, stored and handled in Ar-glove boxes at 22±2°C. Technetium concentration, pH_c and E_h were monitored at regular time intervals, and represented in *Pourbaix* diagrams calculated according to the NEA–TDB data selection for Tc [1]. A decrease of [Tc] in the aqueous phase was interpreted as reduction of Tc(VII) to Tc(IV) and subsequent precipitation of $TcO_2{\cdot}xH_2O(s)$. The redox state of Tc in the aqueous phase was further analysed by solvent extraction techniques for selected samples. XANES and EXAFS were used to characterize the redox state and molecular environment of Tc in the heterogeneous reducing systems evaluated.

The solubility of Tc(IV) was studied in 0.5–5.0 M NaCl and 0.25–4.5 M $MgCl_2$ solutions under Ar-atmosphere at 22±2°C. A Tc(VII) stock solution was electrochemically reduced to Tc(IV) and precipitated as $TcO_2{\cdot}xH_2O(s)$ in a $Na_2S_2O_4$ solution at pH_c ~12. About 5 mg of the resulting solid phase were added to each independent batch experiment with the corresponding background electrolyte and reducing system ($Na_2S_2O_4$, Sn(II) or Fe powder). Technetium concentration, pH_c and E_h were monitored with time. After reaching equilibrium conditions, solid phases of selected batch experiments were characterized by XRD and quantitative chemical analysis.

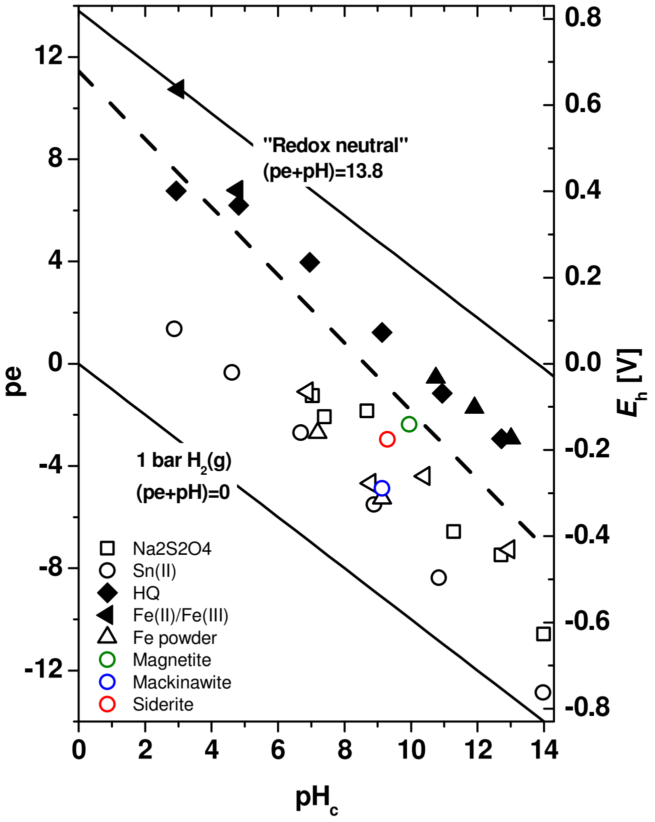

Fig. 1: *Redox behavior of Tc(VII)/Tc(IV) in 5.0 M NaCl. Open symbols indicating reduction to Tc(IV); solid symbols corresponding to samples with no reduction of Tc(VII). Dashed line indicates the Tc(VII)/Tc(IV) borderline calculated according with the NEA-TDB.*

The redox distribution of Tc determined experimentally is in good agreement with the thermodynamically calculated borderline for the chemical reaction $TcO_4^- + 4H^+ + 3e^- \Leftrightarrow TcO_2 \cdot xH_2O(s) + (2-x)\ H_2O$ (Fig.1), thus indicating that E_h and pH are robust and reliable parameters for the prediction of Tc redox behaviour in homogeneous systems. Higher E_h values are observed for samples in highly saline solutions (4.5 M $MgCl_2$) regardless of the reducing system; this was found to influence Tc redox chemistry consistently with the thermodynamically calculated Tc(VII)/Tc(IV) borderline. In heterogeneous systems, EXAFS indicates the predominance of Tc(IV) surface complexes and the absence of Tc solid phases.

Tc(IV) solubility data obtained in NaCl and $MgCl_2$ solutions reveal an increased [Tc] at $4 \geq pH_c \geq 10$. This can be related to the predominance of $TcOOH^+$ and $TcO(OH)_3^-$ aqueous species, respectively, in good agreement with the current hydrolysis scheme selected in the NEA–TDB [1]. The pH–independent solubility reaction $TcO_2 \cdot xH_2O(am) \Leftrightarrow TcO(OH)_2(aq) + (1-x)\ H_2O$ is proposed to control solubility at $4 \leq pH_c \leq 10$. Thermodynamic and activity models (SIT, Pitzer) for the system Tc^{4+}–H^+–Na^+–Mg^{2+}–OH^-–Cl^- are derived based on the newly generated experimental solubility data.

[1] R. Guillaumont, T. Fanghänel, V. Neck, J. Fuger, D. A. Palmer, I. Grenthe and M. H. Rand, eds. "Chemical Thermodynamics 5. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium". ed. E. NEA OECD(2003).