

Technetium interaction with Fe(II)-minerals analysed by spectroscopy and thermodynamics

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Technetium-99 is a β -emitting fission product which needs to be analysed for the safety assessment of repositories for radioactive waste disposal due to its significant inventory in spent nuclear fuel and its long half-life ($t_{1/2} \sim 211.000$ a). Although several oxidation states of Tc are reported in the literature, Tc(VII) and Tc(IV) are the prevailing redox states in the absence of any complexing ligand under non-reducing and reducing conditions, respectively. Tc(VII) is the most stable oxidation state of Tc in suboxic/oxidising environments. It is found as the highly mobile TcO_4^- anion over the entire pH range and shows very high solubility and weak sorption properties. Under reducing conditions, Tc(IV) forms sparingly soluble hydrous oxides $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ and is usually sorbed strongly onto mineral surfaces. Because of the large differences in the aquatic chemistry of Tc(VII) and Tc(IV), an accurate knowledge of Tc redox chemistry is necessary for an appropriate assessment of Tc retention/mobilization processes.

In the present work, the mechanisms for the reduction and uptake of Tc by magnetite (Fe_3O_4) and mackinawite (FeS) are investigated using X-ray absorption spectroscopy, in combination with thermodynamic calculations of the Tc/Fe systems and accurate characterization of the solution properties (pH_m , pe , $[\text{Tc}]$). Batch sorption experiments were performed under strictly anoxic conditions using freshly prepared magnetite and mackinawite in 0.1 M NaCl solutions with varying initial Tc(VII) concentrations ($2 \cdot 10^{-5}$ and $2 \cdot 10^{-4}$ M) and Tc loadings (400–900 ppm). EXAFS data evaluation shows that the mechanisms of Tc(IV) retention by magnetite and mackinawite are strongly dependent on the loading, $[\text{Tc}]_0$ and pH_m . The results provide key inputs for the understanding of the mechanisms driving the reduction and retention of Tc by magnetite and mackinawite under repository-relevant conditions, whilst highlighting the need of coupling classical wet-chemistry techniques, thermodynamic calculations and advanced spectroscopic methods when investigating complex processes or systems such as redox and mineral interfaces.

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