

Interaction of Tc with iron(II) phosphate

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Technetium (Tc) is an element originating mostly from the fission of ²³⁵U and ²³⁹Pu with a yield of 6%.¹ Therefore, ⁹⁹Tc is mainly found in high-level radioactive waste, e.g. from nuclear power or reprocessing plants.² The waste disposal is the subject of numerous studies due to the long half-life of many radionuclides (e.g. ⁹⁹Tc: 2.1 · 10⁵ years)¹ and their high radiotoxicity. One of the most accepted concepts is the deep geological underground repository. A multiple barrier system is planned to reduce the risk of a worst-case scenario, when water ingress could induce the corrosion of the canister containing the waste and, thus, radionuclide release. For the long-term safety, including the construction of effective barriers, the interaction of the radionuclides with different minerals present in the repository needs to be studied at a fundamental level. Tc shows a complex redox chemistry and is considered very mobile compared to cationic radionuclides, due to the presence of the negatively charged TcO₄⁻ under oxidising conditions. However, Tc migration decreases when Tc(VII) is reduced to Tc(IV) since it forms precipitates or is immobilized by mineral surfaces, e.g. with Fe(II) minerals (Figure 1).³

Vivianite (Fe₃(PO₄)₂ · 8 H₂O) is a naturally occurring Fe(II) mineral under reducing conditions⁵ and can be formed by microorganisms.⁶ Phosphate phases are already being considered as an immobilisation matrix for other radionuclides relevant in deep geological repositories (e.g. ²³⁵U, ²³⁷Np, ²³⁹Pu, ²⁴³Am).^{7,8}

This study investigates the retention of Tc by synthetic vivianite particles as a function of pH, Tc concentration and ionic strength on a macroscopic and molecular scale. In addition, Tc(IV) reoxidation experiments were performed.⁴

The synthesis of vivianite was carried out by precipitation from a solution mixture of an iron(II) sulphate and ammonium hydrogen phosphate, as described by Roldán *et al.*⁹ The product was characterised by Raman microscopy, Mössbauer spectroscopy, powder X-ray diffraction and solubility studies with regard to the pH-dependent behaviour under N₂ atmosphere. The identified phase at pH 5.0 and pH 8.0 is vivianite. At pH 12.0 vivianite transforms into Fe(II)(OH)₂. The change in solid morphology due to the mineralogical modification was also observed with scanning electron microscopy.

Batch contact experiments at N₂ atmosphere were carried out to determine the interaction between vivianite particles suspended in water and K₂TcO₄. The Tc concentrations in solution were determined by liquid scintillation counting and the Tc-loaded solid was analysed by X-ray photoelectron spectroscopy (XPS). Kinetic contact experiments of 1 μM TcO₄⁻ show that Tc uptake by vivianite increases with longer contact time at pH 8.0 and is complete after

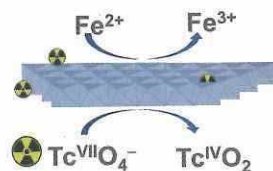


Figure 8: Schematic representation of the reduction of K₂TcO₄ on Fe(II)-minerals.

20 days, while no Tc retention takes place at pH 6.5. The Tc-containing solids from experiments at pH 5.0 and pH 12.0 were analysed by XPS to determine the oxidation state of the Tc and Fe. The results show that Tc(IV) was present on the solid surface in all samples analysed. It indicates that Tc removal at high pH values is due to the reductive immobilization of Tc(VII) to Tc(IV) by vivianite. However, at acidic pH values (pH 5.0) Tc(VII) reduction occurs without decreasing the Tc concentration in solution, but by XPS, formerly dissolved Tc(IV) could be detected on the solid surface.

To investigate the remobilisation of reduced Tc(IV), samples obtained after completion of Tc retention experiments at different pH were exposed to ambient atmosphere and Tc concentration was monitored for six months. Under oxidising conditions, no remobilisation of Tc takes place at pH values above pH 8.0. The immobilisation of Tc by vivianite remains complete over the course of six months. This shows a slower Tc(IV) reoxidation than in Tc(IV)-containing FeS₂ mineral phases, where reoxidation starts after 64 days.¹⁰ Additionally, an increase of Tc retention was determined at pH 2.0 and pH 3.0. This can be explained by a time-delayed immobilisation of Tc by the dissolved Fe(II).¹¹

Those promising results show a high affinity of vivianite towards Tc, aided by the reduction of Tc(VII) to Tc(IV) by structural Fe(II).

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