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Insights into the Enigmatic $TcO_2{\cdot}xH_2O$ Structure via Atomistic Simulations

AUGUSTO F. OLIVEIRA[1], AGNIESZKA KUC[2], THOMAS HEINE[3,4,5] AND ANDREAS C. SCHEINOST[2,6]

[1]Helmholtz-Zentrum Dresden - Rossendorf e.V.
[2]Helmholtz-Zentrum Dresden-Rossendorf e.V. (HZDR)
[3]Technische Universität Dresden
[4]Helmholtz-Zentrum Dresden-Rossendorf
[5]Yonsei University
[6]European Synchrotron Radiation Facility (ESRF)
Presenting Author: a.faria-oliveira@hzdr.de

Technetium is the lightest element without a stable isotope. The β-emitting ^{99}Tc is especially relevant for nuclear waste management due to its long half-life (ca. 2.1×10^5 years) and relatively high formation yield (≥6%) in ^{235}U and ^{239}Pu nuclear reactors. In this context, redox reactions at mineral/water interfaces are crucial for the safety of nuclear waste repositories.

In the absence of complexing agents, Tc exists in water as Tc(VII) and Tc(IV). The former predominates in non-reducing conditions as TcO_4^-(aq), which is highly mobile in the environment due to its solubility and weak interaction with adsorbents. Studies show that Fe(II) minerals can reduce Tc(VII) to Tc(IV), which is then immobilized by adsorption onto or incorporation into the oxidized Fe mineral and by precipitation as $TcO_2{\cdot}xH_2O$. However, even in the simpler case (precipitation) the structure of $TcO_2{\cdot}xH_2O$ remains controversial.

Lukens et al. [1] demonstrated that, despite being amorphous, $TcO_2{\cdot}xH_2O$ has a well-defined local structure. Based on EXAFS measurements, they proposed that $TcO_2{\cdot}xH_2O$ forms linear chains of equally spaced edge-sharing $TcO_4(H_2O)_2$ octahedra, with terminal H_2O ligands at the apical positions. Vichot et al. [2] obtained similar results but, despite having extracted only one Tc-Tc distance from the EXAFS, proposed that Tc atoms would be separated by shorter and longer alternating distances as in the monoclinic TcO_2 crystal. More recently, Yalçintaş et al. [3] showed that both models can be fitted equally well to the EXAFS and, thus, the $TcO_2{\cdot}xH_2O$ structure remained unsolved.

In this work, we use *density functional theory* (DFT) to investigate the polymeric $TcO_2{\cdot}xH_2O$ structure. Our calculations reveal that, in contrast to previous models, a zigzag configuration with the terminal H_2O groups at neighboring positions of the octahedra is more likely. The zigzag configuration is energetically more favored and results in a better agreement with the EXAFS measurement.

[1] Lukens et al. (2002), *Environ. Sci. Technol.* 36, 1124-1129.
[2] Vichot et al. (2002), *Radiochim. Acta* 90, 575-579.
[3] Yalçintaş et al. (2016), *Dalton Trans.* 45, 17874-17885.