

XAFS Study of the Chemical and Structural States of Technetium in Fe(III) Oxide Co-precipitates

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Introduction

XAFS has been used to study the chemical state and structural environment of technetium in Fe(III) oxide co-precipitates. ⁹⁹Tc is an abundant fission product which poses a significant environmental hazard due to its long half-life, abundance in nuclear wastes, and environmental mobility as the pertechnetate ion [Tc(VII)O₄⁻] under oxidizing conditions. Tetravalent Tc [Tc(IV)] is the stable valence state under reducing or anoxic conditions where its environmental mobility is significantly lowered by formation of a sparingly soluble, hydrated amorphous oxide precipitate [Tc(IV)O₂·nH₂O(s)]. We have been studying the kinetics and solid products resulting from abiotic reduction of Tc(VII)O₄⁻ by aqueous, adsorbed, and structural Fe(II) to provide insights on Tc migration in microaerophilic groundwaters. The reduction reaction yields Fe/Tc precipitates of variable structures that have not been previously studied. For the homogeneous reaction with aqueous Fe(II) at relatively high Tc:Fe concentrations, the predominant redox product is a solid containing Tc(IV) dimers attached in a bidentate edge-sharing configuration on the surface or unoccupied interior sites of a ferrihydrite-like precipitate. A similar ferrihydrite-type solid is formed on the surface of Fe oxide minerals such as hematite and goethite following the heterogeneous reaction of Tc(VII)O₄⁻ with surface-complexed Fe(II). These co-precipitates greatly slow the oxidation rate of Tc(IV) relative to amorphous Tc(IV)O₂·nH₂O(s), possibly allowing for the long term sequestration of ⁹⁹Tc in stable (bio)geochemical mineral forms that may reduce the long term environmental risk of ⁹⁹Tc subsurface contamination.

Tc in the Environment

- Abundant fission by-product
- ⁹⁹Tc Half-life 2x10⁵ years
- Pertechnetate ion (Tc(VII)O₄⁻) is the stable form in oxidizing conditions and very mobile
- Pertechnetate is the risk driving contaminant at many sites

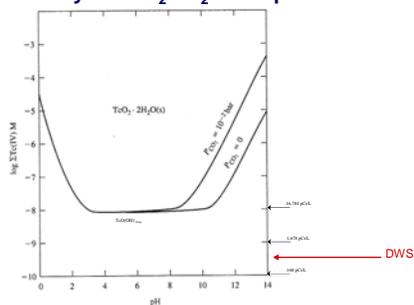
Tetravalent Tc is much less mobile

- However TcO₂·nH₂O solubility still above drinking water standard (DWS)
- Can be easily reoxidized

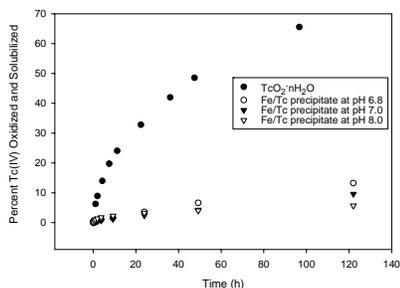
Are Fe-Tc precipitates better?

- Fe(II) is an effective reductant
- Fe-Tc precipitates show reduced potential for reoxidation

Low solubility of TcO₂·nH₂O still problematic



Tc-Fe coprecipitates reoxidize more slowly



Tc-Fe precipitates studied in 3 types of samples

All reactions under strictly anaerobic conditions

Homogeneous reaction

Fe(II) and pertechnetate solutions mixed and buffered to pH 6.8-8, XAS for pH 7 and 8. Precipitates formed with approx 6:1 Fe:Tc

Heterogeneous reaction

Hematite and goethite soaked in Fe(II) solution, then pertechnetate added

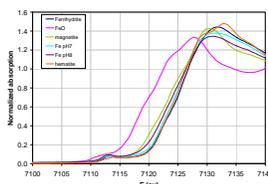
Sediment samples

Ringold and FRC sediment treated with bacteria to produce Fe(II) then exposed to pertechnetate solution

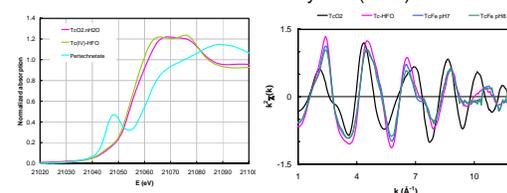
XAFS results

Homogeneous samples – both edges could be studied

Fe edge shows some remaining Fe(II)

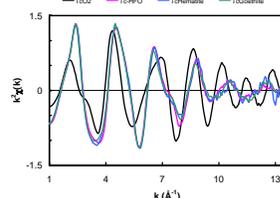


Tc edge shows all Tc is Tc(IV) and EXAFS is similar to Tc in a ferrihydrite (HFO) standard

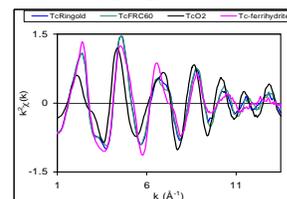


Due to Fe background only Tc edge was studied for the other samples

Hematite and Goethite look similar to homogeneous and Tc-HFO samples



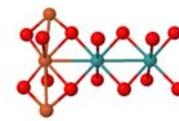
Sediment samples show signs of TcO₂·nH₂O formation



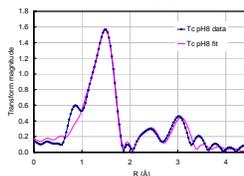
Modeling of EXAFS

TcO₂·nH₂O has previously been determined to form linear chains of edge sharing octahedra. Since the data indicated a similar short Tc-Fe bond we adopted a model where the Tc-O chains are terminated at a Fe-O octahedron. The Tc chain length was a fitting parameter.

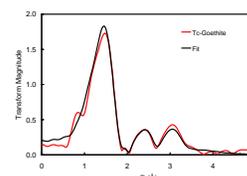
Tc on ferrihydrite starting model – dimer case (Tc – green, O – red, Fe – brown)



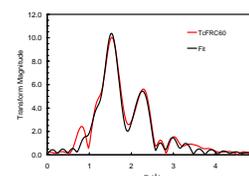
Homogeneous samples Tc-Tc dimers



Goethite and Hematite mostly monomers



Sediment samples show longer chains



Conclusions

The model of TcO₂·nH₂O-like chains bonding to Fe-O octahedra on the surface of a ferrihydrite-like solid fits a wide variety of cases. The length of the chains is varying due to still to be determined parameters, likely the Tc concentration and the availability of reduced Fe.

Acknowledgements

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