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Immobilization of technetium by iron corrosion phases: lessons learned and future perspectives

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Immobilization of technetium by iron corrosion phases: Lessons learnt and future perspectives

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^{99}Tc as fission product in the environment of a repository for high level radioactive waste

- Long half-life ($\tau_{1/2}$ = 0.123 Ma)
- Poorly retained by the natural and technical materials in the repository

Improving the level of knowledge about their **solubility** and **retention** can, if taken into account in the long-term safety assessment, lead to a significant reduction in uncertainty

Fe^{2+}, S^{2-} → $Fe^{II}S_2$ [1,2] → Fe^{3+}, SO_4^{2-}

Tc(VII) → Tc(IV)

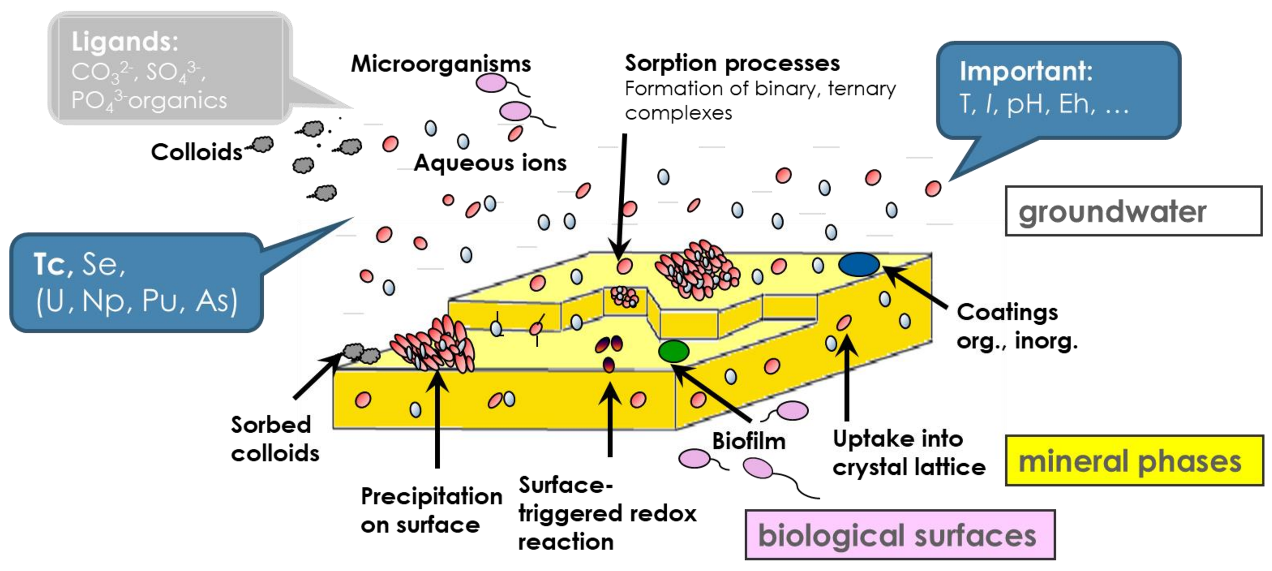
- TcO_4^-
- Almost inert
- **High mobility**

- Different sorption mechanisms [1-5]
- Hardly soluble, TcO_2 [6-7]
- **Reduced mobility**

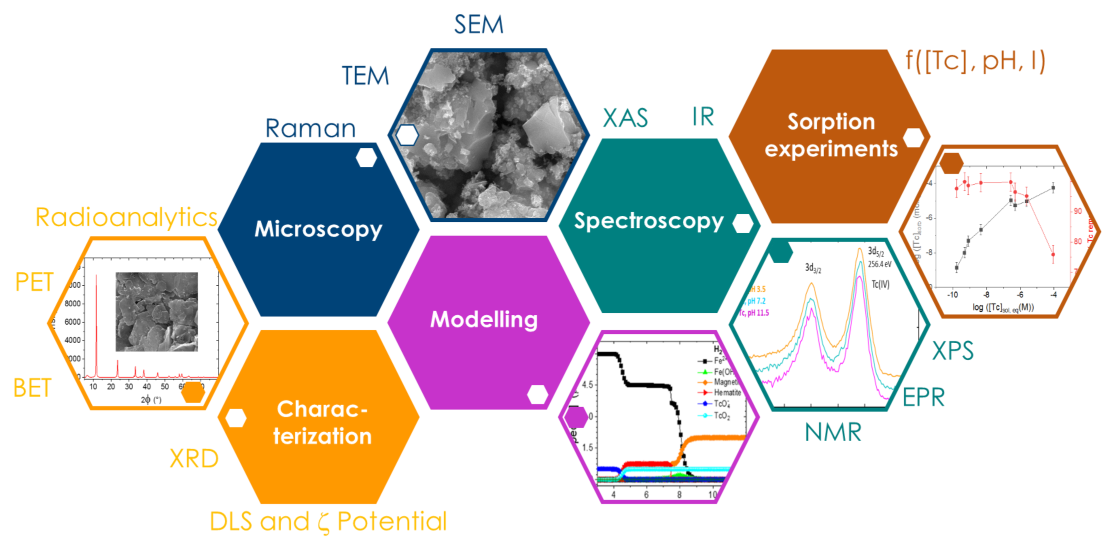
Mobility of contaminants at water-mineral interfaces

Environmental safety assessment

- To consider **all** processes comprehensively
- Thermodynamic databases need **species verification**



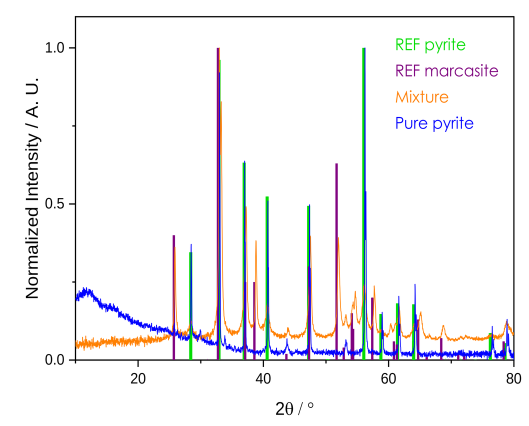
Tool box for comprehensive molecular understanding



Lessons learnt

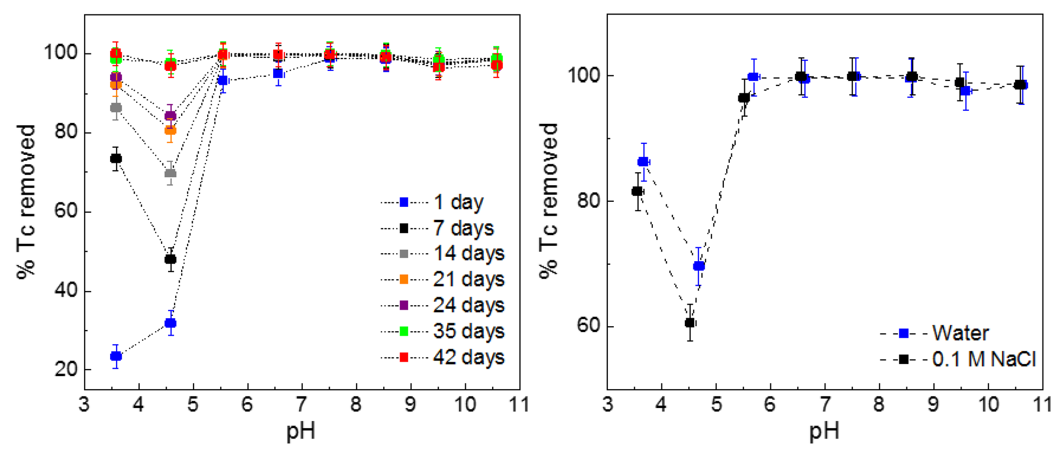
VESPA II project
https://vespa2.grs.de

Characterization of Fe(II) sulfides



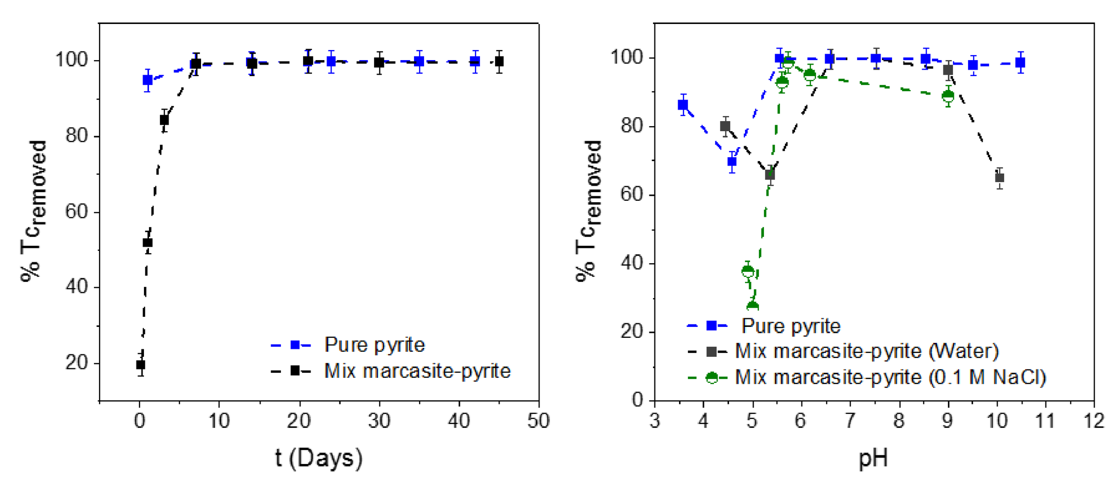
Pure pyrite: BET = 2.0 m^2 g^{-1}, pH $_{IEP}$ = 7.9
Mixture 60:40 marcasite–pyrite: BET = 5.3 m^2 g^{-1}, pH $_{IEP}$ = 7.4

Batch retention experiments of Tc(VII) on pure pyrite [1] …

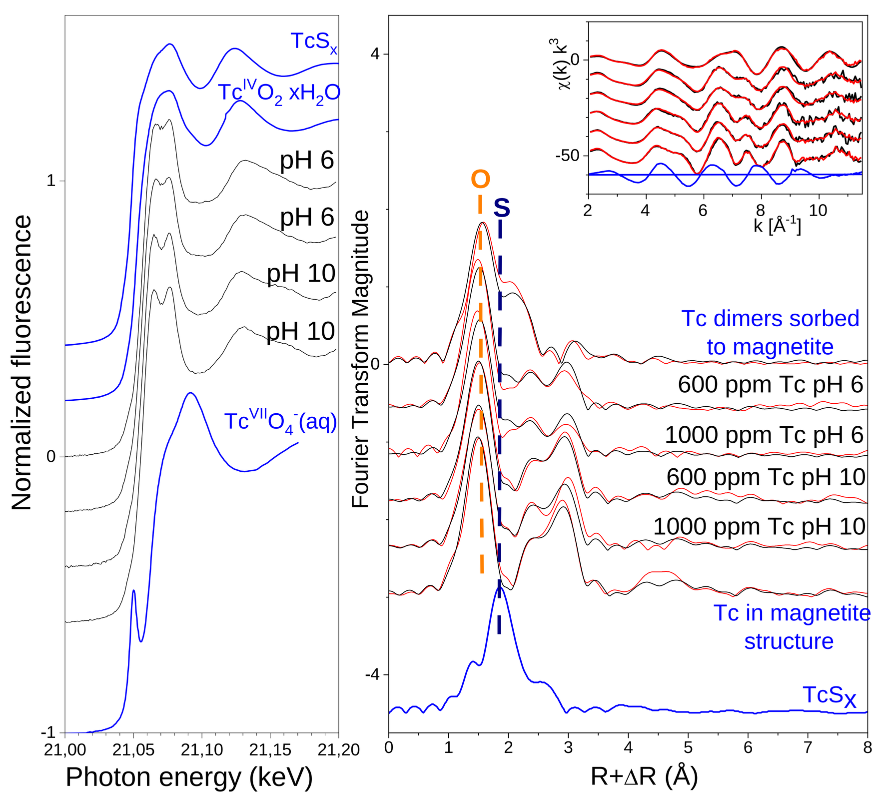


- FeS_2 removes Tc quantitatively at $6 < pH \leq 9$
- Less retention at high pH for mixed sample
- Kinetically controlled processes
- No dependence on ionic strength

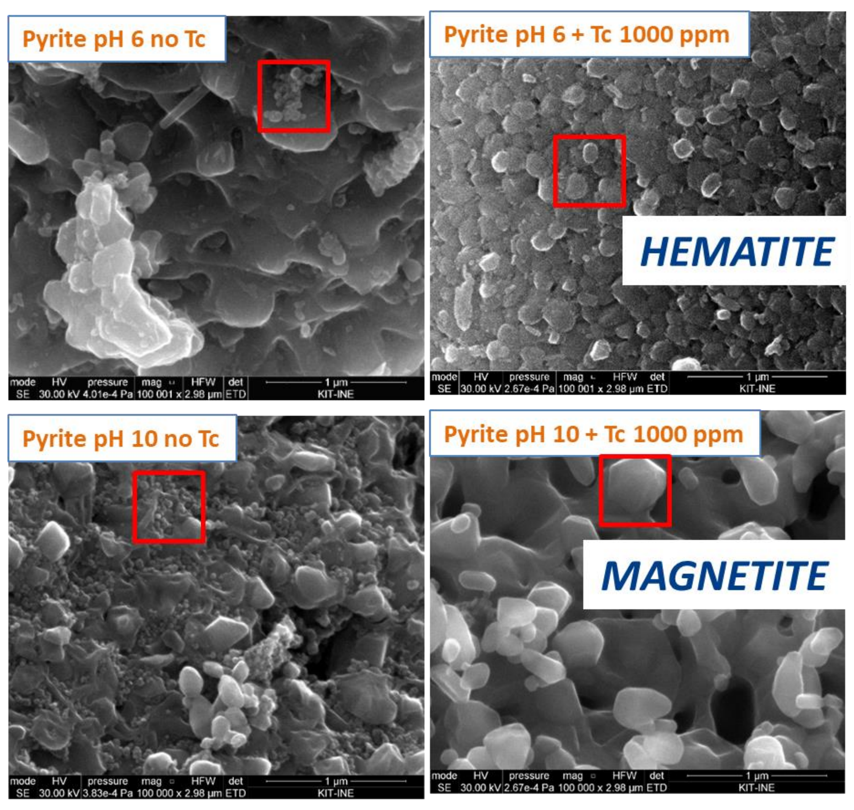
… and on a mixed marcasite-pyrite sample [2]



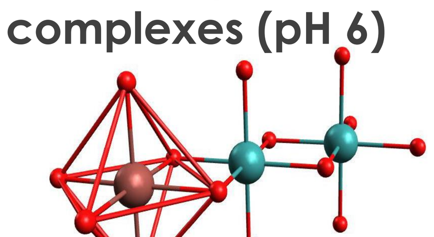
pH dependent retention mechanisms on pure pyrite [1]



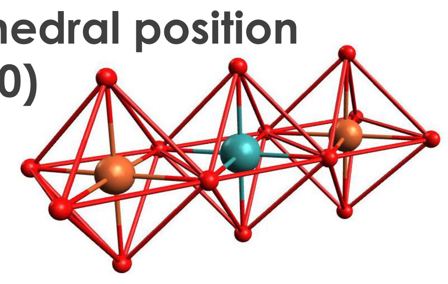
- Tc(IV) coordinated to oxygen



Tc^{IV} dimers sorption as inner-sphere complexes (pH 6)

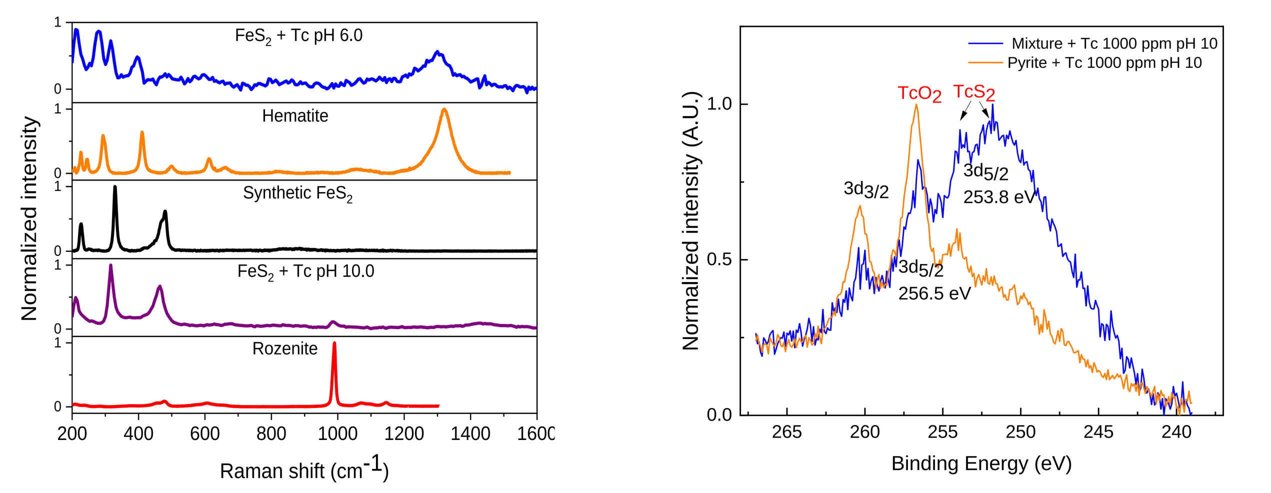


Tc^{IV} incorporation, replacing Fe in octahedral position (pH 10)



- pH dependent identification of secondary mineral phases

The impact of marcasite [2]



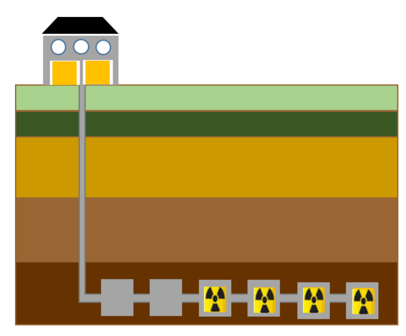
- Retention slower and less effective
- pH 10: Identification of Fe(II)-sulfate mineral
- Presence of TcS_x at all pHs, possibly passivating the surface preventing further Tc reduction

Indication of the role of S^{2-} as reductant in marcasite

Conclusions & Outlook

- Tc removal by FeS_2 minerals is driven by the reduction from Tc(VII) to Tc(IV)
- Identification of secondary minerals is crucial to decipher Tc-mineral molecular interaction
- Different redox functionalities (Fe^{2+} and S^{2-}) are responsible
- pH dependent retention mechanisms on both FeS_2

Reduced Tc mobility is expected in the near- and far-field of nuclear waste repositories where FeS_2 is abundant e.g., induced by microorganism



Future perspectives: study Tc behaviour under more realistic scenarios

TecRad Young investigator group [8]

Tasks in the project

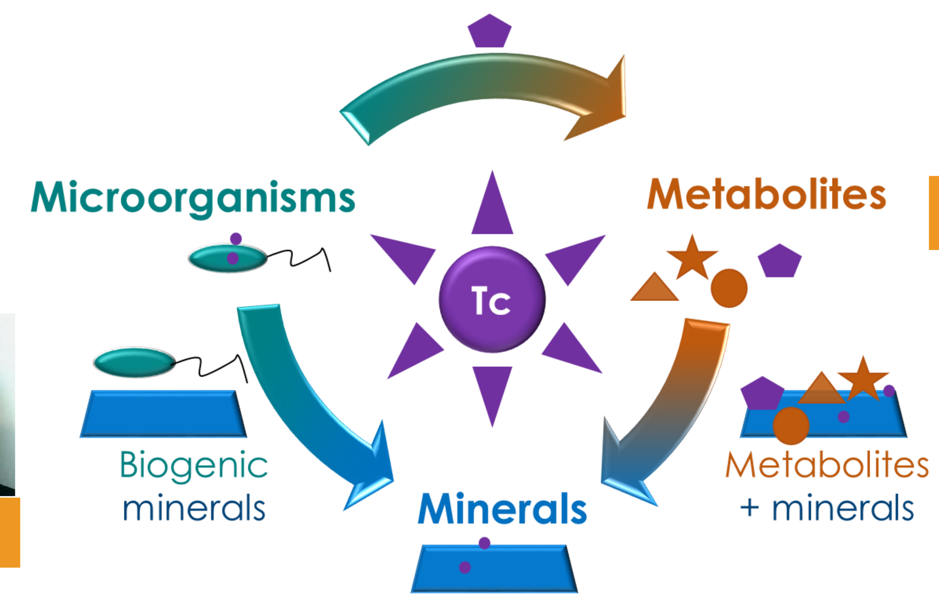
- Development of biogeochemical modelling for redox triggered processes
- Determination of Tc thermodynamic data:
  - Redox chemistry of Tc with organics
  - Sorption of Tc in various oxidation states
- Development of methods to observe in-situ molecular characteristics and redox properties

Interaction of Tc with microorganisms


Irene Cardaio

Development of spectro-electrochemical methods


Arkadz Bureika




Vijay K. Saini

Interaction of metabolites with Tc, and minerals


Caroline Börner

Interaction of Tc with minerals in presence of metabolites

[1] Rodriguez, D. M. *et al. Env. Sci. Technol.* **54**, 2678–2687 (2020). [2] Rodríguez, D. M. *et al. Chemosphere* **281**, 130904 (2021). [3] Mayordomo, N. *et al. J. Hazard. Mater.* **388**, 122066 (2020). [4] Mayordomo, N. *et al. Chem. Eng. J.* **408**, 127265 (2021). [5] Yalçıntaş, E. *et al. Dalton Trans.* **45**, 17874–17885 (2016). [6] I. Baumann, A. et al. *App. Geochemistry* **98**, 321–330 (2018). [7] Duckworth S. B. *et al. Radiochim. Acta* **109(9)**, 681 (2021) [8] TecRad webpage https://www.hzdr.de/db/Cms?pNid=1375.

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