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Tc(VII) reductive immobilization by Sn(II) pre-sorbed on alumina nanoparticles.

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The interaction of highly mobile radioactive elements in the spent fuel with the different technical and geological barriers of a nuclear waste repository needs quantification and mechanistic understanding to allow a reliable safety assessment.
One of the most concerning mobile fission products is Tc-99. It is a long-lived radionuclide (half-life of 0.213 million years) that is expected to occur as Tc(VII) under oxidizing conditions and as Tc(IV) under reducing conditions. The anion pertechnetate (TcO₄⁻) is the main species of Tc(VII) and it is known to be a highly mobile species since it barely interacts with mineral surfaces. On the contrary, TcO2 is the main species of Tc(IV) and it is a hardly soluble solid. Therefore, the reduction of Tc(VII) to Tc(IV) limits the mobility of Tc in water and is triggered by reducing agents such as Fe(II) or Sn(II). [1] In a previous work, we have observed that pre-sorption of Fe(II) on alumina enabled the Tc(VII) reduction at the interface, even at low pH values when Tc(VII) reduction by Fe(II) was expected to be limited due to the low sorption of Fe(II) on alumina. [2] In this study we focus on the impact of Sn(II).
We have performed sorption experiments following a stepwise strategy to ensure that Tc(VII) reduction by Sn(II) occurred at the interface (heteroreduction). i) Sn(II) was sorbed on alumina, ii) the Sn(II) pre-sorbed on alumina solid was isolated and dried, iii) a solution of Tc(VII) was added to this modified alumina, and iv) the yield of Tc removal by Sn(II) pre-sorbed on alumina was analyzed. The resulting Tc-containing solid was analyzed by X-ray absorption spectroscopy (XAS) at the Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility in Grenoble (France).
Re-oxidation experiments were performed in samples where Tc(VII) reduction by Sn(II) was obtained by different pathways: i) Tc(VII) direct reduction by dissolved Sn(II) (homoreduction) and ii) Tc(VII) reduction by Sn(II) pre-sorbed on alumina (heteroreduction).
The results show that Tc(VII) is reduced to Tc(IV) with a high yield (85-100% removal from solution), being maximum at pH values between 3.5 and 9.5, and minimum at pH 10. Re-oxidation studies show that Tc(IV) obtained by heteroreduction presents lower oxidation kinetics than Tc(IV) obtained by homoreduction. These results support that the presence of alumina plays an important role by preventing Tc(IV) re-oxidation.
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Primary authors: MAYORDOMO, Natalia (Helmholtz Zentrum Dresden Rossendorf); RODRÍGUEZ HERNÁNDEZ, Diana Marcela (Helmholtz Zentrum Dresden Rossendorf); ROSSBERG, André (Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Institute of Resource Ecology); SCHEINOST, Andreas (Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Institute of Resource Ecology); Dr KATHARINA , Müller (Helmholtz-Zentrum Dresden-Rossendorf)

Presenter: MAYORDOMO, Natalia (Helmholtz Zentrum Dresden Rossendorf)

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