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

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Abstract. Technetium-99 (^{99}Tc) is a long-lived fission product (2.13×10^5 years) of uranium-235 (^{235}U) and plutonium-239 (^{239}Pu) and, therefore, of great concern for the long-term safe management of nuclear waste. The migration of Tc in the environment is highly influenced by the redox conditions, since Tc may be present in various oxidation states. Depending on the chemical properties of environmentally relevant systems, Tc is expected to mainly occur as Tc(VII) and as Tc(IV) under oxidizing and reducing conditions, respectively. The anion pertechnetate ($Tc(VII)O_4^-$) is known to barely interact with mineral surfaces; this, in turn, enhances its migration in groundwater and favors its entry into the biosphere. On the contrary, the formation of Tc(IV) limits the migration of Tc, since it forms a low soluble solid (TcO_2) and/or species, whose interaction with minerals is more favorable. In the last few decades Tc migration has been focused on the reduction of Tc(VII) to Tc(IV) by various reductants, such as Fe(II), Sn(II), or S(-II), which are either present in solution, taking part in mineral structures (Pearce et al., 2019), or metabolically induced by microbial cascades (Newsome et al., 2014).

We have studied the immobilization of technetium (Tc) by various Fe(II)-containing phases, including Fe^{2+} pre-sorbed on alumina nanoparticles (Mayordomo et al., 2020), Fe(II)-Al(III)-layered double hydroxide (Mayordomo et al., 2021), and Fe(II) sulfides (Rodríguez et al., 2020; Rodríguez et al., 2021). We have combined sorption experiments with microscopic and spectroscopic techniques (scanning electron microscopy, Raman microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, and X-ray absorption spectroscopy) to elucidate the mechanisms responsible for Tc(VII) reductive immobilization.

Those works have been focused on binary systems (i.e., studies of the interaction of Tc with a given reductant). However, the environment is a complex system, where different components often depend on and modify each other. Thus, Tc migration is susceptible and varies, depending on environmental conditions, and should not be studied in an isolated manner. The young investigator group TecRad (HZDR, 2022), funded by the German Federal Ministry of Education and Research, aims at analyzing Tc chemistry from a wider perspective. Our goal is to study the biogeochemical behavior of Tc when it interacts with (i) microorganisms, (ii) metabolites, (iii) Fe(II) minerals, and (iv) Fe(II) minerals in presence of metabolites.

An important part of this project deals with implementing new spectro-electrochemical methods to monitor the in situ the behavior of Tc in solution and at interfaces as a function of the redox potential. With these tools, we aspire to characterize the molecular structures of Tc species under a variable range of redox conditions to broaden the understanding of the chemical behavior of the pollutant.

We aim at generating valuable thermodynamic data (complex formation constants, solubility constants of minerals, redox potentials, and Tc distribution coefficients) that will be used to implement a geochemical modeling able to explain Tc's environmental fate, even under different redox conditions.

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