Technetium retention by green rust chloride

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Techntium-99 (^{99}Tc) is one of the most concerning fission products due to its long half-life ($2.14 \cdot 10^5$ years) and the mobility of the anion pertechnetate (TcO_4^-). [1] However, Tc migration decreases when Tc(VII) is reduced to Tc(IV). This scavenging step is favored by reductive material, among which Fe(II) minerals have been widely studied due to their versatility, low cost and ubiquity. [2]

Green rust is a Fe(II)-Fe(III) mixed hydroxide that possesses adsorption, anion exchange and reduction capabilities. Its presence is expected in the near- and far-field of a nuclear waste repository because it is an iron corrosion product, and it is also formed in the environment when Fe^{2+} interacts with Fe(III) minerals. [3]

Batch contact studies have been performed under a wide range of conditions, i.e. pH (3-11), Tc concentration (nM-mM), and ionic strength (0-0.1 M). X-ray diffraction, Raman microscopy, X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS) provided information on Tc oxidation state and speciation as well as on secondary redox products related to the Tc interaction with green rust. In addition, re-oxidation experiments have been performed during six months.

The results show that green rust removes Tc from solution with efficiencies between 80% (Kd = $8.0 \cdot 10^3$ mL/g) and $\approx$100% (Kd = $9.9 \cdot 10^5$ mL/g) for pH > 6.0, regardless on the ionic strength and the Tc concentration. In contrast, Tc removal for pH < 6.0 drops with decreasing pH, and ranges from 80% to 50% (Kd = $2.0 \cdot 10^3$ mL/g), reaching a minimum at pH 3.5. XPS analysis reveals the predominance of Tc(IV) at all evaluated pH values (3.5 to 11.5), supporting that Tc reductive immobilization is the main retention mechanism. Re-oxidation experiments show that Tc is slowly solubilized when time increases.

$$Kd[mL/g] = ([Tc]_{removed}/[Tc]_{solution}) \times (V/m)$$

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