

Radionuclide-mineral redox interactions: Current progress and future outlook

CHRISTOPHER A. GORSKI^{1*}

¹Department of Civil & Environmental Engineering,
Pennsylvania State University, University Park, PA 16802,
USA (*correspondence: gorski@psu.edu)

Radionuclides, such as technium (Tc) and uranium (U), exist in multiple oxidation states in the environment, which affects their speciation, solubility, and reactivity. In virtually all cases, radionuclide oxidation states are determined by their chemical and biological surroundings. Radionuclides commonly participate in interfacial electron transfer reactions with minerals and amorphous solids that contain redox-active elements, most commonly iron (Fe) and manganese (Mn). The ability to estimate the mechanisms, rates, and extents to which these radionuclide-mineral redox interactions occur is critical both for designing effective radioactive waste storage repositories and remediating existing water contamination. Doing so requires simultaneous knowledge of both the molecular-scale mechanisms by which electron transfer occurs as well as the thermodynamics of the electron transfer step(s).

Here, I will focus on the thermodynamics of radionuclide-mineral electron transfer reactions. Our current abilities to estimate and rationalize reaction rates and extents using thermodynamic values, such as reduction potentials (E_H), is undoubtedly improving, due notably to advances in computational simulations [1] and the development of new electrochemical techniques capable of analysing solid-phase samples. I will discuss these approaches, what information we have gained from them, and their inherent challenges. In parallel, the results yielded from these experimental and modelling advances have been humbling due to the fact that minerals exhibit redox behaviour that is far more complex than previously thought. In many cases, electron transfer to and from minerals is irreversible and cannot be described using simple models, such as the Nernst equation. Additionally, subtle changes in a mineral's morphology and elemental composition may profoundly impact their reduction potential values and subsequent reactivity. Such changes are particularly important when redox reactions induce mineralogical changes, including the structural incorporation or release of radionuclides. I will conclude the talk with where I see this field moving in the future and the critical questions that should be addressed.

[1] Arumugam & Becker (2014) *Minerals*. **4**, 345-387.