

## Redox behaviour of plutonium in the presence of Al-doped iron oxide mineral surfaces: a solid-phase perspective using HERFD-XANES

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Plutonium (Pu) is a radiotoxic element present in used nuclear fuel, in fuel reprocessing products, and at legacy contaminated sites.<sup>1</sup> To facilitate the continued use of commercial nuclear power and address environmental contamination, it is essential to understand Pu fate and transport in subsurface environments, which is tied to its rich redox chemistry (i.e., generally, Pu(IV) is less mobile and Pu(V) is more mobile).<sup>1</sup>

Predictive geochemical models are necessary for long-term performance assessments of potential nuclear waste repositories. However, current geochemical models do not accurately predict actinide behaviour under field conditions and do not account for complexity in mineral assemblages, such as chemical impurities.<sup>2</sup>

Iron oxides (e.g., hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and goethite ( $\alpha$ -FeOOH)) are an integral part of determining the performance of a generic geologic repository (e.g., granite, clay, salt) for used nuclear fuel, influence contaminant fate and transport in the environment,<sup>1</sup> and commonly contain up to ~15% aluminium (Al).<sup>3</sup>

This work tests mineralogically complex systems where Pu(V/VI) is the sorbate, and Al-substituted hematite or Al-substituted goethite are the sorbent. The overall goal is to relate Pu behaviour to the physicochemical properties of the sorbent minerals.

Using M<sub>4</sub>-edge HERFD-XANES we probe the electronic configuration of Pu<sup>4</sup> and quantify the extent of Pu surface-mediated reduction in systems containing Al-substituted hematite and Al-substituted goethite. Our results suggest that Pu sorption to Al-hematite and Al-goethite is slower than to Al-free minerals, although the extent of sorption is comparable as the reactions approach steady state. Stability and surface site properties of Al-substituted minerals may play a role in Pu redox behaviour. Pu(V/VI) surface-mediated reduction to Pu(IV) is observed in our systems via M<sub>4</sub>-edge HERFD-XANES.

Studying the redox behaviour of Pu associated with the solid phase will improve our understanding of surface-mediated reduction and immobilization of Pu in the environment, and its interactions with geologic materials.

(1) Hixon and Powell. *Environ. Sci.: Processes Impacts* **2018**, 20 (10), 1306–1322.

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(3) Hsu et al. *Environmental Science: Nano* **2020**, 7 (11), 3497–3508.

(4) Gerber et al. *Nanoscale* **2020**.