Plutonium desorption from montmorillonite: The role of redox transformations

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Recent investigations of Pu contaminated environments have identified the importance of colloid facilitated Pu transport [1] [2]. Adsorption and desorption of Pu on mineral colloids will likely control the extent of this transport. Pu oxidation state exerts a strong control on its adsorption behavior. However, it has also been demonstrated that certain minerals are able to alter the oxidation state of Pu present on their surface [3] [4]. Depending on the mineral, the rates of surface mediated reduction can vary by orders of magnitude [5]. While Pu desorption from mineral surfaces has not been studied as intensely as adsorption, desorption rates will nonetheless limit the spatial and temporal extent of colloid-facilitated Pu migration. In this work, we quantified Pu-montmorillonite desorption rates using a combination of batch/flow cell experiments and numerical modeling. Our numerical model is based on the Np(V)-geothite adsorption/desorption model reported in [6] but also accounts for Pu surface-mediated redox processes. The model parameters were calibrated by our batch/flow cell data in combination with literature kinetic and equilibrium data

First order desorption rate constants suggest that colloid-facilitated Pu transport is possible at timescales of years or possibly decades. The desorption rates decrease with pH and most likely, with Eh. The desorption is evidently controlled, to a large extent, by the rate of Pu(IV) oxidation to Pu(V). Importantly, these data do not provide evidence for an irreversible sorption process. As a result, colloid-facilitated Pu transport on geological temporal and spatial scales will be limited. Processes in addition to simple adsorption/desorption that may enhance colloid-facilitated transport at geologic timescales will be discussed.

[1] Kersting *et al*. (1999), *Nature* **397**, 56-59. [2] Novikov *et al*. (2006), *Science* **314**, 638-641. [3] Felmy *et al*. (2011), *ES&T* **45**, 3952-3958. [4] Kirsch *et al*. (2011), *ES&T* **45**, 7267-7274. [5] Begg *et al*. (2013), *ES&T* **47**, 5146-5153. [6] Tinnacher *et al*. (2011), *GCA* **75**, 6584-6599.