

Impacts of Si on Se(IV) immobilization on ferrihydrite: An *in-situ* ATR-IR spectroscopic investigation

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The long-lived radionuclide Se-79 is one of the key radionuclides of interest in radioactive waste disposal. Its release from radioactive waste repositories and into groundwater presents serious environmental concerns due to its chemical and radiologic toxicity. Under partly oxidizing conditions typical of shallow repositories, Se exists in the form of highly mobile Se(IV); its migration may be potentially mitigated via interaction with iron minerals [1] present in the components of the repository such as steel overpack, clay buffer, host rock and the overlying soils. At the same time, Si derived from clay alteration and the host rock may potentially compete with Se(IV) for sorption sites on iron mineral surfaces. It is, however, unclear whether Si modifies Se(IV) sorption mechanisms, inhibits Se(IV) sorption or promotes Se(IV) desorption. Understanding the mechanisms underlying competitive processes have implications in modeling the behavior of Se(IV) in actual disposal repositories. Thus, this work aims to clarify the impacts of Si on the mechanisms, degree and stability of Se(IV) sorption on iron oxides.

This work focuses on ferrihydrite, a poorly crystalline ferric hydroxide that is common oxidation product of Fe(II) and is a ubiquitous component of rocks and soils. In order to obtain direct information on sorption mechanisms at the solid-fluid interface, sorption was monitored in a flow-through setup using *in situ* attenuated total reflectance infrared (ATR-IR) spectroscopy. A ferrihydrite film was deposited on a diamond ATR element and Si and Se(IV) solutions at pH 7 to 11 were flowed on the surface. The absorbance of the Se—O and Si—O stretching bands, which provide information on sorbate geometry, was then monitored over time. Generally, Se(IV) sorption was more pronounced at pH 7 and 9 than at pH 11, with the IR spectra exhibiting prominent bands consistent with a bidentate sorption mechanism. In experiments wherein Si was initially adsorbed on ferrihydrite, the absorbance of the Se—O stretching bands increases at a slower rate and attains a lower value than in the absence of Si. This observations suggest that Si inhibits the sorption of Se(IV) on ferrihydrite, likely by blocking sorption sites. In experiments wherein Se(IV) was pre-adsorbed prior to the introduction of Si, the Se—O stretching bands exhibited a decrease in absorbance, indicating desorption. This suggests that Si displaces Se(IV) on sorption sites. Finally, competitive sorption experiments wherein Si and Se(IV) were introduced at the same time were conducted. The results show that while both Si and Se(IV) are adsorbed, Se(IV) sorption proceeded at slower rates than Si, indicating that Si has a greater affinity for surface sites on ferrihydrite than Se(IV).

To summarize, the results show that Si strongly influences the interaction of Se(IV) with ferrihydrite. Given that Si is preferentially adsorbed on ferrihydrite, it inhibits Se(IV) sorption and promotes its remobilization. In the context of the radioactive waste disposal, a key implication of these findings is that in Si-rich environments such as in repositories backfilled with clay, the mobility of Se(IV) is likely to be enhanced. This behavior must be taken into account in safety assessments of radioactive disposal repositories. The approach and results reported in this study also provide a basis to investigate the competition between other species relevant to radioactive waste disposal.

References:

[1] Francisco et al. (2018) *Environ. Sci. Technol.* 52, 4817 –4826.

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