

Effects of Si on the behavior of co-precipitated Se(IV) during Fe-oxide transformation at alkaline conditions

P.C.M. FRANCISCO^{1*}, Y. OZAKI¹, T. SATO¹, T. OTAKE¹

¹Laboratory of Environmental Geology, Graduate School of Engineering, Hokkaido University

*correspondence:

paulcmfrancisco@frontier.hokudai.ac.jp

⁷⁹Se is a radionuclide present in high-level nuclear wastes and is of high environmental interest due to its long half-life and high mobility. The interaction of Se species with Fe-oxides that occur in barrier materials and in the environment surrounding repositories is widely known to be an important immobilization process, with poorly crystalline phases (e.g. ferrihydrite) playing particularly significant roles. However, these metastable phases are expected to transform into stable, crystalline phases in the long-term, potentially leading to the release of previously sequestered elements. Furthermore, the presence of other ligands in the environment (e.g. Si) affects the uptake capacity and transformation kinetics and processes of such phases, which may influence the retention and/or release of sequestered elements. This study aims to clarify the fate of Se (IV) co-precipitated with ferrihydrite during phase transformation and the influence of Si on its behavior. Results of this study may shed light on Se behavior in HLW repositories as well as in other environments (e.g. soils).

Batch co-precipitation experiments of Se (IV) with Fe-oxyhydroxides were conducted in the presence of varying amounts of Si at pH 10. Analysis of residual Se (IV) in the solutions showed that ~90% of Se (IV) was removed from solution and that the amount decreased very slightly with increasing Si. During transformation to hematite and goethite, a fraction of uptaken Se (IV) was released back into solution. The rate of Se (IV) release was increasingly delayed with increasing Si, consistent with the inhibitory effect of Si on ferrihydrite transformation. However, the amount of released Se (IV) also increases with increasing Si. Studies of the solids both before and after transformation using infrared (IR) and x-ray absorption spectroscopic (XAS) techniques, combined with extraction experiments indicated that Se (IV) was sequestered from solution and retained in the solid phases by sorption on Fe-oxide/oxyhydroxide surfaces and not by the formation of an independent phase. These suggest that the release of Se (IV) during transformation may be due to the lower sorption capacities of crystalline Fe-oxides and the competition between Se (IV) and Si for sorption sites. These results show that post-uptake behavior of hazardous elements must be carefully considered.