

Behavior of co-precipitated Se (IV) during the transformation of Fe-oxides at alkaline conditions

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⁷⁹Se is a radionuclide present in high-level nuclear wastes and is of particular environmental interest due to its long half-life. Degradation of waste repositories over time may lead to its release into the wider environment in the form of Se (IV). While Se is an essential element for flora and fauna, it is known to be toxic when present at high concentrations. One of the best-known mechanisms that immobilize Se and limit its mobility in the wider environment is by sorption to iron oxides / hydroxides. These phases may be formed from the corrosion of metal canisters used to contain waste forms under alkaline conditions, providing suitable sinks for Se. Most studies have focused on poorly crystalline ferrihydrite or hydrous goethite (e.g. Hayes et al, 1987; Manceau and Charlet, 1994; Das et al, 2013) due to their high surface areas and reactivity. However, since these phases are metastable with respect to other stable Fe-oxides phases (e.g. hematite, magnetite, maghemite), it is possible that these phases will eventually transform to more stable phases which may result in either the release or retention of previously uptaken Se. There is very limited information on the fate of Se during this transformation process. Thus, it is the objective of this study to clarify the behavior of Se during transformation of poorly crystalline Fe-hydroxides to crystalline Fe-oxides.

Se (IV) was co-precipitated with ferrihydrite by adding base to a solution containing both Fe and Se to raise the pH to 10. The resulting slurries were then aged at 80°C for 4 days to induce transformation. Solids and liquids were then separated by centrifugation and filtration. Solution samples were analyzed for Se concentrations while solids were characterized using x-ray diffraction (XRD), infrared (IR) spectroscopy and x-ray absorption spectroscopy (XAS). Results of solution analyses show that co-precipitation sequesters approximately 90% of Se from the solution. Transformation of the ferrihydrite to crystalline hematite and goethite phases at alkaline conditions results in the release of a fraction of the initially sequestered Se, such that only approximately 50% of the original Se is retained by the solids. Spectroscopic studies of the solids suggest that Se is sequestered from solution by sorption on ferrihydrite and not by the formation of an independent Fe-Se phase. During ferrihydrite transformation to crystalline hematite and goethite, Se is similarly retained by sorption on the crystalline phases. The release of Se during transformation may thus be attributed to the lower sorption capacity of crystalline Fe-oxides for Se. The results of this study thus show that post-uptake behavior of hazardous elements must be considered during long-term assessments of high-level waste repository conditions.

Keywords: Selenium behavior, iron oxide transformation, nuclear waste disposal