Se(-II) immobilization in Fe(II)-(hydro)oxides: Coprecipitation and post-transformation behavior

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As a key long-lived fission product in high-level wastes (HLW), Se-79 is a significant contributor to the long-term radiological hazards associated with geological HLW disposal. Thus, its behavior is of critical importance to the long-term performance assessment of geological HLW repositories. Under reducing conditions in geological disposal environments, Se exists as Se(-II). A potential retardation pathway for Se(-II) species is via interaction with aqueous Fe(II) species and solid phases arising from the corrosion of the steel canister enclosing the waste matrix. At present, the mechanisms of Se(-II) uptake via coprecipitation and interaction with poorly crystalline iron phases and subsequent behavior during phase transformation, are poorly understood.

Batch coprecipitation and crystallization experiments of Se(-II) with Fe(II) phases under N_2 atmosphere and reducing conditions were carried out. Two cases were examined: in the first, the Se(-II) was reacted with aqueous Fe(II) species. In the second case, Fe(II)-hydroxide was first precipitated (slurry) prior to reaction with Se(-II) to simulate Se(-II) interaction with poorly crystalline steel corrosion products. Addition of Se(-II) into the Fe(II) solution/slurry resulted in the immediate formation of black precipitates which were then aged at 90°C for up to 7 days. Solid samples after coprecipitation and aging were then analyzed by XRD, XPS and XAFS to identify mineral phases and Se speciation.

In both cases, solution analyses show efficient initial uptake of Se(-II). In the initial amorphous coprecipitates, spectroscopic results suggest Se was retained as amorphous FeSe/$FeSe_2$ and Se(0) in the first and second cases, respectively. Following aging, Se was completely retained as crystalline $FeSe_2$ alongside magnetite in the first case. In the second case, aging resulted in partial Se release, with the remaining Se likely retained as Se(0) on magnetite surfaces. These findings suggest different Se(-II) retention mechanisms depending on how Se(-II) interacts with Fe(II), providing preliminary constraints on Se(-II) behavior that may help in predicting its long-term migration in geological repositories.

*This study was performed as part of “The project for validating near-field system assessment methodology in geological disposal” funded by METI of Japan.