Effects of pH on the formation and transformation of Fe(II)-Si coprecipitates under anoxic, reducing conditions

P.C.M. FRANCISCO[1*], S. MITSUI[1*], T. ISHIDERA[1], Y. TACHI[1]

[1]Radionuclide Migration Research Group, Japan Atomic Energy Agency, Muramatsu, Tokai, Ibaraki, Japan
Correspondence: paul.francisco@jaea.go.jp; mitsui.seiichiro@jaea.go.jp

The formation of Fe(II)-Si phases at the interfaces of vitrified waste and the surrounding steel overpack in geological disposal systems for radioactive wastes is regarded as a critical process in regulating the dissolution behavior of vitrified waste as well as in preventing the migration of radionuclides that may be released due to the dissolution of the vitrified waste. At present, there is little information on the formation conditions of phases that may form during the interaction of Fe(II) and Si. In this study, we investigate the initial formation of Fe(II)-Si coprecipitates and their transformation to crystalline phases as a function of pH.

Batch coprecipitation experiments of Fe(II)-Si were conducted by mixing solutions of Fe(II) and Si to create mixtures with a Si/Fe molar ratio of ~1. These mixtures were then titrated with base to increase the pH to 7, 9 and 11, which resulted in the rapid formation of greenish precipitates. The precipitates were then aged in the same solution at 60 and 120°C for up to 20 days to induce crystallization. All experiments were conducted in N_2 atmosphere. The solids were then characterized using XRD and FTIR Spectroscopy.

XRD analyses show that the initial precipitates are amorphous. Upon aging, these precipitates transformed into an assemblage dominated by magnetite. FTIR results show the presence of Si-O-Fe bonds, possibly suggesting the formation of Si-Fe phases or the sorption of Si on the transformation products, such as magnetite. With increasing pH, XRD peak intensities for magnetite increase, suggesting that magnetite crystallization is favored at higher pH. Furthermore, peaks that may correspond to Si-Fe phases are also observed with increasing pH. These results provide preliminary data on the phases that may potentially control Si solubility at vitrified waste - steel interfaces and can be used to validate the thermodynamic database prediction for Fe-Si phases.

*This study was performed as part of the "The project for validating assessment methodology in geological disposal systems" and is funded by the Ministry of Economy, Trade and Industry of Japan.