Effect of redox conditions on sulfur and selenium binding in AFm phases

L. NEDYALKOVA[1,2]*, B. LOTHENBACH[2], J. TITS[1], E. WIELAND[1], U. MÄDER[3]

[1]Paul Scherrer Institute, Laboratory for Waste Management, 5232 Villigen, Switzerland (*correspondence: latina.nedyalkova@psi.ch, jan.tits@psi.ch, erich.wieland@psi.ch)

[2] Empa, Laboratory for Concrete & Construction Chemistry, Überlandstrasse 129, 8600 Dübendorf, Switzerland (barbara.lothenbach@empa.ch)

[3] Institute of Geological Sciences, University of Bern, Switzerland (urs.maeder@geo.unibe.ch)

In the context of radioactive waste disposal, AFm phases may play an important role in the immobilization of dose-relevant selenium (^{79}Se) in cement-based low and intermediate level radioactive waste (L/ILW) repositories. The aim of the study is to investigate the ability of AFm phases to bind selenium as well as sulfur, a major competitor for Se binding, in the AFm structure. For this purpose Se(VI)-, Se(IV)-, S(VI)-, S(IV)- and S(II)-AFm phases were synthesized representing a range of possible redox conditions in a cement-based repository. Different analytical techniques (TGA, FTIR and XRD) were used to characterize the synthesized AFm phases. Solubility products were determined from chemical analysis of the liquid phases and the measured pH values. The effect of time (3 months vs. 6 months equilibration time) and pH (high pH of ~13 vs. lower pH of ~12) on the stability of the phases were investigated as well.

The diffraction patterns revealed the formation of well crystalline phases with rhombohedral structure. All of the synthesized products showed different interlayer distances (hkl 003 and 006) but identical position of the main layer peak (hkl 110). From the TGA analyses a total water loss of 12 H_2O for the S(VI)-, S(II)-, Se(VI)- and Se(IV)-AFm, and 11 H_2O for the S(IV)-AFm was determined. These observations suggest intercalation of the Se and S anions in the AFm interlayers giving rise to the differences in the interlayer distances as a function of their size and/or the number of water molecules. For S(VI)- and Se(VI)-AFm phases slightly lower solubility products were obtained than for the reduced S(IV)- and Se(IV)-AFm indicating that the S(VI)- and Se(VI)-AFm are more stable.