Effect of redox conditions on sulfur, selenium and iodine 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)

Under the alkaline and reducing conditions expected in cement-based low and intermediate level radioactive waste (L/ILW) repositories the thermodynamically predominant aqueous species of the dose-determining radionuclides selenium-79 and iodine-129 are SeO_3^{2-}, HSe^-, Se_x^{2-} (with x = 2,3,4) and I^-, respectively. All these anions could potentially exchange for the common interlayer anions found in the structure of the AFm phases in cementitious materials. To study the Se uptake mechanism in AFm phases as well as the effect of the competition with sulfur under reducing conditions, the synthesis of pure $(HS^-)_2$-AFm and $(HSe^-)_2$-AFm phases was attempted. Furthermore, the ability of Se and I to form binary solid solutions between the pairs SeO_3^{2-}-X^{n-} and I^--X^{n-} (with $X^{n-} = SO_4^{2-}$, SO_3^{2-}, $S_2O_3^{2-}$, CO_3^{2-}, OH^-, OH^--CO_3^{2-}) was examined.

XRD analyses revealed an AFm-like (rhombohedral) structure for the synthesized $(HS^-)_2$- and $(HSe^-)_2$-solids with d-spacing of 8.46 Å and 8.27 Å, respectively. Based on XRD observations, the formation of a continuous solid solution was found between the pairs SeO_3-SO_4, I-OH_CO_3 and I-OH, visible by a gradual peak shift of the basal reflexion from one end member to the other. In the case of the I_2-CO_3 pair, a miscibility gap with the composition $0.5 \leq CO_3/(2I+CO_3)$ exists, indicated by the presence of two coexisting phases – an I_2-CO_3-AFm mixed phase and a pure CO_3-AFm.

The experimental data suggests that $(HS^-)_2$-AFm and $(HSe^-)_2$-AFm phases could be potentially stable under the reducing and alkaline conditions expected in a cement-based L/ILW repository after closure. The formation of AFm solid solutions with Se and I anionic species seems to be controlled by the crystal symmetry, the size of the interlayer anion and the hydration state of the phase.