Redox transformations and the disposal of radioactive waste: Influence on Se immobilization

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Safety analysis of a cement-based repository for low- and intermediate level nuclear waste (L/ILW) has shown that ^{79}Se is an important redox-sensitive, dose-determining radionuclide due to its long half-life and weak retardation by common near- and far field minerals. In the sorption data bases currently used for safety analysis it is considered that ^{79}Se is predominantly present as SeO_3^{2-} in the cementitious near field because oxidizing conditions prevail during waste conditioning. With time, however, reducing conditions will establish in the near field caused by oxygen consumption in the course of metal corrosion. In these conditions Se(-II) is expected to be the dominant redox state of Se. Hence, investigations into the interaction of Se(IV) and Se(-II) with cementitious materials and into the reduction of Se(IV) to Se(-II) enable us to assess the long-term fate of Se under the conditions relevant to a cement-based repository.

Sorption studies with Se on cementitious materials indicate that Se(IV) and Se(-II) uptake by hydrated calcium aluminates (AFm) and calcium silicate hydrates (C-S-H) phases, the principal host phases for radionuclides in cement paste, is significant and comparable to the uptake by cement paste. The uptake mechanisms of the Se species, however, are only poorly understood. Wet chemistry experiments suggest that Se(IV) and Se(-II) could be taken up into the structure of the cement phases. In the case of AFm phases, for example, anions bound in the interlayer can be replaced, at least partially, by Se(IV) and Se(-II). This explains why AFm phases are more effective in removing the Se species from solution than C-S-H phases. EXAFS studies were carried out to confirm preservation of the redox states.

EXAFS investigations into redox transformation are ongoing. The first results already suggest that the uptake mechanism of the Se species plays an important role in the reduction of Se(IV) to Se(-II) in cementitious materials.