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## Competitive uptake behaviour of radionuclides in cementitious material

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Cement is an important constituent of the engineered barrier systems in underground repositories for low and intermediate level radioactive waste. Cement is used to solidify and stabilize the waste materials and, furthermore, it is used in huge amounts for the construction and backfilling of the cavern. The release of radionuclides from the cementitious near field into the underground is retarded due to their strong interaction with cement mineral phases. In hydrated cement, calcium silicate hydrates (C-S-H),  $(\text{CaO})_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z$  are quantitatively the most abundant and most important phases. They are chemically the most stable minerals in a cementitious environment and exhibit a wide diversity of structural sites exposed for cation binding. Three different modes of heavy metal interaction with C-S-H phases can be envisaged: 1) surface complexation, 2) uptake in the interlayer, and 3) incorporation in the octahedral Ca sheets.

In this study, 11 Å tobermorite, a crystalline C-S-H phase, was doped with both Nd and Zn in order to investigate whether or not the competition between the two metals has an influence on the binding mechanism and the coordination environment of these metals in the C-S-H structure. On the basis of previous EXAFS studies a structural model for the site occupation of Zn in C-S-H phases was proposed.  $\text{Zn}(\text{O},\text{OH})_4$  tetrahedra substitute for silicate bridging tetrahedral and/or they are bound at terminal silicate chain sites, thus suggesting Zn binding in layer positions of C-S-H phases rather than the interlayer. In contrast, spectroscopic studies on lanthanide binding to crystalline C-S-H phases indicate that Eu (and Nd) forms inner sphere surface complexes with the C-S-H surface in the early phase of the sorption process. However, with time, Eu and Nd binding into the structure of crystalline C-S-H phases occurs, occupying positions in the interlayer and the Ca layer of the C-S-H structure. Therefore, Nd and Zn are expected to be taken up into the structure of C-S-H phases whereby they occupy neighbouring crystallographic positions. In this study Zn K-edge and Nd LIII-edge EXAFS spectroscopy was used to discern the possibility of backscattering contributions from neighbouring Zn and Nd atoms on the absorption spectra.

The Zn and Nd doped 11 Å tobermorite samples had metal concentrations of 50000 ppm, while the reaction times varied from one to six months. X-ray absorption spectroscopic data suggest that Nd has an influence on the incorporation of Zn in the tobermorite structure. The Zn K-edge EXAFS data exhibit distinct differences in the presence and absence of Nd as neighbouring element. Zn has a tetrahedral coordination environment with Zn-O distances of 1.96 Å, whereas Nd is octahedral coordinated with Nd-O distances of 2.45 Å. These findings indicate that competitive uptake of metal cations with similar sorption behaviour by C-S-H phases can take place, which deserves further attention in future assessments of the safe disposal of radioactive wastes in cement-based repositories. Currently molecular modelling calculations are ongoing to better constrain the uptake mechanism involved.

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