

Retention of selenium by cementitious materials under reducing radioactive waste repository conditions

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Cementitious materials play a crucial role as barrier for radionuclide transport in low and intermediate level radioactive waste repositories, where ⁷⁹Se is an important redox-sensitive and dose-determining radionuclide. In current sorption databases for the cementitious near-field, only sorption data for Se(IV/VI) have been considered. Robust sorption data on reduced Se species in general, and a sufficiently detailed mechanistic understanding of their retention in cementitious environment are, however, lacking.

The aim of this work is to investigate the immobilisation of Se under the reducing conditions existing in a cement-based repository ($-230\text{mV} < \text{Eh} < -750\text{ mV}$). Under these conditions, Se(IV) and Se(-II) are the dominating redox states. In this study, Se(-II) was obtained by electrochemical reduction of Se(IV) in solution. Completion of the reduction process was determined by UV-Vis spectroscopy. Se(IV) and Se(-II) sorption kinetic studies were carried out on various synthetic cement components, such as calcium silicate hydrates (C-S-H) and hydrated calcium aluminates (AFm), the principal host phases for radionuclides in hydrated cement. In addition, Se(IV) and Se(-II) sorption experiments were performed with TiO₂ as reference solid, stable under alkaline conditions, at pH = 10.0 and 13.3, in the absence of Ca and presence of 10⁻³ M Ca. XANES studies allowed the determination of the redox state of sorbed selenium.

The sorption tests revealed that the uptake of Se(IV) by C-S-H phases is much stronger than expected. R_d values measured on C-S-H phases are approximately two orders of magnitude higher than R_d values measured on TiO₂. This high affinity of the C-S-H phases for Se(IV) anions is partially explained by the high specific surface area of these solids. Furthermore, R_d values for Se(IV) on various AFm phases are correlated with their interlayer spacing. The sorption of Se(-II) on the different cementitious materials was found to be weaker than the sorption of Se(IV).