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U(VI) uptake by co-precipitation and adsorption in cementitious systems

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Cementitious materials used for engineered barriers in repositories for nuclear waste are known to retard the migration of radionuclides. Calcium silicate hydrate phases (C-S-H), the principal component of hydrated Portland cement, play an important role in radionuclide immobilization. This may take place via co-precipitation processes during the solidification of the waste materials. Degradation of the solidified waste with time may cause the release of radionuclides into the near-field pore water which, however, is followed by adsorption on the cementitious materials. Thus, a detailed understanding of the two immobilization processes (co-precipitation, adsorption) will significantly improve long-term predictions of the safe disposal of radioactive wastes.

For the present study C-S-H phases were synthesised by mixing calcium hydroxide and sodium metasilicate solutions in de-ionized water and in alkaline solution ([Na]=0.114 M, [K]=0.18 M, pH 13.3) to obtain solids with varying CaO:SiO₂ (C:S) ratios. The pH of the equilibrium solutions ranged in value between 11.5 - 12.5 for the first procedure, but was fixed at pH 13.3 in other one. The precipitates formed were characterized with respect to the chemical and mineralogical compositions. In all cases, the main product was identified to be a C-S-H phase with trace impurities (Ca(OH)₂ and CaCO₃) in a few samples.

The kinetics of U(VI) uptake was studied using two procedures: a) Co-precipitation experiments were performed by adding U(VI) to the Ca(OH)₂ solution prior to starting the C-S-H synthesis, b) Adsorption experiments were performed by adding U(VI) tracer to suspensions containing C-S-H phases aged for at least 2 weeks. Equilibrium was reached after approximately 20 days in both adsorption and co-precipitation tests, resulting in high distribution ratios (R_d) ($R_d > 1 \text{ m}^3 \text{ kg}^{-1}$ in the pH range 11.5 - 12.5, $R_d > 10^2 \text{ m}^3 \text{ kg}^{-1}$ at pH 13.3). It was found that R_d values were similar finally in both types of experiments, though the uptake by co-precipitation was faster than that by adsorption early in duration. Furthermore, no dependence on the C:S ratio of C-S-H phases was observed. The above findings suggests that in the adsorption experiments, U(VI) can rapidly diffuse into the gel-like structure of C-S-H and that both the external and internal sorption sites of C-S-H are readily accessible irrespective of the C:S ratio. Complementary spectroscopic studies were carried out on a few samples to elucidate the local structure of U(VI) in the C-S-H phase.

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The role of geochemistry in the research on geological disposal of high-level radioactive waste in a deep Boom Clay in Belgium

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Introduction

SCK•CEN is conducting a large R&D programme to evaluate and demonstrate the feasibility and safety of the geological disposal of vitrified high-level waste and spent fuel in a Boom Clay layer. The role of the geological formation is to prevent or retard the release and transport of radionuclides into the biosphere by geochemical processes such as immobilisation and sorption. To be able to predict radionuclide transport to validate safety assessment studies, one needs to understand the geochemical processes along the pathway to the biosphere: the conditions at the interface of the waste/engineered barrier/host formation, changing geochemistry at the interface due to disturbances (oxidation, alkaline front,...) and the properties of the host formation. The R&D programme consists of characterisation, laboratory batch and column experiments, *in situ* experiments, and is strongly linked to geochemical and transport modelling.

Overview of geochemical related studies

- The geochemistry of the Boom Clay porewater forms a necessary basis to build a Boom Clay Model: determination of the composition of the interstitial clay water and its relation with the Boom Clay mineralogy, determination of Eh, pH and pCO₂ (for *in situ* conditions).

- Investigation of the interaction of HLW glass or UO₂ (simulating spent fuel) with clay and clay water by relating experimental results with modelling predictions. Special emphasis is on generation and impact of secondary phases.

- Investigation of the impact of oxidation (due to excavation) of an alkaline front (coming from the concrete construction materials) on the host rock mineralogy and geochemistry and its possible consequences on the radionuclide retention processes (changes in speciation, solubility). Reactive transport models are used to simulate the movement of water, heat and various solutes.

- Investigation of radionuclide (*e.g.* U, Np, Se) speciation and solubility under the Boom Clay geochemical conditions in order to develop conceptual models describing the radionuclide transport built on a fundamental understanding of the underlying retention and transport mechanisms.

For all these studies geochemical modelling tools are used for pre-modelling (blind predictions) and post-modelling (extraction of data, validation of data/processes and updating of Boom Clay model database).