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Uranium(VI) retention by calcium aluminosilicate hydrates (C-A-S-H) – Impact of temperature, ionic strength, and organic ligands

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Concepts for the safe disposal of high-level radioactive waste in deep geological formations to ensure isolation from the biosphere are based on a multi-barrier system. Cementitious materials are one component of the geotechnical barrier, used as backfill material, for borehole sealing and to enforce the mechanical stability of tunnels. Calcium silicate hydrate (C-S-H), the principal binding phase of conventional concrete, is known to provide a high sorption capacity for trivalent to hexavalent actinides [1-3]. In modern concretes, Al-containing compounds such as blast furnace slag or fly ash are added, leading to formation of calcium aluminosilicate hydrate (C-A-S-H). To systematically study the influence of Al on both the structure of C-A-S-H phases and their U(VI) retention properties in comparison to C-S-H phases, three series of samples were synthesized in the absence and presence of U(VI). They comprise samples with Ca/Si molar ratios of 0.8, 1.2 and 1.6, representing different alteration stages of concrete, and increasing Al/Si molar ratios of 0, 0.06 and 0.18 within each series. Furthermore, the impact of temperature (25°C, 100°C, 200°C) on the structure of C-A-S-H phases and on the U(VI) retention mechanism was studied. Structural characteristics of the cementitious phases were obtained from powder X-ray diffraction as well as ²⁷Al and ²⁹Si solid-state magic angle spinning nuclear magnetic resonance spectroscopy. Al tetrahedra were identified to occupy bridging positions of the Si chain and cross-linking positions. Enhanced temperatures were found to increase the crystallinity of the material with the appearance of neoformed crystalline phases. U(VI) luminescence spectroscopy was applied to characterize the U(VI) binding. Several U(VI) species (surface-sorbed or C-A-S-H interlayer absorbed) are forming in different amounts, depending on the composition of the C-A-S-H phases.

Finally, to study the stability (or reversibility) of the U(VI) retention by the C-A-S-H phases in the presence of (i) high ionic strength pore waters and (ii) organics originally present as admixtures in cement-based materials, leaching experiments were conducted. In these experiments, simulated pore waters of complex solution composition and solutions containing gluconate as a representative of organic ligands that may be present under repository conditions, respectively, were used. The leaching experiments were conducted over extended timescales of up to 6 months. The results showed a high retention of U(VI) in the C-A-S-H phases under both abovementioned solution conditions. In conclusion, the immobilization of U(VI) by cementitious material via sorption and/or incorporation processes has important positive implications for limiting uranium migration during geological disposal of radioactive waste.

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[2] Gaona et al., Environ. Sci. Technol. 45, 8765-8771 (2011).

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Primary author: Dr SCHMEIDE, Katja (Helmholtz-Zentrum Dresden - Rossendorf, Institute of Resource Ecology, Bautzner Landstraße 400, 01328 Dresden, Germany)

Co-authors: Dr HUITTINEN, Nina (Helmholtz-Zentrum Dresden - Rossendorf, Institute of Resource Ecology,

Bautzner Landstraße 400, 01328 Dresden, Germany); Mr SHAMS ALDIN AZZAM, Salim (Helmholtz-Zentrum Dresden - Rossendorf, Institute of Resource Ecology, Bautzner Landstraße 400, 01328 Dresden, Germany); Dr BRENDLER, Erica (TU Bergakademie Freiberg, Institute of Analytical Chemistry, Leipziger Straße 29, 09599 Freiberg, Germany); Dr KRETZSCHMAR, Jerome (Helmholtz-Zentrum Dresden - Rossendorf, Institute of Resource Ecology, Bautzner Landstraße 400, 01328 Dresden, Germany)

Presenter: Dr SCHMEIDE, Katja (Helmholtz-Zentrum Dresden - Rossendorf, Institute of Resource Ecology, Bautzner Landstraße 400, 01328 Dresden, Germany)

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