

U(VI) sorption by Ca-bentonite at pH 8-13: Spectroscopic investigation of retention mechanisms

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Bentonite is considered as buffer and backfill material in deep geological repositories for radioactive waste. Therefore, profound understanding of radionuclide retention processes at the bentonite surface under environmentally relevant conditions is essential for a long-term safety assessment. Such conditions can involve high pH, as hyperalkaline cement pore waters evolve from corroding concrete within a repository. Since the U(VI) sorption behavior at alkaline conditions is still poorly understood, batch experiments were combined with spectroscopic investigations in order to gain insight into the underlying retention processes on the molecular level.

pH-dependent batch sorption experiments (pH 8-13) in a diluted Gipshut solution (2.5 M NaCl, 0.02 M CaCl₂, 0.02 M Na₂SO₄, 0.0051 M KCl) at different carbonate concentrations (absence, 0.5 and 100 mM) showed a decreased U(VI) retention in the presence of carbonate up until a certain pH (pH 9.5 or pH 11, depending on [CO₃²⁻]) due to the formation of weakly sorbing (calcium) uranyl carbonate complexes in aqueous solution, confirmed by time-resolved laser-induced fluorescence spectroscopy (TRLFS). This is in accordance with previous studies [1]. However, also in the presence of carbonate, U(VI) retention is increased in even stronger alkaline solutions, which is attributed to the preferred formation of hydrolyzed U(VI) species at these conditions.

In order to clarify the mechanisms responsible for the very strong U(VI) retention in the pH range 10-12 (absence and 0.5 mM CO₃²⁻), uranyl complexes on the bentonite surface were examined directly, using site-selective TRLFS and EXAFS (ESRF, Grenoble). Selective excitation of different sorption species by varying laser energy allowed the identification of both, surface complexation and, to a smaller degree, surface precipitation. EXAFS spectra did not show any indication of precipitates, verifying that adsorption is the dominant retention process and precipitates form only as small fractions, below the EXAFS detection limit. According to atomic distances and coordination numbers for U-O_{eq}, U(VI) surface complexes shift from a 5-fold to a 4-fold coordination in the equatorial plane with increasing pH.

[1] Marques Fernandes (2012) *Geochim. Cosmochim. Acta* **93**, 262-277.