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Effect of Ca^{2+} on the sorption of uranium(VI) and humic acid on natural clay

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In various countries clay is discussed as possible host rock for a nuclear waste repository. The interaction of the clay with actinides, especially U(VI), is the focus of our work. Sorption experiments were performed to estimate the actinide migration in clay formations. Also the influence of humic acid (HA) is investigated. HA are ubiquitously found in natural environments and can interact with e.g. actinides of the nuclear waste. Natural clay contains HA and fulvic acid like organic matter, which can be released from the clay [1]. HA also forms stable colloids. Due to this behavior HA can influence the mobility of actinides, e.g. U(VI), in a nuclear waste repository.

Opalinus clay (OPA) from Mont Terri, Switzerland was studied. Batch sorption experiments were performed in order to determine the sorption ability of U(VI) ($[\text{U}] = 1 \times 10^{-6} \text{ M}$) onto OPA in the absence and presence of HA ($[\text{HA}] = 10 \text{ mg/L}$, 50 mg/L) and of HA in the absence and presence of U(VI) using synthetic OPA pore water (OPAWA, [2], pH 7.6, $I = 0.39 \text{ M}$) and NaClO_4 (pH 3-10, $I = 0.1 \text{ M}$) as background electrolyte. During these studies a large influence of calcite on the sorption behavior of U(VI) and HA was determined. Calcite presents a fraction of 13% in OPA and its ions occur also in the OPAWA ($[\text{Ca}^{2+}] = 0.03 \text{ M}$, $[\text{CO}_3^{2-}] = 5 \times 10^{-4} \text{ M}$). In OPAWA, U(VI) forms with the ions in solution the neutral aquatic complex $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ [3]. This complex dominates the speciation with a fraction of 99%. In sorption experiments it was shown, that this complex adsorbs weakly onto OPA. Normalized to the specific surface area of OPA ($\text{BET} = 41.6 \text{ m}^2/\text{g}$) the U(VI) sorption was determined with $0.05 \pm 0.002 \mu\text{g U}/\text{m}^2 \text{ clay}$. In further sorption studies it was shown that HA has no influence on the U(VI) sorption onto OPA. This was also proved by speciation calculations, which showed that also in the presence of HA the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ complex is the dominating species in solution. In order to interpret the sorption data onto OPA, additional zeta potential measurements were performed, where between pH 0 and 7.5 a negative zeta potential for OPA was determined.

The HA sorption onto OPA in OPAWA was determined with $3.57 \pm 0.01 \mu\text{g HA}/\text{m}^2$ (10 mg/L) and $17.28 \pm 0.15 \mu\text{g HA}/\text{m}^2$ (50 mg/L). In the presence of U(VI), a slight increase of HA sorption ($D = 0.3 \mu\text{g HA}/\text{m}^2$) was observed for $[\text{HA}] = 50 \text{ mg/L}$. Species calculations showed that Ca^{2+} ions influence also the HA speciation, because Ca^{2+} is complexed by HA. Ca^{2+} is present in such a high concentration, that it saturates the binding sites of HA. Thus, only few binding sites, about 0.1% according to speciation calculations, are available for the complexation of U(VI). Consequently, U(VI) and HA have no effect on each other during the sorption studies. These experiments show the large influence of the calcite fraction of the OPA and thus the resulting composition of the OPAWA on the U(VI) and HA sorption. Thus, calcite should be taken into account for the safety case analysis of a nuclear waste repository.

[1] F. Claret et al., Sci. Total Environ. 317, 2003, 189.

[2] F.J. Pearson, PSI Internal Report TM-44-98-07, Switzerland, 1998.

[3] G. Bernhard et al., Radiochim. Acta 89, 20

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