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Report:

The U(VI) sorption ($[U]_0 = 1\text{x}10^{-4}$ M) onto opalinus clay (OPA), a natural clay from Mont Terri, Switzerland, was studied in the absence and presence of humic acid (HA) ($[HA]_0 = 10$ mg/L). OPA has a very complex composition. Beside clay minerals, also calcite, quartz and pyrite are contained. Because of its heterogeneity it is not known which mineral acts as main adsorbent. Thus, U(VI) surface species onto OPA were studied using EXAFS spectroscopy. During the experiments the influence of pH value, CO_2 presence, HA presence and background electrolyte (0.1 M $NaClO_4$, pH 3.2, 6.8, 7.4, 8.4; OPA pore water, pH 7.6, I = 0.39 M [1]) on the U(VI) sorption were investigated. The samples were measured as wet pastes. The U L_{III}-edge EXAFS spectra ($E_0 = 17185$ eV) were measured in fluorescence mode at room temperature. The EXAFS spectra were analyzed using the suite of programs EXAFSPAK [2]. The theoretical scattering phases and amplitudes were calculated using the scattering code FEFF8.2 [3].

At pH 3.2-6.8 and at 7.4-8.4 two types of EXAFS spectra were measured. For pH 3.2, beside two axial oxygen atoms, O_{ax}, of the uranyl unit (R = 1.764 ± 0.004 Å) and five equatorial oxygen atoms, O_{eq}, (R = 2.31 ± 0.01 Å) also a Si/Al shell (R = 2.751 ± 0.009 Å) was fitted. These results point out the U(VI) sorption onto the clay fraction of OPA. But in comparison with literature data for kaolinite [4] the U-Si/Al distance is very short. The U(VI) complexation with HA could also be excluded, because of the too short U-O_{eq} distance compared with values published for uranyl humate complexes [5]. Speciation calculations showed, that independent of CO_2 and HA presence and background electrolyte, always $Ca_2UO_2(CO_3)_3$(aq) is the dominating species in solution between pH 7 and 9 due to dissolution of the calcite fraction of the clay. Therefore, for pH values 7.4-8.4 the structural data of swartzite were used to fit the spectra. The obtained EXAFS spectra are still under investigation. However, due to their similarity it can be assumed, that there is no significant influence of background electrolyte, CO_2 and HA presence on the formed U(VI) surface complexes.

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