

Mechanisms of uranyl removal from aqueous solution by sandstone and volcanic rock under acidic and alkaline pH conditions

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An understanding of the molecular-level interactions of actinides at mineral surfaces is critical in developing geochemical speciation models to predict potential impacts of the geological disposal of uranium. In this study, we combine Fourier transform infrared (FTIR) spectroscopy, X-ray absorption spectroscopy (XAS), and surface complexation modelling (SCM) to investigate the speciation of U(VI) on the surfaces of sandstone and volcanic rock. Experiments were conducted in acidic (pH 5.5) and alkaline (pH 11.5) aqueous solutions of 0.1M NaCl in the presence and absence of bicarbonate (2 mM). FTIR spectroscopy and SCM were used to characterise the rock surfaces. We found that the sandstone had two proton-active functional groups, attributed to iron surface sites, with pKa values of 5.08 and 8.81. The volcanic rock had three proton-active functional groups with pKa values of 4.83, 6.51, and 8.89, from silicates and iron minerals, based on model protonation constants in the literature.

XAS analyses showed that in the sandstone system, U(VI) is adsorbed at pH 5.5 as a bidentate complex to one Si atom when bicarbonate is not present. When bicarbonate is present, the uranyl carbonate is coordinated with one Si atom. At pH 11.5, uranyl is either adsorbed as a monodentate complex to one Si atom or is precipitated as a U(VI) mineral such as uranophane when bicarbonate is not present in the initial solution. When bicarbonate is present at pH 11.5, U(VI) precipitates as a Na-clarkeite type mineral or remains as a uranyl carbonate surface complex.

For the volcanic rock system, uranyl adsorbs to Si at pH 5.5 as an outer sphere complex, regardless of the presence of bicarbonate in the system. In the bicarbonate-free pH 11.5 volcanic rock system, uranyl is adsorbed as a monodentate complex to one Si atom and precipitates as a Na-clarkeite type mineral. In the presence of bicarbonate at pH 11.5 in the volcanic rock system, U sorbs as a bidentate carbonate complex to one Si atom. The increased understanding of U(VI) speciation gained from this study will aid in constraining the mobility of these uranyl species in proposed repository systems.