

The ternary sorption system U(VI)-phosphate-silica explained by spectroscopy and thermodynamic modelling

H. Foerstendorf, M. Stockmann, M. J. Comarmond,¹ K. Heim, R. Steudtner, K. Müller, V. Brendler, T. E. Payne¹
¹Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia

Spectroscopic data of sorption processes potentially provide direct impact on Surface Complexation Modelling (SCM) approaches. Based on spectroscopic data of the ternary sorption system U(VI)/phosphate/silica strongly suggesting the formation of a precipitate as the predominant surface process, SCM calculations accurately reproduced results from classical batch experiments.

Phosphate is known to influence uranium sorption in natural systems and model minerals.^[1, 2] In the presence of phosphate, the spectroscopic results of the sorption processes of U(VI) on SiO₂, a major component of soils and rocks, strongly suggested the predominant formation of a precipitation at the oxide surface. Surface Complexation Modelling (SCM) was used for predictive modelling and provided insight on the proposed sorption processes.

EXPERIMENTAL. The performance of the batch experiments, *in situ* IR experiments, and SCM calculations are described elsewhere.^[3]

RESULTS. The tracking of the sorption processes by *in situ* IR spectroscopy is accomplished by consecutive acquisition of spectra with a time resolution in the sub minute range. Within the first 10 minutes after sorption of U(VI) in the presence of phosphate was induced, the spectrum exhibits a weak positive band (marked by * in Fig. 1A) reflecting the $\nu_3(\text{UO}_2)$ mode of the uranyl(VI) ion. This band evolves with ongoing sorption and shows an increased intensity in the spectrum of the late sorption process which is shown with reduced ordinate scaling for clarity (Fig. 1B). In the frequency range above 950 cm⁻¹, superimposed bands at 1125 and 994 cm⁻¹ develop with ongoing sorption (Fig. 1B). A comparison with spectra of an aqueous solution and of a precipitate obtained from U-phosphate solutions (data not shown) and earlier investigations suggests the formation of

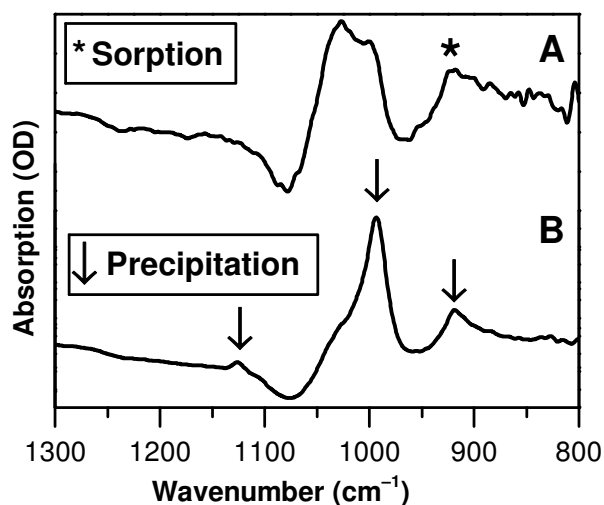


Fig. 1: Mid-IR spectra obtained within the first 10 minutes (A) and after 60 minutes of exposure time of an aqueous U(VI)/P solution (B) at pH 4. The bands marked by (*) and (↓) represent sorption complexes and precipitates at the SiO₂ surface, respectively. Note that the ordinate scaling of the latter spectrum is reduced by a factor of 0.3 for clarity ([U]_{init} = [P]_{init} = 20 μM, 0.1 M NaCl).

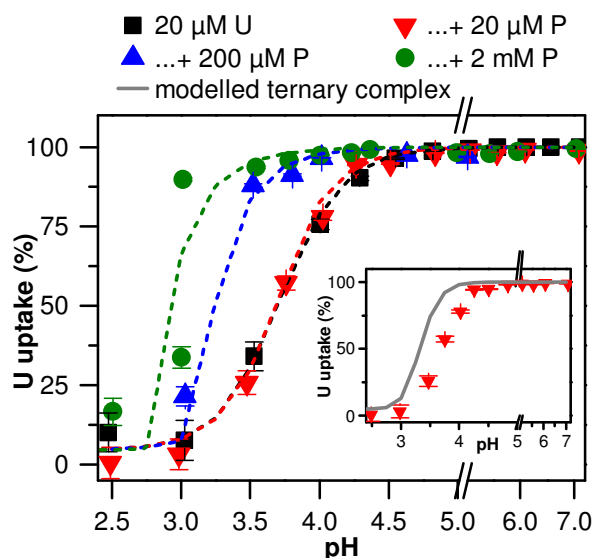


Fig. 2: Uranium(VI) uptake onto SiO₂ in the presence of different phosphate concentrations. Total [U] = 20 μM; Total [P] = 0 μM (black squares), 20 μM (red triangles), 200 μM (blue triangles) or 2,000 μM (green dots) (SiO₂ mass loading = 10 g L⁻¹; 0.1 M NaCl; equilibrium with air; 25 °C). Predictive results of Surface Complexing Modeling for the batch experiments performed at given phosphate concentrations are plotted as dashed lines. Inset: The respective batch and SCM results for [U] = [P] = 20 μM if formation of a ternary surface complex is considered. Note that for clarity reasons an axis break was added in the abscissa and only the largest error bars are shown at low pH values.

a surface precipitate.^[4] In addition, from *in situ* IR and luminescence spectroscopy on the binary sorption system U(VI)-silica, the formation of two uranyl(VI) surface species are strongly suggested.^[3, 5]

According to the spectroscopic results and literature data, the two binary uranyl(VI) surface species $\equiv\text{SiO}_2\text{UO}_2^0$ and $\equiv\text{SiO}_2\text{UO}_2\text{OH}^-$, and relevant solid phases – most probably Na-Autunite – are likely to be formed under the prevailing conditions and were considered during the predictive sorption modeling. The results clearly demonstrate that both processes, adsorption and precipitation, contribute to the removal of U(VI) from the aqueous phase. Both binary surface species in addition to the surface precipitate Na-Autunite describe the experimental data quite well as shown in Fig. 2 (dashed lines). By considering the ternary surface complex an overestimation of the experimental data, mainly for the 20 μM U, 20 μM P system, can be observed (Fig. 2, inset). While the key findings of the present work shows that a uranyl-phosphate ternary species is not required to explain the experimental data, the formation of ternary surface species might occur during the sorption processes as transient species being relevant only under highly diluted conditions.^[3]

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