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The structure of uranyl sorbed on smectite clays: experiment and modelling

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Clays are considered as a potential barrier material for radioactive waste disposal. In addition, clay minerals are highly abundant in nature, which makes it an essential task to study interaction of radionuclides with them in order to reasonably manage contaminated sites.

Investigation of the structures of sorbed species is essential for further modelling of migration processes, bioavailability, etc. The most effective way to experimentally study local structure in such systems is synchrotron-based x-ray absorption fine structure spectroscopy (EXAFS). However, experimental data provide only information about geometrical parameters, while actual configuration and localization of complexes might be only guessed.

The aim of this work was to study the local structure and localization of UO_2^{2+} sorbed on smectites by combining experimental and theoretical approaches. Molecular dynamic simulations with ClayFF force field were implemented to test different models of UO_2^{2+} sorbed on basal surfaces and compare them with experimental results. Samples of uranyl sorbed on clays of different origin in a wide range of pH 3-8 and initial uranyl concentrations 10^{-7}-10^{-5} M were prepared. Large scale atomistic modelling of UO_2^{2+} sorbed on external basal surface evaluates geometric parameters that contradicts with experimental results, while the model of uranyl in interlayer space gave reasonable interatomic distances.

The analysis of EXAFS spectra for model samples of UO_2^{2+} sorbed on smectites of various deposits in vide range of pH and UO_2^{2+} concentrations indicates that there is no significant influence of the smectite clay mineral structure and studied ranges of external conditions on surface complexes formed. Comparison of experimental interatomic distances with atomistic models of UO_2^{2+} sorbed on external or interlayer basal surfaces and recently published DFT-calculations indicate the formation of edge complexes and UO_2^{2+} in interlayer space.

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