Molecular mechanisms of Cs^+ binding to the hydrated surfaces of illite, smectite, and interstratified illite/smectite clays

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Cesiums isotopes (^{137}Cs, ^{134}Cs, ^{135}Cs) contained in spent nuclear fuel are important components of high-level radioactive waste. Cs^+ is highly soluble and highly mobile in aqueous phase. Its uptake in soils is known to be dominated by cation exchange reactions with their clayey component. Clays are also considered as important natural and engineered barriers in the design of geological nuclear waste repositories. In France, the Callovo-Oxfordian (COx) clay formation is considered for this purpose.The clayey component of COx consists mostly of illite, smectite and interstratified illite/smectite (I/S) minerals.

We have performed a series of molecular dynamics (MD) computer simulations in order to quantitatively assess the molecular scale mechanisms controlling the adsorption of Cs^+ cations with the basal surfaces of illite, smectite, and I/S. A set of new structural models of illite, smectite, and I/S have been constructed to more accurately account for the natural disorder in the structural isomorphic substitutions of Al/Si and Mg/Al substitutions in the tetrahedral and octahedral clay sheets, respectively.

The newly developed models allowed us to identify several structurally different energetically favorable adsorption sites at the basal surfaces of all three clay substrates. Cs^+ sorption properties above each individual site on the surfaces of illite, smectite, and I/S were individually characterized and quantitatively compared in terms of their surface distributions, most stable adsorption distances, and free energies of adsorption. The equilibrium constants for surface adsorption and ion exchange reactions Cs^+–Na^+ and Cs^+–K^+ were also calculated and compared with available experimental data.