FPMD study of Ni(II) complexes adsorbed on edge surfaces of clay minerals

CHI ZHANG[1], XIANDONG LIU[1]*, XIANCAI LU[1]

[1] State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, P. R. China
(*corresponding: xiandongliu@gmail.com)

Clay minerals distribute widely in soils and sediments, and play crucial roles in transport and retention of toxic heavy metal cations. Because of the large surface areas and porosities, clays are widely applied as adsorbent materials in environmental engineering and as backfill materials in geological disposal sites for nuclear wastes. In recent years, lots of experiments have focused on the complexations of cations on clay minerals. However, owing to many factors these studies cannot give atomic-scale information of the complexes, which greatly limits the understanding of relevant interfacial processes. Therefore, it is imperative to uncover the underlying adsorption mechanism by theoretical methods.

In this study, in the pursuit of a microscopic understanding of the effects of temperature on the adsorption of heavy metal cations on clay edges, we conducted first principles molecular dynamics (FPMD) simulations to investigate Ni(II) complexes adsorbed on (010) surfaces of 2:1-type phyllosilicates at 300K and 423K. Two types of surface binding sites (i.e. ≡SiO and octahedral vacant sites) are studied. In order to obtain the desorption free energies of Ni(II) complexes at both temperatures, a series of constrained FPMD simulations were performed.

The derived microscopic complexing structures and free-energy values provide physical basis for understanding the complexations of divalent heavy metals in environments at elevated temperature, such as geological repository for nuclear wastes. These results are useful in future experimental and modeling research, e.g., in interpreting experimental observation and predicting the surface complexation of cations.