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# Bonding state of Cs adsorbed on clay minerals investigated by HERFD-XANES using CAS and TES

**AKIKO YAMAGUCHI**[1], TADASHI HASHIMOTO[2], TAKUMA OKUMURA[3], SHINYA YAMADA[4], MASAHIKO OKUMURA[5] AND YOSHIO TAKAHASHI[6]

[1]The University of Tokyo
[2]RIKEN
[3]Tokyo Metropolitan University
[4]Rikkyo University
[5]Japan Atomic Energy Agency
[6]Graduate School of Science, The University of Tokyo

Clay minerals significantly influence the environmental behavior of various elements through adsorption reactions. Radioactive cesium (Cs) released from the Fukushima Daiichi Nuclear Power Plant accident in Japan was strongly adsorbed onto clay minerals, resulting in persistent fixation in surface soils even a decade later. Although this strong adsorption has been widely recognized, its underlying mechanism remains unresolved. Our previous study suggested that the hydration enthalpy of $Cs^+$ and the size matching between $Cs^+$ and the cavities in tetrahedral sheets both contribute to this behavior [1]. However, additional factors, such as the bonding state, may also play an important role.

To explore this possibility, we employed high-energy-resolution fluorescence-detected X-ray absorption near-edge structure (HERFD-XANES) spectroscopy, which provides finer spectral features than conventional XANES. The white-line position in XANES typically shifts depending on the speciation of the absorbing element. Since Cs has only one valence state, peak shifts can be attributed to differences in bonding characteristics, namely the degree of covalent versus ionic bonding. Although such shifts are subtle, HERFD-XANES enables their detection.

HERFD-XANES spectra were collected using two systems: one is a crystal analyzer spectrometer (CAS), which offers high energy resolution, <4 eV full width at half maximum (FWHM), and the other is a transition-edge sensor (TES), which provides slightly lower resolution (~6.5 eV FWHM) but can detect a broad energy range exceeding 2 keV in a single setup. Measurements were performed on several Cs compounds and on $Cs^+$ adsorbed to vermiculite, a representative clay mineral.

Peak shifts measured using both CAS and TES showed strong correlation with the nucleophilic constant ($E_n$), which quantitatively represents the bonding character of Cs compounds. These results demonstrate that HERFD-XANES peak positions can serve as indicators of bonding states. The HERFD-XANES peak for $Cs^+$ adsorbed on vermiculite appeared at higher energy than those of other Cs compounds, suggesting a more ionic bonding environment. This interpretation was further supported by $L\alpha_1$-normalized $L\beta_1$ X-ray emission spectra and resonant inelastic X-ray scattering maps obtained with the TES during a single XANES scan.

[1] Yamaguchi et al. (2024), J. Colloid Interface Sci. 661, 317.