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An EXAFS Investigation of Cesium Adsorption on Clay Minerals

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Beamline(s): X19A, X18B

Introduction: Contamination of soils by highly soluble radionuclides, such as ^{137}Cs , is particularly dangerous because of their ability to move with aqueous media in the subsurface. Because Cs^+ ion does not form strong complexes with dissolved inorganic or organic ligands (e.g., EDTA), the sorption of the free ion on minerals is the dominant factor controlling its speciation, and environmental fate. The major sorbents in soils are generally thought to be the layer-type silicates that bind Cs at the frayed edge sites (FES), external basal sites, or within the interlayer [1,2]. Here we used EXAFS spectroscopy to better understand the speciation of Cs adsorbed onto two common clay minerals vermiculite, and montmorillonite.

Methods and Materials: The clay minerals used were saturated with Cs by equilibrating once with 0.5 M CsCl [1h], twice with 0.1 M CsCl [1h], and once with 0.05 M CsCl [8d]. The Cs-saturated clays were then treated twice with 0.01 M NaCl to displace Cs^+ from sites with lower Na^+ - Cs^+ selectivity. Cs EXAFS was performed at the National Synchrotron Light Source (NSLS) on beamline X19A using a Stern-Heald fluorescence detector. X-ray absorption spectra were collected from -200 to +700 eV about the L_{III} -edge of Cs (5012 eV). The spectra were analyzed using the WinXAS program.

Results: The Cs EXAFS spectra of Cs-saturated vermiculite and montmorillonite show two principal coordination shells. The first shell, at an uncorrected distance of about 2.7 Å, represents the shortest Cs-O bonds. The second Cs-O shell, found for more distant oxygens, at an uncorrected distance of 3.9 Å. The first peak is fit with a Cs-O shell at a distance of 3.2 Å, while the later peak is fit with a larger Cs-O shell at 4.25 Å. Aluminum and Si shells would also result from IS Cs coordination; however, no Cs-Al or Cs-Si shells were required to fit the data. Although such complexes are likely to be present, their small size at long radial distances prevents their detection. However, differentiating the coordination environments that are present is possible based on the careful analysis of the two Cs-O shells. Based on the exchange data and prior studies [3-5], we assigned OS complexes to short Cs-O, and IS complexes to long Cs-O bonds. The inner-sphere adsorption complex may have occurred within the interlayer or at frayed edge sites, and was less extractable than the outer-sphere complexed Cs. Cesium sorbed into OS complexes is easily exchangeable with Na^+ and thus is mobile in the environment while IS sorption complexes may cause partial collapse of the interlayer, effectively limiting Cs mobility and bioavailability. While further research is required to fully determine the structure of these disordered Cs sorption complexes, these data indicate the value of EXAFS in analyzing Cs coordination in natural matrices.

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