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Determination of Site Specific Binding Environments of Surface Sorbed Cesium on Clay Minerals by Cs-EXAFS

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Abstract: Transport behavior of ^{137}Cs in the environment is regulated by surface sorption reactions on clay mineral surfaces. To provide greater understanding of Cs transport processes, XAFS investigations of the local environments of ^{137}Cs sorbed to clay minerals were conducted on Cs-Ca exchanged clay suspensions at the Cs LIII-edge. With decreased surface loadings of Cs, the Cs local environment exhibited increased long range order beyond 6 Å. Identification of Cs in expanded, semi-collapsed and collapsed interlayer environments was determined by correlating radial distances and Fourier transform peak amplitudes representing Cs-O and Cs-Al/Si in the octahedral and tetrahedral layers. Despite the difficulties of analyzing XAFS data of adsorbed atoms in multiple environments, isolation of Cs in more specific sites by selective exchange should allow detailed analysis and identification of predominant binding environments of cations to clay surfaces.

1. INTRODUCTION

The ability to develop adequate models for predicting the fate of inorganic contaminants in both surface and subsurface environments is highly coupled to an accurate description of the partitioning of these constituents between the solid and solution phases and ultimately on the capability to provide specific molecular-level information on species distribution in both of these phases. A radionuclide contaminant of particular interest is ^{137}Cs . To date, little work has been done to directly identify the nature of Cs binding sites in aquated clays in situ. X-ray absorption fine structure (XAFS) spectroscopy is well suited to probe Cs coordination environments in clays since it is capable of very detailed molecular structure determinations.

2. PRELIMINARY STUDIES

In previous investigations, we have used XAFS to investigate the average local environment of solution and solid phase complexes of Cs with Dibenzo-18-Crown-6 ether (Cs-D18C6) [1, 2]. Results of the analysis of the Cs LIII edge data from the crown ether solutions identified the presence of ternary crown-ether-Cs-Br contact pairs. Results from the analysis of the Cs LIII edge XAFS measurements made on the dried Cs-D18C6 complexes showed that, upon evaporation, the Cs atom's local environment changes from a crown-ether complex to a predominantly crystalline CsBr environment separate from the crown-ether. This recrystallization during drying illustrates the importance of in situ methods for the chemical speciation of soluble complexes. A more in-depth discussion of the data acquisition and analysis used for all these experiments, the Cs LIII-edge results as well as the Br K-edge results is presented elsewhere [2].

3. Cs SORPTION TO CLAYS

A number of Cs exchanged and fractionally exchanged ($\text{Cs}_x\text{Ca}_{100-x}\text{Cl}$) phyllosilicate minerals including smectite (SWy-1), illite (Silver Hill) and phlogopite mica [3] (representing a trend of non-collapsed to completely collapsed interlayer clays) were examined. Fluorescence measurements were made on aquated suspensions loaded in polypropylene bags.

One likely site of Cs binding in 2:1 clay minerals is the ditrigonal cavity that arises from six corner sharing silica tetrahedra. This cavity consists of six pairs of lone pair electron orbitals emanating from the surrounding ring of oxygen atoms; analogous to the Crown ether system described earlier. The reactivity of the ditrigonal cavity is governed by the electronegative charge distribution in the phyllosilicate structure. Isomorphic substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet and substitution of Fe^{2+} or Mg^{2+} for Al^{3+} in the octahedral sheet increases localized negative charge that in turn effects surface complexation behavior [4].

The resulting $\chi(k)*k^3$ data for the smectite and illite ($x = 10\%$) and mica samples are shown in Fig. 1 a-c. The Fourier transforms ($2.5 \text{ \AA}^{-1} - 9.0 \text{ \AA}^{-1}$) of the data representing the smectite and illite series are shown in Figs. 2a and 2b respectively. The Fourier transforms of the $\chi(k)*k^3$ data ($2.5 \text{ \AA}^{-1} - 9.0 \text{ \AA}^{-1}$) for the smectite and illite clay ($x = 10\%$) and the mica are shown in Fig. 2c. Qualitative inspection of these data illustrates several trends. For the Cs-saturated clays ($x = 100\%$), limited long range ordering can be deduced. However, at decreased Cs surface loadings, via exchange with Ca (Figs. 2a and 2b), the Cs local

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environment exhibits increased long range order beyond 6 Å. Inspection of the Fourier transforms in Fig. 2c shows similar peak amplitudes for the mica and illite clay. This is consistent with the majority of the Cs ions residing within the collapsed layers of the illite clay. In Fig. 2c, the Fourier transform representing the smectite clay shows peak amplitudes approximately 3 to 4 times smaller than either the mica or the illite clay. In addition, the peak locations for the smectite sample are shifted to higher r -values. These trends are consistent with the Cs ions in the smectite being in a more disordered environment in expanded layers (i.e. the Cs ions being loosely associated with a single ditrigonal cavity at the clay surface). Another interesting trend in the Fourier peak amplitudes is seen for the smectite series near 2 Å (Fig. 2b). Although all other peak amplitudes increase with decreasing Cs/Ca concentration, the peak amplitudes near 2 Å decrease with decreasing Cs/Ca concentrations. This peak (when appropriately phase shifted) is located at an approximate Cs-O radial distance for hydrated Cs. This trend is consistent with the hypothesis that the more tightly bound Cs (most prominently seen when $x = 10\%$) are less hydrated than the loosely bound Cs (most prominently seen when $x = 100\%$). These qualitative results, however, do not eliminate the possibility of Cs sorption to the clay surface in places other than the ditrigonal cavity.

Future studies of these systems will include detailed FEFF6 simulations of the Cs ion local environments in these different sites. Then, a more detailed analysis may be done not only to identify the general sites, but to address the question of distortions of the different sites with the introduction of the Cs ion.

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Figure 1: Six merged $\chi(k) \cdot k^3$ data sets representing the quality of data from a smectite (a), illite (b) and

Figure 2: Fourier transforms of experimental Cs LIII edge $\chi(k) \cdot k^3$ data depicting Cs introduced to a smectite clay via 1 M $\text{Cs}_x\text{Ca}_{100-x}\text{Cl}$ water solution where $x = 10\%$, 50% , and 100% . (a) Fourier transforms of data representing Cs introduced to an illite clay via 1 M $\text{Cs}_x\text{Ca}_{100-x}\text{Cl}$ water solution where $x = 10\%$, 50% , and 100% . (b) Fourier transforms of data representing Cs in a collapsed interlayer double-cage site (thin solid line), Cs introduced to illite clay via 1 M $\text{Cs}_{10}\text{Ca}_{90}\text{Cl}$ water solution (dotted line), and Cs introduced to smectite clay via 1 M $\text{Cs}_{10}\text{Ca}_{90}\text{Cl}$ solution (thick solid line). Note that the amplitude of Cs in mica is approximately twice as large as the amplitude of Cs in smectite, possibly indicating surface sorption to a single electronegative cage site.

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