



Regular Article

Molecular dynamics simulations of cesium adsorption on illite nanoparticles



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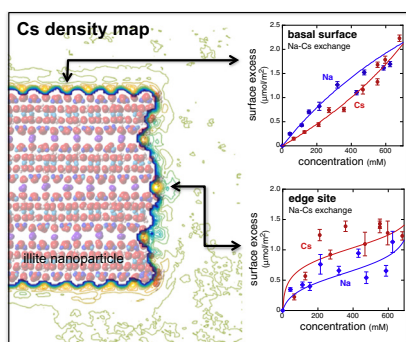
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GRAPHICAL ABSTRACT



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ABSTRACT

The charged surfaces of micaceous minerals, especially illite, regulate the mobility of the major radioisotopes of Cs (^{134}Cs , ^{135}Cs , ^{137}Cs) in the geosphere. Despite the long history of Cs adsorption studies, the nature of the illite surface sites remains incompletely understood. To address this problem, we present atomistic simulations of Cs competition with Na for three candidate illite adsorption sites – edge, basal plane, and interlayer. Our simulation results are broadly consistent with affinities and selectivities that have been inferred from surface complexation models. Cation exchange on the basal planes is thermodynamically ideal, but exchange on edge surfaces and within interlayers shows complex, thermodynamically non-ideal behavior. The basal planes are weakly Cs-selective, while edges and interlayers have much higher affinity for Cs. The dynamics of Na–Cs exchange are rapid for both cations on the basal planes, but considerably slower for Cs localized on edge surfaces. In addition to new insights into Cs adsorption and exchange with Na on illite, we report the development of a methodology capable of simulating fully-flexible clay mineral nanoparticles with stable edge surfaces using a well-tested interatomic potential model.

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1. Introduction

Any future reliance on nuclear energy to play a major role in lessening our dependence on fossil fuels brings with it a need to address the potential for long-term environmental contamination by radioisotopes [71]. Two isotopes of cesium, ^{135}Cs and ^{137}Cs , are among the most important contaminants associated with the nuclear fuel cycle because of their high fission yield, long half lives (2.3×10^6 and 30 a, respectively), high solubility in water, and metabolic similarity to potassium. These radioisotopes are key concerns in the geologic storage of radioactive waste [60,35,17], the management of legacy sites contaminated during the development of nuclear power [28,70], and the remediation of soils contaminated by catastrophic releases such as those that occurred at the Chernobyl and Fukushima Daiichi nuclear power plants [31,104,105]. In the Fukushima region, in particular, ^{137}Cs is the main source of external radiation dose five years after the nuclear disaster of March 2011. The most important process controlling the solubility and mobility of cesium in soils, sediments, and sedimentary rocks is the formation of strong surface complexes with clay minerals [1] and particularly with the micaceous minerals, illite, vermiculite, and mica [28,40,11,63,65]. Cesium adsorption on illite is of particular importance in the geologic storage of radioactive waste, because illite often dominates the mineralogy of fine-grained sedimentary rocks considered for use as host formations [94,35,17].

Studies of the adsorption of Cs by illite have a long history [96,83,27,15,22,87,90,74,76,14,61,62,8,106,53,3,25,6,100]. Recent efforts have deployed a combination of wet chemistry experiments [102,4,26], high-resolution imaging [47,63,95,34], synchrotron X-ray spectroscopy [29,42], and atomistic-level simulations [68,93,44,107] to gain detailed insight into Cs adsorption mechanisms, selectivity, and kinetics. The emerging view from these studies is that Cs adsorption involves at least three types of surface sites: *basal sites* located on the external basal surfaces of illite particles, *slow sites* located in anhydrous illite interlayers, and *high affinity sites* of unclear nature. Adsorption on the basal sites is rapid (< 24 h), reversible, and weakly selective (Table 1). The slow sites have slow adsorption and desorption kinetics (likely weeks to months) and a higher total capacity than the basal sites. Finally, the high affinity sites have a very small total capacity and a very high affinity for cesium and other weakly hydrated cations (K^+ , NH_4^+). The high-affinity sites and slow sites are particularly important, because they control the long-term migration of cesium in the geosphere [20,100,84].

Despite the importance of the high-affinity and slow sites of illite for cesium fate and transport, important questions remain unanswered regarding the properties of these sites. First, the structure of the high affinity sites is a continuing topic of investigation [46,62,93,68]. The predominant hypothesis is that they occur in “wedge” regions where illite or vermiculite interlayers transition

from a collapsed state to an expanded state [18,102,68,107]. The existence of these regions is supported by electron microscopy observations showing that weathering induces a discernible “fraying” at the edges of illite and mica crystals [62,34], perhaps associated with the replacement of K by solvated Ca near the extremities of the anhydrous interlayers [34]. Second, the cation exchange kinetics and selectivity of the slow sites remain poorly understood, in part because of a lack of long-term adsorption and desorption studies. For example, some studies have hypothesized that basal and slow sites have essentially the same Na–Cs exchange selectivity [4], whereas atomistic simulations suggest that Cs is much more selectively retained in anhydrous clay interlayers than on external basal surfaces [79]. The few geochemical modeling studies that described slow sites as distinct surface sites treated them as ideal cation exchangers [22,100] despite evidence that these sites, at least in some cases, form interstratified structures in which Cs displaces K in some interlayers but not in others [69]. Finally, the adsorption-desorption kinetics of the slow and high-affinity sites remain incompletely understood. For example, several studies have shown that solution chemistry strongly affects the kinetics of adsorption on slow sites [4] and desorption from high-affinity sites [25], perhaps through a mechanism analogous to the well known salinity-dependence of smectite clay swelling [86,45]. Geochemical models of cesium adsorption on illite almost invariably ignore the slow sites [14,91,35,33] or assume that their properties are identical to those of the basal sites [4] or the high-affinity sites [100]. The range of values of Na–Cs and K–Cs exchange selectivity coefficients used in surface complexation models is shown in Table 1.

The questions listed above persist in part because the three types of surface sites are challenging to isolate experimentally. For example, spectroscopic or elemental mapping results are challenging to obtain at the very low surface loadings characteristic of the high affinity sites. Atomistic simulation techniques such as molecular dynamics (MD) simulations and density functional theory (DFT) calculations can, in principle, circumvent these difficulties by allowing a direct observation of individual Cs ions on different surface sites. Existing simulation studies have probed cesium adsorption in the interlayer nanopores of swelling clay minerals [64,97,78,79,10,44], in anhydrous clay interlayers [79,93], and at illite and vermiculite wedge sites [68,107]. However, no existing atomistic simulation study has examined cesium adsorption selectivity on different surfaces of a single illite particle, because of two methodological challenges. *Ab initio* MD (i.e., time-dependent DFT) simulations are limited to timescales up to ~ 100 ps that are significantly shorter than the characteristic timescales of Cs migration on hydrated clay surfaces (on the order of nanoseconds [64,10]). Classical MD simulations can probe timescales up to ~ 100 ns, but their predictions can be highly sensitive to the choice of inter-atomic potential parameters. The most well-tested inter-atomic potential model for clay-water systems, the CLAYFF model of Cygan et al. [23], was designed to simulate the basal surfaces of infinite clay particles, and its ability to describe the edge surfaces of clay particles is not well established. In fact, even the detailed microstructure and stoichiometry of clay edge surfaces remains poorly constrained [16,9,67].

Here, we present the first ever atomistic simulation study of Cs adsorption on three binding sites (basal, edge, and interlayer) of a model illite nanoparticle. To account for the slow migration of Cs near clay surfaces, our simulations used relatively long (50 ns) classical MD simulations in combination with thermodynamic integration calculations (i.e., alchemical transformations wherein short-range interaction potential parameters for Na are incrementally adjusted to Cs at different sites on the illite surface). In addition to new insights into Cs adsorption on illite, a significant outcome of our study is the development of a methodology capable

Table 1

Cation exchange selectivities of the high affinity and basal sites used in surface complexation models of Cs adsorption on illite and related minerals. Some models also include an intermediate affinity site of unclear mechanistic basis. The table shows the range of values used in existing models of illite surface chemistry [15,74,14,91,54,100,36,17,33,4,29]. For comparison, values for smectite basal surfaces are shown in the last column as calculated by Bourg and Sposito [11] based on previous studies. Cesium exchange selectivity on smectite increases with layer charge (values are reported for smectite layer charges ranging from 0.7 to 1.4 mol_e kg⁻¹). The notation K_{eq}^{ij} refers to the equilibrium constant for the replacement of *i* by *j* on illite surface sites.

Site type	Illite basal site	Illite high affinity site	Smectite basal site
$\log K_{\text{eq}}^{\text{Na/Cs}}$	1.6–2.0	6.6–7.2	0.7–1.7
$\log K_{\text{eq}}^{\text{K/Cs}}$	0.4–1.1	4.1–5.5	0.2–1.2

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