



Cesium sorption reversibility and kinetics on illite, montmorillonite, and kaolinite

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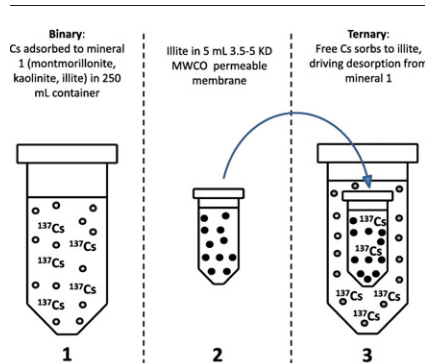
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HIGHLIGHTS

- Permeable membrane used to examine desorption of ^{137}Cs in the presence of two minerals.
- Ternary experiments carried out of over >500 days.
- Cs is reversibly sorbed to kaolinite and montmorillonite.
- Ternary experiments indicate a slow kinetic effect on Cs desorption from illite.

GRAPHICAL ABSTRACT



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ABSTRACT

Understanding sorption and desorption processes is essential to predicting the mobility of radionuclides in the environment. We investigate adsorption/desorption of cesium in both binary (Cs + one mineral) and ternary (Cs + two minerals) experiments to study component additivity and sorption reversibility over long time periods (500 days). Binary Cs sorption experiments were performed with illite, montmorillonite, and kaolinite in a 5 mM NaCl/0.7 mM NaHCO₃ solution (pH 8) and Cs concentration range of 10^{-3} to 10^{-11} M. The binary sorption experiments were followed by batch desorption experiments. The sorption behavior was modeled with the FIT4FD code and the results used to predict desorption behavior. Sorption to montmorillonite and kaolinite was linear over the entire concentration range but sorption to illite was non-linear, indicating the presence of multiple sorption sites. Based on the 14 day batch desorption data, cesium sorption appeared irreversible at high surface loadings in the case of illite but reversible at all concentrations for montmorillonite and kaolinite. A novel experimental approach, using a dialysis membrane, was adopted in the ternary experiments, allowing investigation of the effect of a second mineral on Cs desorption from the original mineral. Cs was first sorbed to illite, montmorillonite or kaolinite, then a 3.5–5 kDa Float-A-Lyzer® dialysis bag with 0.3 g of illite was introduced to each experiment inducing desorption. Nearly complete Cs desorption from kaolinite and montmorillonite was observed over the experiment, consistent with our equilibrium model, indicating complete Cs desorption from these minerals. Results from the long-term ternary experiments show significantly greater Cs desorption compared to the binary desorption experiments. Approximately ~45% of Cs desorbed from illite. However, our equilibrium model predicted ~65% desorption. Importantly, the data imply that in some cases, slow desorption kinetics rather than permanent fixation may play an important role in apparent irreversible Cs sorption.

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1. Introduction

Significant quantities of radioactive cesium (Cs) have been released to the environment. These releases have occurred as a result of nuclear weapons testing (Klement, 1965), nuclear accidents at Chernobyl, Russia and Fukushima, Japan (Castrillejo et al., 2016; Steinhäuser et al., 2015), and leaks from high level waste storage sites such as Hanford, USA (Zachara et al., 2002) and Mayak, Russia (Novikov et al., 1998). The persistence of ^{137}Cs ($t_{1/2}$ 30.1 y) in the environment can pose substantial health concerns. The U.S. EPA regulates the amount of beta emitting radionuclides in drinking water such that the equivalent dose is <4 mrem per year (United States Environment Protection Agency, 2009). This dose corresponds to a maximum ^{137}Cs concentration of 7.4 Bq/L or 1.7×10^{-14} M. Thus, ^{137}Cs is considered a drinking water hazard even at trace concentrations. The environmental contamination and potential health risks associated with ^{137}Cs necessitate understanding its behavior in the environment. Understanding this behavior may also guide remediation strategies for Cs clean-up in the environment and help to design strategies for the safe storage of radionuclides present in spent nuclear fuel.

Sorption and desorption processes play a large role in controlling the fate of Cs in the environment. Sorption to immobile soils or sediments will limit the transport of Cs in solution, while sorption to colloids (defined as <1 μm particulates) may enhance mobility. If Cs is sorbed to minerals, then its desorption behavior will affect its bioavailability and in the case of mineral-colloid association, the extent of transport.

Due to their high sorption capacity and their ubiquity in nature, aluminosilicate clays are particularly important in controlling Cs behavior in natural systems. Cs sorption reversibility on clay minerals with high, intermediate, and low Cs affinities (illite, montmorillonite, and kaolinite, respectively) was the focus of this study. Illite is a non-expanding 2:1 (2 tetrahedral silica layers sandwiching an octahedral alumina layer, TOT) aluminosilicate clay. Cesium sorption to illite has been described as a cation exchange process on either the basal/planar, edge, or interlayer sites (Staunton and Roubaud, 1997). Weathering near the edges of the illite expands the interlayer producing wedge or frayed edge sites (FES) (Jackson, 1963). These FES sites are highly selective for Cs (Rich and Black, 1964; Bolt et al., 1963; Brouwer et al., 1983). As a result, while illite has much lower cation exchange capacity (CEC) than montmorillonite, at Cs concentrations below 10^{-7} M, illite will sorb more Cs than montmorillonite per unit mass (Sawhney, 1970; Komarneni and Roy, 1980).

Montmorillonite is a 2:1 smectite clay with an expanding interlayer (Jackson, 1963) that allows for increased interaction between cations in solution and those in the clay interlayer. The high CEC of montmorillonite leads to its high affinity for Cs (Sawhney, 1970; Sawhney, 1972; Hsu and Chang, 1995; Komarneni and Roy, 1979).

Kaolinite is a 1:1 aluminosilicate non-expanding clay. Sorption of Cs to kaolinite occurs by cation exchange at permanently charged sites on the basal surfaces of the mineral (Swartzen-Allen and Matijevic, 1974; Kim et al., 1996; Kim and Cygan, 1996; Ohnuki and Kozai, 2013; Reinoso-Maset and Ly, 2014). Due to its low CEC and absence of FES sites, kaolinite sorbs Cs less effectively than montmorillonite or illite.

In terms of desorption behavior, research has focused on whether Cs is irreversibly sorbed by clay minerals. In this context we mean that sorption is considered to be reversible if $K_{\text{d,sorption}} \approx K_{\text{d,desorption}}$ (Missana et al., 2004). However, determining true irreversibility can be difficult because sorption and desorption behavior can be affected by the solution composition, kinetics, Cs concentration; and the presence of multiple sorption sites with differing Cs affinities (Comans et al., 1991; Bostick et al., 2002; Missana et al., 2004; Iijima et al., 2010).

In the case of montmorillonite and montmorillonite dominated clays, sorption is believed to be reversible (Missana et al., 2004; Iijima et al., 2010), however recent work has shown that some fixation of intrinsic Cs may be achieved by the addition of divalent cations before desorption (Fukushi et al., 2014; Fukushi and Fukiage, 2015). Similarly, Cs

is readily desorbed from the surface of kaolinite (Shahwan et al., 1999; Erten et al., 1988). However, the behavior with illite is more complex with apparent irreversible behavior observed in some cases. This irreversibility has been attributed to sorption to high affinity FES, and their subsequent collapse that prevents access to the sites (Sawhney, 1972). High concentrations of Cs have been shown to exacerbate interlayer collapse leading to apparent irreversible sorption behavior. A time dependence on the amount of reversibly sorbed Cs has been attributed to diffusion of Cs from FES to the interlayer sites of illite (Comans and Hockley, 1992). However, more recently a time dependent increase in sorption irreversibility has been observed at timescales too short to be explained by diffusion processes (De Koning and Comans, 2004).

Most sorption/desorption studies are conducted as single mineral binary batch experiments over short time periods (days to weeks). However, in the environment, Cs will interact with multiple minerals simultaneously and over long time scales. This presence of multiple minerals is especially important to consider in the case of colloid-facilitated transport of Cs and previous column experiments have demonstrated that Cs can be desorbed from mobile colloids and adsorbed on the immobile host minerals (Zhuang et al., 2003; Turner et al., 2006). Previously, De Koning and Comans (2004) examined Cs sorption reversibility on illite with ammonium hexacyanoferrate (HCF) which has a high selectivity and capacity for Cs. The high sorption affinity of HCF ensures that solution Cs concentrations are low and drives desorption of Cs from illite. In our current work, we employ a similar approach but use illite to drive desorption. This novel approach has the advantage of being more representative of natural environments.

In this work, we evaluate Cs sorption to illite, montmorillonite, and kaolinite over a wide range of initial Cs concentration that extends to low, environmentally relevant concentrations. We perform binary Cs sorption and desorption experiments with illite, montmorillonite, and kaolinite across an initial Cs concentration range of 10^{-3} to 10^{-11} M. We then examine long-term Cs sorption/desorption behavior in two-mineral ternary experiments. By keeping the two mineral phases physically separated using a Spectra/Por® Float-A-Lyzer® dialysis bag, we are able to examine the contribution of each mineral to the overall sorption and evaluate the competitive sorption and desorption of Cs in ternary experiments over a period of nearly 17 months. This method provides a means to evaluate component additivity (Davis et al., 1998), reversibility, and desorption kinetics in the presence of clay minerals over environmentally relevant timescales.

2. Materials and methods

2.1. Materials

All solutions were prepared using ACS grade chemicals without further purification and ultrapure water (Milli-Q Gradient System, >18 M Ω ·cm). Fithian illite from Rochester, NY (Ward's Science), SWy-1 montmorillonite (Clay Minerals Repository), and KGa-1b kaolinite (Clay Minerals Repository) were used in this study. Preparation of homoionic SWy-1 Na-montmorillonite has been previously reported (Zavarin et al., 2012) and the same method was also used for the preparation of illite and kaolinite. Briefly, the minerals were prepared by mixing 100 g/L of the mineral in 0.001 M HCl for 30 min in order to remove soluble salts and impurities. Next, 0.03 M H₂O₂ was added for 30 min to minimize the oxidative and reductive potential of any remaining impurities as well as removing trace organic material. The clay suspensions were then centrifuged for 6 h at 2500g and the supernatant (calculated to contain particles <50 nm diameter) was discarded. The wet solids were transferred to 6000–8000 Da molecular weight cut off (MWCO) dialysis bags and suspended in a 0.01 M NaCl electrolyte solution and dialyzed for seven days to homoionize the minerals. It is possible that there still exists some intrinsic Cs and this may have an effect on the sorption processes. However, the effect is likely to be small and no further consideration is given in this work. The minerals were extruded

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