



Americium sorption on smectite-rich natural clay from granitic ground water



S. Kumar^a, A.S. Pente^b, R.K. Bajpai^c, C.P. Kaushik^b, B.S. Tomar^{a,*}

^a Radioanalytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

^b Waste Management Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

^c Technology Development Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

ARTICLE INFO

Article history:

Received 19 July 2012

Accepted 27 May 2013

Available online 6 June 2013

Editorial handling by S. Stroes-Gascoyne

ABSTRACT

Because of their significant retention capability, clay minerals have been proposed as a potential engineered barrier in high level nuclear radioactive waste disposal repositories. Smectite-rich natural clay is being considered as a backfill and buffer material for the Indian repository program. In the present study the sorption of Am by the clay, from granitic ground water, has been investigated. To identify the minerals in the clay controlling the sorption process, the adsorption isotherm of Eu(III), a chemical analogue of Am(III), was determined on montmorillonite–kaolinite clay mixtures having 0–20 wt% kaolinite. The effect of experimental parameters, such as, pH, ionic strength, and the presence of cation and anions on Am(III) sorption was further investigated to develop a sorption model for the natural clay. Overlapping adsorption isotherms of Eu(III) obtained for different montmorillonite–kaolinite clay suspensions established montmorillonite as the main sorbent for Eu/Am(III) in the natural clay. Americium(III) sorption increases with pH in three distinct stages: at lower pH values (<4) the sorption is virtually insensitive to pH, then rises sharply (4–7) and subsequently attains a constant value at higher pH values (>8). Decreasing ionic strength increases the sorption at pH < 6 indicating the dominant role of ion exchange reactions at lower pH. A surface complexation model, developed for natural clay by including ion exchange site and amphoteric sites present at edges, simulates the sorption profiles at varying pH and ionic strength well and confirms the montmorillonite fraction as the sorbent controlling Am(III) sorption. The presence of Ca(II) as well as anions (Cl⁻, NO₃⁻) does not affect Am(III) sorption on clay under granitic ground water pH and ionic strength conditions. However, the profile of Am(III) sorption to Ca(II)-equilibrated clay differs from that for Na-equilibrated clay corroborating weaker exchange of Ca(II)-Am(III) in comparison to Na(I)-Am(III). The presence of SO₄²⁻ in the sorption system lowers Am(III) sorption at lower pH values. Modeling the sorption data indicated the participation of SO₄²⁻ containing Am surface species. The thermodynamic model developed for sorption onto natural clay was checked for Eu(III) sorption from granitic ground water at pH 6.1. The model simulates the sorption at lower metal ion concentration while there is deviation at higher metal ion concentration. Inclusion of more types of surface sites and the effect of organic material need to be tested to correct the model for this deviation.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The safe and effective isolation of spent nuclear fuels and their processed forms, away from biosphere, has been proposed through their disposal in deep geological repositories (DGR). The isolation is made effective by the natural and engineered multi-barrier system constructed around the disposed waste. The engineered barrier is composed mainly of natural clay minerals while the natural barrier could consist of a salt dome, clay or granitic rock (Schwyn et al., 2012). The Indian DGR scheme aims at disposing the vitrified nuclear high level waste in granitic host rock (Bajpai, 2008). A key function of the multi-barrier concept is the retardation of radio-

nuclides' migration leading to attenuation of their release to the biosphere. Sorption of radionuclides on both the host rock and the engineered barrier is a primary chemical reaction in the retardation processes (Missana et al., 2008; Lutzenkirchen, 2012). Though comprehensive studies have been carried out to study the sorption of long-lived radionuclides on different clay minerals under various geochemical conditions (Coppin et al., 2002; Bradbury and Baeyens, 2002, 2005, 2006; Tetre et al., 2006; Guo et al., 2009; Galunin et al., 2010; Bouby et al., 2011; Lutzenkirchen, 2012), there is a need of sorption data for smectite rich clays, which are being evaluated for their use as the engineered barrier in the Indian repository program.

Smectite-rich natural clays, such as, FEBEX bentonite, MX-80, etc. have been considered for DGR programs worldwide (Lutzenkirchen, 2012). These clays are 2:1 phyllosilicates wherein an

* Corresponding author. Tel.: +91 22 25595006; fax: +91 22 25505151.

E-mail address: bstomar@barc.gov.in (B.S. Tomar).

aluminous (AlO₆) octahedral layer is sandwiched between two siloxane (SiO₄) tetrahedral layers. This structural moiety is attached to another such moiety through H-bonding and produces the behavior generally associated with clay, such as, ability to undergo strain without fracturing, very low hydraulic conductivity, high cation sorption capacity, and ability to swell upon water absorption. Due to their swelling characteristics, these clays establish close contact with the waste form and the host rock. Further, their high ion exchange capacity hinders the leakage of radionuclides from the repository to the geosphere and biosphere. Transport through clay barriers to the far-field areas has, however, been reported to be changed by the ground water chemical conditions, such as, presence of Ca(II) ions (Galunin et al., 2010), dissolved organic content (Bouby et al., 2011; Joseph et al., 2011), and minor phases present in the clay (Hartmann et al., 2008; Montavon et al., 2009), etc.

Kinetics of Am(III) sorption on smectite-rich natural clay minerals have, in general, been found to be fast (Lujanene et al., 2012). Model calculations of Eu(III) sorption on mixtures of smectite and illite clays suggest increasing sorption with increasing smectite content in the mixture (Lutzenkirchen, 2012). In the modeling of adsorption–desorption of Eu(III) on Na–bentonite, reversibility has been observed over pH 4–8 (Guo et al., 2009). The degree of microscopic reversibility has, however, been found to decrease with increasing pH (Coppin et al., 2003). These results and similar observations for other radionuclides, such as Cs(I), Sr(II), and Pu(IV), have been explained mechanistically by considering two distinct processes of sorption occurring on clay surfaces, viz., ion exchange and surface complexation (Reiller and Bradbury, 2006; Reiller, 2007, 2008). Formation of an outer sphere complex on the ion exchange sites at lower pH values favors fast exchange while reversibility at higher pH values is obstructed by the formation of inner-sphere complexes. Strong competition of monovalent background cations to sorbing Am(III) on montmorillonite at lower pH values further indicates the prevalent existence of a cation exchange mechanism (Bradbury and Baeyens, 2005). A sharp increase in Am(III) sorption over a narrow pH range and insensitivity of sorption to varying ionic strength at higher pH values, in the same study, indicates the existence of more than one mechanism for the sorption process. Formation of two types of surface complexes has been found by combined Time-Resolved Laser Fluorescence Spectroscopy (TRLFS) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy study of the sorption of trivalent actinides onto smectite (Stumpf et al., 2001, 2004; Tetre et al., 2006).

Cations present in the groundwater have also been shown to affect Am(III)/Eu(III) sorption to clay surfaces. In the case of sorption of the lanthanide on smectite clays in the presence of Ca(II), metal ion distribution (distribution coefficient, K_d) to the clay surface decreased with increasing Ca(II) concentration in the contact solution (Galunin et al., 2010). This has been explained in terms of Ca(II)–Ln(III) competition, which causes displacement of the lanthanides from cation exchange sites leading to the observed decrease in the K_d value. On the other hand, in the experimental and modeling study of sorption on montmorillonite, this competition by divalent metal ions has been reported to be selective in favor of Eu(III) (Bradbury and Baeyens, 2005).

Groundwater or pore water contains many anions, such as, sulfate, silicate, phosphate, and organic molecules, which can complex metal ions and thus affect their uptake on clay surfaces (Reiller, 2012). The ubiquitous anion is carbonate which, in the absence of any explicit source such as calcite mineral, may come from atmospheric CO₂ and, owing to the formation of carbonate species at higher pH values, may change the metal ion uptake behavior (Guo et al., 2009). A significant decrease in Eu(III) sorption has been observed at pH > 8 in the presence of atmospheric CO₂ in comparison to that in the absence of CO₂. Negating the role of carbonate

species, Hartmann et al. (2008) did not observe a different result in Eu(III) sorption on Opalinus clay and Callovo–Oxfordian clay at pH > 7 in Ar atmosphere and in aerobic conditions. Recently, Cm(III) complexation with organic matter extracted from natural clay, has been investigated (Claret et al., 2005; Courdouan et al., 2008). The asymmetric flow field–flow fractionation method applied to the interaction of bentonite colloids with Eu in the presence of humic acid has shown Eu(III) preferential speciation with humic colloids (Bouby et al., 2011).

Natural clays are generally mineral assemblages and the overlapping sorption behavior of different phases can modify the sorption behavior of a metal ion on such substrates in comparison to that in the pure clay phase case. Effects of minor phases in the clay sample on Eu/Cm(III) sorption has been investigated by Hartmann et al., (2008) with Opalinus clay and Callovo–Oxfordian clay using TRLFS and surface complexation modeling. One of the conclusions of this study was that the surface speciation of Eu(III) is linked to the main phase of the clay mineral and it negated the role of minor components, calcite and quartz, in Eu(III) uptake. A similar observation was made in the “bottom-up” approach of Eu(III) sorption modeling on MX-80 bentonite (Bradbury and Baeyens, 2011). Contradicting these results, significant Am(III) speciation was found in the minor phase (at the carbonate sites) in sorption from natural ground water on three Smectite clay minerals varying in the content of carbonate and Fe minerals, (Lujanene et al., 2012).

Smectite-rich natural clay has been selected for evaluation of its suitability for the Indian deep disposal repository program (Pente, 2009). An operational model for metal ion sorption in the natural system should take into account the effect of each factor of the diverse geochemical conditions. The present study aims at developing a model for Am/Eu(III) interaction with the smectite-rich clay in granitic ground water, using sorption experiments and surface complexation modeling of the sorption profiles. Studies have been carried out to find the main sorbent for Am(III) in the natural clay by evaluating the Eu(III) adsorption isotherm for different montmorillonite–kaolinite mixtures. Further, the effect of different chemical conditions of granitic groundwater for Am(III) sorption on the clay was studied by batch sorption, adsorption isotherms, and surface complexation modeling. The surface complexation model developed in synthetic ground water was checked with the actual ground water.

2. Materials and methods

2.1. Materials

All the chemicals used in experiments were of analytical grade. Clay samples have been collected from Western India and used after minor dressing at the site. Details on the origin and washing are given elsewhere (Pente, 2009). For the purpose of the present study, the clay sample was analyzed for (a) major, minor and trace elements by X-ray fluorescence, (b) chemical analyses for organic

Table 1a
Physicochemical characteristics of the clay sample.

Characteristics	Value
Surface area (N ₂ -BET method) (m ² g ⁻¹)	79.6
Pore volume (cc/g)	0.087
Cation exchange capacity (meq/100 g)	76
Total carbon content	<0.05%
Total organic carbon	<0.05%
Composition (by X-ray diffraction), (wt%)	Montmorillonite (~90), kaolinite (~10), silica (trace)

Download English Version:

<https://daneshyari.com/en/article/6335328>

Download Persian Version:

<https://daneshyari.com/article/6335328>

[Daneshyari.com](https://daneshyari.com)