



X-ray absorption fine structure spectroscopy study of Eu(III) sorption products onto amorphous silica and γ -alumina: Effect of pH and substrate

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ABSTRACT

A molecular level understanding of metal ions sorption onto solids is necessary for modelling the sorption process in a predictive manner and thus for planning of the safe disposal of nuclear wastes. In this study, we have used X-ray absorption fine structure spectroscopy (XAFS) in conjunction with batch sorption and solubility studies to investigate the effect of pH and substrate on the formation and structure of Eu(III) sorption products on two environmentally relevant mineral oxides, namely amorphous silica and γ -alumina. 0.1 mM Eu solution was contacted with silica and alumina over pH 4–8 in an ionic medium of 0.1 M NaClO₄. Batch sorption data indicates a stronger sorption capacity of alumina in comparison to silica. Silica solubility is orders of magnitude higher than that of alumina over pH 3–8. The pH (6–8) and metal ion concentration in the XAFS samples corresponds to the undersaturated to oversaturated state with respect to Eu(OH)₃ precipitation. Modelling of the EXAFS spectra indicates: (1) the formation of a Eu sorption product at pH ~6 in the form of a small atomic cluster wherein Eu binds to oxygen atoms on both solids in a monodentate corner sharing and edge sharing manner, (2) alumina prefers an edge sharing mode with increasing pH over silica, (3) both solids form a surface precipitate containing Eu at higher pH values, with the sorption product being richer in Eu content at the silica surface, and (4) the appearance of a Eu–Eu neighbour distance of ~3.5 and 4.0 Å for alumina and silica, respectively. The Eu–Eu distances for sorption samples, compares with the 3.67 and 4.09 Å Eu–Eu distances in Eu(OH)₃, and thus substantiate the edge and corner sharing preference for alumina and silica, respectively. Though Eu forms similar sorption products on silica and alumina over pH 6–8, there is a distinct difference in their formation pattern at the two surfaces.

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1. Introduction

A major factor controlling the migration of contaminants in aquatic systems is their sorption onto the solids present in the environment, either in the form of a fixed rock structure or colloidal sized particles [1,2]. Retention and thereby partitioning of the metal ions in these sorption processes proceeds through mechanisms involving adsorption, formation of a metal ion precipitate on the solid surface or a metal ion co-precipitate with the dissolved part of the solids [3–5]. As more sorption data is being generated in macroscopic observations, the requirement of linking this information with molecular-level sorption mechanisms intensifies so that predictive models for the sorption processes as a function of various other system variables can be developed. These studies assume special significance for actinides having low solubility, e.g., Pu, Am, etc., which may enter into water bodies as a result of different nuclear activities, such as disposal of nuclear high level waste in deep

underground repositories, accidental release of actinides from operating power plants, underground nuclear tests and re-entry of nuclear powered satellites into earth, and can be a matter of concern for human health [6–9].

Surface Complexation Modelling, a mechanistic description developed to explain metal ion sorption at a solid–water interface, envisages a sorption reaction similar to aqueous complexation reactions with solid surface sites, for example a silanol ($\equiv\text{SiOH}$) site on a silica surface [10]. Assuming Langmuir isotherm behaviour, it reproduces the sorption behaviour at lower metal ion concentrations, that is at a lower surface coverage. At a higher surface coverage surface precipitation becomes the dominant mechanism and the surface speciation varies from pure metal hydroxides to a solid solution comprising of a metal ion and the central atom of the solid substrate [11]. According to Dzombak and Morel [10], surface precipitation should be considered once the dissolved sorbate concentration exceeds one-tenth of its solubility or one half of the total surface site concentration.

Experimental studies on metal ion sorption establish the dependence of sorption on environmental variables such as pH, Eh, ionic

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strength, temperature and presence of ligands [12–14]. These chemical conditions change the speciation of the metal ion and thus affect its sorption on mineral surfaces. Sverjensky reviewed the Eu redox transformation under varying temperature and pressure in water ranging from surface water to reducing medium water, and observed significant Eu(II/III) oxidation state fractionation at higher temperatures and in the presence of complexing ligands such as carbonate, sulfate and chloride [15]. In the sorption of Eu(III) on γ -alumina over different pH (4–8) under varying ionic strength (0.001–0.1 M NaClO₄) and metal ion concentration (10^{−9}–10^{−5} mol/l) Rabung et al. observed the formation of an inner sphere complex of Eu(III) on the alumina surface [16]. Further, the existence of three different surface complexes, (Al–O–Cm(OH)_x)^(2−x) (H₂O)_{5−x} (x = 0–2) over the studied pH was established by a Time Resolved Fluorescence Spectroscopy (TRFS) investigation of Cm(III) sorption on γ -alumina under similar experimental conditions [17]. In the potentiometric and modelling study of neodymium sorption at a rutile (TiO₂)–water interface [18], Ridley et al. observed a systematic increase in the Nd(III) sorption with increasing temperature. The experimental results were rationalized by considering a unique “tetradentate” configuration of Nd(III) on the rutile surface, wherein the sorbing cation bonds directly with two adjacent “terminal” and two adjacent “bridging” surface oxygen atoms. In the modelling study of the sorption of rare earth ions on several oxides [19], Piasecki and Sverjensky observed the proportion of mono- and tetradentate surface species varying as function of pH, ionic strength, surface coverage and type of oxide. The results infer a weaker monodentate (relative to the tetradentate complex) complex of trivalent lanthanides on rutile compared with hematite or silica. The dependence of sorption characteristics on the system variables results from the interfacial chemical reaction associated with sorption in the electric field at the oxide–water interface, which, in turn, depends on the metal ion speciation on the surface.

Direct evidence of surface speciation of metal ions on solid surfaces has been obtained from synchrotron based X-ray absorption fine structure (XAFS) spectroscopic studies [20–22]. Analysis of the X-ray absorption spectrum (extended X-ray absorption fine structure, EXAFS, and X-ray absorption near edge structure, XANES) provides structural information, including the identification, number and bond lengths of the neighbouring atoms around the probe atom, and thus enables the structure of the surface species to be delineated [23]. Very few literature studies have probed trivalent lanthanides/actinides speciation on silica and alumina surfaces using XAFS. In an EXAFS study of Nd and Lu sorption on silica [24], no effect of pH on the surface speciation was found in the pH range 6–9, with the formation of an edge sharing surface complex of Nd/Lu on the silica tetrahedra. In another EXAFS study for the mechanism of Eu retention on calcium silicate hydrates, even in the metal concentration and pH range amenable to precipitation there was no evidence of Eu(OH)₃(s) on the solid surface [25]. Fourier transforms of EXAFS spectra of Eu for both adsorption and precipitation samples was found to exhibit comparable structural features, pointing to similar crystallographic environments [25]. An EXAFS investigation of Nd- and Lu-sorbed on layered silicate, hectorite ([Mg_{2.77}Li_{0.66}]Si₄O₁₀(OH)₂), however, shows distinct spectral dissimilarities when compared with the spectral features observed for silica [24]. In a Cm(III) sorption study on γ -alumina [17], an EXAFS investigation was carried out using Gd and Lu as probe atoms, wherein the authors concluded that a mononuclear monodentate speciation existed on the surface, though shells beyond the first neighbour could not be explicitly delineated in this study. Dardenne et al. [26] observed monodentate Lu sorbed species on hematite (iron oxide/hydroxides are isomorphous to alumina) at pH 8, while edge sharing bidentate binding of Lu was obtained on amorphous 2-line hydrous ferric oxide above pH 5.5.

Silica (SiO₂) and alumina (Al₂O₃) are two ubiquitous oxide minerals in the geological environment. Apart from their geological importance, these solids present two structurally different substrates; Si atoms are tetrahedrally surrounded by oxygen atoms in silica, whereas Al is present in both the tetrahedral as well as octahedral sites of the close-packed arrangement of oxygen atoms in alumina. Surface site silanol (≡SiOH) in silica is, therefore, attached to a tetrahedron and the aluminol (≡AlOH) site in alumina is attached either to a tetrahedron or an octahedron, which may cause a significant change in the surface reactivity of these two solids towards metal ions. Silica and alumina are substrates with different dielectric constants [19] which causes a difference in the solvation environment of the two solids. Piasecki and Sverjensky [19] explained the difference in binding characteristics of trivalent lanthanides on various mineral oxides as a result of varying solvation characteristics of the solids. Investigation of Am(III)/Eu(III) binding to the aluminol (≡AlOH) site is also important for understanding the metal ion speciation on clay surfaces, in view of the finding that metal ion complexation to aluminosilicate clays happens primarily at the aluminol site [13].

In this work, we have examined Eu(III) sorption onto amorphous silica (am-SiO₂) and γ -alumina (γ -Al₂O₃) in near neutral pH conditions (6–8) with X-ray absorption fine structure spectroscopy. Eu(III) has been chosen considering it as an analogue for various long-lived trivalent lanthanides and actinides [12]. The absorption spectra were collected for samples equilibrated with Eu(III) solutions under- and over-saturated with respect to solid Eu-hydroxide with the aim of elucidating the role of pH and mineral substrate on influencing the local atomic coordination and binding of trivalent lanthanides/actinides to naturally occurring mineral oxides.

2. Experimental

2.1. Materials and characterization

Silica and alumina were purchased from M/s. Aerosil Ltd. and M/s. Degussa India Ltd., respectively, and were used as received. They were characterized for surface area by BET analysis and crystalline phase by X-ray diffraction (XRD) analysis. The europium used in the study was purchased from M/s. Indian Rare Earth India Ltd. in its oxide form. It was dissolved in conc. HNO₃ under heating and the dried residue was dissolved in 0.1 M HNO₃. The Eu concentration in the stock solution was determined by complexometric titration using EDTA [27]. Silica and alumina suspensions were characterized for Zeta potential using a Malvern Zeta Sizer nano-ZS. To study the solubility of these solids under different pH conditions, the same amount (3 g/l) of the two solids were equilibrated with 0.1 N NaClO₄ solution at different pH values for 24 h and subsequently the suspensions were centrifuged at 16500 rpm for 1 h. The required volume of the supernatants was aliquoted and assayed for the amount of dissolved silicon or aluminum using ICP-AES. The pH in the experiment was measured using a combination glass electrode based pH meter (M/s. Lab India Pvt. Ltd., India).

2.2. Sorption study

One hundred micromolar solution of Eu(III) containing ¹⁵⁴Eu radiotracer was equilibrated with 1 g/l silica and alumina suspensions for 24 h at 25 (±1) °C. A kinetic study (at pH 5), similar to the sorption study, was carried out to find the time required for attainment of equilibrium in the sorption process. The study showed 24 h as sufficient for attainment of the equilibrium sorption. Suspensions were made in the near neutral pH range (pH 6–8) relevant to environmental aquatic chemistry. Before equilibration with the metal ions, the solids were suspended in 0.1 M NaClO₄

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