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Analytical approaches to the speciation of lanthanides at solid-water interfaces

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ABSTRACT

We review the analysis of lanthanide speciation at solid-water interfaces. We summarize the various mechanisms of lanthanide interaction with sorbent surfaces, such as surface complexation, precipitation and surface-induced redox reactions. There are a wide variety of available analytical techniques for understanding the speciation of lanthanides on surfaces and the reaction mechanisms of sorption. We also review recent advances in the utilization of quantum chemistry that widen the scope of lanthanide speciation studies. We review, summarize and discuss in detail the speciation of lanthanides, mainly Eu(III), at natural or synthetic mineral surfaces, and the available analytical techniques. We aim to collate valuable information about recent results for surface speciation analysis of lanthanides at solid-water interfaces.

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1. Introduction

The highly radioactive nuclides associated with processing nuclear fuels and disposal of nuclear wastes are known to possess long half-lives and high levels of mobility in the environment [1–5]. Many lanthanides (Ln) are known to possess highly adsorptive properties, causing them to bind to not only mineral particles, but also colloids and natural organic matters, thus influencing their migration and diffusion through the environment and their bioavailability [1]. Evidence suggests that minerals are the key sorbents responsible for controlling the fate and the transport of lanthanides in natural systems [6–9]. The physicochemical behavior of trivalent lanthanides in the natural environment is mainly dominated by the species of lanthanides. Thereby, the analysis of the lanthanide species is crucial to evaluate the interaction of lanthanides at solid-water interfaces. High-affinity sorbents can enable the collection of trace and ultratrace levels of lanthanides, making them ideal candidates for evolving environmental remediation technologies and critical resource-recovery processes [1,10–13]. Lanthanide elements (plus yttrium) account for approximately 40% by mass of the atoms resulting from fission products of uranium and plutonium and are thus present in significant quantities in nuclear fall-out and nuclear waste streams [1]. The sorbents can strongly affect the transport of lanthanides due to several physicochemical processes, such as sorption/desorption, oxidation-reduction reaction, surface precipitation or incorporation of the sorbed lanthanide species into the solid matrix [1–4,6–8]. Fundamental insight into the interaction mechanisms and processes occurring at the solid-water interfaces is therefore of strategic importance. For reliable and trustworthy predictions of the physicochemical behavior of lanthanides in the natural environment, it is necessary to analyze the speciations and the microstructures of adsorbed lanthanides at solid-water interfaces. However, most published papers focused on the sorption of radionuclides on different kinds of clay minerals, oxides or nanomaterials at the macroscopic and microscopic level [1–5]. The analysis of lanthanide speciations at solid-water interfaces needs systematic, intensive and comprehensive investigation and study, and reviews of lanthanide speciation analysis are rare.

Reactions of the light lanthanide ions [La(III) to Lu(III)] at the solid-aqueous solution interface have attracted much attention in recent years. Many studies on speciation analysis of lanthanides in natural and artificial environments were carried out. Two main adsorption mechanisms have been highlighted for lanthanides:

- surface complexation at the edges of the clay particles (inner-sphere interaction); and,
- ion exchange (outer-sphere interaction).

The predominance of one mechanism over the other may depend on the type of lanthanide and its concentration [7,9]. However, depending on the geochemical conditions and the type of minerals, reactions other than mere adsorption, such as surface-induced redox reactions and lanthanide incorporation into the solid matrix, are possible [14–17]. The main parameters controlling sorption mechanisms and determining the extent of sorption are pH, redox conditions, total lanthanide-ion concentration, the type of mineral-surface functional groups, and the dynamic properties of the mineral in contact with the aqueous solutions [14–18].

Different and complementary approaches are proposed and applied to analyze radionuclide speciations and microstructures at the molecular level at solid-water interfaces, namely experimental determination with appropriate spectroscopic analytical tools [3,8–10,19] and computer modeling based on the use of thermodynamic data [6,10,13,20,21]. The models, such as surface-complexation models (SCMs) [22–25], provide insight into the trends in the formation of surface complexes, while spectroscopic ap-

proaches, such as X-ray absorption fine structure (XAFS) spectroscopy [6,9,10,14,16] and time-resolved layer fluorescence spectroscopy (TRLFS) [3,8–10], can directly provide the information on sorption speciations at the molecular scale, which are crucial for the analysis of the radionuclide species at solid-water interfaces.

We also briefly introduce other spectroscopic approaches, such as Raman and attenuated total reflection Fourier-transform infrared (ATR-FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and nuclear magnetic resonance (NMR) spectroscopy [1–8,19]. Multi-techniques, the combination of two or more tools mentioned above, can help to probe lanthanide speciation widely in a convincing manner and thus contribute to more accurate elucidation of the interaction mechanisms between lanthanides and sorbents.

A recent review by Geckeis et al. [22] dealt comprehensively with the various mechanisms of actinide interaction with mineral surfaces. Geochemical models and quantum-chemical approaches were applied to analyze sorption reactions and to elucidate actinide-surface structures and tentative binding modes. Another focus is the speciation of actinides (Th, U, Np, and Pu) in aqueous solutions and on solids common in the environment, as well as their interactions with mineral surfaces, organic matter, and microorganisms [26]. More detailed analysis on aquatic actinide chemistry and the related thermodynamics is available [27].

Our previous review summarized available studies on actinide and lanthanide interaction with mineral surfaces, including detailed descriptions of analytical methods [28]. Tan et al. [28] discussed examples of actinide/lanthanide interface reactions in order to elaborate mechanistic insight provided by individual spectroscopic techniques, such as TRLFS and extended XAFS (EXAFS). We also review some density functional theory (DFT) studies about the analysis of lanthanides on mineral surfaces.

The present review deals comprehensively with speciation analysis for various mechanisms of lanthanides with natural minerals or the compositional complex surfaces of the substrates obtained, including inner/outer-sphere surface complexation, surface precipitation and surface-induced redox reactions. We critically review lanthanide speciation at solid-water interfaces by using SCMs and spectroscopic analysis, such as EXAFS, TRLFS, XPS, Raman spectroscopy and ATR-FT-IR.

In addition, we review and discuss a quantum-mechanics approach leading to definitive information on the structure analysis of the adsorbed lanthanide speciation at the molecular level at the solid-water interfaces. In Fig. 1, we give an overview of the interactions between lanthanides and solid-water interfaces, and the analytical and experimental techniques used in the analysis of lanthanide species. Table 1 also summarizes, the advantages and the disadvantages of different analytical approaches. This review is not intended to cover all published results in this field, as we only focus on a few notable works that may enlarge the researcher's view on speciation analysis and interactions of lanthanides at solid-water interfaces.

2. Speciation analysis for different sorption mechanisms

Lanthanide speciation depends on a variety of factors, such as temperature, pH, redox conditions, and the nature of the presence and the concentration of complexing inorganic and organic ligands [22,49]. Different speciations have substantially different behaviors and exhibit very different properties, such as stability, complexation, diffusion and migration in the environment. The analysis of lanthanide speciation is essential and primarily necessary for the long-term assessment of the performance of nuclear waste repositories and radionuclide migration in the environment, and designing remediation processes [2,4,5].

The interactions between lanthanides and the sorbents are related to certain factors, such as the structure and the composition of the

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