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Account / Revue

Molecular approach of the uranyl/mineral interfacial phenomena

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Abstract

In order to understand, at a molecular level, the mechanisms involved in the interactions between radionuclides and minerals, both thermodynamic and structural investigations, using spectroscopic techniques, are presented. However, the natural clays are rather complex minerals. Therefore, it is first necessary to perform these studies on simple substrates such as single crystal and oxides, and then extrapolate the obtained results on the natural minerals. We examine in this review the sorption processes of the hexavalent uranium onto montmorillonite, TiO_2 (powder and single crystal), silica and alumina as well. The corresponding sorption constants are determined using the results obtained with the following techniques: laser-induced spectrofluorimetry, X-ray photoelectron spectroscopy, second-harmonic generation and X-ray absorption spectroscopy. In addition, for TiO_2, these results are compared with theoretical calculations using periodic density functional theory, which gives the atom distribution at the interface and the relative energy stabilities of the different surface complexes. ***To cite this article: R. Drot et al., C. R. Chimie 10 (2007).***

Résumé

Afin de comprendre, à l'échelle moléculaire, les mécanismes impliqués dans les interactions entre radionucléides et minéral, des études thermodynamiques et structurales sont présentées. Les argiles constituant une famille de substrats complexes, il est nécessaire de réaliser ce type d'étude sur des phases unitaires représentatives, afin d'extrapoler ensuite ces résultats aux solides naturels. Sont examinés, dans cette revue, les processus de sorption de l'uranium hexavalent sur la montmorillonite, TiO_2 (poudre et monocristal) et également sur l'alumine et la silice. Les constantes de sorption correspondantes sont déterminées en utilisant les résultats structuraux obtenus à l'aide des techniques spectroscopiques suivantes : spectrofluorimétrie laser, spectroscopie de photoélectrons X, génération de seconde harmonique et spectroscopie d'absorption X. De plus, pour TiO_2, ces résultats sont comparés à des calculs périodiques utilisant la théorie de la fonctionnelle de la densité, qui permettent d'accéder à la distribution des atomes à l'interface ainsi qu'à la stabilité relative des complexes de surface. ***Pour citer cet article : R. Drot et al., C. R. Chimie 10 (2007).***

Keywords: Sorption; Uranyl ion; Montmorillonite; Titania; Spectroscopies; Surface complexation modeling; DFT calculations

Mots-clés : Sorption ; Ion uranyle ; Montmorillonite ; Oxyde de titane ; Spectroscopies ; Complexation de surface ; Calculs DFT

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1. Introduction

The performance assessment of an underground geological nuclear waste disposal is one of the major issues of the nuclear fuel cycle. One of the main concerns related to the safe storage of nuclear waste in an underground repository is the migration of radiotoxic elements through the geosphere [1,2]. In this field, the interaction between solute and solid surfaces, which is mainly governed by sorption/desorption processes, is a crucial point. The precipitation/solubility phenomena of the radionuclides have to be taken into account, as well. Therefore, a detailed knowledge of the mineral–water interface is of fundamental interest since the corresponding interfacial reactions play a significant role in the geochemical regulation of metals. They are, however, inherently complex and require to quantify several physico-chemical parameters to build a predictable model. These phenomena depend mainly on parameters such as the pH, the redox potential, the ionic strength of the aqueous medium, the concentration and speciation of the radionuclides of interest (taking into account the solid precipitates), the specific surface area and the density of functional surface groups of the substrate. Different approaches of the sorption processes are usually used: empirical models using a partition factor (Kd), mechanistic models such as macroscopic ion exchange or microscopic surface complexation [3–12]. Nevertheless, using only these models, the experimental data simulations do not give unambiguous results. Indeed, these determinations without any experimental validation could yield, for instance, to the choice of arbitrary surface complexes. Consequently, the precise determination of the corresponding thermodynamic constants is not an easy task and an accurate understanding, at a microscopic scale, of the mechanisms involved is imperative before any modeling. Therefore, it is necessary to relate the expected surface complexes to the structure of the surface coordination complexes. Up to now, most of the published works present a thermodynamic or a structural point of view, but only a few have used structural results as an experimental constraint in the modeling procedure [13–17].

We present, in this review, the necessity of a combined use of four structural techniques, which allows one to investigate the sorption mechanisms at a molecular scale and thus identify the species involved in the retention processes: laser-induced fluorescence spectroscopy (LIFS), X-ray photoelectron spectroscopy (XPS), surface second-harmonic generation (SSHG) and grazing X-ray absorption spectroscopy (GI-XAS). In addition to the experimental investigations, ab initio calculations were also performed. Sorption of the uranyl ion onto montmorillonite and rutile titania will be considered as illustrative purpose to present the applied methodology, since under environmental conditions, uranium typically occurs in the hexavalent form as the mobile aqueous uranyl ion (UO_2^{2+}). Then, the sorption of this ion onto solid surfaces has been widely studied because this process has a significant effect on transport properties [3,10–12,18–20].

Although the characteristics of clay materials such as low permeability, high sorption capacity and plasticity make them an effective barrier against radionuclides' migration [21], only few works were devoted to the microscopic study of uranium sorption on clay minerals, especially in acidic pH ranges [18–23]. Montmorillonite is a clay mineral formed by two-dimensional sheets of tetrahedral SiO_4 alternating with sheets of octahedral $Al(O,OH)_6$ [24]. Its retention capacities for fission products or actinides are acknowledged [22,25–31]. The existence of both exchange and edge sites' surface complexes on montmorillonite were already experimentally demonstrated using molecular spectroscopic probes [22,23,25,32,33]. Because montmorillonite presents several types of sorption sites, uranyl sorption mechanisms on this mineral are expected to be complex. However, based on its alumino-silicate structure, this clay can be viewed as an assemblage of "basic structural units", which could be represented as "Al-edge site" and "Si-edge site". Consequently, the investigation of the U(VI) sorption mechanisms onto both alumina and silica solids and the comparison of the obtained results with those obtained for the U(VI)/montmorillonite system have allowed one to clearly identify the sorbed uranyl species on montmorillonite.

The rutile titanium dioxide was considered under both powdered and single crystal forms. Due to its high chemical stability over a wide range of pH values, this solid is an interesting mineral model. Moreover, an average repartition of the different crystallographic orientations of rutile powders has been established, with the $TiO_2(110)$ orientation as the main one [34–36]. The aim of the study was to account for the powder retention properties from a molecular study of the different crystallographic planes of titania. Moreover, despite its very particular properties, sorption processes of very few actinides were studied considering this oxide. Then, the structural investigation of the interactions between the hexavalent uranium ion and TiO_2 surface appeared particularly pertinent. Finally, to provide support to the experimental investigations, theoretical calculations were performed. As an example, the interactions between uranyl ions and the $TiO_2(110)$ single crystal