

Uranyl sorption mechanisms onto titanium dioxide: from crystal to powder

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Mécanismes d'interaction de l'uranyle avec l'oxyde de titane : du monocristal à la poudre

La rétention des radionucléides et leur répartition parmi différentes phases minérales co-existantes est au cœur de la gestion des déchets nucléaires. Ces dernières années, plusieurs études se sont focalisées sur la détermination de constantes de sorption fiables, en couplant une approche macroscopique et une approche microscopique. Le travail présenté ici concerne les mécanismes de sorption de l'uranyle sur une surface d'oxyde : l'oxyde de titane, phase rutile, considéré sous forme de poudre et de monocristaux. Le but est de déterminer les sites de surface actifs vis-à-vis de la sorption de l'uranyle. Dans le cas du monocristal, les plans cristallographiques sont parfaitement définis et la distribution des atomes de surface est connue. Ainsi, en comparant la sorption de l'ion uranyle selon différentes orientations cristallographiques et la sorption de ce même ion sur la poudre correspondante, les sites responsables de la rétention de U(VI) par la poudre peuvent être identifiés. De plus, ces résultats expérimentaux sont comparés à des calculs ab initio de chimie quantique.

Within the framework of nuclear waste storage in geological repository, the safety assessment requires a complete knowledge of the mechanisms involved at the aqueous solution/mineral interface. Since radionuclides migration through the geosphere is mainly governed by sorption and precipitation phenomena, it appears to be fundamental to investigate the retention processes at a molecular level. In such a way, the major experimental limitation arises from the difficulty to extract a local phenomenon contribution from the macroscopic system. Therefore, the use of atomic scale modelling makes possible to evaluate the contribution of each component of the global system.

We present here the studies of the interaction mechanisms between uranyl ions and the rutile TiO_2 oxide. This solid substrate is interesting because it can be found under both powder and single crystal forms, which allows to study the retention processes on perfectly characterized crystallographic planes. Since the repartition of the different crystallographic orientations are known for the powder, the results obtained for the single crystals can directly be used to account for the powder retention properties. By using complementary spectroscopic techniques such as Time Resolved Laser-induced Fluorescence Spectroscopy (TRLFS), X-ray Photoelectron Spectroscopy (XPS), Diffuse Reflectance Infra-red Fourier Transformed spectroscopy (DRIFT) and Surface Second Harmonic Generation spectroscopy (SSHG), it is possible to accurately determine the nature of the reactive surface sites as well as the surface species.

Furthermore, in order to better understand the interfacial interactions, atomic calculations will provide support to the experimental data by bringing complementary insights. Among all kinds of simulations, *ab initio* type calculations are the most accurate ones, even if they can treat only small systems (from a few tens up to about one or two hundred

atoms). The purpose of this part is to provide a theoretical support to the experimental investigation.

Moreover, two approaches exist to mimic the system: a periodic approach where the system is infinitely repeated in the three dimensions, and a cluster one where the system is isolated in vacuum.

Experimental investigation

In a first step, the acidity properties of the solid have been investigated. The DRIFT and XPS experiments have clearly shown that the solid, in suspension in solution, is fully hydroxylated. The intrinsic acidity constants associated to the acid-base behaviour of the solid surface have been determined from the surface oxygen charges calculated using the Pauling valence bond (CD-MUSIC approach). Then, for the powdered samples, potentiometric titration experiments were performed and were successfully modelled (Constant Capacitance Model) taking into account the natural repartition of the different crystallographic planes of titania: for the studied rutile powder, the preferential crystallographic orientations are (110), (100) and (101) in the ratio 60/20/20. Thus, only the double layer inner-capacitance value remained as an adjustable parameter.

In a second step, Atomic Force Microscopy was carried out in order to verify that no surface precipitation occurs for the higher surface coverages. Moreover, these analysis have also evidenced that the U(VI) sorption is homogeneous indicating that there is no uranium cluster formation during the sorption process. These observations were corroborated by SSHG experiments (mainly for (001)), which have also shown that the sorption occurs, in a first step, onto preferential surface symmetry axis. The spectroscopic measurements (TRLFS and XPS) clearly evidenced that there are two different surface reactive sites towards uranyl

ions on both (110) and (001) crystallographic planes as well as on the powdered samples.

These sites are made up with surface oxygens linked with one or two titanium atoms, respectively. The corresponding two uranyl surface species were observed whatever the pH value ranged from 1 to 5. Nevertheless, the relative quantities of these species depend on the surface coverage (figure 1).

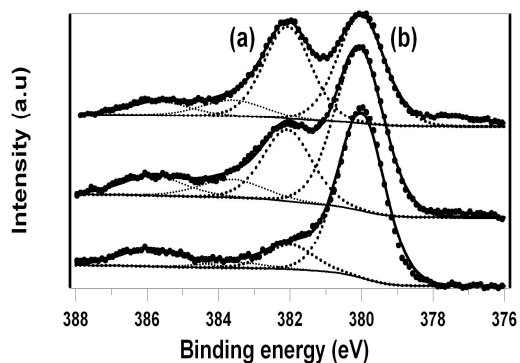


Fig. 1 : U4f7/2 XPS spectra of U(VI) sorbed onto (110) crystallographic face. (a) and (b) denote the two surface species.

All the spectroscopic characteristics of these uranium species (fluorescence spectra and associated decay times, binding energies) were found to be the same for the powder and (110) and (001) crystallographic planes. Moreover, DRIFT experiments have clearly shown that reactive surface oxygen atoms remained protonated after uranyl sorption indicating that all these surface atoms are not affected by the metal sorption.

Finally, the sorption edges defined for powders were then fitted on the basis of the constraints brought by the spectroscopic investigation (figure 2), which allowed to perform the fit with a minimal number of adjustable parameters and then allowed a more accurate determination of the sorption constants values.

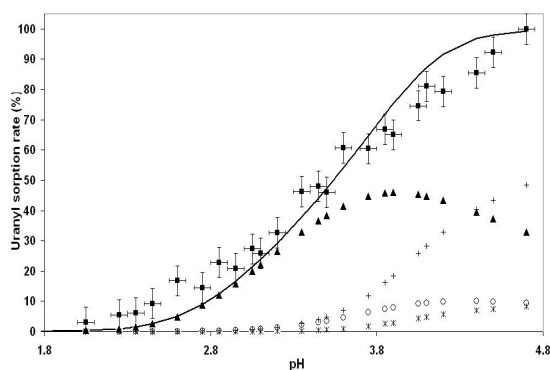


Fig. 2 : U(VI)/rutile sorption edge and corresponding modelling (CCM model) according to the structural investigation

Theoretical calculations

In the theoretical part, two different approaches, using density functional calculations, were used. First, TiO₂ (110) surface was modelled with periodic slabs in order to investigate clean surface relaxations, water adsorption, and finally, interaction of uranyl ions with the mineral surface. The aim of this first step was to identify the most probable UO₂²⁺ sorption sites and to establish their relative energy stabilities as a function of the surface coverage.

Bulk rutile TiO₂ as well as the (110) face parameters were optimized and were found to be in good agreement with experimental data and previous theoretical works. A five layers model, with its most internal layer frozen to bulk positions, was found to be a good model to mimic the TiO₂(110) surface. As reference data for the sorption process, hydration of the uranyl ion using periodic approach was studied. As already experimentally found, solvation energies tend to favour the pentahydrated system [UO₂(H₂O)₅]²⁺ in aqueous solution. From localized calculations, an overall 0.91 electron transfer between the first coordination shell and the uranyl ion was calculated which clearly demonstrates the importance of the solvent effect in the modelling. Then, the simulation of the uranyl ion sorption on a five layers hydroxylated TiO₂(110) model was investigated. Three different sorption sites were investigated. The saturation of the uranyl ion first coordination shell, by three water molecules, was taken into account in order to get more reliable structural parameters relative to experimental data.

Moreover, starting from the previous TiO₂ (110) relaxed structure, stoichiometric (TiO₂)_n clusters were used to simulate the (110) rutile surface (figure 3). This cluster approach was done in order to study, from a local point of view, the interaction of one uranyl ion with the TiO₂ (110) surface for the different possible sorption sites.

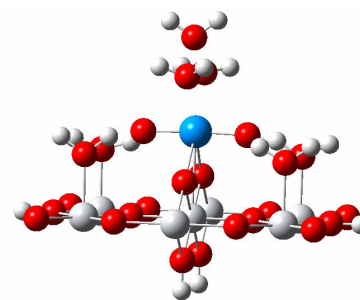


Fig. 3 : Example of one cluster model used to investigate the uranyl sorption on the TiO₂ (110) face.

Each theoretical result is directly compared with the experimental data summarized above and both methodologies (periodic or localized) gave similar results in agreement with these data. This original theoretical study correlated to the experimental investigation leads to an acute representation of the retention processes of radionuclides on mineral surfaces.

