

Study of uranyl sorption onto hematite by in situ attenuated total reflection–infrared spectroscopy

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Abstract

In this paper, we present results of ATR-IR spectroscopy of uranyl complexes adsorbed on hematite. This method allowed the in situ recording of infrared spectra of uranyl sorbed on hematite in presence of aqueous solution and to detect one peak at 906 cm^{-1} attributed to the antisymmetric O=U=O stretching. The intensity of the peak increases with pH, but its shape does not evolve, indicating that the same surface species is responsible for the sorption in the pH range 5–8. The reversibility experiments confirm that the hematite deposit reacts in the same way as dispersed suspensions. Measurement of the stretching frequency of nitrate ions coming from electrolyte showed a pure electrostatic adsorption and exclude the formation of a ternary complex with uranyl.

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1. Introduction

The long term safety of radioactive waste depositories is based on the sorption of radionuclides on engineered and natural barriers placed around the depositories. To predict the safety of such depositories at very long term, it is necessary to extrapolate sorption data measured at the laboratory scale, to real systems and to very long times. Models used for this purpose must represent as accurately as possible the real sorption processes, otherwise the long term prediction may be hazardous. Knowledge of the structure of surface complexes is an important factor, together with the determination of complexation constants. We have to differentiate between inner- (IS) and outer-sphere (OS) complexes, determine the inner-sphere complex structure (typically monodentate or bidentate) or characterize ternary complexes (typically solid/ligand/metal). Fitting of experimental sorption data is not sufficient for that purpose, since it often leads to several possible sets of surface complexes [1,2]. Spectroscopic methods are quite suitable for

bringing information on surface complexes, but ex situ methods such as X-ray photoelectron spectroscopy (XPS) and diffuse reflectance spectroscopy (DRIFT) must be performed on dried samples. Dehydration may modify the structure of surface complexes, as suggested by Hug who has shown the conversion of monodentate to bidentate complexes of sulfate on hematite [3]. X-ray absorption spectroscopy (XANES, EXAFS) has been used to investigate the surface complexes geometry both on dry and wet samples. EXAFS has been already applied to the sorption of the uranyl ion on ferric oxides [4].

Due to its ability to probe chemical bonds, infrared spectroscopy remains a technique of choice to analyze surface complexes. However, since water strongly absorbs IR, methods based on internal reflection spectroscopy have been developed to analyze wet samples: use of the evanescent wave forming in water in contact with a medium with a higher refractive index in which an IR radiation is propagating, limits the absorbance of water and probes a thin sample layer [5]. This technique, called attenuated total reflection (ATR), can be performed directly onto metallic oxides suspensions, but Hug and Sulzberger [3,6] developed a procedure of coating the ATR element by a layer of colloidal mineral particles. For reviews addressing the

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current state of knowledge in the use of ATR-IR to determine surface complexes between inorganic ions and oxy-hydroxides surfaces, the reader is referred to McQuillan [7] (2001) and Lefèvre [8] (2004).

Characterizing the interactions between uranyl ions and ferric oxides is important for numerous environmental problems involving contamination by uranium. For example, the sorption of uranium ions released from nuclear wastes or former mining [9] onto minerals or corrosion products is a key process controlling the migration of this element in natural and engineered barriers. Thus, many studies on uranyl sorption onto ferric oxy-hydroxides surfaces have been carried out. Some of them have only brought macroscopic information, as the distribution coefficient (K_D) or the effect of solution composition (pH, ionic strength, carbonate, etc.) on the sorbed quantity [10]. The first results on the surface speciation of uranyl in presence of solution were obtained by EXAFS [4], indicating the formation of a bidentate complex between uranyl ions and ferric oxides surface. EXAFS results are based on the measurement of the distances between the sorbed ion and the surrounding shells. It would be interesting to test this result by other in situ spectroscopic methods, which determine the bond vibration modes.

In this paper, we present results of ATR-IR spectroscopy of uranyl complexes adsorbed on hematite. Until now, ATR-IR has been used to characterize surface complexes of “light” oxoanions MO_n^{m-} (CO_3^{2-} , SO_4^{2-} , PO_3^{2-} , etc.) through the absorption of IR by M–O stretching [8]. For heavier oxoions, like UO_2^{2+} , the analysis is possible by recording the double bond (U=O) stretching. The sorption/desorption kinetics and the influence of pH and uranyl concentration were investigated. Nitrate ions at the surface of hematite were also followed by ATR-IR, in order to correlate their sorption as counterions to the surface charge and to study the possible formation of a ternary complex “hematite/nitrate/uranyl.”

2. Materials and methods

2.1. Hematite synthesis

Hematite colloids were synthesized by hydrolysis of ferric ions in a boiling solution [11]. 350 mL of water was heated at 90 °C in a pyrex glass flask with a reflux condenser and a magnetic stirring. A solution of $FeCl_3$ (0.15 M, 50 mL) was added by a peristaltic pump at a rate of 40 mL/h. After the addition, the suspension was heated 6 h, then cooled, and kept in the solution. High resolution transmission electron microscopy (HR-TEM) images (not shown) indicate presence of particles of ca. 25 nm. The crystallinity of the particles is confirmed by the presence of periodic fringes.

2.2. Turbidimetry

Turbidity measurements of uranyl solutions were performed with a Hach 2100N turbidimeter.

2.3. Layer deposition

The deposition procedure of hematite colloids was optimized to obtain a thin layer on the whole surface of the crystal, by varying several parameters (particles concentration, alcohol addition, temperature, etc.). The hematite suspension was mixed with an equal volume of propanol. 25 μ L of the suspension was spread with a micropipette tip on a 45° ZnSe crystal, whose temperature was kept at 50 °C by a thermostated bath. This heating allows a rapid drying of the solution, and the addition of the mixture was repeated several times. The total mass added on each face was about 0.5 mg. Micro-Raman spectroscopy was used to determine the distribution of the hematite deposit and to check that the whole surface of ZnSe is covered.

2.4. ATR measurement

Measurements were performed in a homemade liquid cell containing 6 mL and connected to a 500-mL polyethylene vessel through a peristaltic pump. The geometry of the ZnSe crystal (5 × 10 × 2 mm) and its double-sided coating lead to 25 reflections. $NaNO_3$ 0.01 M was used as a background electrolyte due to the absence of absorption in the mid-IR range (except around 1370 cm^{-1} where NO_3 stretching takes place) and its low complexing properties towards uranyl ions. The experimental procedure was similar to that of Peak et al. [12], allowing to adjust and measure pH and to add uranyl stock solution. Nitrogen is continuously flowed over the solution to avoid CO_2 contamination. The colloid film was in contact with the aqueous solution which was circulating at 1 mL/min. Spectra were recorded at a resolution of 4 cm^{-1} with 128 co-added scans, with a dry air purged Nicolet spectrometer using OMNIC software for the data processing. Due to the drift of the baseline with time (the experiments lasted several hours), spectra for uranyl have been corrected by shifting the whole spectra to zero absorbance at 1000 cm^{-1} . The coated crystal was first washed by flowing the electrolyte solution ($NaNO_3$ 0.01 M), then the background spectra were recorded. The spectra of sorbed uranyl/nitrate ions were recorded every 5 min by flowing a 10^{-5} M uranyl solution with increasing pH. This concentration was found to be the lowest value leading to a sufficient signal/noise ratio. When the increase in the spectrum intensity with time is less than 5%, corresponding to about 15–20 min, the equilibrium state was assumed to be reached and the pH was raised by addition of NaOH. This equilibration time is consistent with a fast sorption process, supported by the observation by Giammar and Hering [13] on goethite where completion was reached in a single rapid step.

3. Results and discussion

3.1. Review of previous spectroscopic results on uranyl sorption onto metal oxy-hydroxides

The uranyl ion UO_2^{2+} is as a linear molecule (O=U=O), with a U=O distance in the range 0.17–0.19 nm [14]. There

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