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Sorption of sulfate ions onto hematite studied by attenuated total reflection-infrared spectroscopy: Kinetics and competition with other ions

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Abstract

In this paper, after a short discussion about the use of attenuated total reflection-infrared spectroscopy (ATR-IR) to study sorption of inorganic ions onto iron oxides, results of ATR-IR spectroscopy of surface complexes adsorbed on hematite are presented. Kinetics of sorption of sulfate ions was followed, showing an equilibrium after half an hour. The infrared band was assigned to a monodentate surface complex with a low contribution of a bidentate complex with help of second-derivative spectral analysis. The effect of several ions (SeO_4^{2-}, ReO_4^-, UO_2^{2+}) after sorption of sulfate (10 μM) was investigated. Selenate ions (10–100 μM) were shown to compete with sulfate ions, while perrhenate ions (1–100 μM) did not desorbed sulfate complexes. Experiments were also carried out in the hematite–sulfate (10 μM)–uranyl (10 μM) system, but no ternary complex was observed.
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1. Introduction

The long term safety of radioactive waste depositories is based on the solubility and 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. The validity of the models used for this purpose depends on the accuracy of the description of sorbed species and sorption processes. Fitting of macroscopic results, such as the sorbed fraction of ions *vs* pH, can lead to several sets of surface complexes (Lützenkirchen, 2002; Duc et al., 2006) and thermodynamic sorption constants, due to the number of adjustable parameters and electrostatic models. Methods must be developed to differentiate between inner- (IS) and outer-sphere (OS) complexes, to

determine the surface inner-sphere complex structure (typically monodentate or bidentate) or characterize ternary complexes (typically solid/ligand/metal).

Ex situ spectroscopic methods can bring some information on surface complexes, but a drying step is usually needed before analysis by X-ray photoelectron spectroscopy (XPS) or by diffuse reflectance spectroscopy (DRIFT). 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 (Hug, 1997). X-ray absorption spectroscopy (XANES, EXAFS) and time-resolved laser fluorescence spectroscopy (TRLFS) have been often used to investigate the surface complexes on both dry and wet samples. More recently, attenuated total reflection (ATR) infrared spectroscopy has been shown to gain information on the symmetry of sorbed species in presence of solution (Lefèvre, 2004). This technique can be performed directly onto metallic oxides suspensions (Tejedor-Tejedor and Anderson, 1990), and a quantitative spectral analysis is possible using a procedure where the ATR element is

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coated by a layer of colloidal mineral particles (Hug, 1997). In this method, only a short depth (a few micrometers) of the layer of particles is probed by the evanescent wave (Mirabella, 1993), thus avoiding the strong water IR absorption.

The sulfate/hematite system was chosen to illustrate the use of ATR-IR spectroscopy in sorption studies. Sulfur isotopes are not present in high activity long live radioactive wastes, but ^{35}S is released to the environment by gas-cooled nuclear power plants in the UK (Collins and Cunningham, 2005). More important is the behavior of sulfate ions present in natural waters in the sorption of radioactive pollutants. Thus, on metallic oxides, the presence of sulfate ions may promote uptake of cations (Ostergren et al., 2000; Swedlund and Webster, 2001) but competes with other anions (Wu et al., 2002).

In the present study, after a short review of the use of ATR-IR method to study sorption of inorganic ions onto iron oxides, we describe several results obtained on the hematite–sulfate system illustrating a particular possibility of ATR-IR to study sorption kinetics, speciation of surface complexes, and interaction with other ions (selenate, perrhenate, nitrate and uranyl).

2. Materials and methods

2.1. Chemicals

All chemical reagents were analytical grade and were used without further purification. Water was of Milli-Q quality (Millipore). Hematite colloids (particles of ca. 25 nm) were synthesized by hydrolysis or ferric ions in a boiling solution (Lefèvre et al., 2006).

2.2. Layer deposition

The deposition procedure of hematite colloids was optimized to obtain a thin layer on the whole surface of the ATR ZnSe crystal, by varying several parameters (particles concentration, alcohol addition, temperature, . . .). Finally, the drying at 50 °C under a nitrogen flow of drops of a mixture of ethanol (50 vol.%) and the hematite suspension (3 g L^{-1}) was chosen. The total mass added on each face was about 0.2 mg. Micro-Raman spectroscopy was used to obtain a cartography of hematite and to check that the whole surface of ZnSe is covered by colloidal particles.

2.3. ATR measurement

Measurements were performed in a homemade liquid cell containing 6 mL of solution and connected to a 500-mL polyethylene vessel through a peristaltic pump. The geometry of the ZnSe crystal and its double-sided coating lead to 25 reflections of the infrared beam. NaCl or NaNO$_3$ 0.01 M were used as background electrolytes and expected to be inert under these conditions. The experimental set-up was similar to that of Peak et al. (1999), allowing adjusting
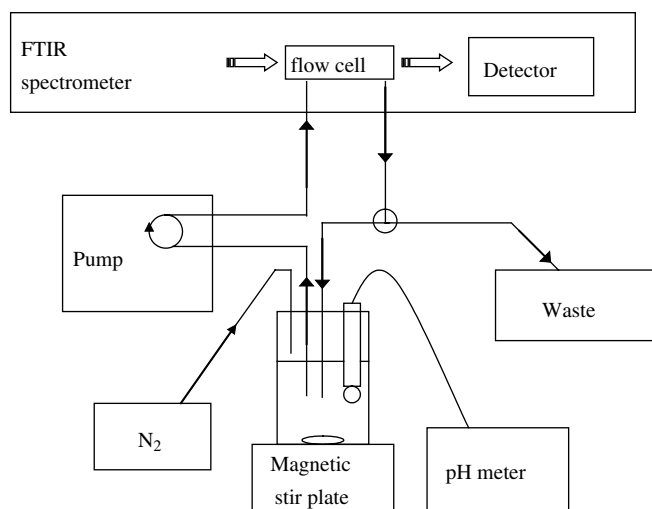

Fig. 1. Experimental set-up.

and measuring pH and to add sorbing species stock solution (Fig. 1). The colloid film was in contact with the aqueous solution which was circulating at 1–3 mL min^{-1}. Spectra were recorded with a resolution of 4 cm^{-1} with 64-256 co-added scans, with a Nicolet spectrometer using OMNIC software (Thermo-Nicolet) for the data processing. The coated crystal was firstly washed by flowing the electrolyte solution to waste, then the solution was circulating in closed circuit and the background spectra were recorded.

For competition with anions (perrhenate, selenate), a sulfate solution was firstly flowed to waste, then a background was recorded. The cell was then rinsed by flowing a sulfate-free solution to waste. Then, a sulfate-free solution with a competing anion was flowed in closed circuit, and the spectra were recorded.

3. ATR principles

Attenuated total reflection spectroscopy is based on the existence of an evanescent wave in a medium of lower index of refraction ($n_{water} = 1.33$) in contact with an optically denser medium ($n_{ZnSe} = 2.4$) in which a light is introduced (Mirabella, 1993). The evanescent field decays exponentially in the lower index medium according to the following equation:

$$E = E_0 \exp\left[-\frac{2\pi}{\lambda_1}(\sin^2\theta - n_{21}^2)^{1/2}Z\right] = E_0 \exp(-\gamma Z) \qquad (1)$$

where $\lambda_1 = \lambda/n_1$ is the wavelength of the radiation in the denser medium, λ is the wavelength in free space, θ is the angle of incidence with respect to the normal, $n_{21} = n_2/n_1$, where n_1 and n_2 are respectively, the refractive index of the optically denser and rarer medium, and Z is the distance inside the solution from the surface. Due to this relation, the light probes only a few micrometers, and the depth of penetration, d_p, is expressed as

$$d_p = \frac{10\,000}{2\pi v n_1}\left(\sin^2\theta - n_{21}^2\right)^{-1/2} \qquad (2)$$