Applied Geochemistry 94 (2018) 28–34

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Adsorption of uranyl tricarbonate and calcium uranyl carbonate onto γ-alumina

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ARTICLE INFO

Keywords:
U(VI) tricarbonate and calcium uranyl carbonate
γ-Alumina
U(VI)-Carbonato surface complexation
TRLFS
ATR-FTIR spectroscopy

ABSTRACT

The uranyl tricarbonate moiety, exemplified by $UO_2(CO_3)_3^{4-}$, $CaUO_2(CO_3)_3^{2-}$, and $Ca_2UO_2(CO_3)_3(aq)$, is potentially expected to consist of mobile uranyl(VI) species in the aquifer of a deep geological repository for spent nuclear fuel. Time-resolved laser fluorescence spectroscopy (TRLFS) for the U(VI) surface speciation on γ-alumina was utilized to investigate the effect of various uranyl tricarbonate species on U(VI) adsorption. Under the prevailing carbonate conditions, the emission bands of the species of U(VI) adsorbed onto γ-alumina were found at 467.6 ± 0.1, 487.1 ± 0.1, 507.5 ± 0.1, 530.0 ± 0.1, and 552.8 ± 0.2 nm and were blueshifted compared with those of the U(VI)-hydroxo surface complexes. The shift to the shorter wavelengths was attributed to the spectral feature of bis- and/or tris-carbonato U(VI) complexes found in aqueous uranyl(VI) species and uranium (VI) minerals with two to three carbonate ions. The results obtained from attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy have confirmed the formation of U(VI)-carbonato surface complexation on γ-alumina in a bidentate manner. Based on identical spectroscopic properties, which were observed independently of the presence or absence of calcium ions in the uranyl tricarbonate system, a similar manner of U(VI) tricarbonate adsorption can be assumed, regardless of the absence or presence of calcium. According to the results from this work and comparison with previous studies, U(VI)-carbonato surface complexation tends to be favorable on mineral surfaces with a higher point of zero charge (pH_{PZC}) such as alumina. Regarding the retention of U(VI) in the aquifer, the results presented in this work provide new insight and interpretation of U(VI) adsorption in carbonate-rich groundwater.

1. Introduction

The migration of the actinides in the natural environment is affected by various geochemical reactions, e.g., precipitation/dissolution, complexation, sorption, and the redox process. The sorption reaction is one of the most important retention processes so that the migration of long-lived radioactive elements in the deep geological repositories for high-level radioactive waste is strongly dependent on the sorption capacity of a host rock when the engineered barriers are degraded. Uranium is a radiotoxic and chemically toxic heavy metal and is abundant in spent nuclear fuel. Uranium in the hexavalent oxidation state, U(VI), remains stable and mobile in oxidizing water. Therefore, the understanding of U (VI) sorption on natural rock formations is necessary to assess the disposal safety. At the mineral-water interface, various metal oxides and hydroxides provide sorption sites for U(VI). Alumina (Al_2O_3) has been widely studied as an interesting U(VI) sorbent (Baumann et al., 2005; Chang et al., 2006; Chisholm-Brause et al., 2001, 2004; Drot et al., 2007; Froideval et al., 2006; Gabriel et al., 2001; Kowal-Fouchard et al., 2004; Sylwester et al., 2000; Gückel et al., 2012; Müller et al., 2013) because it is an analogue of structural and functional properties of the aluminosilicates.

Uranyl tricarbonate, $UO_2(CO_3)_3^{4-}$, is the dominant uranyl species under atmospheric CO_2 and alkaline conditions and has been considered as a species that is hardly adsorbed because of its considerably negative charge (Duff and Amrhein, 1996). The uranyl tricarbonate moiety occurs even at neutral and weakly alkaline pH in carbonate-containing aqueous systems by complexing with calcium and forming ternary calcium uranyl carbonate species, $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3(aq)$ (Bernhard et al., 2001). These ternary Ca-UO_2-CO_3 species are the main uranyl species in the pH range from 7.5 to 9.0 at mM concentrations of Ca^{2+} based on chemical thermodynamic data (Bernhard et al., 2001; Dong and Brooks, 2006; Endrizzi and Rao, 2014; Lee and Yun, 2013) and field studies (Baik et al., 2015; Schmeide et al., 2014). A few studies on the effect of these ternary species on U (VI) sorption have been reported. Batch sorption experiments have shown that the U(VI) uptake onto ferrihydrite, quartz (Fox et al., 2006),

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https://doi.org/10.1016/j.apgeochem.2018.05.004
Received 30 November 2017; Received in revised form 3 May 2018; Accepted 8 May 2018

bentonites (Meleshyn et al., 2009), goethite-coated sand, natural sediments (Stewart et al., 2010), and clay (Joseph et al., 2013) significantly decreased in the presence of calcium ions in neutral and weakly alkaline solutions with carbonate and concluded that the formation of calcium uranyl carbonate impeded the sorption of U(VI). In the U(VI) sorption study on pristine diorite at the Äspö Hard Rock Laboratory (HRL, Sweden), the uranyl tricarbonate moiety was involved in U(VI) adsorption in the groundwater of the HRL, where $Ca_2UO_2(CO_3)_3(aq)$ is predominantly present (Schmeide et al.).

In spite of the considerable role of the uranyl tricarbonate moiety in U(VI) retention, many studies of carbonate-bearing U(VI) adsorption have exclusively reported on iron oxides (Bargar et al., 1999, 2000; Wazne et al., 2003). The participation of carbonate in U(VI) surface complexes may be dependent on the surface charge of the minerals, but the impact of carbonate on U(VI) surface complexation onto other minerals is still unclear. In addition, a very few studies have been performed using spectroscopic techniques to examine the effect of $UO_2(CO_3)_3{}^{4-}$, $CaUO_2(CO_3)_3{}^{2-}$, and $Ca_2UO_2(CO_3)_3(aq)$ on U(VI) surface complexation.

The purpose of this work is a spectroscopic identification of U(VI) complexation on γ-alumina in aqueous systems where the uranyl tricarbonate moiety is predominant. For this purpose, two types of spectroscopy, TRLFS (time-resolved laser fluorescence spectroscopy) and ATR-FTIR (attenuated total-reflectance Fourier transform infrared) spectroscopy have been employed complementarily. TRLFS is a very sensitive tool for the study of U(VI) and thus has been introduced for investigating the chemical behavior of U(VI) not only in aqueous solutions but also at mineral-water interfaces. Here, the spectral properties obtained from U(VI) species chemical behavior onto γ-alumina was analyzed for U(VI) surface speciation. ATR-FTIR and electrophoretic mobility measurements were utilized to identify U(VI)-carbonato complexation on the γ-alumina surface.

2. Experimental section

2.1. Materials

The specific surface area of γ-alumina (Sigma-Aldrich 544833) was measured to be $141.5 \pm 0.5\,m^2/g$ using the N_2-BET (Brunauer-Emmett-Teller) method. Scanning electron microscopic (SEM) images and XRD patterns of γ-alumina are given in the Supplementary Material.

Solutions with a concentration of 89 μM U(VI) were prepared to form the uranyl tricarbonate moiety (i.e., the UO_2-CO_3 sample) by diluting a stock solution of $UO_2(NO_3)_2{\cdot}6H_2O$ (Merck) in 0.83 M $HClO_4$. The initial carbonate concentration of the UO_2-CO_3 samples was adjusted to 0.025 M by addition of Na_2CO_3. The pH was adjusted by $HClO_4$/NaOH in the range of 7.5–9.0. For the subsequent complexation of calcium uranyl carbonate $Ca(ClO_4)_2$ was spiked to the UO_2-CO_3 samples. The Ca-UO_2-CO_3 samples were filtered through a 20 nm syringe filter to remove precipitates of $CaCO_3(s)$. After filtration, the calcium concentration in the Ca-UO_2-CO_3 samples was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) from 0.6 to 3.3 mM. Prior to sorption experiments, TRLFS measurements of the UO_2-CO_3 and the Ca-UO_2-CO_3 samples were carried out to confirm the formation of the uranyl tricarbonate and calcium uranyl carbonate complexes. TRLFS results of the solutions showed comparable spectroscopic data with the previous study (Lee and Yun, 2013) in terms of fluorescence spectra and lifetimes, indicating the successful formation of $UO_2(CO_3)_3{}^{4-}$, $CaUO_2(CO_3)_3{}^{2-}$, and $Ca_2UO_2(CO_3)_3(aq)$. In addition, the calculation of aqueous U(VI) speciation based on thermodynamic data suggested the predominance of the uranyl tricarbonate moiety in UO_2-CO_3 and Ca-UO_2-CO_3 samples (Supplementary Material). For comparison, 10 μM U(VI) solutions were prepared at pH 7.5 and 9.0 under an Ar atmosphere ($O_2 < 5$ ppm) and 23 μM U(VI) solutions were prepared containing 3×10^{-4} M Na_2CO_3 (low carbonate condition) at pH 7.5. The ionic strength of all solutions was maintained at 0.1 M with H/$NaClO_4$. All samples were prepared using deionized water (18.2 MΩ) at room temperature (22–26 °C). At the 3×10^{-4} M carbonate concentration, the U(VI) speciation was calculated using the OECD-NEA database (Guillaumont et al., 2003) with PHREEQC 3.0 software (Parkhurst and Appelo, 2013). The formation constants of the uranyl species at an ionic strength of I = 0.1 M were corrected using the specific ion interaction model (SIT) (Ciavatta, 1980).

2.2. Sorption experiment

The batch sorption experiments were carried out by mixing the prepared U(VI) solutions and γ-alumina in 15 mL polypropylene centrifuge tubes. The γ-alumina was blended with the prepared U(VI) solutions at a solid/liquid ratio (SLR) of 5 g/L. The suspensions were stirred for 2 days (a preliminary experiment indicated that the adsorption reached equilibrium after 1 day). During the sorption experiments, the pH was monitored and remained stable within ± 0.1. After 2 days of reaction time, the solid and liquid phases were separated by centrifugation (30 min at 9360 g, Hanil Scientific Inc., Smart R17 Plus) and then syringe-filtered with a pore size of 20 nm. The separated solids were investigated using TRLFS. Inductively coupled plasma-mass spectrometry (ICP-MS) was employed to measure the amount of U(VI) remaining in the supernatants. The tube wall sorption was observed in the sample under an Ar atmosphere (< 3% of the initial U(VI)) and the U(VI) loss by adsorption to the container for the other samples was negligible. All batch sorption experiments were performed in triplicate at room temperature (22–26 °C).

2.3. TRLFS analysis

For fluorescence spectroscopic measurements on aqueous U(VI) species in prepared U(VI) solutions and adsorbed U(VI) species on γ-alumina, aqueous and suspended samples were exposed to the fourth harmonic beam (266 nm) of a Nd:YAG laser (Quantel Brilliant, pulse duration: 6 ns, and pulse frequency: 10 Hz). The emitted fluorescence of the samples was transferred to a Czerny-Turner spectrometer (Andor, SR-303i-A) coupled with an ICCD camera (Andor, DH734-18F-C3) via an optic fiber. A fluorescence standard reference material (NIST, SRM 936a) was utilized to calibrate the spectral responsivity over the wavelength region of interest. To measure the fluorescence of the U(VI) species adsorbed onto minerals, a separated solid was re-suspended after the sorption experiments by adding background electrolyte with the same pH, initial concentration of carbonate, and ionic strength to the original aqueous solutions. The suspended sample was stirred during TRLFS measurements. The Voigt function was used for fluorescence peak fittings. All TRLFS measurements were performed at room temperature (22–26 °C).

2.4. ATR-FTIR analysis

Suspensions were prepared for the ATR-FTIR spectroscopic analysis of the U(VI) species adsorbed onto γ-alumina. The chemical condition of the γ-alumina suspension was very similar to that of TRLFS, except that the ionic medium changed from H/$NaClO_4$ to H/NaCl. For preparing the γ-alumina suspension in the carbonate-containing system, γ-alumina particles were dispersed in 0.025 M Na_2CO_3 solution with 5 g/L SLR. The initial U(VI) concentrations in the suspensions were 10^{-4} and 10^{-3} M by diluting a stock solution of $UO_2(NO_3)_2{\cdot}6H_2O$ (Merck) with 0.1 M HCl. The ionic strength was maintained at 0.1 M with NaCl and the pH was adjusted to 7.5 with HCl. After 2 days, γ-alumina was separated in the suspension by centrifugation (30 min at 9360 g, Hanil Scientific Inc., Smart R17 Plus) and then re-dispersed by addition of an aliquot of supernatant to obtain a high SLR of approximately 500 g/L. For comparison, a 5 mM U(VI) solution was prepared at pH 8.8 and 0.1 M H/$NaClO_4$. U(VI)/γ-alumina suspensions and U(VI) aqueous