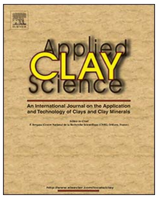
Applied Clay Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Applied Clay Science

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



Research paper

Exploring the relationship between Th(IV) adsorption and the structure alteration of phlogopite

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ARTICLE INFO

Keywords:
Thorium
Adsorption
Phlogopite
Structural transformation
Alteration

ABSTRACT

The adsorption of Th(IV) and the structural transformation of phlogopite were explored using batch, extraction, and spectroscopic approaches in this study. The batch experiments showed that ion exchange, surface complexation, and precipitation were predominant for Th(IV) adsorption on phlogopite under the observed pH ranges. XRD patterns showed that phlogopite was indeed transforming into the vermiculite- and/or montmorillonite-like minerals during Th(IV) adsorption, which indicated that the adsorption of Th(IV) could enhance the weathering process of phlogopite. Such weathering process could be attributed to the intercalation of hydrated Th(IV) ions instead of K^+ ions locating at the interlayer sites, and then induced the expansion of the interlayer with a d-spacing of ~14 Å. Higher temperature and initial Th(IV) concentration were benefit for the structural transformation, but the presence of alkaline cations inhibited the expansion process following the order of $Rb^+ > K^+ > Na^+ \approx Li^+$, which is strictly consistent with their hydrated radii and energy. Fulvic acid (FA) affected the distribution of Th(IV) on phlogopite to a large extent, which induced different adsorption mechanisms for Th(IV) and the alteration process of phlogopite structure. The results clearly showed a positively relationship between the immobilization ability for Th(IV) and alteration degree of phlogopite structure, which is very important to understand the mutual interaction of radionuclides and micaceous minerals in the environment.

1. Introduction

Fission-based nuclear energy provides reliable power as the 21st century unfolds, responding to the enormous threat of global climate change and the decreasing availability of fossil fuels (De Robbio 2011). The management of irradiated/spent nuclear fuel is one of significant challenges for the development of nuclear power, which still desiderates many technical improvements, such as the remediation of contaminated surrounding soils and groundwater by radionuclides (Stout et al. 2006; Wu et al. 2016; Pan et al. 2017). Thorium (Th) is a potential alternative solution for energy sources because of its abundant storage and low price, especially less producing of plutonium and radioactive waste in comparison with uranium fuel (Heuer et al. 2014; Torapava et al. 2009). The early strip-mining, however, has contaminated the surrounding in ways of radiation hazard, heavy metals and ammonia-nitrogen pollution, and acid pollution, which can threaten the atmosphere, the aquatic ecosystem and the edatope at a long-term perspective (Gammons et al. 2003; Garcıa-Sánchez et al. 1999; Kumar et al. 2008; Zhu et al. 2015).

As a lithophile element, dissociative Th(IV) prefers to enrich in silicate minerals, for example, micaceous minerals (Larimer and Anders 1970). As is well known, the typical dioctahedral and trioctahedral micas behave differently in surface characters and adsorption ability, which is directly due to the dissolution of potassium ions from their surface and interlayer. The dissolution of K^+ is affected generally by the orientation of hydroxyl and the charges in octahedral sheet caused by isomorphous replacements (Ames 1983; Maslova et al. 2004). In trioctahedral micas, each hydroxyl ion locates above three Mg^{2+} ions and under one K^+ ion, and the dipole orients perpendicular to the octahedral layer and, accordingly, perpendicular to the cleavage planes (Maslova et al. 2004). The special arrangement, thus, implies that the interlayer-K^+ presents an increasing mobility relative to dioctahedral

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https://doi.org/10.1016/j.clay.2017.11.026
Received 10 July 2017; Received in revised form 17 November 2017; Accepted 20 November 2017

Please cite this article as: Wu, H., Applied Clay Science (2017), https://doi.org/10.1016/j.clay.2017.11.026

micas (Righi et al. 1999; Środoń 1999). A fast chemical weathering can happen from mica structure to vermiculite- and/or montmorillonite-like structure in the presence of coexisted ions and proton attack. All of above is the characteristics phlogopite possessed, and the superior adsorption performance and mix-layer structure can be observed (Bigham et al. 2001; Righi et al. 1999; Środoń 1999).

Generally, adsorption capacity of geologic materials is commonly evaluated by cation exchange capacity (*CEC*) (Loomer et al. 2013; Pan et al. 2017). However, our work showed that *CEC* cannot precisely estimate the adsorption capacity of minerals in the case of the structural alteration during the adsorption process (not published). Several cations with hydrated radius close to K^+ (1.38 Å), such as Cs^+, Ca^{2+}, and Mg^{2+}, are able to interact with the interlayer sites and resulted in the changes of adsorption ability and capacity (Tamura et al. 2014). Hitherto, there are no reports on discussing how a large hydrate cation, as an example of Th(IV) with high hydrate energy (−6136 kJ/mol), is contributing to the structural transition of micas (Bushiri et al. 2013; Smith 1977). However, it is essential and critical to evaluate the migration, enrichment, diffusion, and redistribution of Th(IV) and to draw up a suitable plan for in-situ remediation around mill tailings.

In this study, batch experiments and X-ray diffraction (XRD) characterization were adopted to explore the interaction and mechanism between Th(IV) and phlogopite, including the synchronous alteration of phlogopite structure. The effect of the polluted factors was discussed in detail, including pH, temperature, and the competitive cations. The contributions of the different adsorption sites (mainly planar site and interlayer site) on phlogopite were also evaluated through the sequential extractions. These studies are essential to clarify the migration behavior and environmental risk of Th(IV) and the chemical weathering of phlogopite.

2. Experimental

2.1. Materials

All chemicals were purchased at analytic purity and used without any further purification. Phlogopite was sourced from Lingshou County (Hebei, China), and prepared in Milli-Q water (18.2 Ω) as a stock suspension, which was equilibrated in aqueous phase for 3 months before the characterization and batch experiments. Th(IV) stock solution was prepared by dissolving thorium nitrate tetra-hydrate ($Th(NO_3)_4 \cdot 4H_2O$) in the Milli-Q water and kept at pH ~3.0 by adding negligible hydrogen nitrate. Fulvic acid (FA) extracted from natural soil had been characterized previously (Fan et al. 2008).

2.2. Batch experiments

All batch experiments were carried out at ambient conditions. The particular amount of stock solutions of back-ground electrolytes (i.e., Li^+, Na^+, K^+, and Rb^+), Th(IV), FA, and phlogopite suspension were added in 10 mL polyethylene test tubes with scrap to achieve the desired concentrations, and the total volume was maintained at 6.0 mL with Milli-Q water. For each system, pH values were adjusted by adding the negligible $HClO_4$ and/or NaOH solution, and then put them into an incubator shaker (IS-RDD3, Crystal Technology & Industries, Inc.) in a given contact time and temperature. After the adsorption achieved equilibrium, solid and liquid phases were separated by centrifugation at 12,000 rpm for 30 min. Concentrations of Th(IV) and FA in the supernatant (equilibrium concentration, C_e, mol/L for Th and mg/L for FA) were analyzed by spectrophotometry methods at visible (660 nm with Arsenazo III) and ultraviolet wavelength regions, respectively. It was verified that the presence of FA had no effect on Th(IV) determination. The adsorption percent, concentration in solid phase (C_s, mol/g for Th (IV) and mg/g for FA), and solid-liquid partition ratio (K_d, L/g) are calculated as follows:

$$Adsorption\,(\%) = (C_0 - C_e)/C_0 \times 100\% \quad (1)$$

$$C_s = (C_0 - C_e)/(s/l) \quad (2)$$

$$K_d = C_s/C_e \quad (3)$$

where C_0 (mol/g for Th(IV) and mg/g for FA) is the initial concentrations of Th(IV) or FA, and s/l (g/L) is the solid-to-liquid ratio in the adsorption system. All the experimental data were the averages of duplicate or triplicate experiments, and the relative errors of the data were less than 5.0%.

2.3. Effect of FA addition sequence

In the following four control tests, the detailed methods are identified to the Section 2.2.

(1) **System I** [Phlogopite + Th(IV)]: 0.6 g/L phlogopite suspension was pre-equilibrated with the variable concentrations of Th(IV) solution for 48 h (I = 0.01 M $NaClO_4$, at ambient temperature).
(2) **System II** [{Phlogopite + Th(IV)} + FA]: 0.6 g/L phlogopite suspension was pre-equilibrated with the variable concentrations of Th (IV) solution for 24 h (I = 0.01 M $NaClO_4$, at ambient temperature). Then, 48 mg/L FA solution was added, and the systems were shaken for another 24 h.
(3) **System III** [Phlogopite + {Th(IV) + FA}]: a series of Th(IV) solution was pre-equilibrated with 48 mg/L FA for 24 h. Then, phlogopite suspension (0.6 g/L) was added, and the systems were shaken for another 24 h.
(4) **System IV** [{Phlogopite + FA} + Th(IV)]: 0.6 g/L phlogopite suspension was pre-equilibrated with 48 mg/L FA for 24 h (I = 0.01 mol/L $NaClO_4$ solution, at ambient temperature). Then, a series of Th(IV) solution were added, and then the systems were shaken for another 24 h.

2.4. Sequential extraction

Sequential extraction was performed to identify the adsorption mechanism of Th(IV) on phlogopite in the binary (FA-free) and ternary (the presence of FA) systems according to the well-developed method (Guo et al. 2007; Martin et al. 1998; Rauret et al. 1999). In the sequential extracted experiments, Ca^{2+} was used to replace the weak adsorption species formed with basal/edge sites, such as the ion exchange and outer-sphere complex, and NH_4^+ was used to extract intercalated Th(IV) (Petit et al. 1999; Rigol et al. 1998; Springob 1999).

Here, Th(IV)-loading phlogopite samples were strictly identical to those in the Section 2.3. After adsorption experiments, solid samples were recovered and rinsed rapidly with Milli-Q water for the subsequent extraction experiments. Extracted fractions were defined as follows: (i) fraction 1 (F_1) extracted by 1.0 M $CaCl_2$ solution, which is classified as the ion exchange and outer-sphere complex species, (ii) faction 2 (F_2) extracted by 1.0 M ammonium acetate (NH_4OAc) solution, which is assigned to the adsorbed Th(IV) locating at the interlayer sites of phlogopite (Martin et al. 1998; Virtanen et al. 2013), and (iii) residual fraction (F_3), involving inner-sphere complex species coordinated with oxygen on phlogopite and/or oxygenated groups of FA. The contents of Th(IV) in each fraction was determined by spectrophotometry method as mentioned in the Section 2.2.

2.5. Characterization

Solid samples were recovered and vacuum freeze-dried for the subsequent characterization and measurements. Compared with air-dried method, vacuum freeze-drying is much more likely to show up the adsorption state at the phlogopite/water interface (Liu et al. 2000). X-Ray fluorescence (XRF) was performed with the XRF Panalytical Magix PW2403 spectroscope. Brunauer-Emmett-Teller (BET) surface area was