

Luminescence Studies of U(VI)-Laponite System in Aqueous Phase

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1. Introduction

Mineral surface adsorption of radionuclides is one of fundamental geochemical processes to be elucidated for long-term safety analysis of deep geological disposal techniques of spent fuels. Uranium(VI) adsorption onto clay minerals has been studied to understand the sorption mechanism particularly at the surface of the characteristic platelet structures. For decades time-resolved laser-induced fluorescence spectroscopy (TRLFS) has been a valuable tool for the chemical speciation of U(VI) adsorbed on various mineral phases. Although the surface-adsorbed U(VI) species exhibit strong luminescence enhancement in general, however, the TRLFS-based U(VI) speciation data of colloidal mineral phases are still limited and inconsistent within literature available [1].

In this study, we attempt to understand the basic U(VI) luminescence characteristics arising from the interaction with a synthetic nano-clay mineral, i.e., Laponite RD[®]. Although laponite shares a 2:1 silicate structure with the smectite natural clays such as montmorillonite, its primary particles are fairly monodispersed with a disk-like shape having a diameter in the range 25–30 nm and thickness of 0.92 nm. So, it offers a large area of surface binding sites, particularly from the edge of the platelet structures. At low concentration it can form a homogeneous and transparent aqueous solution depending on pH and electrolyte concentrations (ionic strength). Thus, U(VI)-laponite system can be a good model system for investigating U(VI)-clay interactions and speciation using TRLFS.

2. Results and Discussion

2.1 Properties of laponite aqueous solutions

Laponite RD[®] (Southern Clay Products Inc. USA) was used as received. It forms highly thixotropic, clear gels when dispersed in water at a 2 wt% concentration. In this study the final concentration of

laponite in aqueous samples was maintained at 0.1–0.2 wt%, where completely dissolved forms of laponite can be obtained. Due to the non-spherical shape of laponite platelets, the particle size distribution appears multi-modal when analyzed using dynamic light scattering (DLS) (Zetasizer NanoZS, Malvern), as shown in Fig. 1. It is evident that at such low concentration levels cluster or aggregate formation of laponite particles is effectively suppressed for more than a week.

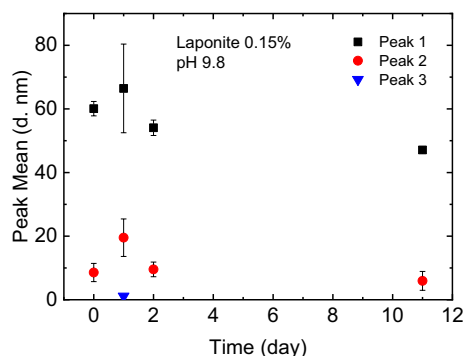


Fig. 1. Monitoring the particle size distribution of an aqueous sample containing 0.15% Laponite (pH 9.9). DLS analysis results show 2-3 main peaks at different sizes.

2.2 U(VI) sorption equilibria

Strong sorption behaviors of U(VI) are observed in a wide pH range, i.e., 4–9. When monitored using an ultracentrifuge technique, only trace amount of U(VI) is detected in a supernatant solution in this pH range after the removal of laponite-gel precipitates. (data not shown). Thus, we conclude that the majority of U(VI) exists in forms of surface complexes on the laponite nano-colloids in the pH region explored in this study. The zeta potential values of the aqueous U(VI)-laponite colloidal system are measured in the range of -30 ~ -40 mV, which indicates the negative charges of the basal plane of clay particles play dominant role in the colloidal behaviors of laponite. In recent studies, however, the U(VI) sorption equilibrium on smectite clay occurs primarily via the reactive edge sites, i.e., silanol ($\equiv\text{SiOH}$) and aluminol ($\equiv\text{AlOH}$) surface groups [2,3].

2.3 TRLFS study of U(VI)-laponite system

For TRLFS study a pulse laser (355 nm, 2~3 mJ) was used with a repetition rate of 10 Hz. An intensified CCD (iStar, Andor Technol.) was employed for the gated detection of luminescence. Deconvolution of TRLFS data using PARAFAC analysis was carried out by implementing N-way331 in Matlab [4]. Ten data sets of 10 μM U(VI) in a pH range of 7 to 10 were analyzed (0.1 wt% of laponite). Deconvolution with three components converged with a core-consistency value (75%). Details of TRLFS techniques and spectral deconvolution methods will be discussed in the presentation. The summarized results of the PARAFAC analysis with three components are shown in Figs. 2-3.

In this study our investigation aims to analyze the long lifetime luminescent species, of which typical luminescence lifetimes are $> 50 \mu\text{s}$. Fig. 2 displays the deconvoluted luminescence spectra of three major U(VI) species identified from the PARAFAC analysis. Interestingly, the species of the longest lifetime appears as a dominant adsorbed species at $< \text{pH } 7.5$ (A in Fig. 2).

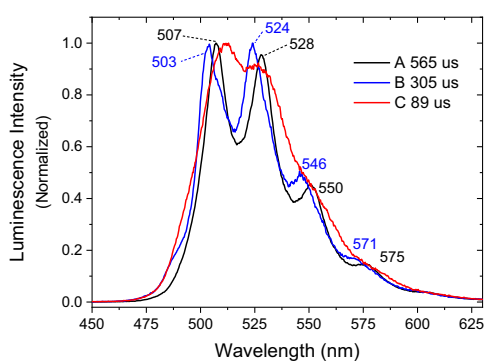


Fig. 2. Normalized deconvoluted luminescence spectra of the three U(VI) species adsorbed on laponite at pH 7-10. The luminescence lifetime of each species is shown in the legend.

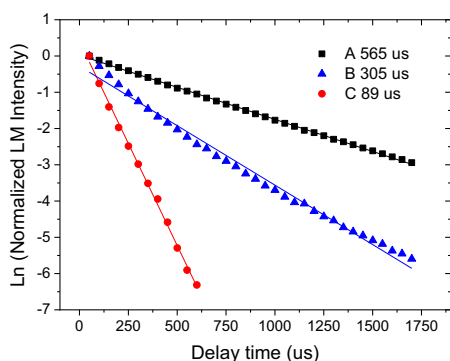


Fig. 3. Luminescence decays of the three species of Fig. 2 as a function of delay time.

On the other hand the species B and C are observed at higher pH regions, i.e., 7.5-8.5 and > 8.5 , respectively. Species C is found to contribute to the featureless luminescence spectra with absence of the multiple peak pattern at higher pH region. Combined with the batch sorption results we conclude that all three U(VI) species represent adsorbed species on laponite, specifically inner-sphere complexes at edge sites of the plate structures. More details will be discussed in the conference presentation.

3. Conclusion

By using a synthetic nano-clay mineral material (laponite) and TRLFS techniques the fundamental sorption behaviors of U(VI) were investigated. Luminescence kinetic data were deconvoluted using PARAFAC analysis and examined with the results from on the batch sorption equilibrium analysis. Three major luminescent U(VI) species are identified, each of which appears as an adsorbed species on laponite in a pH-dependent manner.

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