PC03: การวิเคราะห์รูปแบบการยึดจับของยูเรเนียม (VI) กับชั้นแร่ โดยเทคนิค time-resolved laser-induced fluorescence spectroscopy

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บทคัดย่อ

การเคลื่อนย้ายของสปีชีส์ของยูเรเนียม เกิดจากกองหินและเหมืองแร่เก่าถูกชะล้างโดยน้ำผิวดินเป็นส่วนนใหญ่ จำเป็นต้องมีการศึกษาเส้นทางการเคลื่อนที่ สปีชีส์ และปริมาณของสารประกอบยูเรเนียมที่เคลื่อนย้าย วัตถุประสงค์ของการวิจัยนี้คือการวิเคราะห์อัตรกิริยาระหว่างชั้นแร่ที่เป็นของแข็ง กับสปีชีส์ของยูเรเนียมที่เคลื่อนที่ในรูปแบบต่าง ๆ เช่นการดูดซับ การตกตะกอน และการเกิดเป็นแร่ยูเรเนียมทุติยภูมิ โดยใช้เทคนิค time-resolved laser-induced fluorescence spectroscopy (TRLFS) ซึ่งสามารถวิเคราะห์สปีชีส์ของยูเรเนียมปริมาณน้อย ซึ่งให้สัญญาณฟลูออเรสเซนที่มีลักษณะเฉพาะ ได้แก่ความเข้มข้น และ สมบัติเฉพาะของสปีชีส์ของยูเรเนียมที่เกิดการเรืองแสงในตัวอย่าง ซึ่งมีสอง ลักษณะเฉพาะคือ ตำแหน่งของพีคที่มีค่าสูงสุด และระยะเวลาของการเกิดสัญญาณ เทคนิคนี้ไม่เพียงแต่ใช้วิเคราะห์ยูเรเนียม (VI) ในสารละลายน้ำเท่านั้น แต่ยังใช้วิเคราะห์ยูเรเนียมที่เคลือบบาง ๆ บนของแข็งได้ด้วย ผลวิเคราะห์การดูดซับยูเรเนียม (VI) ในผิวแร่กิบบ์ไซต์ และมัสโคไวต์ได้แสดงไว้ในงานวิจัยนี้ สัญญาณสเปกตรัมบ่งชี้ของยูเรเนียม (VI) มีประโยชน์ในการวิเคราะห์รูปแบบการยึดจับของยูเรเนียมที่อยู่ในรูปต่าง ๆ เช่น คอลลอยด์ ยูเรเนียมที่เคลือบบาง ๆ อยู่บนหิน ที่เป็นส่วนประกอบเล็กน้อยในดิน และในผลผลิตจากกากนิวเคลียร์

คำสำคัญ: **เหมืองแร่ยูเรเนียม, ยูเรเนียม (VI), time-resolved laser-induced fluorescence spectroscopy**

The Analysis of Uranium Binding Form with Mineral Phases by Time-resolved Laser-induced Fluorescence Spectroscopy

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Abstract

Uranium migration is mainly occurred when mobile uranium species from rock piles and old mines are washed by surface water. It is necessary to study the pathway, the species, and the amount of migrating uranium compounds. The objective of this research is to investigate the interactions between solid mineral phases and

mobile uranium species such as sorption, precipitation and forming secondary uranium minerals by time-resolved laser-induced fluorescence spectroscopy (TRLFS). This technique has shown to be able to detect a trace amount of uranium (VI) species in both solution and solid phases. TRLFS delivers a fluorescence signal with characteristic features related to the concentration and speciation of fluorescent species in the sample. These features include, the positions of the peak maxima, and characteristic lifetimes of the signals. Results show fluorescent signals of absorbed uranium species on gibbsite and muscovite surfaces. The spectroscopic signatures of these uranium (VI) minerals are useful in identifying uranium (VI) species as colloids, thin coatings on rocks, minor components in soils, or alteration products of nuclear waste.

Keywords: Keywords: Uranium mining, uranium (VI), time-resolved laser-induced fluorescence spectroscopy

1. Introduction

An improved understanding of the mechanisms of radionuclide sorption on rocks and soils is predominantly based on the identification of the coordination environment of the adsorbed radionuclide species on respective minerals. Knowledge about the dispersal behaviors of mobile uranium in the surrounding of former mining facilities and stock piles caused by uranium mining is necessary in order to get an appropriate risk assessment for the environment. Floating fluids like water in the environment would contact soils and rocks. If those fluids come in contact with uranium bearing solids, they will take up uranium in a special extend and transport it away. Later, if external conditions like temperature or pH value would be different, the uranium could leave the fluid phases. We have to know, in which way and amount that uranium originated from the fluids will be received by solid phases. With known sorbed species, the sorption reaction equations are known. That equations help to find all thermodynamic data which are necessary for calculating the sorption capacity of a rock by means of special computer programs. Soils and rocks are assembled by different small mineral particles. Therefore, it is important to investigate the sorption behaviors of the single minerals as little parts to get a comprehensive picture about sorption behaviors of the rocks in the surrounding of uranium mining facilities. A similar scenario would be essential for the nuclear waste disposal sites as well. The biggest sorption capacity will have minerals with a big specific surface. In this present study, the mineral gibbsite, as a relative simple hydroxide, and the mineral muscovite, as a more complex mica, were investigated by TRLFS as a first step in the direction to describe the sorption behaviors of the whole rocks.

2. Materials and Experiments

2.1 Mineral samples

Gibbsite is a mainly occurring weathering product of Al containing and rock forming minerals. The gibbsite used in this work, hydrargillite [$AlH_3O_3 \cdot xH_2O$], was purchased from Merck. The average particle size of the powder was 12.2 μm, determined by laser diffraction device. The specific surface area of the gibbsite was determined with a five-point N_2-BET, yielding 1.5 m^2/g.

Muscovite, a dioctahedral 2:1 phyllosilicate (ideally $KAl_2[Si_3AlO_{10}](OH)_2$), is a common rock-forming mineral and major constituent of many rocks and thus a potentially important sorbent of uranium. In principle, there are three possible binding sites for heavy metals on muscovite: (1) adsorption to the basal plane surface through equatorial coordination of the heavy metal with two adjacent surface oxygen atoms from a siloxane [SiO_4] tetrahedron, (2) cation exchange for interlayer potassium, and (3) adsorption onto the aluminol groups in octahedral coordination of the muscovite edge-surfaces. The investigations presented here were made on muscovite platelets of approximately 1 cm^2 and 5 mm thick.

2.2 Sorption experiments on gibbsite

The batch experiments concerning the sorption behavior of uranyl on gibbsite were carried out in air atmosphere at an ionic strength of 0.1 M $NaClO_4$ and at different pH values with a stepping of 0.5 from 3.5 to 9.5. For each point, 0.5 g gibbsite was weighed in polyethylene tubes, and 40 ml $NaClO_4$ solution was added. Then the pH was adjusted by NaOH and $HClO_4$ solutions, controlled and readjusted over two weeks. After uranium was added, the pH value was readjusted again. After a contact time of 2 days in the overhead mixer the gibbsite was separated by centrifugation, and the uranium in the centrifugation was measured by ICP-MS.

2.3. Sorption experiments with muscovite

Muscovite platelets of approximately 1 cm^2 and 5 mm thick were immersed in 0.01 M $NaClO_4$ solution, and the pH was adjusted to 7.0. At this pH a maximum of uranium (VI) sorption had been expected. The pH was readjusted each day until it was stable. A uranyl (VI) stock solution was added to achieve a total uranium (VI) concentration of 1×10^{-5} M. A contact time of 60 h ensured complete U (VI) sorption. Then the final pH was measured, and the uranium concentration

in solution was determined by ICP-MS. With the obtained uranium contents in solution and on the container walls, the total amount of sorbed uranium was calculated; 72.6% ± 5% of the initially added U (VI) was adsorbed.

2.4. TRLFS for analyzing the uranyl sorption on mineral surfaces

The method is usable for fluorescent ions such as U (VI) or Cm (III), Am (III), Np (III) and Eu (III) – U (VI) signals could be evaluated until concentrations down to 10^{-8} M U. U (VI) and its compounds shows a characteristic fluorescence spectrum, with a typical position of peak maxima and a typical fluorescence life time, both characteristic for the U (VI) speciation. The TRFL spectrum from a U (VI)-species usually has 6 maxima. The life time of a fluorescence signal depends from character and number of signal quenching species in the closest neighborhood from the U atom, the so called “quenchers”.

TRLFS system consists of a Nd:YAG diode laser, with an excitation wavelength of 266 nm. The emitted fluorescence radiation was focused into a spectrograph and the resulting spectra were measured by a diode array. The delay time after the excitation laser pulse ranged from 0 to 6500 ns. For further details concerning the set up of the TRLFS equipment and operation modes, see Geipel et al.[1] Every spectrum was measured 3 times, for each spectrum 100 laser shots were averaged. 31 spectra at steadily increasing delay times were collected totally for one time-resolved spectrum. The evaluation of spectroscopic data was performed with in-house software by Brendler *et al*[2] to obtain the fluorescence lifetimes and the single component spectra. The fluorescence decay function was determined, and the best approximation gave a bi-exponential decay function $y = y_0 + A_1e^{-(x-x0)/t1} + A_2e^{-(x-x0)/t2}$ yielding two fluorescence decay times t_1 and t_2.

3. Results and Discussion

3.1 TRLFS on gibbsite

The TRLFS spectrum of the uranium sorbed on gibbsite at pH 6 is shown in Fig. 1. The peak at 532 nm is the laser-dispersions peak (second order of excitation radiation at 266 nm). The percentage of uranyl(VI) sorption vs pH, between pH 3.5 and pH 9.5 is showed in Fig.2.

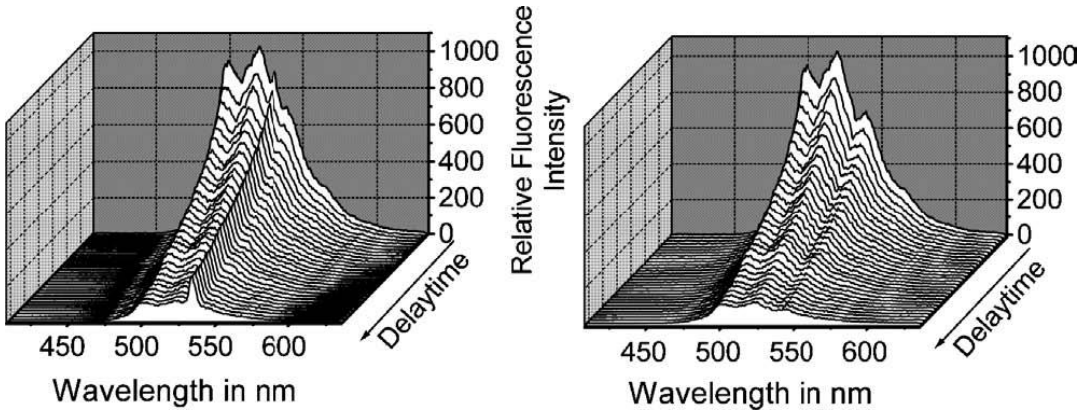

Fig. 1 TRFLS spectra of U(VI) sorbed onto gibbsite at pH 6, the left side showing the raw spectra, and the right side giving the spectra after correction for the laser dispersion peak.

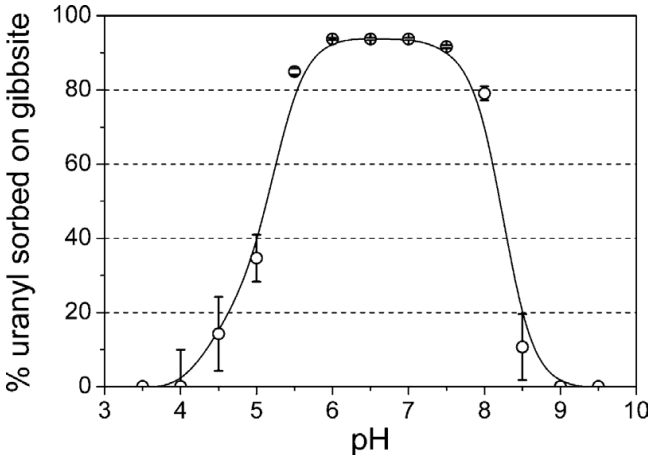

Fig. 2 U(VI) sorbed onto gibbsite vs pH (sorption curve)

TRLFS measurements were carried out on the above described samples to obtain spectroscopic information on the adsorbed uranyl(VI)-gibbsite surface species. These investigations on fluorescent uranium(VI) species yield two kinds of characteristic information: the position of the fluorescence emission bands and the fluorescence lifetime.[3] The fluorescence lifetime varies depending on the number of neighboring water molecules surrounding the uranium(VI) atom. Such characteristic spectral information is then useful in identifying fluorescent aqueous uranium species as well as uranyl(VI) surface species adsorbed on minerals.

Fig. 3 shows the determination of the fluorescence lifetime of uranyl(VI) sorbed onto gibbsite at pH 6. The samples at pH below 5 or above 8.5 with very weak signal intensities due to low sorption ratios, could not be processed in this way and are therefore omitted.

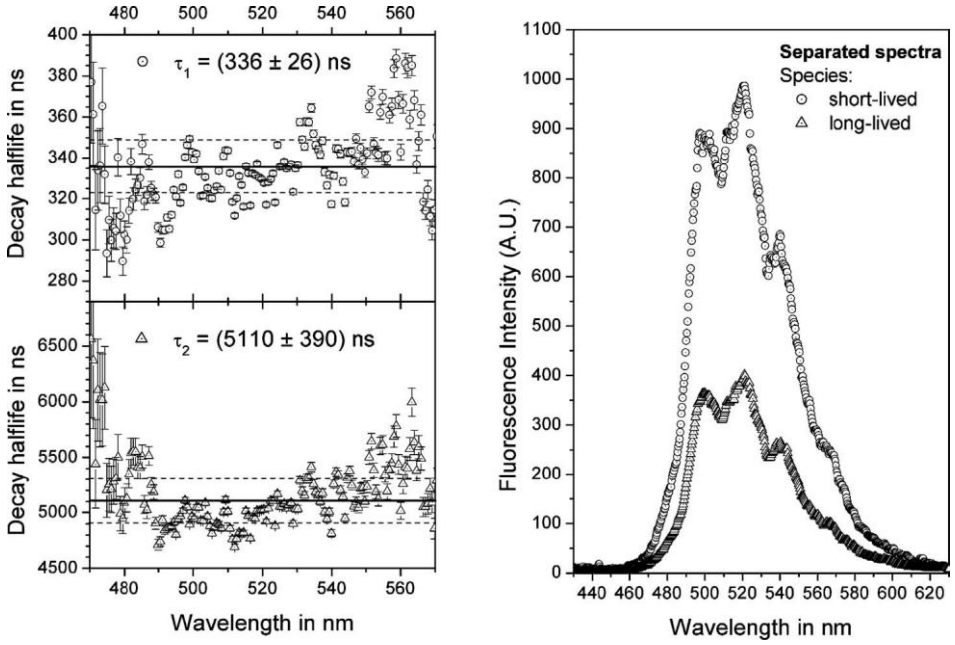

Fig.3 Fluorescence decay lifetimes of U(VI) sorbed onto gibbsite at pH 6 (left-hand side) with the solid line marking the average and dashed lines giving the uncertainly limits of the mean (error 2 σ) and a single component spectra (right-hand side)

Two different fluorescence lifetimes indicating two uranyl surface species on gibbsite with a faster and a slower fluorescence decay, were identified in the pH region 5 to 8.5. Those lifetimes are t_1 = 330 ± 115 ns and t_2 = 5600 ± 1640 ns, representing the short and the long-lived species, respectively. The deconvoluted fluorescence spectra reveal six characteristic fluorescence emission bands that are almost identical for both uranyl (VI) surface species. Due to the pronounced coincidence of all the fluorescence peaks, the two adsorbed uranium (VI) surface species, i.e., the short-lived and the long-lived species, are assumed to be similar in their coordination environment throughout the investigated pH range. They should thus have identical numbers of hydroxyl groups in their first coordination sphere, as different numbers of hydroxyl groups cause changes in the spectral features.[4] Considering the discriminative fluorescence lifetimes, the two distinguishable surface species should differ only in their respective water content.[5]

From the TRFLS measurements, two adsorbed uranyl(VI) surface species on gibbsite are present. The first one with the lifetime of 330 ns is attributed to a bidentate mononuclear inner-sphere surface complex in which the uranyl(VI) is bond to two OH^- groups. The second surface species with the significant longer fluorescence lifetime of 5600 ns was attributed to small clusters

consisting of sorbed polynuclear surface species. The relative number of water molecules in the coordination environment of the uranyl atoms is smaller, because H_2O in the coordination environment of uranyl(VI) quenches the fluorescence lifetime.

3.2 TRLFS on muscovite

The fluorescence emission bands are show in Fig 4. The spectra of the basal plane surface of muscovite showed almost no U(VI) fluorescence signal, indicating that U(VI) does not significantly adsorb onto that surfaces

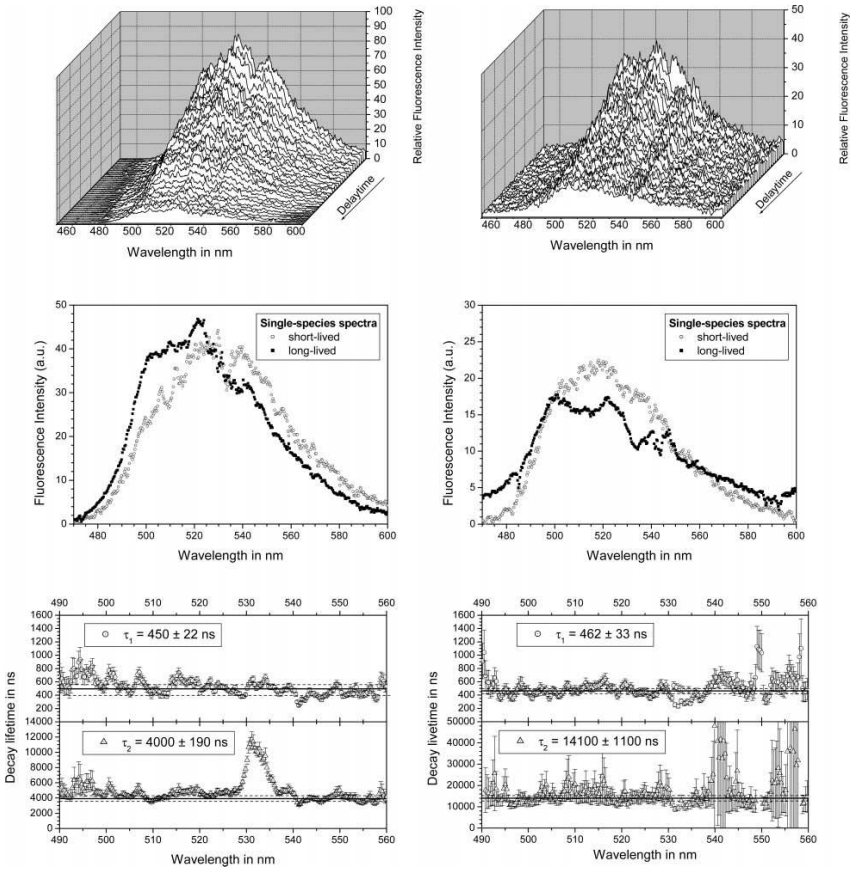

Fig.4 TRLF spectra (top); convoluted single spectra at t = 0; (middle) and fluorescence decay lifetime (bottom)

However, the strong fluorescence signal was obtained from the edge surface, showing that U(VI) adsorption occurs predominantly onto edge-surfaces. The deconvoluted TRLF spectra of the adsorbed U(VI) surface species on muscovite edges indicated two surface species with different fluorescence lifetimes: 450 ± 22 ns and 4000 ± 190 ns. The peak maxima are shifted significantly

relative to the values for the free uranyl ion in perchlorate medium. Due to the pronounced shift to higher wavelengths, it is assumed that the two adsorbed uranium(VI) edge-surface species on muscovite differ in their coordination environment. Namely, they should have different numbers of hydroxyl groups in their first coordination sphere, as different number of hydroxyl groups cause changes in the spectra features.[6] Also the different lifetimes indicate a different number of quenchers, very likely water molecules.

4. Summary

Two adsorbed uranyl(VI) surface species on gibbsite were identified in the pH range of 5.0 to 8.5 based on their fluorescence emission bands and their distinct different fluorescence lifetimes. The surface species with the short-lived fluorescence lifetime with the lifetime of 330 ns is attributed to a bidentate mononuclear innersphere surface complex in which the uranyl(VI) is bound to two reactive OH^- groups at the broken edge linked to one Al. The second surface species with the significant longer lifetime with 5600 ns, was attributed to small sorbed clusters consisting of polynuclear uranyl(VI) surface species. In this context, the longer fluorescence lifetime of the long lived uranyl surfaces species at pH 8.5 is explained by the growing average size of the adsorbed polynuclear uranyl surface species.

The surface species with the distinctively longer fluorescence lifetimes of 4000 ± 190 ns on edges of muscovite platelets are interpreted as an amorphous U(VI) condensate or nanosized clusters of polynuclear uranyl(VI) surface species with a diameter of 1-2 nm. The size of the species correlates with the fluorescence lifetime, i.e., the larger the particles, the longer the fluorescence lifetime. The precipitation of nanosized uranyl(VI) clusters that form during sorption experiments of uranyl(VI) with mineral surfaces seems to be a process that has been generally overlooked. However, to better describe and model sorption experiments, the precipitation of solid uranyl(VI) phases as nanosized, poorly crystalline particles should also, in addition to surface complexation models, be considered.

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