

## Chemical Interaction between U(VI) and Eu(III) ions on a Silica Surface

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### 1. Introduction

Understanding the chemical behavior of actinide in groundwater flow is important for assessing the possibility of its migration with water flow in the radioactive waste disposal site. Precipitation/dissolution in groundwater and adsorption/desorption onto a geological solid surface would determine its migration. The sorption in a geochemical system was expected to be a reaction on a naturally equilibrated surface. However, the construction of a waste disposal facility could disturb this equilibrium state, induce a new reaction environment and affect a nanoscopic surface reaction of actinide.

Uranium is ubiquitous in the natural environment and a representative element in a nuclear fuel cycle and in a high level radioactive waste. In oxic environments, it is typically present as uranyl oxocation ( $\text{UO}_2^{2+}$ ), which is easily adsorbed and thereby removed from a solution in the near neutral pH range. This adsorption would form a new surface condition to give an unexpected adsorption behavior for other actinide ions. Eu(III) frequently is used as a chemical analogue of Am(III) and Cm(III) in migration chemistry.

The adsorption phenomena has been interpreted with the help of a SCM (surface complexation model). Some spectroscopic techniques such as EPR (Electron Paramagnetic Resonance), IR (InfraRed), EXAFS (Extended X-ray Absorption Fine Structure) and TRLFS (Time Resolved Laser Fluorescence Spectroscopy) have been used for the identification of a modeled adsorbing species. In the case of fluorescence elements, TRLFS has advantages over other techniques for its high sensitivity being proportional to laser source intensity and good selectivity depending on specific transition and lifetime. This technique can be applied to a species on a solid surface not absorbing light such as silica. U(VI) and Eu(III) have fluorescent properties reflecting their coordination structure. In this study, the interaction between U(VI) and Eu(III) on a silica surface was studied by a fluorospectroscopic technique.

### 2. Experimental

$\text{UO}_2^{2+}$  and  $\text{Eu}^{3+}$  in a  $\text{HClO}_4$ - $\text{NaClO}_4$  (0.1 M) solution was adsorbed onto a silica (amorphous, specific surface area=375  $\text{m}^2/\text{g}$ , 8.3 g/L) by adjusting pH with  $\text{CO}_2$  free NaOH at room temperature in a nitrogen atmosphere. After equilibration for a day, the silica was separated by centrifugation (15,000 rpm, 30 min, Centrikon T-2060, Kontron), and the concentration in an aqueous phase was determined by using ICP-AES (ULTIMA2C, Jobin Yvon). The silica was transferred to an optical quartz

cell and the fluorescence was measured. The excitation spectra were measured by using a fluorospectrometer (Series 2, SLM-Aminco). The emission spectra and lifetime were measured by using TRLFS (constructed in laboratory). The experimental setup was similar to the system described in the previous work [1] (refer to Fig. 1). A pulsed Nd:YAG laser (5000 Series, B.M. Industries) operating at 355 nm (the third harmonic) with a repetition rate of 20 Hz (8 mJ) was used as the excitation source. The emitted fluorescence light was passed through a monochromator (HR-250, Jobin Yvon) coupled to a PMT (R928, Hamamatsu). The fluorescence intensity at a certain wavelength as a function of time was collected by using a digital oscilloscope (9450A, Lecroy) to evaluate the fluorescence lifetime. Fluorescence spectra were measured by using a gated integrator (SR225, SRS) with a gate delay time of 50  $\mu\text{s}$  and a gate width of 2  $\mu\text{s}$ .

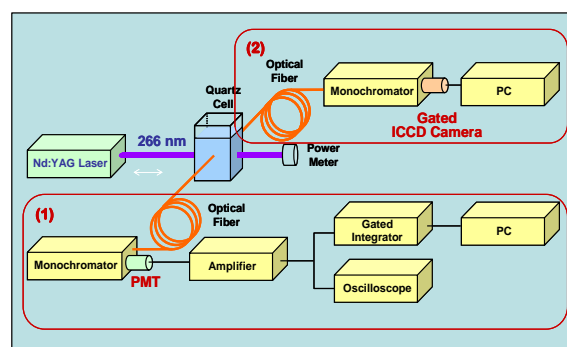


Fig. 1. Schematic diagram of TRLFS.

### 3. Results and discussion

3.1. U(VI) effect on Eu(III) adsorption. The measured sorption ratios of Eu(III) in the presence and absence of U(VI) at various pHs were shown at Table 1.

Table 1. Eu(III) adsorption at various pHs in the presence of U(VI).

[U(VI)] mM	Eu(III) ratio adsorbed (pH)			
	[Eu(III)]=0.02 mM			
0.00	0.01(4.9)	0.05(5.7)	0.50(6.3)	0.98(6.8)
0.2	0.04(4.5)	0.31(5.9)	0.74(6.3)	0.99(6.8)
1.7	0.06(5.0)	0.41(5.8)	0.83(6.3)	0.99(6.8)

The sorption of Eu(III) was increased by the presence of U(VI) in the range of adsorption edge. On considering that U(VI) has a larger adsorptivity than Eu(III) due to its higher effective nuclear charge, The adsorbed U(VI) chemically interacted with Eu(III) on a silica surface to increase its adsorption. In the solution

without complexing ligand, various hydrolyzed U(VI) species of  $\text{UO}_2(\text{OH})^+$ ,  $\text{UO}_2(\text{OH})_2^0$ ,  $\text{UO}_2(\text{OH})_3^-$ , and/or  $(\text{UO}_2)_3(\text{OH})_5^+$  were adsorbed onto a surface. The hydroxyl group of adsorbed U(VI) species provide a new site for an Eu(III) adsorption. U(VI) bridges between silica surface and Eu(III) to form a structure of  $\equiv\text{Si-O-U(VI)-O-Eu(III)}$ . The increased adsorption by U(VI) suggests that the bridged species was more stable than a directly adsorbed species of  $\equiv\text{Si-O-Eu(III)}$ .

**3.2. Confirmation of U(VI)-Eu(III) interaction by fluorescence measurement.** The formation of U(VI) bridged Eu(III) surface species could be confirmed by an Eu(III) fluorescence emission induced by U(VI) excitation. The emission spectra for U(VI)-Eu(III) on a silica surface were observed on exciting U(VI) with laser of 355 nm wavelength, where excitation of Eu(III) can be ignored, as shown in Fig. 2. The spectra showed an increasing Eu(III) emission and decreasing U(VI) emission with increasing Eu(III) concentration due to an energy transfer from U(VI) to Eu(III). Energy can be transferred from an exciting to an emitting moiety through radiation, collision and chemical interaction modes. Since Eu(III) has weak excitation bands within the emission wavelength range of U(VI), the energy transfer through radiation mode was not expected. The fluorescence quenching of U(VI) by Eu(III) in an aqueous solution was explained by a collision and/or a static mechanism involving complex formation between Eu(III) and  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  [2]. In additional experiments, the excited U(VI) on a silica surface did not transfer energy to an aqueous Eu(III) ion at pH 5. This implies that the energy of excited U(VI) was transferred only to a chemically interacting Eu(III).

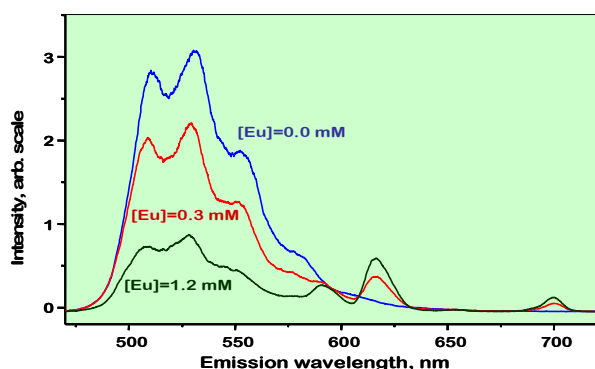


Fig. 2. Fluorescence emission spectra of U(VI)-Eu(III) on a solid surface at pH 7.  $\lambda_{\text{ex}}=355$  nm.  $[\text{U(VI)}]=0.12$  mM.

The decreasing U(VI) emission intensity with increasing Eu(III) concentration indicated a deactivation of excited U(VI) by Eu(III) due to energy transfer. This should result in a decreasing of lifetime for U(VI) fluorescence as shown at Fig. 3. The plot of logarithmic value of intensity against time shows no linearity, suggesting the presence of various species. However, the initial slope shows a rapidly decreasing lifetime with increasing Eu(III) concentration. This also implies an increased U(VI)-Eu(III) chemical interaction and

energy transfer on a silica surface with increasing Eu(III) concentration.

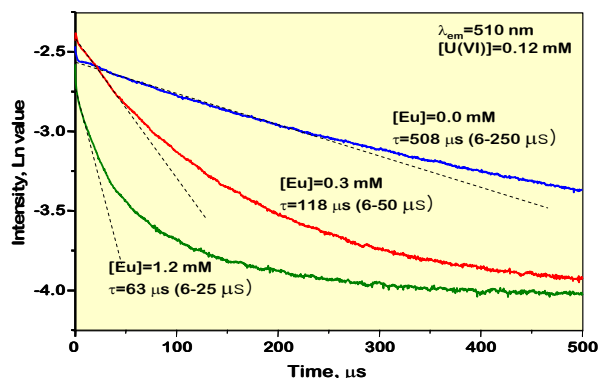


Fig. 3. Lifetime measurement of U(VI) on silica surface with Eu(III) at pH 7.

#### 4. Summary

The interaction between U(VI) and Eu(III) on a silica surface was studied by fluorospectroscopic technique. U(VI) increased the adsorption of Eu(III) by providing a new surface hydroxyl group site for the formation of  $\equiv\text{Si-O-U(VI)-O-Eu(III)}$  which was more stable than the species of  $\equiv\text{Si-O-Eu(III)}$ . This chemical interaction was supported by the energy transfer from U(VI) to Eu(III). The emission intensity of Eu(III) increased while the emission intensity and lifetime of U(VI) decreased due to an energy transfer from U(VI) to Eu(III).

#### Acknowledgements

This work was supported by the Nuclear Research and Development program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology.

#### REFERENCE

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