

## Spectroscopic properties and formation constants of ternary Ca-UO<sub>2</sub>-CO<sub>3</sub> complexes at high temperatures

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### I. Introduction

In the deep geological repository for high-level radioactive waste, the waste can come into contact with groundwater and migrate if the engineering barriers are degraded. The temperature of groundwater may be increased due to the thermal gradient (typically +3 °C/100 m) and the decay heat produced from radioactive waste. The migration behavior of uranium, which is the dominant element of spent nuclear fuel, is strongly influenced by complexation with various ions and ligands present in natural water. Especially, the ternary uranyl complexes with calcium and carbonate has been considered as main uranyl complexes in neutral and weak alkaline groundwater under ambient atmosphere. In field studies, the predominance of ternary calcium uranyl carbonate species, CaUO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>2-</sup> and Ca<sub>2</sub>UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>(aq), was clearly observed<sup>1,2</sup>. Due to the importance of these ternary species, many studies have addressed thermochemical data of CaUO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>2-</sup> and Ca<sub>2</sub>UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>(aq)<sup>3-5</sup>. However, all data have been produced at room temperature and no result has been reported on temperature effect. The main objective of this work is the determination of spectroscopic properties and the formation constants of ternary calcium uranyl carbonate species at high temperature up to 70 °C by means of time-resolved laser fluorescence spectroscopy (TRLFS).

### II. Methods

Initially, 1×10<sup>-4</sup> m uranium solutions were prepared by diluting a stock solution, UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 1.1 m HClO<sub>4</sub>, and the initial carbonate concentration was set to 0.02 m by adding Na<sub>2</sub>CO<sub>3</sub> at 25 °C. Then, solutions were transferred to and stored in cooling/heating block for controlling temperatures in the range of 10-80 °C. The pH<sub>c</sub> of the solutions was set to 8.0 with HClO<sub>4</sub> while adjusting ionic strength to 0.1 m H/NaClO<sub>4</sub>. Ca(ClO<sub>4</sub>)<sub>2</sub> was spiked to form ternary uranyl complexes. Deionized water (18.2 MΩ) was used to prepare all solutions. The total concentrations of calcium were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES).

The fluorescence measurements of U(VI) solutions were carried out by an excitation of the fourth harmonic beam (266 nm) of Nd:YAG laser (Quantel Brilliant B). The emitted fluorescence was delivered by optical fiber to Czerny-Turner spectrometer (Andor, SR-303i-A), which is connected to the ICCD camera (Andor, DH734-18F-C3). For the temperature-dependent uranyl complexation, the sample cell was put into a hollow copper block where a temperature-controlled water flowed in to keep the sample temperature constantly.

In order to determine the Ca<sup>2+</sup> concentrations in solutions, an EDTA titration was carried out. The slope analysis was performed to determine the stoichiometric number of calcium and the formation constants of CaUO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>2-</sup> and Ca<sub>2</sub>UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>(aq). Details of the slope analysis are given elsewhere<sup>3,5</sup>.

### III. Results and Conclusions

Figure 1 shows fluorescence spectra of ternary Ca-UO<sub>2</sub>-CO<sub>3</sub> complexes at various temperatures (10, 25, 40, 55, and 70 °C). Five peaks at 466-485-505-527-511 nm were observed without any change in peak positions at all temperatures. Contrarily, the spectral width became broader and both fluorescence intensities and lifetimes decreased as increasing temperatures. This reduction in intensities and lifetimes indicates that the main quenching mechanism is dynamic.

At 10 °C, both EDTA titration and slope analysis were performed. The slopes of the linear fit were determined to be 1.01 ± 0.08 and 1.87 ± 0.35 at low and high Ca<sup>2+</sup> concentration, respectively. These slopes indicate the stoichiometric number of Ca<sup>2+</sup> complexation with UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup>, providing the formation of CaUO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>2-</sup> and Ca<sub>2</sub>UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>(aq). Two

intercepts of the linear fit on the y-axis suggesting the stepwise constants in 0.1 m ionic strength were found to be  $\log K'_{113} = 2.35 \pm 0.23$  and  $\log K'_{213} = 4.26 \pm 0.80$  for  $\text{CaUO}_2(\text{CO}_3)_3^{2-}$  and  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ , respectively.

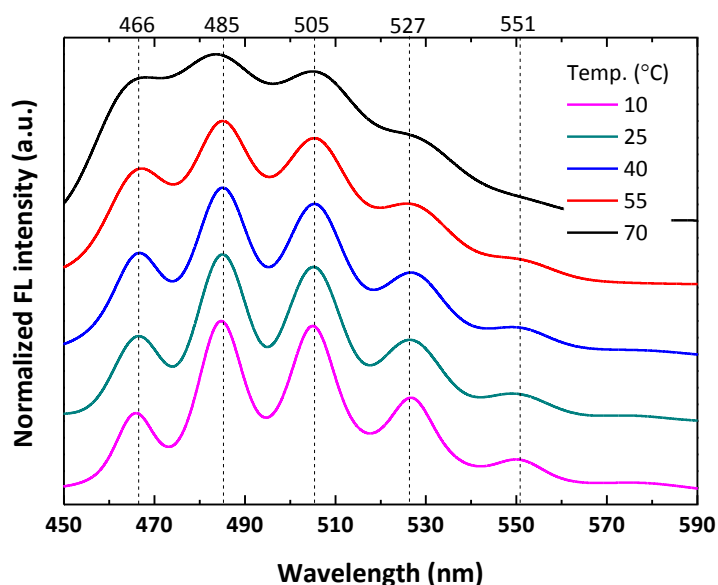


Fig.1. Fluorescence spectra of Ca-UO<sub>2</sub>-CO<sub>3</sub> complexes at [Ca<sup>2+</sup>] = 1.65 mM and pH 7.5 at varying temperatures of 10, 25, 40, 55, 70 °C.

#### ACKNOWLEDGMENTS

This work was supported the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP: Ministry of Science, ICT and Future Planning, No. 2016M2B2B1945252) and the Nuclear Safety Research Program through the Korea Foundation of Nuclear Safety (KOFONS, No. 1305032), granted financial resource from the Nuclear Safety and Security Commission (NSSC), Republic of Korea.

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