

# Chemical Behavior and Solubility of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}(\text{cr})$ at $T = 22$ and $80^\circ\text{C}$ in Dilute and Saline NaCl Systems

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## 1. Introduction

A comprehensive knowledge of uranium chemical behavior is indispensable for the prediction of radionuclide migration in contaminated sites in the environment. According to the omnipresence of carbonate and calcium ions, aqueous ternary Ca-UO<sub>2</sub>-CO<sub>3</sub> species are foreseen to be predominant complexes in natural groundwater system. Particularly, the solubility of U(VI) could be controlled by  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}(\text{cr})$  solid phase (also known as liebigite) where aqueous Ca-UO<sub>2</sub>-CO<sub>3</sub> complexes dominate the overall aqueous U(VI) species. Although of the relevance of the Ca-UO<sub>2</sub>-CO<sub>3</sub> system, there are still significant lack of relevant experimental data for determining thermodynamic data for the solid  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}(\text{cr})$ , which is essential for the reliable interpretation of U(VI) migration behavior in nature.

The objective of the present work is to investigate the solubility and stability of  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}(\text{cr})$  in various NaCl concentrations at  $T = 22$  and  $80^\circ\text{C}$ , under weakly alkaline pH condition.

## 2. Experimental

Batch-series solubility experiments were performed under ambient air condition. Well-characterized  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}(\text{cr})$  solid phase provided by Helmholtz-Zentrum Dresden-Rossendorf was equilibrated with  $\approx 0.03$ ,  $0.51$ , and

$5.61$  m NaCl solutions for 132 days at two different temperatures of  $T = 22 \pm 3$  and  $80 \pm 5^\circ\text{C}$ . The  $\text{pH}_m$  ( $-\log m_{\text{H}^+}$ ) values were initially adjusted to be  $\text{pH}_m = 7.9 - 8.2$  by using HCl/NaCl solutions. After reaching equilibrium, post-experimental analyses of the solid were performed by means of powder XRD, SEM-EDX, and chemical analysis digestion (ICP-MS/OES).

## 3. Results

The experiment results showed the clear presence of  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}(\text{cr})$  solid phase, controlling the solubility of U(VI) in  $\approx 0.03$ ,  $0.51$  m NaCl solutions at  $T = 22^\circ\text{C}$ . However, notable transformation from the initial U(VI) solid phase to  $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}(\text{cr})$  (also known as andersonite) was observed for  $5.61$  m NaCl solution at  $T = 22^\circ\text{C}$ , (based on the characteristic XRD patterns and quantitative chemical analysis by ICP-MS/OES). Similarly, dramatic changes in U(VI) solid phases were identified for all samples equilibrated at elevated temperature, indicating remarkable transformation of initial  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}(\text{cr})$  to  $\text{CaU}_2\text{O}_7 \cdot 3\text{H}_2\text{O}(\text{cr})$  and/or  $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$  along with calcite.

As shown in Fig. 1, the solubility data presented significantly high U(VI) concentrations at  $[\text{NaCl}] \leq 0.51$  m at  $T = 22^\circ\text{C}$ . The stoichiometric ratio of  $[\text{Ca}] : [\text{U}] \approx 2 : 1$  derived by ICP-MS/OES analysis supported the presence of  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}(\text{cr})$

after the solubility experiments. On the other hand, relatively decreased concentrations of aqueous U(VI) were determined at  $[\text{NaCl}] = 5.61 \text{ m}$  at  $T = 22^\circ\text{C}$ , in accordance with the presence of transformed  $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}(\text{cr})$  based on the solid phase characterization after solubility experiments.

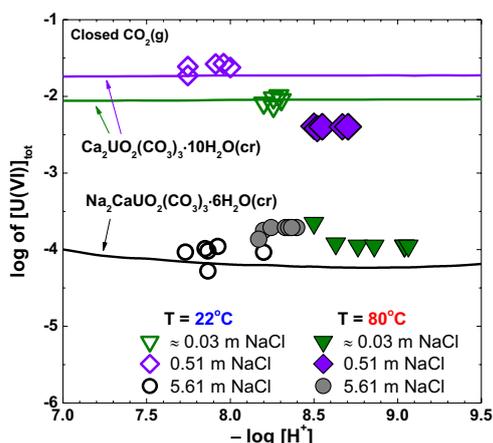


Fig. 1. Solubility of U(VI) observed at  $T = 22$  and  $80^\circ\text{C}$  (symbols). Lines represent the calculated solubility at  $T = 25^\circ\text{C}$  based on chemical thermodynamic data obtained in the present work and taken from the literatures [1,2].

In addition, remarkably changed solubility tendency was identified at  $T = 80^\circ\text{C}$ , compared with that obtained at  $T = 22^\circ\text{C}$ . Relatively shifted  $\text{pH}_m$  values towards further alkaline condition referred to the degassing of  $\text{CO}_2(\text{g})$  driven by the elevated temperature. Considerably lower concentrations of U(VI) were measured for samples at  $[\text{NaCl}] \leq 0.51 \text{ m}$  at  $T = 80^\circ\text{C}$  in comparison to analogous samples equilibrated at  $T = 22^\circ\text{C}$ , complementally indicating the transformation of initial U(VI) solid phase.

The solubility results, quantitatively obtained in this work, and chemical thermodynamic data describing the formation of aqueous Ca-UO<sub>2</sub>-CO<sub>3</sub> complexes [1] were employed to derive solubility products of  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}(\text{cr})$  and  $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}(\text{cr})$ .

## 4. Conclusion

The stability and aqueous solubility of  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}(\text{cr})$  was investigated at various NaCl concentrations at  $T = 22$  and  $80^\circ\text{C}$ . The experimental evidences and chemical thermodynamic data obtained in the present work provide better understating of chemical behavior of U(VI) in the context of geologic disposal of radioactive waste.

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