

## Effect of organic ligands on uranium release from uranophane dissolution

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### 1. Introduction

Uranium (U), a crucial element in energy production for nuclear power plants (NPPs), is naturally present in the Earth's crust, typically at concentrations ranging from 1 to 3 parts per million (ppm). However, in areas known as technogenic origin sites, which include locations where nuclear weapons have been tested, the concentrations of uranium can be significantly higher. For instance, the Semipalatinsk Test Site (STS) in North-East Kazakhstan has reported abnormally high uranium concentrations [1]. These concentrations were found in the surface waters (up to 62 µg/l) and bottom sediments (up to 540 mg/kg). Furthermore, such anthropogenically introduced uranium in contaminated soils is characterized by a high degree of potential mobility in the area.

The mobility of uranium is primarily governed by its oxidation state and the solubility of the uranium mineral. Uranium in its +4 oxidation state (U(IV)) forms less soluble and more stable compounds than uranium in its +6 oxidation state (U(VI)), which is more easily mobilized.

The oxidation or reduction of uranium is influenced by various factors, ranging from inorganic physicochemical parameters (like pH, Eh, pO<sub>2</sub>, pCO<sub>2</sub>) to organic and microbial enzymatic mechanisms. [2].

For instance, citrate and humic acids, common constituents of organic matter (OM) fraction in a sediment, are known to play a significant role in enhancing the mobility of uranium. These components can form complexes with uranium, thereby increasing its solubility and facilitating its transport in the environment [3-4]. This is particularly relevant when considering the fate of uranium in OM-rich sediments and its potential impact on environmental health and safety.

Moreover, research has been conducted on uranium deposits and the formation of uranium minerals in uranium-contaminated soil. One such mineral is uranophane  $\text{Ca}(\text{UO}_2)_2\text{SiO}_3(\text{OH})_2 \cdot 5(\text{H}_2\text{O})$ , a secondary uranium silicate mineral found in silicon-rich sediment. Uranophane is present in both uranium mining deposits and spent nuclear fuel repositories [5-6].

Limited data exist on how organic ligands from the OM influence the dissolution of uranophane and the subsequent release of uranium. Therefore,

understanding the fate of uranium necessitates the consideration and modelling of multi-component relationships. In this study, we synthesized uranophane and conducted a thorough analysis of its batch dissolution in the presence of citrate and humic acid. Specifically, this work aims to investigate how changes in the concentration of citrate and humic acid affect the release of uranium from uranophane into an aqueous solution over time.

### 2. Experimental Methods

#### 2.1. Uranophane synthesis

All solutions were formulated using ultrapure deionized water (DIW) and chemicals of reagent grade, at ambient temperature unless otherwise stated. The synthesis commenced with the addition of 50 mg of 2% HNO<sub>3</sub> U ICP-MS calibration standard (1000 ppm, PerkinElmer Pure Plus) to a 250-mL glass beaker. Subsequently, 0.21mmol of 10 mL sodium metasilicate (Sigma Aldrich) was introduced to the beaker while maintaining constant vigorous stirring (300-400 rpm) with a magnetic stirrer throughout the synthesis. The pH of the solution was gradually adjusted to 3 using solid calcium hydroxide powder. As the calcium hydroxide (Sigma Aldrich) was slowly added, an additional 60 mL of DI water was supplemented to the solution. The pH of the solution was then further adjusted to 10 by the addition of a carbonate-free saturated 0.1 M NaOH solution (Sigma Aldrich). The NaOH was added dropwise, allowing the pH to equilibrate after each addition. The addition of NaOH resulted in the formation of a yellow precipitate. The solution was then transferred to a polyethylene bottle and heated at 96°C for 96 hours. Some water was evaporated during this process, but not to the extent of drying the sample. The color of the solid became a slightly brighter yellow during this process. To eliminate any unreacted cations and anions, the slurry was centrifuged for 5 min at 3500 rpm, the supernatant was decanted and discarded, and 30 mL DIW was added; this process was repeated three times. To enhance the crystallization of the synthesized

Table 1. Uranophane synthesis conditions

Sample	Additional heating
Uranophane	None
	135°C for 1 week

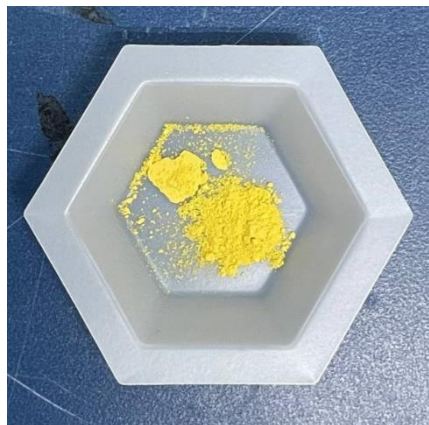


Fig. 1. Synthesized uranophane powder post-heat treatment at 135°C for one week

uranophane, the solid was placed in a 10 mL Parr reactor Teflon with the mother liquor as the background solution. The resulting 10 mL slurry was placed in the Teflon insert of Parr reactor and heated at 135 °C for 1 week. The Parr reactor was allowed to cool to room temperature before opening. All the solid were collected and rinsed by washing the sample several times with DIW and filtering the rinsate.

## 2.2. Characterization

The identity of the uranophane was verified by X-ray diffraction (XRD), using Rigaku Miniflex II. The XRD pattern of the synthesized uranium sample was analyzed with Rigaku PDXL software (Materials Data Incorporated, California) using the International Centre for Diffraction Data (ICDD) XRD database. The diffractogram of the solid was measured after the sample was fully dried after washing and ground into a fine powder that was placed on a glass slide sample holder.

## 3. Results and Discussion

The Table 1 summaries synthesis conditions explored in the uranophane synthesis. The uranophane synthesized through a process of additional heating treatment at 135°C for one week is illustrated in Fig. 1. A close examination of Fig. 1 reveals the solid to exhibit a vibrant yellow hue, a characteristic trait of uranophane.

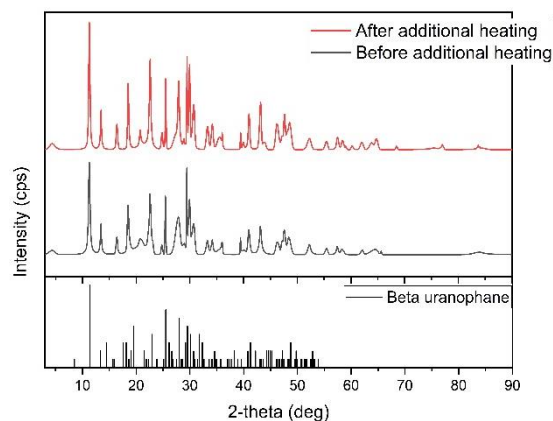


Fig. 2. Uranophane XRD before and after additional heating at 135°C for 1 week with relative to the reference of uranophane beta

The Fig. 2. shows the XRD diffractogram before and after additional heating at 135°C for 1 week in the mother liquor. The overall diffractogram pattern matches with the uranophane XRD reference. From the Fig. 2, additional heating treatment helps to improve overall crystallinity of the sample. The major uranophane peak (11.41 at 2-theta) becomes more predominant after the additional heating and resolution between the peaks becomes more distinct.

## 4. Conclusion

This study aimed to evaluate the synthesis of uranophane using U 2% HNO<sub>3</sub> ICP-MS standard. It was established that using additional heating treatment at 135°C for extended period of time helps to improve the crystallinity of the sample.

This is ongoing work and further work on the batch dissolution study of synthesized uranophane in the presence of varying concentrations of OM ligands, citrate and humic acids, will be provided to estimate the U release.

## 5. Acknowledgments

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