

Uranium(VI) Solubility and Hydrolysis in NaCl Solutions at Elevated Temperatures

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The present work is integrated into the German research project *ThermAc*, which aims at improving the scientific understanding and the available thermodynamic database for the chemistry of actinides in conditions of elevated temperatures, relevant in the context of high-level nuclear waste disposal. *ThermAc* is formed by eight German and European research institutions and it is coordinated by KIT-INE. Repositories for high-level radioactive waste are expected to feature elevated temperature conditions over a significant period of time, during early stages of operation. In scenarios involving early canister failure, radionuclides may contact aquatic systems at relatively high temperatures. Adequate scientific tools must therefore be provided in order to model the chemical and physical reactions of actinides at elevated temperatures and predict their potential release from a repository. Among different actinides, uranium is relevant in the context of nuclear waste disposal: it composes the largest portion in the inventory of radioactive waste, with U(VI) being the most stable oxidation state under anoxic and oxidising conditions. In agreement with these considerations, we undertook a solubility and hydrolysis study on U(VI) at different temperatures and in dilute to concentrated NaCl solutions. The present contribution summarizes our current experimental and modelling results.

Undersaturation solubility experiments with U(VI) were conducted in 0.10, 0.51 and 5.15 mol/kg NaCl solutions within $4 \leq \text{pH}_m \leq 14$ (with $\text{pH}_m = -\log m_{\text{H}^+}$). Solutions in the acidic pH range ($\text{pH}_m = 4-7$) were equilibrated with metaschoepite, $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$, whereas solutions prepared in the neutral to alkaline pH range ($\text{pH}_m = 7-14$) were equilibrated with sodium uranate, $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$. Batch samples were prepared in screw-cap, gastight and chemically inert PTFE flasks. Leaching tests carried out on these vessels confirmed that no release of organic content (as quantified by TOC) into solution occurred during the solubility experiments at elevated temperature. Solubility experiments were conducted at $T = 25, 55$ and 80°C , in all cases with solid phases previously equilibrated at $T = 80^\circ\text{C}$. Samples were stored in compact ovens accommodated in an Ar glovebox, allowing to work strictly under inert gas atmosphere. Batch solutions were periodically sampled: U(VI) concentration in solution was determined by ICP-MS after filtration with tempered syringe filters (PTFE membrane, $0.2 \mu\text{m}$ pore size, *Acrodisc*, Pall Co.); pH_m was measured at the same temperature of equilibration, using a glass electrode and housing the flasks in a customized dry-block heater. The proton concentration was measured using combination glass electrodes (type ROSS, Orion) calibrated against standard pH buffers equilibrated at the same temperature of the samples measured. In salt solutions of ionic strength $I_m \geq 0.1$ mol/kg, the measured pH value (pH_{exp}) is an operational apparent value related to m_{H^+} by $\text{pH}_m = \text{pH}_{\text{exp}} + A_m$. A_m values were determined in the present work as a function of temperature and NaCl concentration. After attaining equilibrium conditions, solid phases were characterized by XRD, quantitative chemical analysis and SEM-EDS.

Preliminary results show that $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$, equilibrated in aqueous solutions at $T = 80^\circ\text{C}$, is transformed into a Na-U(VI) phase, even in the acidic range and in conditions of relatively low concentration of NaCl (0.1 mol/kg). Results from experiments conducted in NaCl 0.51 mol/kg at $T = 80^\circ\text{C}$ show that the solubility of $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$ is significantly increased at elevated temperature, up to two orders of magnitude, with respect to room temperature conditions (Figure 1). This effect is mainly due to the enhanced hydrolysis of

U(VI) at higher temperatures, as a result of the increased acidity of water. The solubility at $T = 25\text{ °C}$ of $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$ previously tempered at $T = 80\text{ °C}$ is noticeably decreased (0.5 orders of magnitude), compared with previous solubility data collected at $T = 25\text{ °C}$ for non-tempered $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$ [2]. Thermodynamic modelling of the data collected at $T = 25$ and 80 °C provided very preliminary – but reasonable – estimates of the enthalpies of solubility and hydrolysis of U(VI) in the alkaline range. Forthcoming results from solubility experiments at $T = 55\text{ °C}$ and new results from experiments at $T = 80\text{ °C}$ will provide a reliable set of data for modelling the chemical behavior of U(VI) in both the acidic and the alkaline range at different temperatures and ionic strengths.

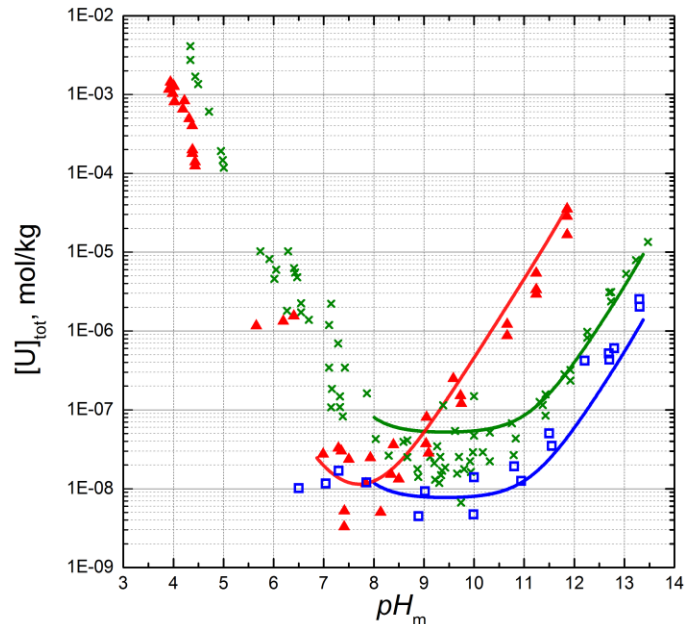


Figure 1 Solubility of $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$ as a function of pH_m . $I = 0.5\text{ mol/kg NaCl}$. Bullets: experimental points. \times Data at 25 °C from ref. [2]; \square Current data at 25 °C , $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{s})$ preliminarily equilibrated at 80 °C ; \blacktriangle Data at 80 °C ; lines are the calculated solubility curves, on the basis of the thermodynamic parameters derived by least-square minimization of these solubility data (Table 1)

References

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