THEREDA – added value to contaminant speciation in brines

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- Karlsruhe Institute of Technology – Institute for Nuclear Waste Disposal
- Technische Universität Bergakademie Freiberg – Institut für Anorganische Chemie
- AF-Consult Switzerland AG

Introduction

Cooperative project THEREDA: establishing a consistent and quality assured database (DB) for elements, temperature and pressure ranges relevant for (nuclear) waste disposal.

Main focus: provision of data for the correct calculation of the solubility of radiotoxic elements in highly saline solutions, *i.e.*, utilizing the Pitzer model for ion-ion-interactions.

Data sources

Major thermodynamic data source: NEA Thermochemical Database [1,2] for aqueous and solid uranium species.

But: exclusion of many relevant reactions due to NEA's very stringent quality demands.

THEREDA: consideration of recently published papers and further unpublished works from KIT-INE, also addressing Pitzer parameters [3]. Also inclusion of thermodynamic data of secondary mineral phases formed in the waste material.

Test calculations

Predictive test calculations: comparison of results based on THEREDA with other Pitzer DB [4,5].

Test cases: published solubility experiments of U(IV) and U(VI) minerals in high saline solution [6–11].

Result: high quality of THEREDA DB.

Tetravalent Uranium

Amorphous U(IV) hydroxide ($U(OH)_4$):
Inaccurate prediction of the solubility using Yucca Mountain Project datasets [4], due to differences in aqueous speciation and Pitzer data (Fig. 1) as well as no data for carbonates ($U(CO_3)_n^{4-2n}$) (Fig. 2) and sulfates ($U(SO_4)_n^{4-2n}$) (Fig. 3).

data0.pit.R2 [5] database not able to model U(IV) chemistry, because there are no thermodynamic data for aqueous uranium species at all, only very few U minerals.

Hexavalent Uranium

Metaschoepite ($UO_3 \cdot 2H_2O$, synonym: Schoepite):
Different solubilities caused by deviating solubility constants in the considered DB ($\Delta \log K°_{sp} \approx 0.52$) as well as different or missing data for the aquatic uranium speciation in [5] (Fig. 4).

Becquerelite ($Ca(UO_2)_6O_4(OH)_6 \cdot 8H_2O$):
Minor deviations due to different solubility data ($\Delta \log K°_{sp} = 0.9$) (Fig. 5).

Soddyite ($(UO_2)_2SiO_4 \cdot 2H_2O$):
Though relevant within the far-field of a nuclear waste disposal, only incorporated in THEREDA so far, allowing a prediction of its solubility (Fig. 6).

THEREDA: provides ready-to-use databases for the common speciation codes (ChemApp, EQ3/6, Geochemist's Workbench, PHREEQC).

Latest release covers tetra- and hexavalent uranium data for the system of oceanic salts containing Na, K, Mg, Ca, Cl, S, C, and Si.

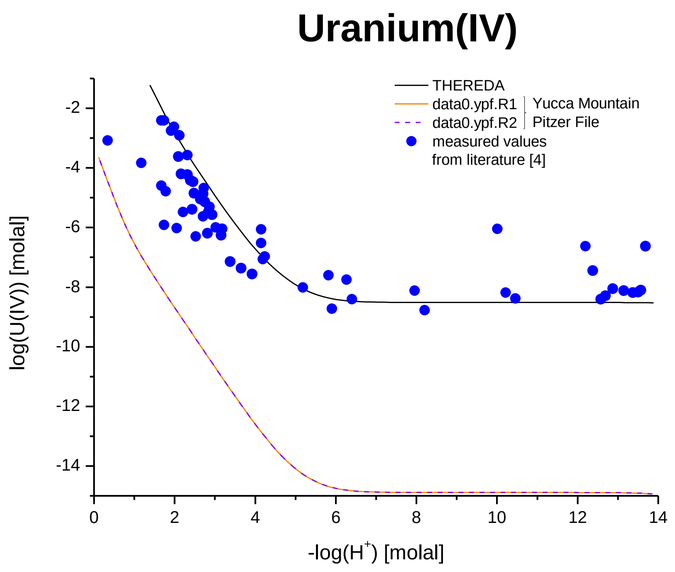

Fig. 1: Solubility of $U(OH)_4$(am) in 1 m NaCl solution at T = 25 °C.

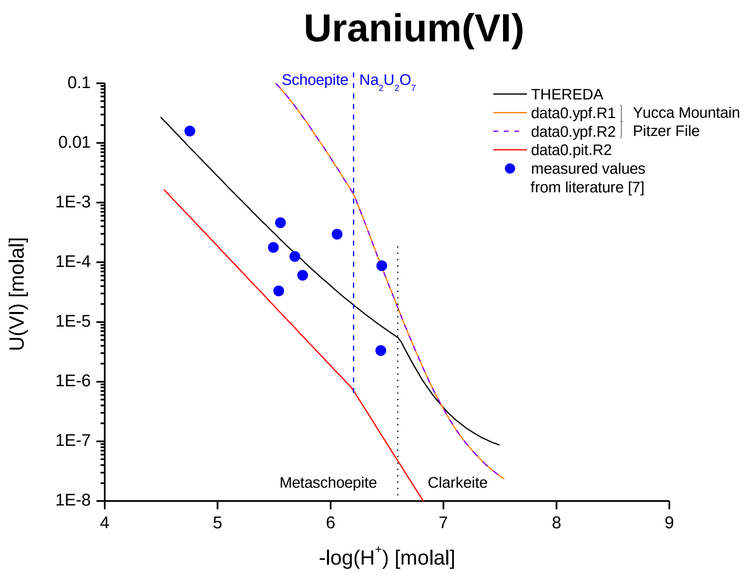

Fig. 4: Solubility of Metaschoepite in 5 m NaCl solution at T = 25 °C.

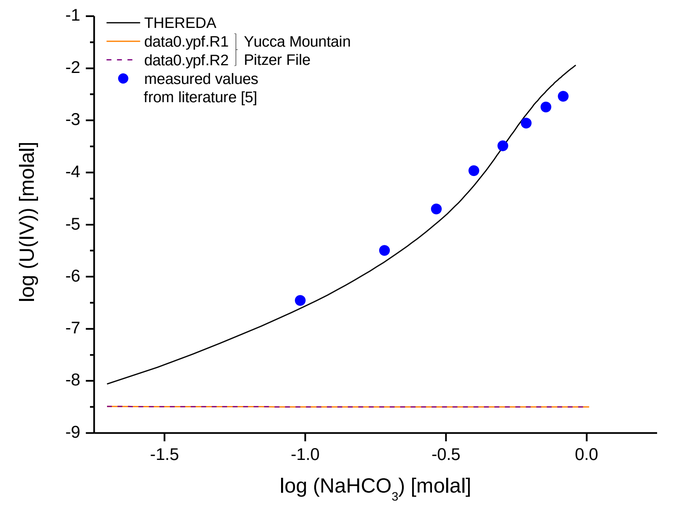

Fig. 2: Solubility of $U(OH)_4$(am) in $NaHCO_3$ solution at T = 25 °C.

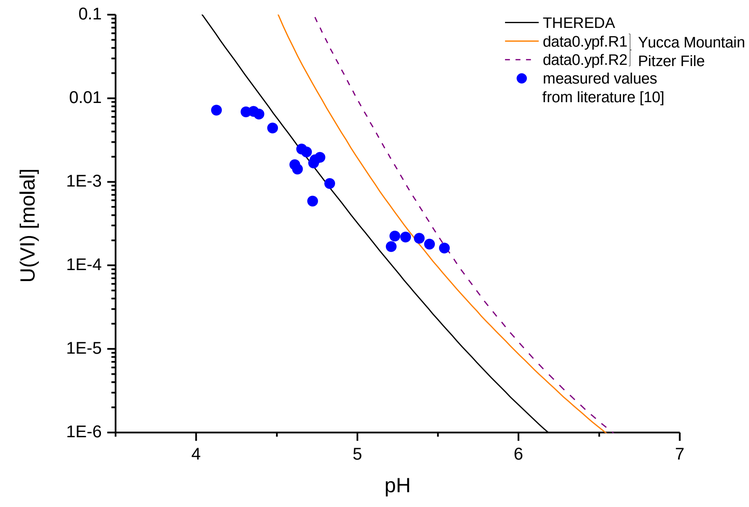

Fig. 5: Solubility of Becquerelite in 1 m $CaCl_2$ solution at T = 25 °C.

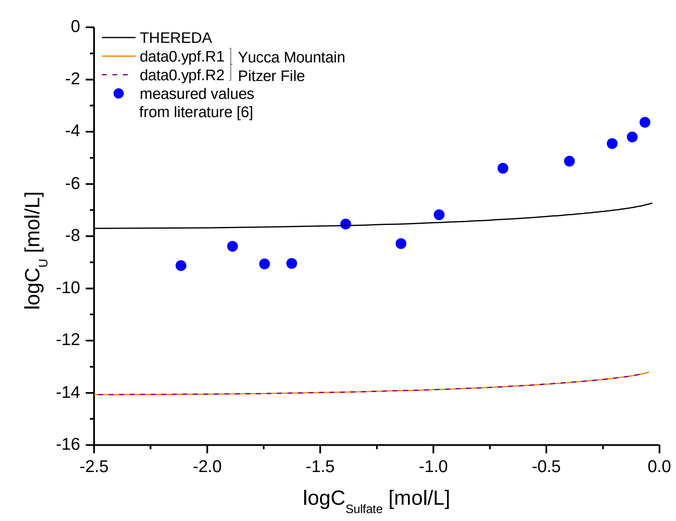

Fig. 3: Solubility of $U(OH)_4$(am) in Na_2SO_4 solution at T = 25 °C and $\log(c_{H+}) = -4.5$.

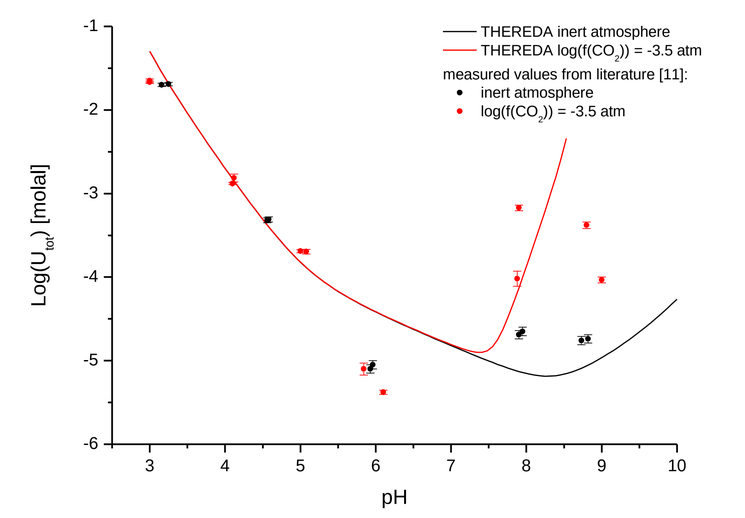

Fig. 6: Solubility of Soddyite in 0.1 M $NaClO_4$ solution at T = 25 °C.

Conclusions

The revealed discrepancies illustrate the need for further database efforts. Joint benchmark activities help identifying missing or less reliable data, enhance the quality of all databases, and thus, eventually increase the confidence in modelling results.

An upgrade for this release is already in progress and will include U(IV/VI) phosphate data.

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This project is jointly funded by the Federal Ministry of Education and Research (BMBF), the Federal Ministry of Economics and Technology (BMWi), and the Federal Office for Radiation Protection (BfS) with funds from the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU).

Bundesministerium für Bildung und Forschung
Bundesministerium für Wirtschaft und Energie
Bundesministerium für Umwelt, Naturschutz, Bau und Reaktorsicherheit
Bundesamt für Strahlenschutz

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