NUCLEAR WASTE DISPOSAL AND SAFETY

Safety Research for
Nuclear Waste Disposal

THEREDA REVISITED – PROJECT STATUS IN 2013

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The Project

- Design of waste repositories requires reliable thermodynamic data to predict the geochemical behaviour of contaminants
- Need: aqueous speciation, solubility limiting solid phases and ion-interaction parameters
- Challenges: Incomplete sets of major and trace elements, inconsistencies between species considered and corresponding formation constants / activity models, restricted variation ranges of parameters (temperature, density, pressure, ionic strength)
- Action: Launch of THEREDA in 2006

The Partners and Goal

- Gesellschaft für Anlagen- und Reaktorsicherheit mbH, Braunschweig (Coordinator)
- Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology
- Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal
- TU Bergakademie Freiberg, Institute of Inorganic Chemistry
- AF-Consult Switzerland AG, Baden (Switzerland).

Main objective: a centrally administrated and maintained database of verified thermodynamic parameters for environmental applications in general and radiochemical issues in particular

The Chemistry

- Actinides, Fission and Activation Products:
  - Pa, Th, U, Np, Pu, Am, Cm
  - Rb, Sr, Tc, Cs, Sm, Nd, Ra
- Matrix:
  - System of oceanic salts: Na^+, K^+, H^+, OH^-, Mg^{2+}, Ca^{2+}, Cl^- , SO_4^{2-}, CO_3^{2-} / HCO_3^- / CO_2(aq) – H_2O containing the elements Na, K, Mg, Ca, Cl, S, C
  - Hydrated cement phases (including Al, Si)
- Ion-Ion-Interactions:
  - Pitzer approach
  - (SIT & extended Debye-Hückel)

Releases / Extended Interface

- Six new official releases since Migration 2011, all based on Pitzer (in bold: additions to the hexary system of oceanic salts)
  - Na, Mg, Ca – Cl – **Am(III), Nd(III), Cm(III)** – H_2O(l) (2011-11-23)
  - Na, K, Mg, Ca – Cl, SO_4 – **HCO_3/CO_2(g)** – H_2O(l) (2012-02-21)
  - Na – Cl – **Np(V)** – H_2O(l) (2012-11-30)
  - Na, Mg, Ca, K – Cl, SO_4 – **HCO_3/CO_2(g) – Cs** – H_2O(l) (2013-01-28)
  - Na, K, Mg, Ca – Cl, SO_4 – **HCO_3/CO_2(g) – Si, Al** – H_2O(l) (2013-07-04)
  - Na, K, Ca – Cl – **HCO_3/CO_2(g) – Th(IV), Np(IV), Pu(IV)** – H_2O(l) (2013-08-04)
  - Additional release for U(IV) and U(VI) is planned for the near future.
- Download as separate files (www.thereda.de → navigation menu: THEREDA Data Query → Tailored Databases) in five formats: generic ASCII type and specific to geochemical speciation codes (PhreeqC, EQ3/6, ChemApp, Geochemist's Workbench – GWB).
- Access to data records is now also possible through interactive forms (menu: THEREDA Data Query → Single Data Query // Complex Systems), both with export options as CSV or MS Excel file.
- New interactive web-based tool for data entry and editing – though only visible to members of the editorial board of THEREDA.
- Eight issued technical papers (Downloads → Documentations) add transparency and promote the transition of THEREDA into an open information and discussion platform – covering the database itself as well as geochemical modeling at large.

Quality Assurance (QA)

- Major milestones in QA:
  - Integration of a new auditing scheme,
  - Monitor data selections
  - Automatic logging system storing all data changes in separate files
  - Extension of the internal calculation scheme for mutually dependent thermodynamic data to check for data consistency and plausibility.
- An illustration of THEREDA's capability: the solubility of freshly precipitated $Nd(OH)_3$(am) in 3.86 m $CaCl_2$ solution.
- Calculations compared to predictions (based on two databases from the Yucca Mountain Project – data0.ypf.R1/2) and experimental results (Fig. 1).
- Deviations in the weak alkaline range due to different solubility constants for Nd(III) hydroxides ($\Delta \log K Nd(OH)_3$(am) ≈ 3.3).
- The missing increase of Nd(III) solubility in higher alkaline range ($-\log(mH^+) > 10$) using the data0.ypf.R1/2 databases is a consequence of different aqueous speciation, especially for anionic and ternary Ca-Nd-$(OH)_x$ complexes.

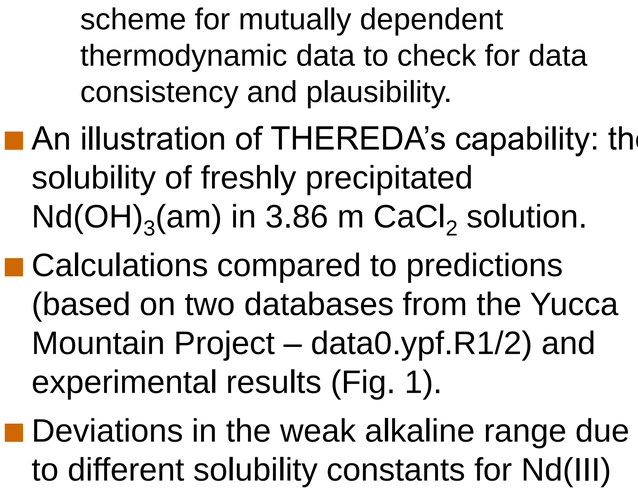

Fig. 1: Solubility of amorphous/crystalline $Nd(OH)_3$(am) in 3.86 m $CaCl_2$ solution (lines: database predictions, symbols: experimental data from Neck, V.; Altmaier, M.; Rabung, T.; Lützenkirchen, J.; Fanghänel, T.; Pure and Applied Chemistry 81, 2009, 1555–1568.).

Surface Complexation

- A holistic view of geochemical processes must include sorption phenomena.
- Thermodynamically consistent treatment: only possible with surface complexation modeling (SCM).
- Support for models implemented in PhreeqC and GWB: Diffuse Double Layer Model (DDL), Constant Capacitance Model (CC), Non-electrostatic Model (NE), 1p*K*-Basic Stern Model (1p*K*-BS).
- Stored for each mineral: specific surface area, surface binding site density, surface protolysis constants (p*K*). Capacitance values will be kept for the CC and the 1p*K*-BS model. Surface complex formations constants (log*K*) are entered for given combinations of mineral, ligand, and model.
- Currently SCM data are stored for 298.15 K only, but adaptation to temperature-dependent functions is possible.
- The extension towards SCM required the synchronization of various table designs (e.g. for solids and bibliography) and the introduction of numerous new tables, coupled to new data categories.
- Severe general problems: speculative species, unreliable, contradicting or missing thermodynamic parameters.

- ***We are looking forward to receive helpful feedback on THEREDA and are hoping for intensified interactions of the THEREDA database project with the international user community.***

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