THEREDA – THERMODYNAMIC REFERENCE DATABASE FOR NUCLEAR WASTE DISPOSAL IN GERMANY

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The disposal of radioactive waste including the assessment of long-term safety is still an open question in Germany. In addition to the still pending decision about the repository host rock (salt, granite, or clay) the basic necessity of a consistent and obligatory thermodynamic reference database persists. Such a database is essential to assess potential failure scenarios accurately and to make well founded predictions about the long-term safety. Specific needs for waste repository and remediation projects in Germany are comprehensive datasets also covering high temperatures and high salinities. Against this background, available databases do not suffice and are limited in their use, partly because of high restrictions and resulting incompleteness of reactions. Other databases rely on heterogeneous and therefore inconsistent data leading to incorrect model calculations. Due to these deficiencies THEREDA, a joint project of institutions leading in the field of safety research for nuclear waste disposal in Germany, was started. It will provide consistent thermodynamic datasets and enhance the transparency and reliability of safety analyses.

I. INTRODUCTION

Radioactive waste and chemo-toxic substances are hazardous to human health and to the environment. Hence they should be kept away from the biosphere for long periods of time. The choice of a repository location should promote the isolation of contaminants in the host rock over geological periods.

Performance assessment studies have to take into account water intrusion scenarios with a subsequent release of radionuclides. Depending on the surrounding host rock formation, but of course also on the design of the waste containment and engineered barrier systems, the resulting aqueous solutions may exhibit very high ionic strength, as is the case in brines generated in salt rock, but also clay pore waters may reach considerable ionic strengths. It is thus essential to address all relevant reactions under widely varying environmental conditions. Only then the amount and fluxes of radionuclide emission into the biosphere can be modeled.

To characterize the chemical behavior of radioactive waste and chemo-toxic substances in aqueous solution, the knowledge of various physico-chemical parameters is essential:

- Composition and solubility products of relevant solid phases (pure minerals as well as solid solutions)
- equilibrium constants for complex formation (including hydrolysis) and redox reactions
- activity coefficients for solid solutions
- activity coefficients describing interactions of species dissolved in electrolyte solutions

The last category is in particular inevitable for model calculations in high saline solutions, as being present in salt host rocks.

The importance of reliable thermodynamic data for the use in long-term safety analyses of geological repositories has been acknowledged internationally since decades. For selected actinides (U, Np, Pu, Am) and fission products (Tc, Zr, Ni, Se) a thermodynamic database from the Nuclear Energy Agency of the Organisation for Economic Cooperation and Development (NEA/OECD) is available[1], being permanently updated and extended. However, as a result of high demands for quality this database is rather restrictive and therefore incomplete for extensive modeling calculations. E.g., there are 197 solids in the NEA uranium database, but only five uranium minerals out of about 250 natural occurring ones made their way into the recommended data set. This has been pointed out (but unfortunately not corrected for) also by the Nagra/PSI data base[2].

The use of further established databases (NBS tables, CODATA, IUPAC) is limited, especially when dealing with solutions of high ionic strength. Moreover, they lack data on many relevant radionuclides and other toxic metals.

Other thermodynamic databases were assembled in the context of specific final repository projects in the USA and in Switzerland and have been adapted to the respective projects[3].

Therefore, a direct adaptation of already existing databases proved to be not sensible, especially when taking into account that Germany will have further requirements not relevant in other countries. First, the selection of a specific deep geological repository for high level radioactive waste (HLRW) is still an open question. Different host rock formations (salt, clay, granite) are currently surveyed in Germany, which implies varying solution compositions and ionic strengths. Second, the time frame for intermediate storage of the nuclear waste is not fixed yet, thus there are also concepts to be discussed coping with temperatures as high as 150 °C. Third, as there is not clear yet whether a German repository will be used for HLW, ILW and LLW simultaneously or not (then implying more than one deposit) the composition of the waste may vary considerably, too, again with effects on the temperatures to be dealt with.

II. OBJECTIVE

Geochemical modeling of the near-field and far-field processes occurring in repositories for radioactive waste in the different rock formations currently under discussion in Germany poses special demands on a database with respect to the:

- relevance of species (main and trace elements),
- applicability in highly concentrated solutions,
- consistency, documentation, traceability and quality assurance.

Therefore a consortium was founded with the main objective of developing a comprehensive and internally consistent thermodynamic reference database fulfilling these demands. The collaboration includes institutions leading in the field of safety research for nuclear waste disposal in Germany, with some project partners being directly involved in long-term risk assessment ensuring risk-informed insight. It shall provide reliable and trace-able answers to corresponding questions by means of consistent thermodynamic data for geochemical calculations. A thermodynamic database, THEREDA[4], is now developed that:

- enables the prediction of the activity, speciation and solubility of relevant toxic elements,
- is applicable from low to high ionic strengths,
- fulfils specific German quality requirements, and
- will be the compulsory reference database for performance assessment studies.

To obtain synergistic effects aiming on a better overall cost-benefit ratio THEREDA will also address geochemical questions in relation to chemo-toxic waste already stored in Germany in various underground facilities.

THEREDA supports storage of an arbitrary number of stoichiometric condensed phases and mixed phases (gas phase, aqueous phase and solid solutions). In addition, provision is made for models which account for the non-ideality of mixed phases.

III. METHODOLOGY

THEREDA is a joint venture of institutions, leading in the field of safety research for final disposal of radioactive waste in Germany. An overview of the project coordination and the structure of THEREDA is given in Fig. 1.

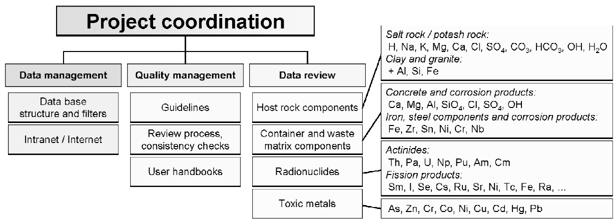

Fig. 1. Project coordination and structure of THEREDA.

III.A. Data coverage

An intensive collection and review of thermodynamic data includes species and phases with:

- host rock components (HMW-database[5] completed with Al, Si and Fe),
- container and waste matrix components (species of concrete and corrosion products and steel components),
- radionuclides (actinides and fission products like U, Np, Pu, Am, Cm, Pa, Th, Tc, Cs, Sm, I, Se, Sr, Ni, or Ra),
- toxic metals (Zn, Cr, Co, Cu, Cd, Hg, Pb) and As.

In the first stage of the project, THEREDA will comprise data of 28 elements relevant to a final storage of nuclear waste, with more than 2000 species.

III.B. Quality management

Within the project THEREDA, we seek to compile data of high quality, internal consistency and traceability, mainly from existing databases, and to complement this basis particularly with datasets for high saline systems (Pitzer and SIT parameters) and systems at elevated temperatures. Persistent data gaps are closed via data of higher uncertainty or estimated values. The identification of such gaps can also aid decisions about the targets and priorities of future experimental programs.

Each dataset included in THEREDA is documented in detail and gets a grade of quality attached. Information about solid phase modification (like "crystalline" or "amorphous") is mandatory for any editor and specific marks are designated to indicate whether dissolution/ precipitation is kinetically controlled or not. Well known examples of differences in solubility of orders of magnitude between solids precipitating from over-saturated solutions and well crystalline "technical" products are the tetravalent actinides (see, e.g., Neck & Kim[6] or Altmaier et al.[7] for details.). Consequently, higher grades of quality are allocated to thermodynamic parameters derived from experimental data, namely from non-thermochemical experiments, whereas estimated values determined from systematic trends in thermodynamic behavior (Linear Free Energy Relation-ships and other regressions or correlations) or from studies of chemical analogs get lower ratings. The fundamental philosophy here is that the omission of species and related reactions almost always generate larger errors than using respective data accepting a large uncertainty. The inherent storage of all associated data uncertainties provides for a later quantification of specific errors by numerical uncertainty and sensitivity analysis. Furthermore, the quality of data sources (primary or secondary literature, peer-reviewed or non-certified) is categorized.

The quality management in the project THEREDA covers three levels of evaluation including:

- rating of single data,
- internal and external reviews, validation and consistency check of the database,
- documentation for users (structure of parameter files, handbooks instructing users and editors).

To guarantee the consistency of datasets inside the thermodynamic database, different conversion paths are available (Fig. 2). Other important consistency rules require linking those parameters that were originally derived simultaneously from the same experimental raw data. In addition, some parameters are linked to specific sets of chemical species and are only valid within this combination.

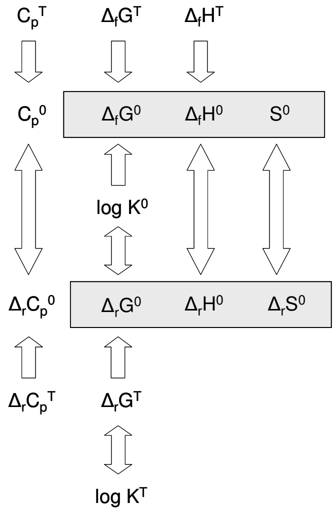

Fig. 2. Elemental conversion steps between data types in THEREDA

III.C. Data management

Both data management and technical realization of THEREDA are using a databank system based on PostgreSQL and running on an Apache web server. An overview of the data flow paths is given in Fig. 3. One of the major goals of the project is to rely on open source software to minimize the risks of vendor dependence and incompatibilities, and to keep the long-term running costs for database maintenance low.

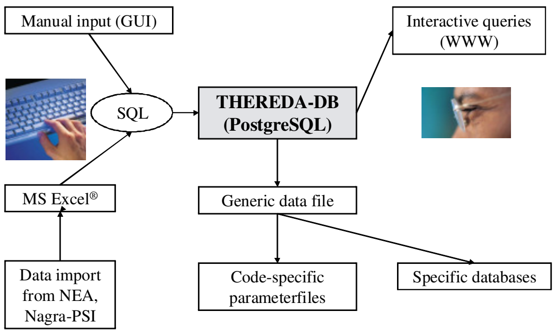

Fig. 3. Scheme of data management in THEREDA.

The database is filled through manual data input and the import of data from existing databases. All data will be stored in a generic and openly documented ASCII format. Specific user-defined queries and restrictions allow downloading subsets of the stored data in a generic and publicly documented ASCII format. Programmed export filters will be provided for a conversion of such subsets in formats specifically required by speciation and reactive transport codes. Moreover, external users can write their own specific parsers to convert the data to the needs of their specific codes. The generic format shall also ensure easy and long term readability.

The web presence and the internal communication between the project partners (intranet) are realized by means of the PostgreSQL-database as well.

IV. CONCLUSION / POTENTIAL APPLICATIONS

The data compiled and evaluated by THEREDA can be utilized for all final repository systems discussed in Germany. The reliability of modeling calculations and the practicability of uncertainty and sensitivity analyses is facilitated by a comprehensive documentation and transparency of the thermodynamic reference database. In contrast to existing databases, internal consistency and compatibility of the contained datasets in THEREDA will be permanently ensured. Custom-designed data, extracted from the database and converted to file formats required specifically by geochemical codes (such as EQ3/6, PHREEQ-C, GWB, ChemApp), allow a widespread use in the fields of storage of radioactive waste or chemo-toxic substances and remediation of contaminated sites. Respective long-term safety analyses will be made more reliable, comparable and traceable.

We hope that THEREDA can serve as an instrument for research control. Preferences for experimental programs in the future can be given based on an identification and ranking of gaps within thermodynamic datasets.

THEREDA will represent a source of information on thermodynamic data that will be publicly accessible, fully documented, and free of charge via www.thereda.de, thus hopefully attracting users from other communities, too. The expected feedback from scientists, regulators, implementers and other stakeholders is welcome and will be serving as an additional tool for quality assurance.

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