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ThermoChimie

Technical report

ThermoChimie guideline 3: Validation and verification

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The ThermoChimie database was first developed in 1995 by Andra, the French national radioactive waste management agency. They have since been joined by Radioactive Waste Management (RWM) from the UK, and ONDRAF/NIRAS from Belgium.

ThermoChimie provides an accurate and consistent set of data specifically chosen for use in modelling the behaviour of radionuclides in waste packages, engineered barriers, and both the near surface and deep geosphere. The database can be used to model the speciation and solubility of a wide range of stable and radioactive elements, organics, and solid phases including cements, clay minerals and degradation products (such as zeolites). The database is suitable for use within the range of conditions expected in both near-surface and geological disposal facilities: pH 6-14, ionic strength up to SIT, Eh within the stability fields of water, and temperatures from 15 to 80°C.

ThermoChimie is intended for use across the radioactive waste management community, to support repository performance assessment, research and development activities and decision making. To maximise their utility the data are therefore provided in formats suitable for use with common geochemical modelling codes. The database can be viewed and downloaded from the project website: https://www.thermochimie-tdb.com/, where additional information and supporting documents are also available.

This document is the third guideline for the ThermoChimie database. It gives details of the different verification and validation procedures applied to the database with the aim to guarantee its completeness and accuracy.

ONDRAF/NIRAS

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Radioactive Waste Management

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ThermoChimie guideline 3: Validation and verification

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1. Introduction

The reliability of a thermodynamic database is often judged by its ability to explain independent experimental data gathered from either laboratory experiments or field observations. Validation of the selected thermodynamic data is then an essential part of its development. For the ThermoChimie database, validation exercises play a key role, providing relevant information on its consistency and accuracy.

Validation and verification procedures play an important role in ensuring that all the relevant aqueous species and solid phases are included in the database. These procedures also provide information on the consistency and accuracy of the database and whether adequate uncertainty is assigned to less reliable data.

This guideline explains the different verification and validation exercises carried out as part of the ThermoChimie database development (see Figure 1).

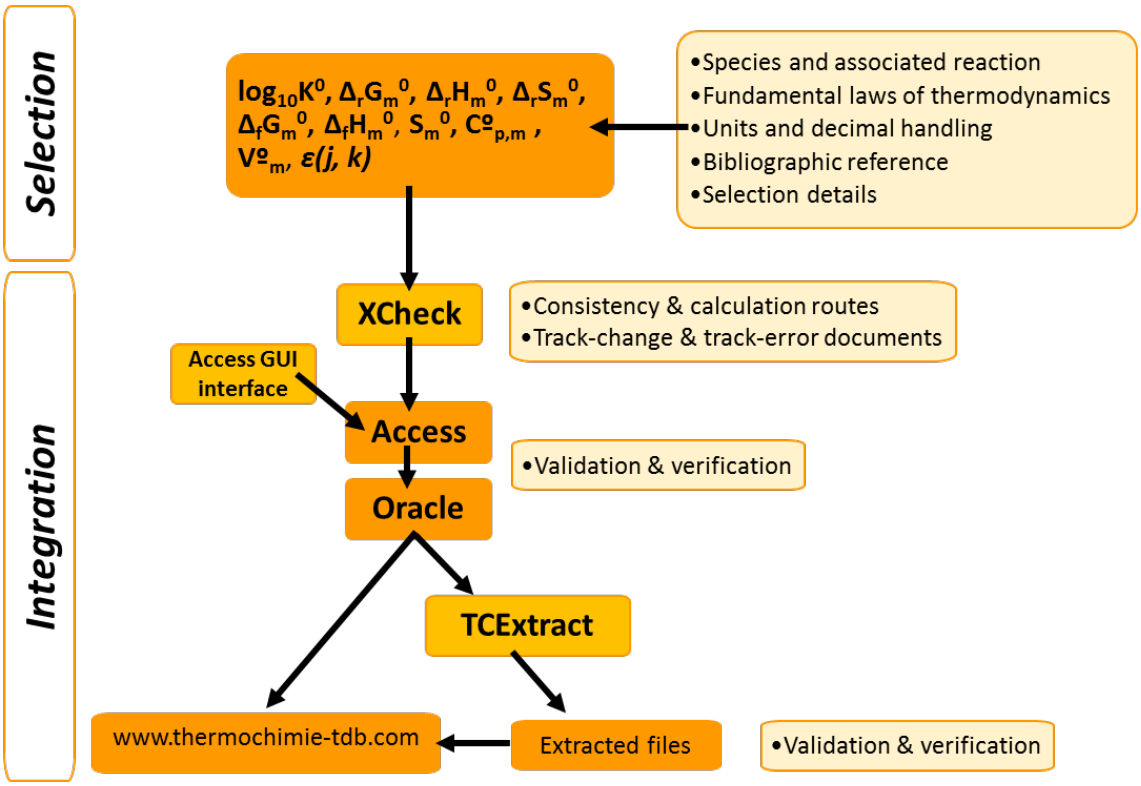

Figure 1. Summary of the ThermoChimie data integration procedure, including validation and verification steps (from Guideline 2: Data integration and consistency).

The terms “verification” and “validation” are sometimes used interchangeably, but in this document they refer to different procedures.

Verification refers to the process of determining whether the database has been properly implemented as intended by the developer. In the specific case of ThermoChimie, verification

refers to all the processes used to check that the data are correctly stored and correctly extracted in formats for use with the different geochemical codes (such as PhreeqC, Crunch, ToughReact, Geochemist's workbench, etc.)[1].

On the other hand, **validation** is used to determine the ability of the database to describe an experimental or natural system (within the intended limits of temperature, pH, etc. of ThermoChimie). Therefore, the validation process includes a set of exercises developed to ensure that the database is accurate and exhaustive, and able to achieve the geochemical modelling tasks for which it has been designed[2].

2. Verification

The ThermoChimie database verifications are designed to check that: a) data are correctly stored in the database, and b) data are not lost, altered or modified during the storage, recalculation or extraction routines.

The following types of verification exercises are used:

1. **Direct comparison** between different versions of the ThermoChimie database. When a new database version is ready to be released, database administrators perform a direct comparison between the new version and former versions. The main objective of the exercise is to ensure that data are not lost or altered when they are introduced into the Access/Oracle versions of ThermoChimie. These comparisons increase the traceability of the database and ensure that all the changes between the new version and former ones are included in the corresponding track-changes and track-errors document (see Guideline 4: Data traceability).

2. **Benchmarking exercises.** In these exercises, a geochemical model is run several times with different geochemical codes (PhreeqC, Crunch, ToughReact, Geochemist's workbench, etc.), using the ThermoChimie database. The calculations are restricted to those conditions (temperature, pH, etc.) for which the database is designed. The following geochemical models, covering different systems, can be run:

    - Radionuclide solubility and speciation under clay or cement conditions.
    - Radionuclide solubility and speciation at different temperatures.
    - Organic speciation under clay or cement conditions.
    - Speciation of major ions as a function of temperature.

[1] Further details on data integration procedures and extraction can be found in the Introduction to ThermoChimie Guidelines and in Guideline 2: Data integration and consistency.
[2] Further details on ThermoChimie database objectives and principles of development are detailed in the Introduction to ThermoChimie guidelines.

- Radionuclide and major ion speciation under different ionic strength conditions, using different ionic strength correction approaches (SIT, extended Debye-Hückel, Davies)
- Determination of the cement phases present in cement at a specific stage of degradation.
- Calculation of the porewater composition in equilibrium with the Callovo-Oxfordian formation at different temperatures.
- Simplified 1-D transport calculations.

Note that not all the geochemical codes are capable of handling all these calculations; thus, only the appropriate codes are used for each exercise.

It is worth mentioning that the verification exercises are performed before a major ThermoChimie version is released, or when significant updates and improvements are made to the extraction tool. The results obtained from these verification exercises check that the data has been correctly extracted into formats for use with the different geochemical codes (see Guideline 2: Data integration and consistency). In addition, these exercises are necessary to adapt the extracted files to the needs of the different codes.

3. **Modelling of experimental data.** In these exercises, experimental data used in the development of ThermoChimie are modelled using ThermoChimie and an appropriate geochemical code. Some examples of this type of verification exercises are:

    - Radionuclide solubility calculation and comparison with the original experimental data used for updating the database.
    - Organic speciation calculation and comparison with the original experimental data used for updating the database.
    - Radionuclide and major ions speciation under different ionic strength conditions calculation and comparison with the original experimental data used for updating the database.
    - Definition of cement phases predominance diagrams.
    - Drawing activity diagrams involving clay minerals.

    The performance of the database in these modelling exercises verifies whether data are correctly stored in and properly extracted from the database.

3. Validation

Validation determines how accurately the database can describe an experimental or natural system. Besides the accuracy of the thermodynamic database, the validation process also checks understanding of the physicochemical processes occurring in the system, the suitability

of the user's input parameters and geochemical model proposed, together with the capabilities of the chosen geochemical code

Validation exercises have to be performed within the designed limits of ThermoChimie. As the database includes a large number of solid phases and aqueous species it is not possible to test all of them simultaneously. Therefore, different validation exercises are performed to cover the different scenarios of interest. The validation exercises are frequently focused on the systems that have been updated in that specific database version (see Guideline 4: Data traceability). For example: if the cement system has been significantly updated in a particular ThermoChimie release, the validation exercises will be tailored to cover cement systems.

Four different types of validation exercises are available, but the choice of one or another validation test is obviously dependent on the availability of the data.

1. **Direct comparison exercises** involving ThermoChimie and another thermodynamic database. These comparisons are focused on checking the species and minerals included in the database and the numerical values of the thermodynamic parameters. The similarities and discrepancies between ThermoChimie and other databases can highlight additional data (available in the other database but not in ThermoChimie) and check the completeness of ThermoChimie. The aim of the exercise is to ensure that the database contains the data needed to explain the behaviour the studied systems.

   The databases selected to be used in the comparison exercises have to fulfil the following requirements:

   - Their field of application must be comparable with that of ThermoChimie;
   - Databases have to be public, available through public web sites or through public printed documents;
   - Their development must be independent of ThermoChimie development.

   Some examples of databases that can be included in the comparison exercises are, among others, the **Nagra-PSI TDB** of the Paul Scherrer Institute (PSI) (http://www.psi.ch/les/database); the **Thereda database**, a cooperative project of several institutions working on radioactive waste disposal in Germany (https://www.thereda.de/); the **JNC database** of the Japan Atomic Energy Agency (JAEA) (https://migrationdb.jaea.go.jp/cgi-bin/db_menu.cgi?title=TDB&ej=1) or the **LLNL database** of the Lawrence Livermore National Laboratory (https://www.llnl.gov).

2. **Benchmarking exercises.** Selected geochemical models are implemented in a specific geochemical code and simulated using ThermoChimie and other thermodynamic databases. The obtained results are compared and the differences are rationalised. For this type of exercise, a literature review is required to identify an example geochemical model that fits in the application field of ThermoChimie.

An example validation exercise is that designed for checking the performance of the SIT approach. ThermoChimie uses the Specific ion Interaction Theory (SIT) for ionic strength corrections. Other databases use different ionic strength correction approaches (e.g. Pitzer or extended Debye-Hückel equations). For this specific case, validation involves modelling of solubility data obtained at high ionic strengths, using different databases with different ionic strength corrections.

3. **Modelling of experimental data.** A validated thermodynamic database provides good agreement between calculated and experimental data. To achieve this, the literature is reviewed to gather experimental data that have not been previously used in the data selection process. These new sets of data are then modelled using ThermoChimie and an appropriate geochemical code. The performance of the database in simulating the new data is tested and the obtained results are rationalised in the view of the consistency and the exhaustivity of database.

   Data used in the validation exercises must be: i) reliable, as the experiments must be performed with a sound scientific basis, without systematic errors, ii) detailed, including an extensive analysis of the aqueous phase, solid characterization, etc. and iii) independent, that is, the experimental data should not have been previously used in the selection and updating of ThermoChimie. This is a limiting step in the process, because many reliable experimental studies available in the literature have already been used for database development.

4. **Simulation of data from natural analogues.** Modelling of natural analogues have also been used in validation exercises, although in a less systematic way. The main limitation of this approach is that it requires a very detailed understanding of the physicochemical processes occurring in the natural system. This knowledge is sometimes limited and as a consequence, the deviations of the simulated results from experimental data are often related to the inaccuracy of the geochemical model more than to the thermodynamic database itself.

   An example of modelling natural analogues is discussed in Bruno et al. (2002) with calculated radionuclide solubilities systematically compared with data gathered from Poços de Caldas (Brazil), Cigar Lake (Canada), Maqurin (Jordan), El Berrocal (Spain), Oklo (Gabon) or Palmottu (Finland).

The validation exercises can highlight possible ways to improve ThermoChimie:

- The exercises are able to point out data discrepancies: significant differences in thermodynamic data for solids or aqueous species in the different databases can lead to mismatched results when running calculations. If addition of the identified data would improve ThermoChimie, they will be included in a new version of the database, following the standard selection procedure.

- Validation exercises are able to pinpoint solid phases or aqueous species not included in ThermoChimie that could be needed to provide an accurate geochemical model of the system. In some cases, this is the driving force to define a specific experimental program to fill the identified data gaps.
- The validation exercises provide insight into the validity of ThermoChimie in terms of ionic strength, temperature, or redox conditions.
- The validation exercises are also a useful way to ensure the database is compatible with the requirements of the different geochemical codes.

4. Summary

This guideline provides information about validation and verification procedures used in ThermoChimie. These procedures are important for ensuring that all the relevant aqueous species and solid phases are included in the database. These procedures also provide information on the consistency and accuracy of the database and can be used to judge whether adequate uncertainty values are associated to the data, especially in cases where data is less reliable. Finally, detailed analysis of the results obtained from these exercises can highlight ways to improve ThermoChimie.

5. Bibliography

Bruno, J., Duro, L. and Grive, M. 2002. The applicability and limitations of Thermodynamic geochemical models to simulate trace element behaviour in natural waters. Lessons learned from natural analogue studies. Chemical Geology, 190, 371-393.