INPUT FROM DITUSC: IDENTIFICATION AND TREATMENT OF UNCERTAINTIES.

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CONTEXT

Strategic study = "think tank–type activities" carried out within the programme to:

- Analyse strategic questions, gaps, and options
- Support programmatic, policy, and implementation decisions
- Identify future R&D needs or priorities

DITUSC aimed to assessing current thermodynamic understanding in support of the Radioactive Waste Disposal Safety Case, with special focus given to a transversal understanding through the colleges of EURAD 2 and with key inputs from End Users

TOWARDS THE ESTABLISHMENT OF A SHARED VISION – "TDB METHODOLOGIES"

Workshop to exchange and define together a shared vision on future priorities (Nantes - November 2025)

Allowed to identification of high-level transversal topics, not directly related to specific systems:

- Verifications of applicability of existing TDBs for specific applications
- Sensitivity studies to identify key parameters for specific applications
- Assessment of related uncertainty through error propagation

Examples of identified processes/systems for which these aspects could be investigated:

→ Speciation
→ Solubility
→ Surface complexation
→ Mechanistic cement models

Increasing complexity

WHITE PAPER - CALL TO ACTION REGARDING “TDB METHODOLOGIES”

Rationale

- Ensure thermodynamic databases are sufficiently exhaustive for complex safety-relevant systems
- Explicitly account for the impact of thermodynamic uncertainties on model outputs

Near-term priorities (3–5 years)

- Joint selection of verification test systems by experts from the three colleges
- Selection criteria: safety relevance, maturity of scientific knowledge, collaboration potential
- Strengthening links with EURAD-2 WPs (e.g. RAMPEC)
- Apply sensitivity analyses to identify key parameters and assess uncertainty impacts

Longer-term priorities (5–10+ years)

- Develop consistent error-propagation methodologies in TDB-based geochemical modelling
- Avoid unrealistic conservatism due to stacking of correlated uncertainties
- Coordinate with (inter)national initiatives (e.g. OECD NEA TDB, TDB programs)
- Invest in advanced computational tools, including AI/ML, for transparent uncertainty treatment

Expected outcome

- Increased confidence in model-based predictions
- Reduced unnecessary conservatism in safety assessments
- More robust and defensible bounding and enveloping scenarios

GEOCHEMICAL MODELLING AND UNCERTAINTIES

Source of uncertainty

- **Conceptual uncertainty**
  - **Choice of thermodynamic database,**
  - **Selection of relevant aqueous species and solid phases,**
  - **Relevance of equilibrium vs kinetics**
  - **Surface complexation models vs empirical Kd approaches**
- **Uncertainty on parameters**
  - **log K, ΔG°, etc.**
  - **Porewater composition and material properties**

→ a **false sense of precision**, while small input variations may produce **strongly non-linear output responses**

Beware

- **Conceptual uncertainty is usually higher than uncertainty on parameters**
- **Non-linear systems and correlations between model input parameters**

  → Process understanding required to constrain uncertainty management/correlations

  → Range of application of models to be specified
- **Deterministic vs probabilistic approaches**

UNCERTAINTIES IN TDBS: 2 EXAMPLES

NEA-TDB: TDB-3 Guidelines for the assignment of uncertainties clearly define how uncertainties on ΔG°, log K, etc. should be estimated → Uncertainties in thermodynamic values should ideally cover the range within which the corresponding data can be reproduced with 95% probability (NEA TDB Guidelines 3, Wanner and Östhols, 1999).

ThermoChimie: The procedure for assigning uncertainty varies between data sources (Guideline 1, TCIII-2023-05E)

- Data obtained from own dedicated experimental programmes → uncertainty estimation by someone familiar with experimental method (EURACHEM, 2012)
- Data obtained from the open literature
  - original experimental sources → different experimental sources: all reliable data are considered / single experimental source: reported uncertainty or appropriate value
  - thermodynamic data compilations → NEA TDB: as reported in CTS reports / Other compilations: uncertainty evaluation based on source data
- Data derived from estimations → uncertainty derived from analogue systems with experimental data
- Data internally calculated → NEA TDB Guideline 3 (Wanner and Östhols, 1999)

PAST PROJECTS ON PROPAGATING UNCERTAINTIES IN GEOCHEMICAL MODELLING

→ There are credible and technically sound attempts (mainly Monte Carlo and surrogate-based approaches)

2023-2024

Marinich et al., 2023 – Miron et al., 2024

Uncertainty in SCM and aqueous complexation – Nagra sorption database. Using MC analyses and Polynomial Chaos Expansion surrogate model

2022

Sochala et al., 2022

Pore water chemistry of the COx clay, combine geochemical modelling (PHREEQC) with Polynomial Chaos surrogate models to propagate uncertainties and perform full statistical and sensitivity analyses

2018

ThermoChimie 2 – Task F2

Comparison MCPhreeqC et Ljunskile for some specific systems

2011-2013

MCPhreeqC in FP7 Crock

MCPhreeqC program is based on a generic Monte Carlo approach, (provided the user can define input distributions and run PHREEQC in batch mode)

2002-2015

LJUNGSKILE (Ekberg et al., 2002, Ödegaard-Jensen et al., 2004 and Malmberg 2015)

LJUNGSKILE program for assessing uncertainties in speciation calculations statistically calculate speciation uncertainties from uncertainties in stability constants, using Latin Hypercube Sampling

2000

MINVAR and UNCCON

MINVAR program gives uncertainties in water composition caused by uncertainties in rock composition

UNCCON program estimates the effect on the calculated solubilities

LESSONS LEARNT ON METHODS AND TOOLS

- **Monte Carlo** (MC) methods are straightforward but computationally expensive and challenging as soon as systems become highly non-linear and/or parameter-rich. Subject to clustering effects in some applications !
- **Latin Hypercube Sampling** (LHS) approaches can significantly improve sampling (reducing clustering effect)
- **Surrogate-based approaches** are a credible way to make uncertainty propagation feasible on complex models whilst providing overall sensitivity and output correlations. Likely to be difficult to develop simple "generic" tools as it requires to develop specific surrogate models.
- All previous attempts remain **isolated** and weren't integrated into "standard" modelling or SA/PA workflows.
- Some softwares are not compatible with the new versions of PhreeqC, would require efforts to update
- **Possible tools?**
  - GibbsStudio software also allows Monte Carlo analysis coupled with PHREEQC. Worth examining as allow systematic workflows to be developed easily !
  - UpSaGems (take advantage of developed libraries for statistics and surrogate models)

THERMOGAP – SUBTASK 4.2

Develop and benchmark workflows for uncertainty quantification in geochemical modelling using UpsaGEMS, GibbsStudio, HPGeochem, and couplings with GEMS and PHREEQC.

Method Development

- Identify key uncertain parameters through sensitivity analysis
- Define uncertainty ranges and probability distributions
- Compare sampling and uncertainty propagation strategies

Demonstration Cases

- RN sorption modelling
  - Confidence interval sampling
  - Bayesian posterior sampling
- Solubility limits and porewater speciation uncertainty

Safety Assessment Relevance

- Test cases coordinated with Task 5 (SA/PA oriented)
- Harmonised approach across partners to ensure complementarity

ThermoGAP
THermodynamic Experimental Research and Methods for Overcoming Gaps in Analysing Performance

Take-home message: Deliver validated, safety-assessment-oriented workflows for geochemical sensitivity and uncertainty analysis.

Thank you for your attention !

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