LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-TR-868425

M3SF-24LL010302062-NEA-TDB Management and International Collaborations in Sorption and Thermodynamic Modeling

M. Zavarin

August 15, 2024

Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

M3SF-24LL010302062-NEA-TDB Management and International Collaborations in Sorption and Thermodynamic Modeling

Crystalline International Collaborations

Prepared for
U.S. Department of Energy
Office of Nuclear Energy
By Lawrence Livermore National Laboratory

Mavrik Zavarin

July 30, 2024

Document Number-20XX-XXXX
National Laboratory Report No. LLNL-TR-868425

NFCSC DOCUMENT COVER SHEET[1]

Name/Title of Deliverable/Milestone/Revision No.	M3SF-24LL010302062-NEA-TDB Management and International Collaborations in Sorption and Thermodynamic Modeling
Work Package Title and Number	Crystalline International Collaborations – LLNL SF-24LL01030206
Work Package WBS Number	1.08.01.03.02
Responsible Work Package Manager	Mavrik Zavarin (Name/Signature)
Date Submitted	8/8/24

Quality Rigor Level for Deliverable/Milestone[2]	☐ QRL-1 ☐ Nuclear Data	☐ QRL-2	☒ QRL-3	☐ QRL-4 Lab QA Program[3]

This deliverable was prepared in accordance with (Participant/National Laboratory Name) QA program, which meets the requirements of:

☒ DOE Order 414.1 ☐ NQA-1 ☐ Other

This deliverable was subjected to:

☒ Technical Review (TR) ☐ Peer Review (PR)

TR Documentation Provided
☐ Signed TR Report, or
☐ Signed TR Concurrence Sheet, or
☒ Signature of TR Reviewer(s) below

PR Documentation Provided
☐ Signed PR Report, or
☐ Signed PR Concurrence Sheet, or
☐ Signature of PR Reviewers below

Name and Signature of Reviewers

Gregory Pope QA — Gregory Pope

Daniel Flowers

NOTE 1: *This form should be filled out and submitted with the deliverable. Or, if the PICS:NE system permits, completely enter all applicable information in the PICS:NE Deliverable Form. The requirement is to ensure that all applicable information is entered either in the PICS:NE system or by using the NFCSC Document Cover Sheet.*

- *In some cases, there may be a milestone where an item is being fabricated, maintenance is being performed on a facility, or a document is being issued through a formal document control process where it specifically calls out a formal review of the document. In these cases, documentation (e.g., inspection report, maintenance request, work planning package documentation or the documented review of the issued document through the document control process) of the completion of the activity, along with the Document Cover Sheet, is sufficient to demonstrate achieving the milestone.*

NOTE 2: *If QRL 1, 2, or 3 is not assigned, then the QRL 4 box must be checked, and the work is understood to be performed using laboratory QA requirements. This includes any deliverable developed in conformance with the respective National Laboratory / Participant, DOE or NNSA-approved QA Program.*

NOTE 3: *If the lab has an NQA-1 program and the work to be conducted requires an NQA-1 program, then the QRL-1 box must be checked in the work Package and on the Appendix E cover sheet and the work must be performed in accordance with the Lab's NQA-1 program. The QRL-4 box should not be checked.*

ACKNOWLEDGMENTS

This work was supported by the Spent Fuel and Waste Science and Technology campaign of the Department of Energy's Nuclear Energy Program. Prepared by LLNL under Contract DE-AC52-07NA27344.

CONTENTS

M3SF-24LL010302062-NEA-TDB MANAGEMENT AND INTERNATIONAL COLLABORATIONS IN SORPTION AND THERMODYNAMIC MODELING

1 INTRODUCTION

This progress report (Level 3 Milestone Number M3SF-24LL010302062) summarizes research conducted at Lawrence Livermore National Laboratory (LLNL) within the Crystalline International Collaborations Work Package Number SF-24LL01030206. The activity is focused on our long-term commitment to engaging our partners in international nuclear waste repository research. This includes participation in the Nuclear Energy Agency Thermochemical Database (NEA-TDB) Project and development of methodologies for integrating US and international thermodynamic databases for use in SFWST Generic Disposal System Assessment (GDSA) efforts.

A continuing focus for FY24 efforts is to support the US participation in the NEA-TDB effort. The focus of FY24 activities was the development of an agreement for a Phase 7 activity that will start in Q1 of 2025. Mavrik Zavarin is now the US representative on both the Management Board and the Executive group to the NEA-TDB. He is also the POC for the Cements State of the Art Report that is undergoing peer review in FY24.

In FY24, we used our position on the NEA-TDB MB and EG to facilitate the integration of NEA-TDB thermochemical data with LLNL's SUPCRTNE thermodynamic database that supports the SFWST GDSA activities. This effort is coordinated with the Argillite work package SUPCRTNE database development efforts (Wolery, 2024). The goal is to provide a downloadable database that will be hosted on LLNL's thermodynamics website which incorporates NEA-TDB data into the LLNL database where appropriate.

We also began engagement with the EURAD2 program that was initiated in FY24 by our European collaborators at the Karlsruhe Institute of Technology (KIT), Germany. The primary focus of the engagement is with WP20: DITUSC Thermodynamic database evaluation program. A kickoff meeting for this activity is planned for early FY25.

Finally, we have been selected to co-host (with Clemson University) the International Conference on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere in 2025 (Migration2025). The meeting will be held September 21-26, 2025, in New Orleans, Louisiana, and will focus on international efforts to understand the risks of radionuclide releases into the environment. This central focus of this conference is on international efforts to develop safe disposal options for nuclear wastes. As such, we are developing a theme focused on US underground nuclear waste repository science.

2 NUCLEAR ENERGY AGENCY THERMOCHEMICAL DATABASE PROGRAM STATUS

The Nuclear Energy Agency (NEA) Thermochemical Database Program (TDB) was conceived of and initiated with the goal to 1) make available a comprehensive, internally consistent, internationally recognized database of selected chemical elements; 2) meet the specialized modeling requirements for safety assessments of radioactive waste and; 3) prioritize the critical review of relevant data for inorganic compounds and complexes containing actinides. Data from other elements present in radioactive waste are also critically reviewed as well as compounds and complexes of the previously considered elements with selected organic ligands. The NEA TDB program is envisioned as the foundational source of thermodynamic data for the US DOE-NE nuclear waste disposal program and is the primary source of thermodynamic data used at LLNL in the development of the SUPCRTNE

code and associated database for use in nuclear waste disposal thermodynamic modeling (see (Wolery, 2024) for details).

The objective of the NEA-TDB program is to produce a database that contains data for all the elements of interest in radioactive waste disposal systems, document why and how the data are selected, give recommendations based on original experimental data, rather than compilation and estimates, document the sources of experimental data, provide internally consistent thermodynamic parameters, and treat solids and aqueous species of the elements of interest for nuclear storage performance assessment calculations.

The qualification of existing data is conducted using documented Guidelines which include several components. A Technical Review is conducted by subject matter experts who critically review experimentally determined literature data, reanalyze the data as necessary, and select data for inclusion in the database. Upon completion of the Technical Review, a Peer Review is undertaken. A second, independent panel of reviewers ensure that the technical reviewers followed the review Guidelines. A Comment Resolution component ensures that the Technical Reviewers address the comments made by the Peer Reviewers. At this time, the volume is readied for final publication. Distribution of the Reviews is completed as open source material and in electronic form via the NEA-TDB website.

Phases VI of the NEA-TDB program was officially started in February 2019 with all participating member parties having signed the Framework Agreement. The first meeting of the Management Board (MB) and the Executive Group (EG) were held at the NEA in Paris, February 19-20, 2019. Lena Evins (Sweden-SKB) was elected Chair of the MB and Stephane Brassinnes (ONDRAF/NIRAS-Belgium) Vice Chair. Canada and the Netherlands joined the Programme for this Phase. Elected to the Executive Group were Chair Marcus Altmaier (INE-Germany), Cindy Atkins-Duffin (DOE/LLNL-USA), Benoit Made (ANDRA-France), Pascal Reiller (CEA Saclay – France), and Kastriot Spahiu (SKB (retired)-Sweden. Some of the projects that were not completed in Phase V were brought forward to Phase VI. Phase VI of the NEA-TDB program, after a two year no-cost extension, will be completed at the end of 2024. The membership, scope, and effort associated with Phase 7 of the NEA-TDB program is being negotiated at this time.

The U.S. representative to the NEA TDB Management Board, Cynthia Atkins-Duffin, retired from LLNL in FY23. Mavrik Zavarin, also from LLNL, replaced her on the Management Board. The Management Board also elected Mavrik Zavarin to replace Cynthia Atkins-Duffin on the Executive Group. Mavrik Zavarin is also the point of contact to complete the Cements State of the Art Report. The Cement SOAR review will be completed in 2024 and is presently undergoing peer review.

Management Board (MB) and Executive Group (EG) meetings were held in Paris on November 6 to 8, 2023. An EG meeting was held in Paris on April 15-16, 2024. Follow-on online meetings were held by the MB on May 29, 2024 to discuss the path forward for a Phase 7 of the NEA-TDB project. A number of other online meeting were held to plan for Phase 7 activities and in response to ongoing Phase VI Blue Book and State-of-the-Art peer review and publications.

The current status of the Phase VI program and the associated reviews are:

- Iron (Part II) Volume – Published online (NEA-TDB website) in January, 2020 (NEA, 2020a) (https://www.oecd-nea.org/jcms/pl_22611/chemical-thermodynamics-of-iron-part-2).
- 2nd Update of the Actinides Volume – Published online (NEA-TDB website) in October, 2020 (NEA, 2020b) (https://www.oecd-nea.org/jcms/pl_37389/update-on-the-chemical-thermodynamics-of-uranium-neptunium-plutonium-americium-and-technetium)

- Ancillary Data Volume – Published online (NEA-TDB website) in June, 2024. Carlos Jove-Colon (USA) served as one of the peer reviewers (NEA, 2024) (https://www.oecd-nea.org/jcms/pl_93961/selected-ancillary-compounds-of-interest-to-radioactive-waste-management)
- Molybdenum Data Volume –The EG took a more active management role in this project (Pascal Reiller is the EG liaison). To motivate the completion of this data volume, a hard deadline for the first internally reviewed draft of the volume was set for December 2023. While this deadline slipped somewhat, all sections are undergoing final review at this time and peer review is anticipated to begin in early 2025.
- Cements State of the Art Report –The NEA Project Coordinator and the EG liaison (Mavrik Zavarin, USA) convened quarterly meetings with the review team. The SOAR is now ready for peer review and the external review team has been assembled. Ed Matteo (SNL) has been confirmed as reviewer. Final publication of the volume is anticipated in early 2025.
- High Ionic Strength Solutions State of the Art Report – The EG has decided to take a more aggressive approach to complete this volume. A number of chapters that were deemed non-essential were removed from the report. The document is presently under review by the NEA-TDB and external peer review will begin in late 2024.
- Organics Update – The initiation report has been completed and the Management Board accepted the report as presented, paid, and closed out the reviewer contracts. The decision was made to defer the start of this effort to a possible Phase 7 of the NEA-TDB Program.
- Lanthanides Volume – This activity is ongoing. Work on this volume continues with anticipated draft submission to NEA-TDB by Q1 of 2025 and external peer review later in 2025.
- High Temperature State of the Art Report – The initiation report has been completed and accepted. The decision was made to defer the start of this effort to a possible Phase 7 of the NEA-TDB Program.
- TDB course –The 7th edition of the TDB course was executed as an in-person event in conjunction with Migration23 in Nantes, France.
- TDB course – The 8th edition of the TDB course is planned for October 10 as a 2.5 hour online course.
- TDB Electronic Database – Currently only maintenance activities such as the populations of the eTDB with the new selected values from the Ancillary and Molybdenum volumes are being undertaken. All available NEA staff resources have been focused on the management, editing, and publication of the review volumes. Thus, updates to the electronic database may not be made until the start of a proposed Phase 7. (https://www.oecd-nea.org/jcms/pl_37223/electronic-database-of-the-tdb-project)

Based on the pace of Phase 6 deliverables and the expressed interest by the NEA-TDB partners not to enter into a Phase 7 until all ongoing activities reach the peer review stage, the MB decided to extend Phase 6 into a second no-cost 1 year extension. This allows Phase 6 to be extended to Q1 of 2025. At that point, we anticipate that the Ancillary Data volume will have been published and the Molybdenum Data volume, Cements SOAR, and High Ionic Strength SOAR will be in the peer review stage. The Lanthanides Data volume will also be nearing the peer review stage. This will also allow

for sufficient time to develop a plan forward for Phase 7 which, if approved, would begin at the end of Phase VI. The MB agreed to defer both the Organic Update Blue Book and the High Temperature State of the Art report to Phase 7. The initiation report have already been approved and revised in anticipation of a Phase 7 start of these activities.

The schedule for preparing a Phase 7 agreement followed this schedule:

- Draft agreement: mid-2024
- Ready for signature: late-2024
- Start of TDB-7: Q1 2025

Discussion of Phase 7 activities has been a priority in 2024. The MB is in agreement that Phase 7 should prioritize the Update to Organics Data volume and the High Temperatures and Pressures SOAR which already have approved initiation reports from Phase VI. Some significant interest in developing a Data Volume on iodine thermodynamics was noted. Discussion of Phase 7 priority research areas are continuing as the draft agreement is being revised and identification of participating countries is established. Depending on the level of participation and the interests of the participating agencies, the scope and effort associated with Phase 7 activities will be defined. We anticipate that a number of initiation reports will be approved by Phase 7 participating countries and the MB in early 2025.

3 PLANNING FOR PHASE 7 OF THE NEA-TDB PROGRAM

In FY24, planning for Phase 7 was underway. A draft agreement was provided to all Phase 6 participating countries in mid-2024. DOE-NE reviewed the draft agreement and did not identify any issues associated with the participation in Phase 7. The NEA-TDB MB also solicited new participants for Phase 7 from the international community. A final Phase 7 agreement will be prepared for signature by participating organizations in late 2024 for a planned March, 2025, start. The NEA-TDB program anticipates that ~3 countries that participated in Phase VI will not join the Phase 7 program. However, there are ~3 new countries that expressed interest in joining the program. Thus, it is not anticipated that the Phase 7 will see a significant reduction in the number of participating countries.

Some notable changes that have been implemented as part of the Phase 7 agreement include the following:

- Based on prior experience, it was determined that a 5-year program (rather than 4-year) was more appropriate for Phase 7.
- Significant new oversight responsibility was placed on both the EG and the lead authors to ensure that schedule delays are avoided.
- All prior phase documents will be in the peer review stage at the start of Phase 7 with the exception of the Lanthanides Blue Book. However, the Lanthanides Blue Book will be approaching the review stage at the start of Phase 7.
- Two efforts have been pre-approved for Phase 7: Organics Update Blue Book and the High Temperature State of the Art Report. Initiation reports and negotiations have already been completed and their start in anticipated in early 2025.
- In Phase 7, we anticipate that, based on the interests of the participating countries, a selection of initiation reports will be identified by the MB for preparation. Initiation reports will evaluate the feasibility of performing thermodynamic reviews on priority radionuclides of interest to the participating countries (e.g. iodine). Depending on the timing, budget, and

input from the MB, these initiation reports may be approved for Blue Book or State of the Art report preparation as part of Phase 7 or Phase 8.

4 ADDITIONAL INTERNATIONAL ENGAGEMENT EFFORTS

We have been selected to co-host (with Clemson University) the International Conference on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere in 2025 (Migration2025). The meeting will be held September 21-26, 2025, in New Orleans, Louisiana (Figure 1), and will focus on international efforts to understand the risks of radionuclide releases into the environment. The central focus of this conference is on international efforts to develop safe disposal options for nuclear wastes. As such, we are developing a theme focused on US underground nuclear waste repository science.

Figure 1. Announcement flyer for the 2025 International Conference on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere (Migration2025), September 21-26, 2025, in New Orleans, Louisiana.

In conjunction with Migration2025, the NEA-TDB will hold an in-person short course on thermodynamic modeling. We have secured classroom space at the conference hotel and are coordinating the activity with the NEA-TDB Management Board. This will be the 9th Edition of the NEA-TDB course and will be held as a full day in-person workshop.

We were approached by the Thermochimie steering committee to hold a workshop in conjunction with the upcoming Migration2025 conference. The Thermochimie steering committee formally approved this plan in 2024 and we have secured a classroom to hold the event in conjunction with the Migration2025 conference. The 2-day event will follow the Migration2025 conference and we anticipate 80 attendees. This workshop will focus on updating the community on the Thermochimie database development efforts of the past years and solicit recommendations and comments from workshop participants regarding the needs of the nuclear waste science communities, ongoing parallel efforts, and plans for future thermodynamic database developments globally.

We have been approved as associate partners of the DITUSC (DITUSC: Development and Improvement of Thermodynamic Understanding for use in Nuclear Waste Disposal Safety Case) project which is being initiated in FY25 as part of the larger EURADII (European Joint Programme on Radioactive Waste Management) effort. The DITUSC kickoff meeting is planned for November 13,

2024, and will be followed by an open 2 day workshop on November 14 and 15, 2024. Both events will be held in Barcelona, Spain, and were scheduled to align with the NEA-TDB Management Board meeting that will be held the following week in Paris, France.

The DITUSC project is focused on the consolidation and improvement of knowledge to predict processes over long timescales in key fields for geological disposal of radioactive waste. Special focus will be given to 1) the identification of data gaps supporting the understanding of the transport behaviour of safety-relevant radionuclides and organics, 2) the thermodynamic description of a set of perturbations (temperature and high saline conditions), 3) the thermodynamic description of solid-solutions and their role in radioactive waste management and disposal, and 4) the interplay of thermodynamics and kinetics. As a "strategic study" withing the EURADII framework, this project aims to develop a white paper summarizing the current thermodynamic understanding and promoting new scientific strategies to further support/improve the use of thermodynamics in the Safety Case of nuclear waste disposal facilities.

In late FY24, we are convening an international workshop on sorption data collection and database development in collaboration with David Garcia (Amphos21), Stephane Brassinnes (Ondraf/Niras), and Vinzenz Brendler (HZDR). The workshop, titled "Sorption data management and database development for radioactive waste management" will take place September 16-17, 2024, in Barcelona, Spain, with participation of nearly all countries with active nuclear waste repository programs. The workshop was developed based on discussions at the NEA-TDB MB and EG meetings in 2023 that supported the concept of aligning efforts to develop consensus among international nuclear waste repository programs regarding this topic. However, sorption was deemed to be outside the scope of the NEA-TDB whose primary focus is thermodynamics. While the NEA-TDB has provided some guidance regarding surface complexation modeling in the past ((NEA, 2001, 2005)), they encouraged the interested parties to develop the topic outside the NEA-TDB and return to the NEA-TDB program to discuss how any new initiatives associated with this topic may be supported in the future (either within or outside the NEA portfolio). A more detailed summary of this effort is provided in the milestone report "M3SF-24LL010301062-Surface Complexation/Ion Exchange Data Integration for Radionuclide Sorption to Clay Minerals" associated with the Argillite International work package (SF-24LL01030106) (Zavarin et al., 2024).

5 PLANNED FY25 EFFORTS

FY25 efforts will support the initiation of and US participation in Phase 7 of the NEA-TDB program as well as supporting the completion of prior phase Blue Books and State of the Art Reports. We anticipate that Phase 7 will be initiated in Q1 of 2025. We will use our position on the NEA-TDB MB and EG to facilitate the integration of NEA-TDB thermochemical data with LLNL's SUPCRTNE thermodynamic database that supports the SFWST GDSA activities. This effort is coordinated with the Argillite work package SUPCRTNE database development efforts.

Based on the result of our Sorption Database workshop in late FY24, we will discuss publication of a manuscript that provides a summary and guidelines for development of sorption databases and associated models to support underground nuclear waste repository efforts. We will actively support the DITUSC project, which is part of the EURADII initiative, as associate partners. We will execute the Migration2025 conference and support associated the NEA-TDB and Thermochimie workshops that will provide critical international engagements and develop consensus and synergy in thermodynamics as it relates to supporting the US nuclear waste repository program.

6 REFERENCES

NEA, 2001. Using thermodynamic sorption models for guiding radioelement distribution coefficient (Kd) investigations. A status report. OECD Publishing, Paris, France.

NEA, 2005. NEA Sorption Project Phase II: Interpretation and Prediction of Radionuclide Sorption onto Substrates Relevant for Radioactive Waste Disposal Using Thermodynamic Sorption Models. OECD Publishing, Paris, France.

NEA, 2020a. Chemical Thermodynamics of Iron, Part 2. OECD Publishing, Paris, France.

NEA, 2020b. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. OECD Publishing, Paris, France.

NEA, 2024. Selected Ancillary Compounds of Interest to Radioactive Waste Management. OECD Publishing, Paris

Wolery, T., 2024. M3SF-24LL010301052-Summary of SUPCRTNE testing and Rev0 database. Lawrence Livermore National Laboratory, Livermore, California.

Zavarin, M., Eguiguren, L., Golla, J., Han, S., 2024. M3SF-24LL010301062-Surface Complexation/Ion Exchange Data Integration for Radionuclide Sorption to Clay Minerals. Lawrence Livermore National Laboratory, Livermore, California.