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M4SF-20LL010302082- Thermodynamic Database for Generic Disposal System Assessment

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Appendix E
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This Deliverable was subjected to:

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Technical Review (TR)

Review Documentation Provided

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☐ Peer Review

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June 15, 2020

M4SF-20LL010302082- Thermodynamic Database for Generic Disposal System Assessment

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1. Introduction

This progress report (Level 4 Milestone Number M4SF-20LL010302082) summarizes research conducted at Lawrence Livermore National Laboratory (LLNL) within the Crystalline International Collaborations Activity Number SF-20LL010302081. The activity is focused on our long-term commitment of engaging our partners in international nuclear waste repository research. This includes participation in the Nuclear Energy Agency Thermochemical Database (NEA TDB) Project (Cindy Atkins-Duffin) and development of methodologies for integrating US and international thermodynamic databases for use in SFWST Generic Disposal System Assessment (GDSA) efforts.

LLNL is supporting the overall objectives of the Disposal Research (DR) Crystalline International Collaborations Research and Development (R&D) control account. The objective of this control account is to advance our understanding of long-term disposal of spent fuel in crystalline rocks (including both granitic and metamorphic rocks) and to develop necessary experimental and computational capabilities to evaluate various disposal concepts in such media. LLNL efforts in the Crystalline International Collaborations work package are focused on the following:

• Continued engagement with the NEA TDB project through the support of Dr. Atkins-Duffin as the SFWST representative for international thermodynamic database development effort. This effort ensures that US GDSA model efforts are aligned with internationally accepted practices for repository performance assessment calculations.

• Dr. Cindy Atkins-Duffin is the Executive Group (EG) liaison to the TDB Cements team and will help coordinate the completion of the Cements report.

• Coordinating and integrating LLNL thermodynamic database efforts (Argillite DR workscope) with international efforts to ensure that GDSA model efforts are performed using internationally accepted thermochemical data.

In FY20, we focused on our longterm commitment to engaging our partners in international nuclear waste repository research. This includes participation in the Nuclear Energy Agency Thermochemical Database Project (Cindy Atkins-Duffin), thermodynamic database collaborations (Tom Wolery), and surface complexation model international collaborations (Mavrik Zavarin).

In FY19 we developed mechanisms for integration of NEA-TDB thermochemical data (new electronic database made available in 2018) with LLNL's thermodynamic databases. A short code was written to import new data and export formatted databases for use in Geochemists Workbench and other reactive transport codes. This effort was coordinated with the Argillite work package database development efforts. The goal for FY20 was to test this code for providing a new downloadable database that will be hosted on LLNL's thermodynamics website which incorporates NEA-TDB data into the LLNL database where appropriate.

As part of our international engagement with surface complexation model development, FY20 efforts included the assimilation of sorption data collected by our international RES3T team partners at the Helmholtz Zentrum Dresden Rossendorf. These data are in the process of being incorporated into LLNL's sorption database and will increase our database to approximately 20,000 individual measurements. A summary of that data will be provided in the Argillite International Collaborations FY20 M4 milestone report.

2. Nuclear Energy Agency Thermochemical Database Program

2.1 History of Project

The Nuclear Energy Agency (NEA) Thermochemical Database Program 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 objective of the 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 an 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.

2.2 History of Phases and New Phase 6 Efforts

Phase I of the NEA-TDB program was conducted between 1984 and 1998. Initial review volumes included Uranium, Americium, Technetium, Neptunium/Plutonium.

Phase II of the NEA-TDB program updated all the actinide volumes. The update is contained in a single volume. Added in this phase were Nickel, Selenium, Zirconium, and the compounds and complexes of the reviewed elements with selected organic ligands - EDTA, ISA, oxalate, and citrate. The Program also conducted a workshop,

"The Use of Thermodynamics Databases in Performance Assessment." The phase ran from 1998-2003.

Phase III of the NEA-TDB program saw the introduction of a second product, State-of-the-Art reports. The first such report covered solid solutions of interest to nuclear waste management. Thorium, Iron (part I), and Tin volumes were added to the published collection.

Phase IV of the NEA-TDB program, conducted from 2008-2014, started the second portion of the Iron review; review of Molybdenum, and; review of Auxiliary Data which includes species and compounds necessary to describe aqueous chemistry of Aluminum and Silicon, data on inorganic species and compounds of elements such as Iodine, Boron, Magnesium, Calcium, Strontium, and Barium.

Phase 5 of the NEA-TDB program, conducted from 2014-2019 took on a second update to actinide and fission product volumes, and two State-of-the-Art reviews - Cement Minerals and High Ionic Strength Aqueous Systems. The design and development of a new TDB electronic database that is compatible with PHREEQC was undertaken.

Phases 6 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. In process projects from Phase 5 were brought forward to Phase 6.

The current status of the Phase 6 program and the associated reviews are:

- **Iron (Part II) Volume** – Published online (NEA TDB website) in January, 2020.
- **2nd Update of the Actinides Volume** – Issues with the Uranium chapter were identified and then resolved by members of the review team. The final draft is now in preparation by the TDB staff before transmittal to the NEA publishing group. Publication of this volume is anticipated in the summer of 2020.
    - This volume will contain a dedication to the late Ingmar Grenthe, renown chemist and one of the founders of the TDB project
- **Ancillary Data Volume** – The full draft volume is now in the peer review process. Carlos Jove-Colon (USA) is one of the peer reviewers.
- **Molybdenum Data Volume** – This review continues to struggle with delivery of information from the team to the NEA and to other teammates. Several rescoping and personnel assignments have been put into place. The EG will take a more visible management role in this project.

- **Cements State of the Art Report** – The team provided a new schedule to the EG. They had not delivered the individual drafts and internal reviews in December as described in their previous schedule of work. The new schedule indicates the individual draft will now be completed by September 2020. Internal reviews would commence in the following summer. There will be a scheduled videoconference at the end of June to status their progress.
- **High Ionic Strength Solutions State of the Art Report** – The deadline for the completion of the first drafts and of all internal reviews was February 2020. A progress report received in April indicated a three month delay in the delivery of the first drafts. The latest information received by the EG is that "there is progress, but it is slow."
- **Organics Update** – The initiation report work is underway. The literature search is projected to be complete by the end of July and the final initiation report submitted by the end of October for review by the MB for their November meeting.
- **Lanthanides Volume** – The initiation team has indicated they intend to submit their final report by the end of June.
- **High Temperature State of the Art Report** – The initiators have submitted a document containing a synopsis of the topics that will be covered and the organization of their initiation report.
- **TDB course** – planned to be held in Paris, November 2020 – The webpage and final outline are available online, including the registration page. Possible impact to this activity from COVID 19 will be evaluated at some later time.

The NEA has announced there will be no "in person" meetings convened for NEA projects through this calendar year. Plans are in progress to convene the annual meeting in November of the Management Board and the Executive Group by virtual means.

3. An Interactive SUPCRT Data Tool for Adding New Species and Outputting New Data Files For Reactive Transport Codes

3.1 Introduction

The goal of this task is to create software to help manage thermodynamic database files as new and improved data become available. The software will ensure that users adding data to databases do so in way that is correct, convenient, consistent with existing data, and in a form immediately useful for reactive transport modeling.

The task consists of two main efforts:

1. Method to add thermodynamic data for new species, or replace thermodynamic data for existing species to the existing database

2. Produce a new data file for the user-specified reaction path code (e.g. PHREEQC, EQ3/6, GWB etc.) that contains the new or modified data formatted for the code of choice.

We choose for this version of the software to work from the SUPCRT data base developed by Helgeson and others at UC Berkeley (Helgeson et al., 1974a,b, 1976, 1981). Our starting file is the SUPCRT version that has been augmented with additional data by Chen Zhu and co-workers at Indiana University and referred to as SUPCRTBL (Zimmer et al., 2016).

We have chosen to use the scripting language Tcl/Tk to create the software. Tcl can be used with all major platforms and Tk provides easy creation of a graphical interface for convenient and fool-proof user input.

3.2 Progress to date

The first task we identified was to code a method to read in the SUPCRT data file and write reactions between all the species (or user-selected subset of species). This would be done using the user-selected set of "basis species" that are specific to the reactive transport code the user is targeting. This code reads in and stores all the data in SUPCRT and allows later manipulation needed to add new species or modify existing ones as desired.

The first version of code to carry out this task was completed in the Fall of 2019. However, in carrying out this work, we identified two additional needs to complete this task. The first involves correcting numerous formatting inconsistencies in the SUPCRT data file that cause our script to fail. Error checking to alert the user was one option, but would necessitate the user having to edit the data file to correct the problem. Because our high-level goal is to make robust software that would not involve user editing (which might not even be an option for some users), we decided to use the script itself to check for and correct these errors. This task was time-consuming and in some ways more difficult than the main task. This task continued on through the end of the year.

The second need is to include phase change data in the algorithm. Although these data are probably not necessary for most applications that we envision (low temperature aqueous systems), the data may be needed for some modeling at elevated temperatures (corrosion near reactors or heated HLW etc.) and providing for this capability now will be much easier than inserting it later. Work on this task is not expected to be difficult, but has not yet started. The SUPCRT data file contains phase change data for many solids. These data will be carried forward along with an input option to add additional phase change data.

3.2 Next steps

The next step is a front end (including GUI) to allow a user to input new or revised data into the SUPCRT database. The code will make sure the data is entered correctly and in a way that is internally consistent with the existing data.

The final step is to provide coding to format the SUPCRT output for the reactive transport code of choice. Both of these steps will take advantage of the code already written to read in the data file and write reactions. We anticipate that these last two steps will take the same amount or less effort than effort to date.

The final task is to take the list of balanced chemical reactions and log K data and re-write it in the format of the desired reactive transport code. This work has not yet been started, but is not expected to involve anything other than providing the correct output format for each code. No additional data manipulation should be needed.

3.3 Summary

Work is in progress to produce a software tool to add new species and to produce enhanced data files for reactive transport codes relevant to the SFWST Generic Disposal System Assessment (GDSA) efforts. The tool is built around the SUPCRT data base as amended by Chen Zhu and co-workers (SUPCRTBL). The code is meant to be used by someone wanting to add new data to SUPCRT and ensure that it is internally consistent with the existing data. The code will produce a new version of the data file needed to run any of several reactive transport codes. Currently we plan to produce files for PHREEQC, EQ3/6, and GWB. Additional file configurations can be readily added to support the GDSA efforts. Furthermore, our code can readily be modified to use data files other than SUCPRT as the starting database. In particular, this code will be applicable to the modified SUPCRT code under development in the Argillite work package and led by T. Wolery for use in the US SFWST Generic Disposal System Assessment (GDSA) efforts. A key goal is to facilitate the integration of US SFWST thermodynamic database development with international thermodynamic database compilations (e.g. the NEA-TDB radiochemical thermodynamic data).

5. Planned FY21 Efforts

A continuing focus for FY21 efforts will be to support the US participation in the NEA-TDB effort and developing mechanisms for integration of NEA-TDB thermochemical data (new electronic database made available in 2018) with LLNL's thermodynamic databases that support the SFWST GDSA activities. This effort is coordinated with the Argillite work package database development efforts. 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. Updating thermodynamic databases and enhancement of our database integration code to ensure that SFWST GDSA efforts are based on current and internationally accepted thermodynamic data will be a key focus in the next fiscal year.

6. Acknowledgments

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