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M4SF-21LL010302062-Update on NEA-TDB Database Development and Database Formatting Tool

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1. Introduction

This progress report (Level 4 Milestone Number M4SF-21LL010302062) summarizes research conducted at Lawrence Livermore National Laboratory (LLNL) within the Crystalline International Collaborations Activity Number SF-21LL01030206. 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.
- 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.

A continuing focus for FY21 efforts was to support the US participation in the NEA-TDB effort and developing mechanisms for integration of NEA-TDB thermochemical data with LLNL's thermodynamic database (SUPCRTNE) that support the SFWST GDSA activities. This task supported three NEA-TDB management board meetings in FY21 that were held in Paris, France (all meetings were conducted remotely in FY21). This effort is coordinated with the Argillite work package database development efforts.

In addition, a goal of FY21 was to create software to help manage thermodynamic database files as new and improved data become available. We continued our effort to produce a code to integrate NEA-TDB thermochemical data (new electronic database made available in 2018) and other newly-available thermodynamic data with LLNL's thermodynamic databases. A short code was written with the goal of importing new data and exporting formatted databases for use in Geochemists Workbench, PHREEQC, EQ3/6, and other reactive transport codes. We decided to use the SUPCRT database as the starting database given it was also used to create the EQ3/6 data base. This effort was coordinated with the Argillite work package database development efforts. The goal for FY21 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, FY21 efforts included the assimilation of sorption data collected by the Japanese Atomic Energy Agency (JAEA). These data are in the process of being incorporated into LLNL's sorption database and will increase our database to approximately 35,000 individual measurements. A summary of that data assimilation effort is reported in section 4 of this report.

2. Nuclear Energy Agency Thermochemical Database Program

2.1 History of Project

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 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 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 via the NEA TDB website.

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 a 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** – Published online (NEA TDB website) in October, 2020
- **Ancillary Data Volume** – The volume is in the final stages of editing and production, expected publication (NEA TDB website) by the end of 2021. 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 has taken a more

visible management role in this project. The current planned publication (NEA TDB website) by the end of 2022.

- **Cements State of the Art Report** – Considerable discussions were conducted by the TDB MB and EG regarding the pace of this review. The review team as asked to provide a realistic schedule to complete the project. The team provided a new schedule to the EG. The NEA Project Coordinator and the EG liaison (Cindy Atkins-Duffin, USA) convened quarterly meetings with the review team to monitor the review teams progress to their schedule. Progress has been steady with a planned publication (NEA TDB website) by the end of 2022.
- **High Ionic Strength Solutions State of the Art Report** – Progress continues to be slow on this project. The next deliverable, first single author drafts and internal reviews of the text are due mid-2021. The current planned publication (NEA TDB website) by the end of 2022.
- **Organics Update** – The initiation report work was delayed and is now underway. This report is due mid-2021.
- **Lanthanides Volume** – The initiation team submitted their final report by the end of June. There was considerable discussion about the initiation report (strategy and approach) at the fall 2020 EG and MB meetings. Several small discussions and a meeting of the Initiators and the EG was convened. Contracting of the review team complied with the new OECD procurement processes and was initiated in early March 2021. Deliverable dates are under discussion.
- **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. A panel of experts to review the identified material is being constructed. Once identified the remaining review scheduled can be planned and contracting initiated.
- **TDB course** – The in-person course planned for Paris in November 2020 was cancelled. An online option was presented as a substitute. 75 people participated and reviewed the opportunity favorably. The possibilities of continuing online presentation of this material either as side event to the in-person meeting or as a separate promotional event are under consideration. The September 2021 course (adjacent to Migration ’21) was postponed.
- **TDB Electronic Database** – In November 2020 the electronic version of the NEA database was upgraded to include the release of a search engine and the inclusion of the SIT1 and SIT2 coefficients. Work is underway at this time to add the data from the recently released Ancillary review data and continue with bug fixes.

The NEA has announced there will be no “in person” meetings convened for NEA projects through this calendar year. The annual meeting in November of the Management Board and the Executive Group will again be conducted virtually.

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 product data files will be made available to all users wanting to use the new thermodynamic data in their modeling calculations. For example, the latest NEA data will be made available for most of the widely used modeling codes. The software itself will be made available to users wanting to create a custom data file for their specific needs.

The task consists of two main efforts:

1. Create a method to add thermodynamic data for new species or set of 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). Historically, SUPCRT was the default database for the EQ3/6 code. 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

We have completed most of Task 2 listed above. The current code reads in and stores all of the information in the SUPCRTBL database. The SUPCRT data file is generic and universal in the sense that it contains the most common species (aqueous, solid, and gaseous) for the elements commonly used in modeling aqueous systems. These data were obtained from critically reviewed sources such as NBS, CODATA, NIST, and Bureau of Mines reports. For most user applications, we anticipate that these data will not be further modified as they are considered the best available.

What the SUPRCT database lacks are data for actinides, rare earths, less-common metals, and other species needed in specific applications. It also lacks the most recent thermodynamic data available from current thermodynamic measurement activities. Our

goal is to make it easy to incorporate these data.into the SUPCRT database with a convenient and relatively fool-proof tool.

Our previous work produced a code that writes a balanced reaction for any user-specified species in terms of the "basis" species for each element. This step is important because SUPCRT contains data for individual species whereas the modeling codes require as input the log K values for reactions between species. Modeling codes each have their own defined basis species that our code knows and uses to write these reactions. Current work has successfully used these reactions to produce an input file to the SUPCRT code to produce log K grids for desired reactions. Because we use SUPCRT itself to compute thermodynamic properties, we should be able to continue to use our code without significant changes as newer versions of SUPCRT become available.

SUPCRTBL is in fact a newer version of SUPCRT with added thermodynamic data for additional aluminosilicate minerals from Holland and Powell (2011), a critically-compiled dataset for arsenic species to allow better modeling of arsenic transport, and updated properties for alumina and silica species important for modeling carbon dioxide sequestration in the subsurface (Zimmer et. al., 2016). Note that the Holland and Powell data required the addition of new equation of state parameters into SUPCRT, a non-trivial task. We have structured our code to have all of the thermodynamic manipulations take place via a call from the Tcl code to SUPCRT, and not carry out any calculations in our code that may be modified or enhanced in the future. Improvements such as these are likely to continue and one of our goals is to ensure our code can easily be used as the SUPCRT data file and SUPCRT code evolve.

SUPCRT is run interactively or in batch mode using a user-created input file. The file tells SUPCRT the reaction or set of reactions for which to compute reaction properties (log K, enthalpy, etc.). Note that there is no error checking of the SUPCRT user input. The user can input an imbalanced reaction and the code will produce thermodynamic data regardless. In contrast, our code uses the previously-computed balanced reactions (using matrix algebra) to create a SUPCRT input file and then calls SUPCRT to compute the reaction properties. This is all done internally by the Tcl code. No user error for the reactions is possible. SUPCRT produces an output file which our Tcl code then parses to find the log K values for the reactions. The log K values are then used to produce the reaction data blocks for the desired reactive transport code (EQ3/6, PHREEQC, etc.). We expect to have all of these features working by the end of FY2021.

3.3 Next steps

The next step is to create a graphical user interface (GUI) to allow a user to accomplish two main tasks. The first task is to input new or revised data into the SUPCRT database. The data may be of any of several forms, such as

- a free energy value for a species at some temperature or set of temperatures
- a log K value for a reaction at some temperature or set of temperatures

- a free energy value for a species at some temperature plus a heat capacity polynomial for that species

Others are possible as well. For each case, the code will make sure that the new data are consistent with existing thermodynamic properties in the SUPCRT data file. For example, if a log K for a reaction is provided, the user will also need to identify the species in the reaction. The code will check to make sure those species are in the current database (which in most cases will be true as these will mainly be the existing "basis" species) and that the reaction is balanced. If new species are present, the user will be asked to provide data for the new species as well. If the reaction is not balanced, the code will balance the reaction and provide a warning to the user. In each case, the code will be structured as much as possible to check user entry and make sure only thermodynamically consistent data are entered. This work is underway and will be the main focus of work in FY2022.

The second task is to allow the user to create a data file with a user specified set of species. For example, the user may only want to use the NEA data in their modeling calculation. Or they may want to add a new set of thermodynamic data for europium while keeping all other rare earth species as they are. A common request is to remove all of the organic species that are not relevant for most calculations that add unwanted clutter to the output file. This will be accomplished using species "tags" depending upon their origin or other properties that will allow them to be user selected as desired. We expect that the user interface will evolve over time once we begin to get feedback from users. The GUI will then be modified both to include requested options, and to add more error-checking of user input.

The final FY2022 task is to take the list of balanced chemical reactions and log K data and rewrite it in the format of the desired reactive transport code. This work is currently underway for the PHREEQC code and we expect to have a working version for PHREEQC this year (FY2021). A similar effort for the other targeted codes (EQ3/6, GWB, and CRUNCH) will be completed in FY2022. This effort is not expected to involve anything other than providing the correct output format for each code. But work to date has found some unexpected inconsistencies in the existing reactive transport data files that will need to be specifically addressed as special cases by our code. No additional data manipulation should be needed.

3.4 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 SFWST Generic Disposal System Assessment (GDSA) efforts. A key goal is to facilitate the integration of SFWST thermodynamic database development with international thermodynamic database compilations (e.g. the NEA-TDB radiochemical thermodynamic data).

4. Japanese Atomic Energy Agency Kd Database Assimilation Effort

In an effort to build an open source database of raw sorption data for use in nuclear waste performance assessment models, we recently reached out to our colleagues at the Japanese Atomic Energy Agency and began the process of assimilating JAEA's large database of sorption data into the LLNL SCIE database. The JAEA Kd database is a web based open source database that contains nearly 70,000 Kd data (Table 1) (https://migrationdb.jaea.go.jp/nmdb/db/sdb/search_1.jsp). The database includes information on both rock and single mineral sorption data. The database also spans a wide range of radionuclides relevant to the nuclear waste programs (Table 2). However, a number of issues needed to be resolved to assimilate these data into the LLNL SCIE database for use in surface complexation/ion exchange database (and ML) development being pursued at LLNL. Key issues to be resolve included the following:

- Conversion of electrolyte composition into units compatible with the LLNL SCIE (mol/L)
- Conversion of gas composition alphanumeric strings into gas fugacity values
- Conversion of various alphanumeric strings (value ranges, "<" and ">" values, etc., into real numbers
- Conversion of Kd data into aqueous and sorbed radionuclide concentration.

Table 1. Summary of Kd data contained in JAEA Kd database by mineral type

Mineral Group	Number
Cementitious materials	7236
Other minerals	12762
Bentonite (smectite)	13995
Basaltic rocks	2178
Granitic rocks	7096
Mudstone (Sedimentary rocks)	3061
Clay minerals	12694
Sandstone	4594
Tuff	2843
Soil	2503
Grout(Cement, Granitic rocks)	826
Total	**69788**

Table 2. Numbers of Kd data per element in JAEA Kd database

Element	Data
Ac	85
Am	2739
Ba	645
Bi	24
C	1000
Ca	301
Cd	310
Ce	277
Cl	175
Cm	93
Co	2078
Cs	11104
Eu	4967
Fe	596
I	1682
K	98
Mg	84
Mn	294
Mo	76
Na	108
Nb	844
Nd	141
Ni	5218
Np	5168
P	11
Pa	471
Pb	1926
Pd	108
Po	64
Pu	3250
Ra	1657
Rb	104
Sb	166
Se	4250
Sm	144
Sn	528
Sr	5531
Tc	2293
Th	1961
U	7616
Zn	1065
Zr	536
Total	**69788**

We developed a Jupiter notebook with ~500 lines of python code to perform the necessary reformatting of the JAEA database and allow for the assimilation of JAEA data into the LLNL SCIE database. The details of this process will not be presented here. However, a summary of the mineral data captured in the conversion process (single minerals only) is reported in Table 3. A list of total data per element is reported in Table 4 and Figure 1. In this first effort to assimilate JAEA data, nearly 17,000 single mineral data were converted into the LLNL SCIE format. This nearly doubles the number of data

that are now available to our surface complexation/ion exchange and machine learning database development efforts. In FY22, we will pursue a more detailed evaluation of JAEA Kd data quality and examine whether additional data can be mined from the JAEA database for other SFWST performance assessment purposes. For example, there are significant number of data for rocks and engineered materials that may be relevant to the SFWST program and we have not yet evaluated whether our data stripping code effectively captured all relevant single mineral data. We will engage directly with the JAEA database group (Dr. Yukio Tachi, Radionuclide Migration Group lead) to facilitate further data evaluation efforts in FY22.

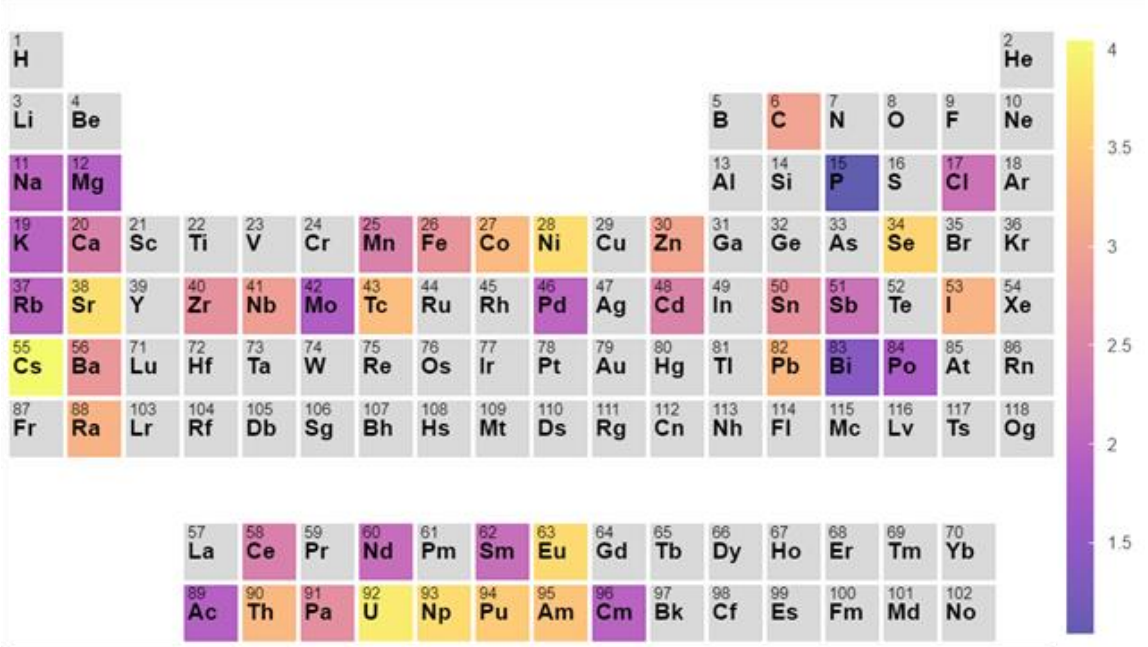

Figure 1. Data distribution patterns in the JAEA Kd database (log(# of data)).

Table 3. Numbers of Kd data per mineral in JAEA Kd single mineral data.

Mineral	Number
Al(OH)3, Al2O3, alumina, corundum	517
albite, anorthite, K-feldspar, orthoclase, microcline, bytownite, oligoclase	206
mica, biotite, Na-biotite, muscovite, phlogopite, Na-phlogopite	554
argillite	146
chlorite	138
vermiculite, K-vermiculite, Na-vermiculite	90
bentonite, Ca-bentonite, Na-bentonite	2832
montmorillonite, Ca-montmorillonite, K-montmorillonite, Mg-montmorillonite, Na-montmorillonite	2003
smectite, Ca-smectite, K-smectite, Na-smectite, saponite	1222
illite, Ca-illite, K-illite, Na-illite, NH4-illite	1633
kaolinite, K-kaolinite, Ca-kaolinite, Mg-kaolinite, Na-kaolinite, NH4-kaolinite	531
halloysite, Ca-halloysite, Mg-halloysite, K-halloysite, Na-halloysite	127
hectorite	12
calcite	812
dolomite	3
cerusite	3
siderite	1
apatite	4
FeO, ferrihydrite, goethite, hematite, magnetite, gama-MnO2, MnO2	1512
SiO2, opal, quartz	817
TiO2	13
sphene	1
gypsum	23
chrysocolla	2
enstatite	23
epidote	16
galena	1
hornblende	34
hornblendite	6
hydrogarnet	3
olivine	1
pyrite	8
serpentine	5
allophane	12
anhydrite	5
attapulgite	3
augite	13
zeolite, Na-clinoptilolite, mordenite, heulandite, clinoptilolite	854
loess	113
NA	2643
Total	**16942**

Table 4. Numbers of Kd data per element in JAEA Kd single mineral data

Sorber	Number
Am	446
Ba	57
Bi	20
Ca	60
Cd	31
Ce	5
Cm	36
Co	141
Cs	3725
Eu	476
Fe	93
I	90
K	5
Mg	65
Mn	19
Na	6
Nb	8
Ni	1853
Np	2122
Pa	123
Pb	1296
Pd	16
Po	6
Pu	353
Ra	155
Rb	7
Sb	1
Se	1431
Sm	11
Sn	47
Sr	204
Tc	163
Th	652
U	3147
Zn	47
Zr	25
Total	**16942**

5. Planned FY22 Efforts

A continuing focus for FY22 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.

As part of our international activities, we will continue our effort to integrate the JAEA Kd database into the LLNL SCIE database framework. To date, we have compile >500 lines of python code that can be used to export JAEA single mineral data Kd data into a format that is compatible with the LLNL SCIE database (~15,000 data). FY22 efforts will focus on code debugging and data quality evaluation. In addition, we are currently discussing data assimilation efforts from nuclear waste program databases in Germany and elsewhere. The overall goal is to produce an open source database that can be shared and integrated with multiple nuclear waste programs internationally.

6. Acknowledgments

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