LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

M4SF-18LL010302082-Thermodynamic Database Development and Identification of Actinide Sequestration in Corrosion Products

M. Zavarin, E. Balboni, C. Booth, T. Wolery, C. Atkins-Duffin

August 17, 2018

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Appendix E
FCT Document Cover Sheet

Name/Title of Deliverable/Milestone	M4SF-18LL010302082: Thermodynamic Database Development and Identification of Actinide Sequestration in Corrosion Products
Work Package Title and Number	SF-18LL01030208 Crystalline International Collaborations - LLNL
Work Package WBS Number	1.08.01.03.02
Responsible Work Package Manager	Mavrik Zavarin (Name/Signature)
Date Submitted	

Quality Rigor Level for Deliverable/Milestone	☐ QRL-1 Nuclear Data	☐ QRL-2	☐ QRL-3	☒ QRL-4 Lab-specific

This deliverable was prepared in accordance with Lawrence Livermore National Laboratory's QA program which meets the requirements of

☒ DOE Order 414.1   ☐ NQA-1-2000

This Deliverable was subjected to:

☒ Technical Review	☐ Peer Review
Technical Review (TR)	**Peer Review (PR)**
Review Documentation Provided	**Review Documentation Provided**
☐ Signed TR Report or,	☐ Signed PR Report or,
☐ Signed TR Concurrence Sheet or,	☐ Signed PR Concurrence Sheet or,
☒ Signature of TR Reviewer(s) below	☐ Signature of PR Reviewer(s) below

Name and Signature of Reviewers

Brian L. Anderson	*Brian Anderson*	
Gregory Pope	*Gregory Pope*	

*Note: 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. QRL for such milestones may be also be marked N/A in the work package provided the work package clearly specifies the requirement to use the Document Cover Sheet and provide supporting documentation.

M4SF-18LL010302082-Thermodynamic Database Development and Identification of Actinide Sequestration in Corrosion Products

M. Zavarin[1], E. Balboni[1], C. Booth[2], T. Wolery[1], and Cindy Atkins-Duffin[1]

[1] Glenn T. Seaborg Institute, Physical & Life Sciences, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA.
[2] Lawrence Berkeley National Laboratory, One Cyclotron Road, Mailstop 70A1150, Berkeley, CA 94720 USA

DISCLAIMER

This information was prepared as an account of work sponsored by an agency of the U.S. Government. Neither the U.S. Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness, of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. References herein to any specific commercial product, process, or service by trade name, trade mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.

Contents

1. Introduction

This progress report (Level 4 Milestone Number M4SF-18LL010302082) summarizes research conducted at Lawrence Livermore National Laboratory (LLNL) within the Crystalline International Collaborations Activity Number SF-18LL010302081. The activity is focused on our long-term commitment of engaging our partners in international nuclear waste repository research. This includes participation in the following activities: actinide sequestration in steel corrosion products (Enrica Balboni), Nuclear Energy Agency Thermochemical Database (NEA TDB) Project (Cindy Atkins-Duffin), thermodynamic database collaborations (Tom Wolery), and surface complexation model international collaborations (Mavrik Zavarin).

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. Specific tasks included in the FY18 effort associated with this milestone include the following:
- Engagement with the NEA TDB Project through the support of Dr. Atkins-Duffin as the DOE Spent Fuel and Waste Sciences and Technologies (SFWST) representative for international thermodynamic database development effort. This effort ensures that the United States Geologic Disposal Safety Assessment (GDSA) model efforts are aligned with internationally accepted practices for repository performance assessment calculations.
- Collaboration with Helmholtz Zentrum Dresden Rossendorf (HZDR) thermodynamic and sorption database development groups in support of the database needs of the SFWST program
- Thermodynamic database development in support of SFWST with particular focus on updating the thermodynamic database to be used for evaluating the mineralogic and geochemical evolution of near-field and far-field repository conditions.
- Investigating the role of steel corrosion on radionuclide sequestration and improved prediction of repository performance. This includes engaging with collaborators at the European Synchrotron Radiation Facility (ESRF) and Stanford Synchrotron Radiation Lightsource (SSRL) to investigate actinide incorporation into oxide phases.

In FY18, LLNL continued their efforts in data collection and model development in support of the SFWST program. In particular, our research focused on identification, quantification, and parameterization of processes relevant for the evaluation of the performance of various repository scenarios under investigation by the SFWST program. Ongoing efforts funded in late FY18 under the Argillite Disposal, Argillite International Collaborations, and Crystalline Disposal work packages are not included in this summary. However, the scope associated with these efforts is reviewed under Ongoing FY18/FY19 Efforts at the end of this report.

Our particular interest in radionuclide sequestration by corrosion products stems from (1) the potential for this process to significant inhibit radionuclide release during canister breaching and (2) from the absence of such processes in most repository performance assessments. Discussions with James Jerden (Argonne National Laboratory) suggest that a model of radionuclide incorporation can be added to the waste package cell of the GDSA model and may lead to a reduction in the source term of mobile radionuclides. Steel corrosion rates have been implemented within the spent fuel matrix degradation process model but have not yet been implemented into GDSA. Results from an experimental and modeling study of radionuclide partitioning into steel corrosion products will facilitate the incorporation of this process into the GDSA as the steel corrosion model is implemented.

LLNL evaluated this process from both an experimental and modeling perspective. Experimentally, LLNL has been in the process of developing methodologies to grow various iron oxides phases (goethite, hematite, magnetite) in the presence of radionuclides. We performed a small number of binary (RN-mineral) coprecipitation experiments to test radionuclide (Pu, Am, Np, and U) partitioning. Experiments are attempting to quantify coprecipitation partitioning and examine the effects of aging and the potential iron oxide recrystallization effects associated with the presence of reduced iron (i.e. Fe(II)).

2. Nuclear Energy Agency Thermochemical Database Program

2.1 History of Project

The Nuclear Energy Agency (NEA) Thermochemical DataBase (TDB) 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 (1) produce a database that contains data for all the elements of interest in radioactive waste disposal systems, (2) document why and how the data are selected, (3) give recommendations based on original experimental data, rather than compilation and estimates, (4) document the sources of experimental data, (5) provide an internally consistent thermodynamic parameters, and (6) 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

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 to 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. In Phase III, the program also added Thorium, Iron (part I), and Tin
volumes to the published collection.

Phase IV of the NEA-TDB program, conducted from 2008 to 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 V of the NEA-TDB program, the currently active phase, 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.

The current status of the program and the associated reviews are:
- Iron, part 2 - The Peer Review is in process. Publication of the volume is
  anticipated at the end of 2018.
- Molybdenum - The Technical Review team required restructuring and
  reassignment of tasks. This was completed and the Peer Review draft is being
  compiled. The anticipated publication of this volume is early 2019 following the
  Peer Review and Comment Resolution processes.
- Auxiliary Compounds – The Peer Review draft is complete and process in its
  early stages. Following Comment Resolution, a publication date of early 2019 is
  planned.

- Second update of Actinides and Fission Products - The Peer Review of the sections on the individual elements are complete and the volume is in the Comment Resolution phase. Publication is anticipated by the end of 2018.
- State-of-the-Art report on Cement Materials - The Technical Review is in process with an expected completion date in mid- to late 2018. Expected publication is in 2019.
- State-of-the-Art report on High-Ionic Strength Solutions - The Technical Review is in process with an expected completion date in mid- to late 2018. Expected publication is in 2019.
- The new electronic database is complete and was made available to the public in June 2018.

Three workshops have been planned to increase awareness, particularly in students and early career staff, on topics of interest in modeling interactions of actinide and fission products with geochemical media. The workshops are being conducted at the ISSP-18 conference in July 2018 (Tours, France); Goldschmidt 2018 in August 2018 (Boston USA), and; The 256th American Chemical Society meeting in August 2018 (Boston USA).

2.3 Preparing for Phase VI

In April 2017, the NEA convened a meeting for interested parties to discuss options for the work plan in Phase VI. Attendees included not only representatives from Phase V, but also included other organizations with interests in actinides and fission product interactions with geologic media. Discussions focused on benefits of continuation of the Program, contents of future workscope, organizational issues, and funding options. Cindy Atkins-Duffin, Mavrik Zavarin, and Don Reed participated for the United States. They Program Management Board convened in November 2017 and took the decision to continue the Program.

Preparing the Program for a new Phase requires reviewing and editing the Framework Agreement. This document is the Agreement between the NEA and the various national programs participating in the Program. Typically, the NEA undertakes their projects in one of two formats - internally funded, directed, and executed or membership funded, directed, and executed. However, in the past, the NEA TDB Program has functioned as a hybrid of these two project types - the workscope was membership funded with the NEA providing a Program Coordinator. Management of the execution of the work was joint between the Program Coordinator and the Executive Group. The NEA determined that the Phase VI effort of the TDB Program will need to be restructured to comport with NEA By-Laws and function in one of the two standard governance models. As a result, in Phase VI, the Program Coordinator will be funded by the membership, significantly altering the amount of work that can be undertaken. It is anticipated the Agreement will be signed and enter into force in the near future. It is also anticipated at this time that COVRA (Dutch nuclear waste processing and storage company) will join the Program as a paying member.

The workscope for Phase VI will include the following review volumes:
- Update of the Organic ligand review
- Lanthanides, and
- Weak Complexes
- State-of-the-Art report on High Temperature data.

The current plan is for Phase VI to enter into force in November 2018 when the next Program Management Board convenes.

3. Corrosion: Plutonium Interaction with Iron Minerals

For the long-term performance assessment of nuclear waste repositories, understanding the interaction of actinide ions with mineral surfaces is imperative. Iron (oxy)hydroxides are common soil minerals and are present in intermediate level radioactive waste [1]. In addition they also form as corrosion products of steel which is a primary structural component of nuclear repositories and of waste canister materials [2]. Studies have shown that Pu(IV) has high sorption affinity for the goethite and hematite surface at circumneutral pH [3-5]. At higher concentration, Pu(IV) colloids form on the goethite surface may undergo a lattice distortion, due to epitaxial growth, which leads to a stronger surface binding compared to other mineral phases, such as quartz [6]. Gaining a detailed understanding of the interactions between iron oxide and plutonium is key in predicting the long-term stability and mobility of plutonium in the natural environment. The hydrous ferric oxide, ferrihydrite (FH), is a common, poorly crystalline, metastable early product of both biotic and abiotic precipitation of iron, and is a precursor to other more crystalline iron oxides such as hematite (Fe_2O_3) and goethite (FeOOH). Ferrihydrite crystallizes to hematite or goethite depending upon solution conditions, pH, ionic strength and temperature [7]. The hematite and goethite formation process begins with ferrihydrite particle aggregation [8], followed by recrystallization within the aggregate via dissolution and reprecipitation processes that occur at the nanoscale [9]. During this process, adsorbed plutonium has the potential to become incorporated into the structure of hematite or goethite. Co-precipitation (or structural incorporation) of co-contaminants into mineral structures most likely involves substitution of the cation site in the mineral or perhaps interstitial incorporation. Crystal chemical constraints that affect incorporation include: i) the cation coordination environment, ii) the cation charge and, iii) a charge balancing mechanism. It has been shown that goethite and hematite are able to accommodate various impurities into their structure including Si, Ti, Mn, Ni and U(VI) [1, 10]. Coprecipitation of plutonium into stable mineral phases, such as iron (oxy)hydroxides, offers a pathway for sequestration with the potential for long term immobilization.

In FY17 we synthesized goethite (FeOOH) and hematite (Fe_2O_3) with varying amounts of plutonium (300, 1000 and 3000 ppm) from a poorly crystalline ferrihydrite (FH) precursor. The initial FH material was obtained according to the following methodologies

– note that the main difference within the two synthetic pathways is the timing of plutonium addition.

- *Method A* or *coprecipitation into FH*: 1 M $FeNO_3.9H_2O$ solution was mixed with Pu(IV), ferrihydrite was then formed by slow addition of 5 M KOH (to pH 11.5 for goethite) or 1 M KOH (to pH 3 for hematite);
- *Method B* or *sorption to FH method*: a KOH (5M or 1M) was slowly added to a 1M $FeNO_3.9H_2O$ solution to form ferrihydrite (final solution pH of 11.5 for goethite and pH 3 for hematite), Pu(IV) was then sorbed onto the ferrihydrite precipitate prior to ferrihydrite alteration to goethite and hematite.

Data reported in FY 17 showed that Pu strongly partitions in the ferrihydrite and goethite solids compared to hematite. In FY18 we focused our efforts in furthering our understanding of Pu-ferrihydrite/goethite interaction through spectroscopy and chemical characterization. The focus of this effort was to understand how the timing of Pu addition (coprecipitation -Method A- or sorption- Method B) to ferrihydrite as precursor to the more crystalline mineral goethite, affects the final form of plutonium associated with these minerals.

3.1 X-ray absorption spectroscopy

Samples FH-A-3000, FH-B 3000, GA-3000 and GB-3000 were selected for X-ray Absorption Spectroscopy (XAS) analysis at the Stanford Synchrotron Radiation Light Source (SSRL). In general, the X-ray Absorption Near Edge Structure (XANES) region of the XAS spectra provides information on oxidation state changes in the samples based on comparisons to standard reference materials. The Extended X-ray Absorption Fine Structure (EXAFS) region is fit to determine the nearby neighbors and their distances from the plutonium site. The XANES region of the spectra confirmed that in all our samples, plutonium is present in the tetravalent oxidation state.

3.1.1 X-ray absorption spectroscopy of ferrihydrite

The EXAFS spectra of samples FH-A-3000 and FH-B-3000 are different, suggesting that plutonium may have different coordination environments in the samples (Figure 1,Figure 2) even though >98% of Pu sorbed in both cases. The FH-B-3000 spectrum could be fit to the model structure of PuO_2, with ~8 O in the first shell at 2.3 Å and four Pu in the second shell at 3.82Å (Table 2). This structural feature indicates that plutonium is likely present as a PuO_2 surface precipitate on sample FH-B-3000. The FH-A-3000 spectrum could not be fit with a PuO_2 model. In FH-A-3000, plutonium is coordinated to six O at 2.29Å in the first coordination sphere (Table 1) and no indication of Pu-Pu backscattering. These results suggest that the timing of Pu addition in the synthesis procedures (Method A or B) affects the final form of plutonium in the ferrihydrite structure (occluded or surface precipitated PuO_2 versus adsorbed or coprecipitation Pu).

Kalmydov et al. [11] examined the interaction of Pu with hydrous ferric oxides isolated from the Mayak, Russia, site and suggested that Pu will initially sorb as a PuO_2 surface precipitate if high Pu concentrations are present but transform to adsorbed Pu as concentrations decrease in the field. However, direct evidence for the surface precipitated and adsorbed structures were not presented and the timescale required for that transition to occur are not known. Importantly, more reduced phases of iron oxide are likely to form during cannister breaching and steel corrosion (e.g. magnetite) in a deep subsurface nuclear waste repository [12]. Sorption of Pu to these more reduced phases has been reported in the literature [13] but evidence for Pu coprecipitation with these phases has not been investigated to date. Nevertheless, the ferrihydrite results clearly indicate that the association of Pu with corrosion products will depend on the timing of Pu release and corrosion product formation.
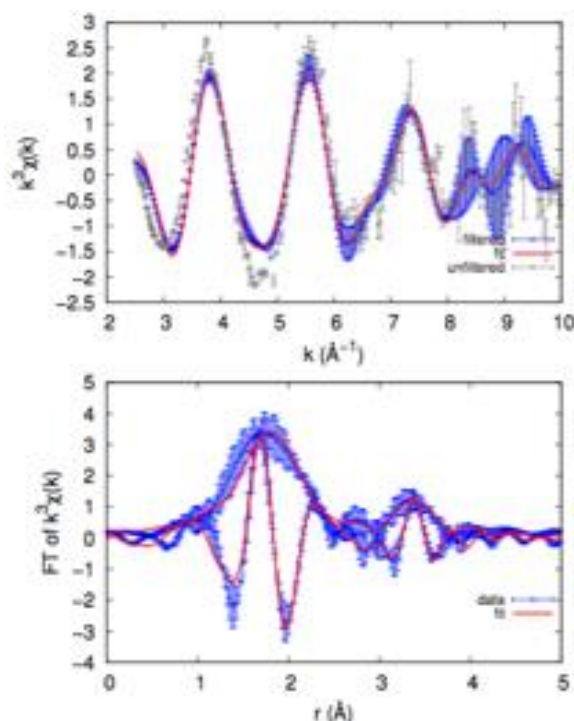

Figure 1. FH-A-3000 EXAFS spectra (top) and Fourier transform in R (Å) (bottom).

Table 1. Fit parameters for EXAFS spectrum of FH-A-3000.

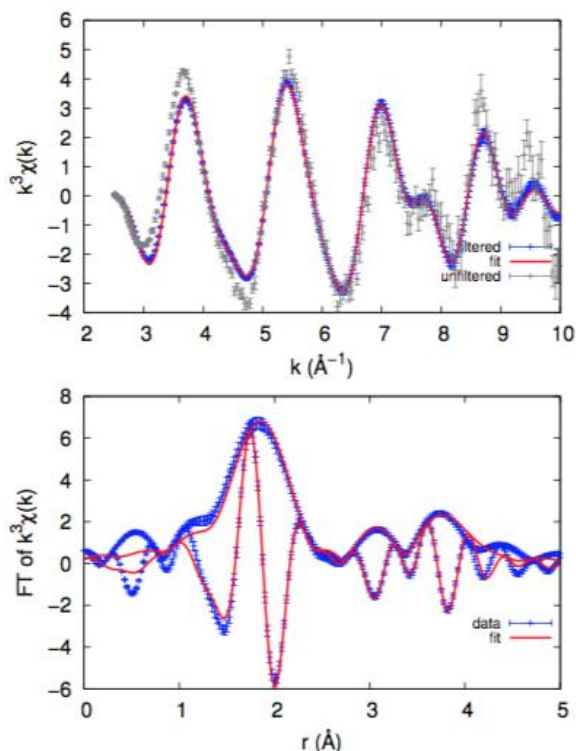|		Sample **A2**	
	N	$\sigma^2(\text{Å}^2)$	$R(\text{Å})$
Pu_O_2.3678.f10	5.5(*)	0.0176(3)	2.29(2)
Pu_O_3.7450.f10	3(2)	0.0037(2)	3.91(2)
ΔE_0		-11.9(14)	
S_0^2		1.000	
$R(\%)$		14.82	

Figure 2. FH-B-3000 - EXAFS spectra (top) and Fourier transform R (Å) (bottom).

Table 2. Fit parameters for EXAFS spectrum of FH-B-3000.

	N	Sample **B2** $\sigma^2(\text{Å}^2)$	$R(\text{Å})$
Pu_O_2.3678.f10	7.7(9)	0.0113(1)	2.324(8)
Pu_Fe_3.4312.f10	3(3)	0.015(1)	3.36(2)
Pu_Pu_3.8666.f10	3(1)	0.0038(1)	3.82(2)
ΔE_0		-11.8(9)	
S_0^2		1.000	
$R(\%)$		5.18	

3.1.2 X-ray absorption spectroscopy of goethite

The precursor ferrihydrite material (FH-A-3000 and FH-B-3000) was aged hydrothermally (3 days at 70°C) to form goethite. The EXAFS spectra of samples GA-3000 and GB-3000 are also different. The G-B-3000 spectrum could be fit to the model structure of PuO_2, with four Pu at a distance of 3.82Å (
Table 4, Figure 4. G-B-3000 - EXAFS spectra (top) and Fourier transform R (Å) (bottom). This structural feature indicates that plutonium is likely present as a surface precipitate or inclusion in sample GB-3000. Presence of surface bound plutonium oxides (i.e. surface precipitates) was confirmed by TEM imaging (Figure 5). The G-A-3000 spectrum could not be fit with a PuO_2 model. In G-A-3000, plutonium is coordinated by eight O at 2.18 Å in the first coordination sphere. These bond distances are slightly

shorter than the Pu-O bond distances of G-B-3000, 2.31(1)Å (
Table 4). The fitting of this data includes one Fe at 3.5 Å and one Pu at 3.8 Å in the 2nd
shell. These results suggest that in this sample, Pu may not be present as a surface
species. The results suggest, again, that the timing of Pu addition to the ferrihydrite
precursor (Method A or B) affects the final form of plutonium in the goethite structure.
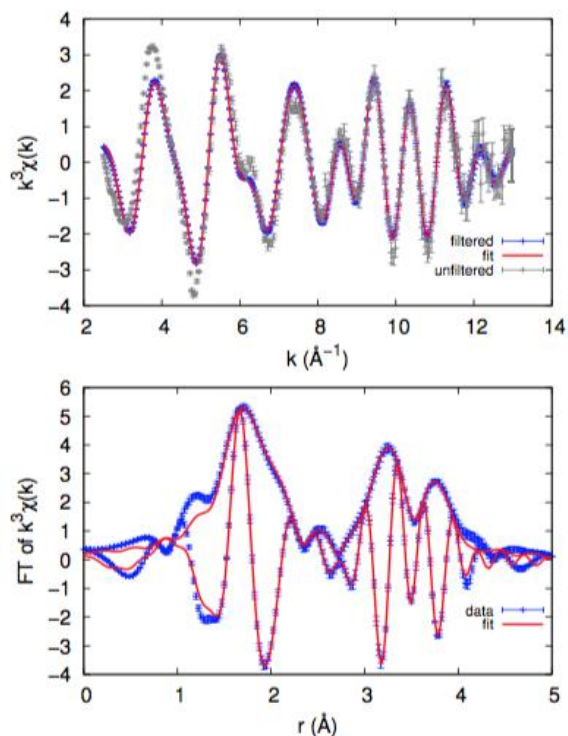

Figure 3. G-A-3000- EXAFS spectra (top) and Fourier transform R (Å) (bottom).

Table 3. Fit parameters for EXAFS spectrum
of G-A-3000.

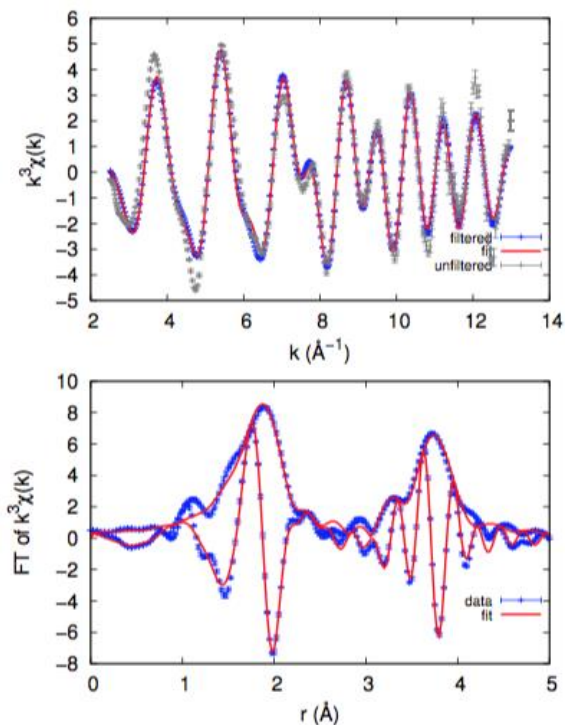|		009b1G	
	N	$\sigma^2(\text{Å}^2)$	$R(\text{Å})$
Pu_O_2.3678.f10	2.5(1)	0.00311(2)	2.180(4)
Pu_O_2.3678.f10	2.42	0.00312	2.338(6)
Pu_Fe_3.4312.f10	1.1(3)	0.00025(1)	3.55(2)
Pu_O_3.7450.f10	2.5(7)	0.0001(5)	3.95(3)
Pu_Pu_3.8666.f10	1.5(10)	0.002(2)	3.799(8)
ΔE_0		-12.0(7)	
S_0^2		1.000	
$R(\%)$		2.80	

Figure 4. G-B-3000 - EXAFS spectra (top) and Fourier transform R (Å) (bottom).

Table 4. Fit parameters for EXAFS spectrum of G-B-3000.

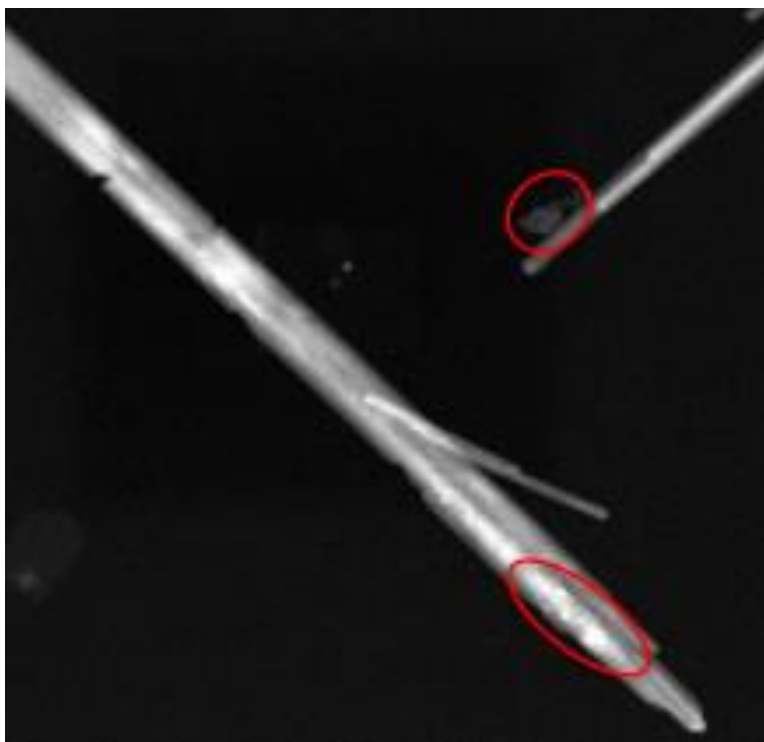|		Sample **B**	
	N	$\sigma^2(\text{Å}^2)$	$R(\text{Å})$
Pu_O_2.3678.f10	7.6(10)	0.01003(8)	2.321(8)
Pu_Pu_3.8666.f10	4.2(10)	0.0038(1)	3.807(5)
ΔE_0		-12.0(10)	
S_0^2		1.000	
$R(\%)$		9.83	

Figure 5. TEM image of G-B-3000 (PuO_2 colloids circled in red).

3.2 Acid leaching of Fe and Pu from Goethite samples

Sample G-A-3000 and G-B-3000 were tested to determine the leaching behavior of Fe and Pu in HNO_3 (0.1-6M). Suspensions were equilibrated in the acid suspensions of different concentrations for 30 minutes prior to centrifugation. Fe measurements were conducted with ICP-MS (ppb-ppm) and UV-Vis (ppm). Pu concentration was determined by Liquid Scintillation Counting (LSC). Results reported in Figure 6 show that the concentrations of Fe leached from both goethite samples (G-A-3000 and G-B-3000) are similar (Figure 6). The leaching of Pu from these solids, however, shows that 2-3 times more Pu is leached from G-B-3000 than from G-A-3000 (Figure 7), suggesting that the association of Pu to G-B-3000 may be different from G-A-3000. Specifically, leaching of Pu from samples that include PuO_2 surface precipitates (Figure 5) is more favorable than when Pu is coprecipitated in the iron oxide phase.
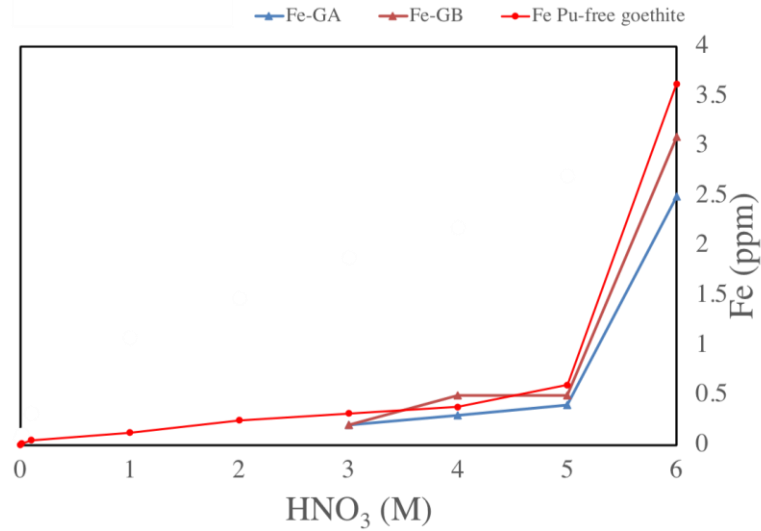
Figure 6. Leaching of Fe(ppm) from G-A-3000 and G-B-3000, measured by ICP-MS (red) and UV-Vis (orange and blue).
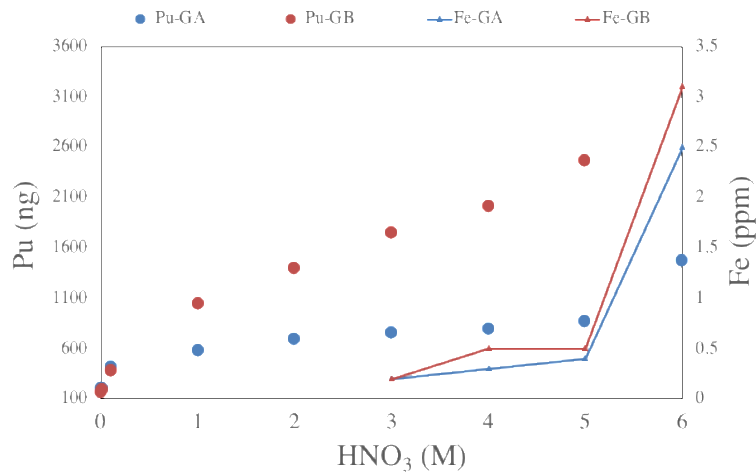

Figure 7. Leaching of Pu from G-A-3000 (blue dots) and G-B-3000 (red dots), and leaching of Fe(ppm) from G-A-3000 (blue line) and G-B-3000 (red line).

3.3 Conclusions

Investigation into the molecular and crystallographic behavior of Pu associated with ferrihydrite and goethite iron oxide phases has led to the following conclusions regarding the potential for Pu sequestration in these solid phases as a result of canister corrosion:

- The timing of Pu release and ferrihydrite corrosion product formation can lead to differences in Pu association: formation of PuO_2 versus coprecipitation of Pu
- Alteration of amorphous ferrihydrite to a more crystalline goethite phase will retain Pu association with the solid phase. However, the nature of Pu association

will be affected by the characteristics of Pu associated with the precursor ferrihydrite.

- • The molecular nature of Pu association with iron oxide phases affects the leaching behavior of Pu. EXAFS and TEM data confirm that Pu association with goethite as a surface precipitate is more labile than the coprecipitate. This has implications to the longterm stability of Pu associated with corrosion products.

As stated earlier, it is likely that more reduced oxide phases (e.g. magnetite) will be favored over the ferrihydrite and goethite phases describe here. The incorporation of actinides into those more thermodynamically favorable phases (under deep nuclear waster repository conditions) is the subject of ongoing effort in FY18/FY19. These efforts are described in section 5 of this report.

3.4 References

1. Marshall, T.A., et al., *Incorporation of Uranium into Hematite during Crystallization from Ferrihydrite.* Environmental Science & Technology, 2014. **48**(7): p. 3724-3731.
2. Music, S., M. Gotic, and S. Popovic, *X-Ray-Diffraction And Fourier-Transform Infrared-Analysis Of The Rust Formed By Corrosion Of Steel In Aqueous-Solutions.* Journal of Materials Science, 1993. **28**(21): p. 5744-5752.
3. Sanchez, A.L., J.W. Murray, and T.H. Sibley, *The adsorption of plutonium-iv and plutonium-v on goethite.* Geochimica Et Cosmochimica Acta, 1985. **49**(11): p. 2297-2307.
4. Zhao, P.H., et al., *Plutonium(IV) and (V) Sorption to Goethite at Sub-Femtomolar to Micromolar Concentrations: Redox Transformations and Surface Precipitation.* Environmental Science & Technology, 2016. **50**(13): p. 6948-6956.
5. Romanchuk, A.Y., S.N. Kalmykov, and R.A. Aliev, *Plutonium sorption onto hematite colloids at femto- and nanomolar concentrations.* Radiochimica Acta, 2011. **99**(3): p. 137-144.
6. Powell, B.A., et al., *Stabilization of Plutonium Nano-Colloids by Epitaxial Distortion on Mineral Surfaces.* Environmental Science & Technology, 2011. **45**(7): p. 2698-2703.
7. Schwertmann, U. and R.M. Cornell, *Iron oxides in the laboratory*, in *Iron Oxides in the Laboratory*. 2000, Wiley-VCH Verlag GmbH. p. i-xviii.
8. Fischer, W.R. and U. Schwertmann, *Formation of hematite from amorphous iron(iii)hydroxide.* Clays and Clay Minerals, 1975. **23**(1): p. 33-&.
9. Combes, J.M., A. Manceau, and G. Calas, *Formation Of Ferric Oxides From Aqueous-Solutions - A Polyhedral Approach By X-Ray Absorption-Spectroscopy .2. Hematite Formation From Ferric Gels.* Geochimica Et Cosmochimica Acta, 1990. **54**(4): p. 1083-1091.
10. Liu, J., et al., *General Strategy for Doping Impurities (Ge, Si, Mn, Sn, Ti) in Hematite Nanocrystals.* Journal of Physical Chemistry C, 2012. **116**(8): p. 4986-4992.

11.   Kalmykov, S. N.; Kriventsov, V. V.; Teterin, Y. A.; Novikov, A. P., *Plutonium and neptunium speciation bound to hydrous ferric oxide colloids*. Comptes Rendus Chimie, 2007, **10**(10-11): p. 1060-1066.

12.   Laaksoharju M., Smellie, J., Tullborg, E-L., Gimeno, M., Hallbek, L., Molinero, J., Waber, N., "Bedrock hydrogeochemistry Forsmark site descriptive modeling SDM-Site Forsmark," SKB R-Report (R- 08-47), SKB, Stockholm, Sweden, 2008.

13.   Kirsch, R.; Fellhauer, D.; Altmaier, M.; Neck, V.; Rossberg, A.; Fanghanel, T.; Charlet, L.; Scheinost, A. C., *Oxidation state and local structure of plutonium reacted with magnetite, mackinawite, and chukanovite*. Environmental Science & Technology, 2011, **45**(17): p. 7267-7274.

4. Thermodynamic Database Development Efforts

As part of our FY18 effort in thermodynamic database development, we prepared a draft report entitled "H2OI95: A Stand-Alone Fortran Code for Evaluating the IAPWS-95 Equation-of-State Model for Water" by T. Wolery. This report will be completed in early FY19 and released as a LLNL technical report. Below, we summarize the report which describes the calculation of the thermodynamic and thermochemical properties of water over a wide range of pressure relevant to SFWST.

H2OI95 is a stand-alone Fortran code for evaluating the IAPWS-95 equation-of-state model (Wagner and Pruss, 2002) for the thermodynamic properties of water. It further evaluates the corresponding thermochemical properties of water consistent with the CODATA recommendations (Cox et al., 1989). The IAPWS-95 model is based on a model equation for the dimensionless Helmholtz energy for which the primary variables are the inverse reduced temperature ($\tau=T_{cr}/T$) and reduced density ($\delta=\rho/\rho_{cr}$). Here T is the absolute temperature (K), ρ is density (kg/m^3), and the subscript "cr" refers to the critical point of water (647.096 K and 22.064 MPa pressure in this model, for which ρ_{cr} is 322 kg/m^3). The code solves four basic types of problems, distinguished by the specified inputs:

    1, Temperature (K) and density (ρ kg/m^3) or reduced density (δ)
    2. Temperature (K) and pressure (MPa).
    3. Temperature (K) on the saturation (liquid-vapor equilibrium) curve
    4. Pressure (MPa) on the saturation curve

Each type of problem is run using a corresponding input (text) file. All but the first type of problem require iteration. For example, to solve for desired temperature and pressure, the reduced density must be adjusted to give the desired pressure. Iteration is accomplished using the Newton-Raphson method, though the secant method is also used in solving the fourth type of problem.

H2OI95 has been used to conduct numerical studies of convergence and the problem of multiple numerical solutions, only some of which correspond to valid results. Obtaining valid results depends mainly on appropriate choice of starting values. The studies made as part of this work supplement those reported by Junglas (2008), which is unfortunately the only other known work addressing these numerical issues. The problem is illustrated by considering case of 500K (less than the critical temperature of 647.096K) and 25 MPa

(somewhat greater than the critical pressure of 22.064 MPa). By varying the starting estimate for the density, three numerical solutions (each corresponding to a different density) were found. Partial results are summarized in Table 5, where κ is compressibility, w is speed of sound, S is absolute (thermochemical) entropy, and G is thermochemical Gibbs energy The mid density solution has a negative compressibility and no value for the speed of sound, as the calculated square of the speed of sound had a negative value. The mid density solution is non-physical and therefore invalid. It is just a numerical artifact. The low density solution has a negative value for the absolute entropy. Therefore it is also invalid. Only the high density solution gives all physically meaningful results. This solution is valid. The density value matches that given by the steam tables of Wagner and Pruss (2002).

Table 5. Partial results of convergence studies for water at 500K and 25 MPa. Cells highlighted in orange contain unrealistic results.

Solution	ρ kg m^{-3}	κ MPa^{-1}	w m s^{-1}	S J kg^{-1} K^{-1}	G kJ mol^{-1}
High density	850.558202	0.930558751 x 10^{-6}	0.133010698 x 10^4	109.1009	-255.0398
Mid density	621.049863	-0.487483957 x 10^{-6}	NC*	111.8598	-254.5668
Low density	331.832991	0.275002785 x 10^{-10}	0.338667401 x 10^6	-2.03222 x 10^{-6}	-4.80574 x 10^4

*Not calculated (w$^2 \leq 0$)

H2OI95 was used to calculate the pressure over a wide range of density at 500K. The results are shown in Figure 8. The pressure curve is extremely irregular, in places approaching near infinite negative and positive values. The curve appears broken because only a limited range of pressure is considered in the figure. Note that calculated pressures can be negative (hence unphysical). The red line marks the previously considered pressure of 25 MPa. Numerical solutions are where this intersects the curve of calculated pressure. Here points C, D, and E correspond to the previously found low, mid, and high density solutions.
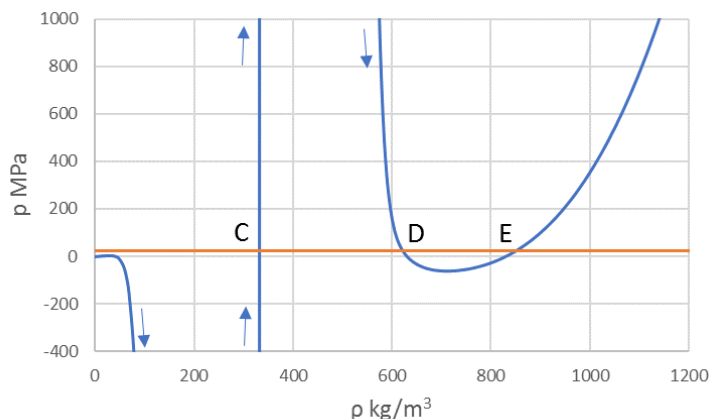
Figure 3. Pressure as a function of density (blue) at 500K. Arrows are shown to indicate curve direction moving outside the field of view. The red line marks a pressure of 25 MPa. For this pressure, C = low density solution, D = mid density solution, and E = high density solution.

For other temperatures and pressures, up to five numerical solutions have been observed. At most, only two solutions can be valid, in the case where the temperature and pressure lie on the saturation curve with one solution (with the lowest density) representing saturated vapor and the other (with the highest density) corresponding to saturated liquid.

The result obtained by the iteration process depends on the starting estimate for the density. Default values in H2OI95 are thought to lead to only physically meaningful solutions. It is noted that the IAPWS-95 model as documented by Wagner and Pruss (2002) does not address convergence studies and is silent on the topic of appropriate starting values for density when calculating water properties as a function of temperature and pressure.

With modification, H2OI95 can be used to support SUPCRT92 (Johnson et al., 1992) and similar codes that compute chemical thermodynamic properties of species and reactions over a wide range of temperature and pressure (273.16-1273K and 0-1000 MPa). The original SUPCRT92 uses a combination of two older equation of state models for water, that of Haar et al. (1984) for most of the range of temperature and pressure, and that of Levelt Sengers et al. (1984) near the critical point.

REFERENCES

Cox J. D., Wagman D. D., and Medvedev V. A., eds. (1989) CODATA Key Values for Thermodynamics. CODATA Series on Thermodynamic Values. Hemisphere Publishing Corp., New York. 271 pp. ISBN 0-89116-758-7.

Haar L., Gallagher J. S., and Kell G. S. (1984) NBS/NRC Steam Tables. Hemisphere Publishing Corporation, Washington, DC. 320 pp. ISBN 0-89116-353-0.

Johnson J. W., Oelkers E. H., and Helgeson H. C. (1992) SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals,

gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. Comp. Geosci. 18, 899-947.

Junglas P. (2008) Implementing the IAPWS-95 standard in MATLAB. Preprint – ICPWS XV, Berlin, September 8–11, 2008.

Cox J. D., Wagman D. D., and Medvedev V. A., eds. (1989) CODATA Key Values for Thermodynamics. CODATA Series on Thermodynamic Values. Hemisphere Publishing Corp., New York. 271 pp. ISBN 0-89116-758-7.

Levelt Sengers J. M. H., Kamgar-Parsi, B., Balfour F. W., and Sengers J. V. (1983) Thermodynamic properties of steam in the critical region. J. Phys. Chem. Ref. Data 12, 1-28.

Wagner W. and Pruss A. (2002) The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. J. Phys. Chem. Ref. Data 31, 387-535.

5. Planned FY18/FY19 Efforts

In late FY18, we received additional funding to support SFWST efforts within the Crystalline Disposal, Argillite Disposal, and Argillite Disposal International Collaborations work packages. These efforts will begin in FY18 with associated milestones that will be completed in mid-FY19. The efforts associated with these three work packages are outlined below. Support for NEA-TDB participation through the Crystalline International Collaborations work package will be minimally supported by the Argillite International Collaborations work package pending additional FY19 funding from the Crystalline International Collaborations work package.

5.1 Crystalline Disposal R&D - Pu incorporation into reduced iron oxide phases

FY18 carryover funding for this work package has focused on completion of experiments examining Pu incorporation into Fe(III) oxide phases (hydrous ferric oxide, goethite, and hematite). However, fuel matrix degradation models suggest that the near field is likely to be reducing at the time of canister breaching, steel corrosion, and radionuclide release. Thus, there is a need to evaluate Pu incorporation into reduced Fe-oxide phases (e.g. magnetite, green rust). The FY18/FY19 scope will identify synthesis methods for reduced Fe-oxide phases and perform Pu sorption and coprecipitation experiments to determine the fractionation of Pu into and onto these phases. Specifically, we will

- Quantify the rate of Pu incorporation to magnetite and green rust
- Characterize the nature and morphology of sorbed and coprecipitated Pu on these phases using Transmission Electron Microscopy
- Determine the oxidation state and near-neighbor environment of Pu associated with these phases to determine whether a direct cation substitution process controls Pu incorporation into these phases using synchrotron based X-ray Absorption Spectroscopy

Beamline access to the Stanford Synchrotron Radiation Lightsource (SSRL) was recently made available through our successful application for beamtime in FY17. Some of this effort may need to be carried past our planned milestone (12/3/18) depending on the

availability and scheduling of beamtime at SSRL. The effort will be coordinated with the FMDM modeling and experimental workscope performed at Argonne National Laboratory.

5.2 Argillite Disposal R&D - Code development in support of the SFWST Thermodynamic database

In FY18/FY19, LLNL will continue and expand our efforts in the development of thermodynamic databases in support of the Spent Fuel and Waste and Science Technology (SFWST) program. Thermodynamic models provide the basis for understanding the stability of solid phases and speciation of aqueous species and modeling the evolution of repository conditions. This effort will be performed in coordination with other US database development efforts. International coordination with the NEA-TDB is supported through crystalline international work package.

We will release the stand-alone program H2OI95 including source code with minimal restrictions (such as a BSD 3-clause license) and make the code available for download on the EQ3/6 website hosted at LLNL (https://www-gs.llnl.gov/energy-cyber-and-infrastructure/geochemistry). This code uses the IAPWS-95 equation of state for water in conjunction with key thermochemical data (CODATA) to compute the thermodynamic and thermochemical properties of water over a wide range of temperature and pressure. We will create an interface subroutine in a modified version of SUPCRT92 so that it can use H2OI95 directly, replacing the usage of an earlier equation of state model and older key thermochemical data. We will write an institutional report on H2OI95 and revise the Part 2 paper on water thermochemistry models for submittal to a suitable journal. We still need to integrate our modified SUPCRT92 with the SUPCRTBL of Zimmer et al. (2016). We will similarly release this and make it available for download on the EQ3/6 website. We will then return to the focus on developing a new thermodynamic database for aqueous species, gases, and minerals. We will be watching for potentially impactful developments by others, including the new paper by Miron et al. (2017) and the forthcoming NEA Ancillary Data volume.

The thermochemical data for some key species including the aqueous species Ca^{2+} and Mg^{2+} are likely to be changed from the CODATA values owing to recent developments, and the NEA recommended data may have to be adjusted to conform from newly chosen values. This would be important to maintain consistency between data for natural minerals on the one hand and substances containing radionuclide elements. However, it will be necessary first to take a hard look at potential changes to the key data for species such as Ca^{2+} and Mg^{2+}, as such changes may inappropriately deprecate key calorimetric results. Our effort at database development will begin with a simple, nearly "sequential" derivation aimed at elucidating differences resulting from alternative values for certain of the key thermochemical data. Such derivations are useful in showing the structure associated with data dependencies. They are useful in identifying key issues and those input data that should be rejected before performing a more general "optimization" process to obtain a higher-level database.

We will develop a project web page with ancillary web pages on which our products can be downloaded. This will expand on a current LLNL web page that provides download of EQ3/6 and its existing thermodynamic databases. All codes will be hosted on an updated EQ 3/6 website hosted at LLNL and available for download.

REFERERENCES

Miron G. D., Wagner T., Kulik D. A., and Lothenbach B. (2017) An internally consistent thermodynamic dataset for aqueous species in the system Ca-Mg-Na–K–Al–Si–O–C-H–Cl. Am. J. Sci. 317, 754-805.

Zimmer K., Zhang Y., Lu P., Chen Y., Zhang G., Dalkilic M., and Zhu (2016) SUPCRTBL: A revised and extended thermodynamic dataset and software package of SUPCRT92. Computers & Geosciences 90 (Part A), 97-111.

5.3 Argilline International Collaborations R&D - Surface complexation and ion exchange database development phase 1: clay minerals

FY18/FY19 effort will focus on surface complexation/ion exchange database development. Effort will be coordinated with international partners involved in similar database development efforts (e.g. Helmholtz Zentrum Dresden Rossendorf RES^{3}T). Two components of database development will be pursued. First, a primary sorption data capture effort will focus on radionuclide (Cs, Sr, U, Np, and Pu) sorption to clay minerals (with particular focus on bentonite/montmorillonite). Second, methodologies for development of a surface complexation/ion exchange constant database from the primary sorption data will be pursued. A key component of that effort will be the integration of commercially available fitting routines (e.g. PEST) that can be linked to surface complexation/ion exchange codes and produce optimized constants and associated parameter uncertainties. The effort will be linked to thermodynamic databases (e.g. EQ3/6, NEA-TDB) to allow for updates to the surface complexation/ion exchange databases as the thermodynamic databases are updated. The effort will allow for testing of various surface complexation (Non-electrostatic, diffuse layer, etc.) and ion exchange (Vanselow, Gapon, etc.) models and will provide flexibility in testing surface complexation/ion exchange conceptual models and numerical constructs.

This effort is coordinated with the thermodynamic database development efforts described in the Argillite work package and in support of the Spent Fuel and Waste and Science Technology (SFWST) program. Thermodynamic models, when combined with surface complexation/ion exchange provide the basis for understanding the stability of solid phases, speciation of aqueous species, partitioning between aqueous and solid surfaces, and modeling the evolution of repository conditions. Thermodynamic database efforts are, in part, supported through crystalline international work package that is focused on US involvement in the NEA-TDB effort.

6. Acknowledgments