

# FCT Quality Assurance Program Document

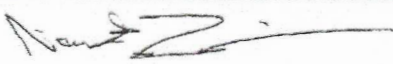
## Appendix E FCT Document Cover Sheet

Name/Title of Deliverable/Milestone M4SF-20LL010301082: Sorption Database and Model for  
Generic Disposal System Assessment

Work Package Title and Number SF-20LL010301081 Argillite International Disposal

Work Package WBS Number R&D - LLNL

1.08.01.03.01

Responsible Work Package Manager Mavrik Zavarin  
(Name/Signature) 

Date Submitted

Quality Rigor Level for Deliverable/Milestone	<input type="checkbox"/> QRL-1 Nuclear Data	<input type="checkbox"/> QRL-2	<input type="checkbox"/> QRL-3	<input checked="" type="checkbox"/> 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

**Technical Review (TR)**

**Review Documentation Provided**

- Signed TR Report or,  
 Signed TR Concurrence Sheet or,  
 Signature of TR Reviewer(s) below

Peer Review

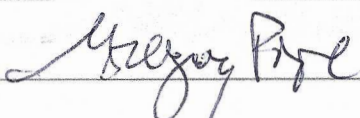
**Peer Review (PR)**

**Review Documentation Provided**

- Signed PR Report or,  
 Signed PR Concurrence Sheet or,  
 Signature of PR Reviewer(s) below

**Name and Signature of Reviewers**

Brian L. Anderson: Brian Anderson

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.



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

# M4SF-20LL010301082-Sorption Database and Model for Generic Disposal System Assessment

M. Zavarin, A. Deinhart, V. Genetti, S. Shipman

June 29, 2020

June 15, 2020

# **M4SF-20LL010301082-Sorption Database and Model for Generic Disposal System Assessment**

**M. Zavarin, Amanda Deinhart, Victoria Genetti, Sam Shipman**

<sup>1</sup> Glenn T. Seaborg Institute, Physical & Life Sciences, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA.

## **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.

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

## Contents

<b>1. Introduction.....</b>	<b>4</b>
<b>2. The RES<sup>3</sup>T Database .....</b>	<b>4</b>
<b>3. Digitized Database Structure .....</b>	<b>5</b>
<b>4. Data Capture Process .....</b>	<b>8</b>
4.1 Unit Conversions.....	9
4.1.1. Data Reported as Percent Sorbed .....	9
4.1.2. Data Reported as Fraction Sorbed.....	9
4.1.3. Data Reported as Kd or Rd.....	10
4.2 Error Propagation .....	10
4.3. Status of Data Digitization Effort.....	14
<b>5. Fitting Raw Sorption Data using PHREEQC-PEST Optimization .....</b>	<b>18</b>
<b>6. Planned FY21 Efforts .....</b>	<b>19</b>
<b>7. Acknowledgments .....</b>	<b>20</b>
<b>8. References .....</b>	<b>20</b>

## 1. Introduction

This progress report (Level 4 Milestone Number M4SF-20LL010301082) summarizes research conducted at Lawrence Livermore National Laboratory (LLNL) within the Argillite International Collaborations Activity Number Activity SF-20LL010301081. The activity is focused on our long-term commitment to engaging our partners in international nuclear waste repository research. The focus of this milestone is surface complexation model international collaborations. Specifically, we are developing a database framework for Spent Fuel and Waste and Science Technology (SFWST) that is aligned with the Helmholtz Zentrum Dresden Rossendorf (HZDR) sorption database development group in support of the database needs of the SFWST program.

The ongoing effort is focusing on surface complexation/ion exchange database development. Effort is coordinated with international partners involved in similar database development efforts (e.g. HZDR RES<sup>3</sup>T). Two components of database development are pursued. First, a primary sorption data capture effort is focused on radionuclide (e.g. 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 are being pursued. A key component of this effort is the integration of commercially available fitting routines (e.g. PEST) that can be linked to surface complexation/ion exchange codes (e.g. PHREEQC) and produce optimized constants and associated parameter uncertainties. A new component of this effort that was initiated in late FY20 is the application of machine learning and data science techniques to this database effort. The data capture effort will be linked to thermodynamic databases (e.g. SUPCRTNE, NEA-TDB) to allow for updates to the surface complexation/ion exchange databases as the thermodynamic databases are updated. The effort allows 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 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 and other thermodynamic database international efforts.

## 2. The RES<sup>3</sup>T Database

The need to develop self-consistent surface complexation/ion exchange models, in concert with thermodynamic models, for nuclear waste repository performance assessment was identified many years ago (Bradbury and Baeyens, 1993). This issue was expressly identified in NEA Sorption project reports (Davis et al., 2005; Ochs et al., 2012). However, significant progress on this issue has been made only recently in

various international nuclear waste repository programs (e.g. (Bradbury and Baeyens, 2009), (Dresden-Rosendorf, 2013), (Geckeis et al., 2013)). Hybrid approaches have also been attempted (Bradbury et al., 2010). The best path forward for developing such databases remains an open question (Geckeis et al., 2013), particularly in cases where generic repositories are being investigated resulting in a need to model radionuclide behavior over a very broad range of solution and mineralogic conditions.

The RES<sup>3</sup>T project is an ongoing effort by HZDR to develop a digital open source thermodynamic sorption database. It includes mineral-specific surface complexation constants that can be used in component additivity models of more complex solid phases such as rocks or soils. It includes an integrated user interface to access selected mineral and sorption data and export data into formats suitable for other modeling software. Data records comprise mineral properties, specific surface areas, characteristics of surface binding sites and their protolysis constants, sorption ligand information, and surface complexation reactions (surface complexation models include the Non-Electrostatic, Diffuse Double Layer, Constant Capacitance, Triple Layer, Basic Stern, and the 1-pK Model as extended to CD-MUSIC). The database also includes a comprehensive list of publications that are the primary sources of the surface complexation data. In total, the database includes over 146 minerals, 148 sorbing ligands, nearly 6700 surface complexation reaction constants, and over 3000 references. The database provides a comprehensive list of reaction constants reported in the literature for a very large number of radionuclide-mineral reaction pairs. However, this database project does not provide recommended values. It also does not capture the primary sorption data or provide information on the aqueous speciation constants used in determining those surface complexation constants. As a result, the RES<sup>3</sup>T project provides a foundation for developing a comprehensive surface complexation database but does not go so far as to provide one. The limitations of the database in its present state were discussed in previous milestone reports (i.e. Zavarin, 2019; Zavarin et al., 2018, Zavarin et al., 2016)

### 3. Digitized Database Structure

To develop a comprehensive sorption database in support of the SFWST program, we focused our FY20 effort to the first component of the database development effort: data digitization to support surface complexation database development. The LLNL database of digital sorption data was developed in Microsoft Access with a series of linked tables as reported in the FY19 milestone report (Zavarin, 2019). Thus, the structure of the database is will not be reported in detail here. However, some enhancements to the database were pursued in FY20 and will be highlighted here (enhancements are *italicized* in the description below). The tables include the following:

1. Reference Table
2. Dataset Table
3. Data Table
4. Mineral Site Density Table
5. Atmospheric CO<sub>2</sub> Table

The Reference Table captures the following information:

1. Unique identifier – supplied by Microsoft Access
2. Reference name – Unique name for reference based on the nomenclature established in the RES<sup>3</sup>T database.
3. Original pdf of manuscript (if DOI not available)
4. *Document DOI*
5. Importer – Name of person performing the data import
6. Original data – Y/N answer to whether the data appear to be original to the reference manuscript
7. *RES<sup>3</sup>T reference* – Y/N answer to whether the reference is contained in the RES<sup>3</sup>T database.
8. In database – Y/N answer to whether the raw data are captured in the database
9. Comments – Ancillary information regarding data digitization

In FY20, we no longer embed the original document PDF into the database. A document DOI was sufficient to provide a direct link to the original document without the burden of increasing the database file size. The database could thus be reduced from 0.5 GB to 0.28 GB. **There are presently 158 references included in the database.**

The Dataset Table captures each set of data included in a reference. By far, this table captures the majority of the metadata required to understand the nature of the batch sorption experiments. A set of data is generally defined as a set of batch sorption data that have a common sorbent concentration and/or other unifying features. For example, a typical dataset would be one sorption envelope in which sorption was measured as a function of pH under otherwise similar solution conditions. However, a dataset could also comprise a single datapoint or an isotherm. The Dataset Table contains the following information:

1. Unique identifier – supplied by Microsoft Access
2. Reference name – Unique name for reference
3. Dataset name – Reference name followed by a figure and dataset number
4. Attachment – jpg of original figure and a .txt file with associated digitized data
5. Mineral – name of mineral
6. *Mineral formula* – *chemical formula of mineral*
7. *Mineral\_source* – *the source of the mineral which may be naturally sourced mineral, synthesized, or purchased through a specific brand*
8. ElectrolyteX – Name of electrolyte ion X
9. ElectrolyteX\_val – Value for electrolyte X
10. ElectrolyteX\_SD – standard deviation for electrolyte X value
11. ElectrolyteX\_units – units of electrolyte X value (e.g. mol/L)
12. Sorbent – Name of sorbent
13. Sorbent\_val – Value of sorbent
14. Sorbent\_SD – standard deviation of sorbent value
15. Sorbent\_unit – Units of sorbent value
16. Mineral\_val – Value of mineral
17. Mineral\_SD – standard deviation of mineral value



18. Mineral\_units – Units of mineral\_val (e.g. g/L)
19. MineralSA – surface area of mineral
20. MineralSA\_SD – standard deviation of mineralSA
21. MineralSA\_units – Units of mineralSA
22. Mineralsites – mineral reactive sites value
23. Mineralsites\_SD – standard deviation of mineral reactive site value
24. Mineralsites\_units – Units of Mineralsites (e.g. sites/nm<sup>2</sup>)
25. CEC – *cation exchange capacity*
26. CEC\_SD – *standard deviation of cation exchange capacity*
27. CEC\_units – *units of cation exchange capacity*
28. GasX – Name of gas in equilibrium with solution
29. GasX\_val – Value of GasX
30. GasX\_SD – standard deviation of GasX value
31. GasX\_units – units of GasX value (e.g. bar)
32. X\_axis – Name of X axis in figure
33. X\_units – Units of X axis
34. Y\_axis – Name of Y axis on figure
35. Y\_units – Units of Y axis

The dataset table has expanded significantly since FY19. **At present, there are 1567 datasets included in the Dataset Table.**

A common problem in understanding sorption data from the literature is to quantify the equilibrium gas conditions during the experiment. This information is often not measured or simply not reported. However, experiments are often described as having been performed in an N<sub>2</sub> glovebox or under atmospheric conditions. In the case of atmospheric conditions, the gas composition can be estimated from the composition of gases in the laboratory at the time of data collection. The most critical component of that estimate is the fugacity of CO<sub>2</sub>. The CO<sub>2</sub> fugacity is critical to any modeling effort as it is well known that formation of carbonate complexes in solution can significantly affect the sorption behavior of many radionuclides. For this reason, we include the table Atmospheric CO<sub>2</sub> in the Access Database. This table contains the fugacity of CO<sub>2</sub> in the atmosphere as a function of time. Thus, for experiments performed under atmospheric conditions, the CO<sub>2</sub> fugacity in the experiments is based on the atmospheric CO<sub>2</sub> fugacity at the date of publication (which is presumed to be close to the date of the actual experiments).

A second issue with regard to datasets reported in the literature are the mineral reactive site densities. The site density on the mineral surface can be measured but is often assumed to be a value that has been previously reported for that mineral or simply based on common values reported in the literature for a variety of minerals. Thus, most modeling efforts use surface site densities that are chosen somewhat arbitrarily. To develop consistency across multiple datasets, we add another table to our database called Mineral\_Site\_Density. This table is intended to regularize the modeling effort by overwriting the original site density values reported in the Dataset Table with a common

site density for all data reported for a specific mineral. Of course, during any modeling effort, the user may choose to use a common site density for a mineral or an author-specified site density.

The final table contained in the database is simply called Data Table and captures the values contained in each Dataset Table entry. This table contains the data extracted from the plots contained in each dataset in the reference. The Data Table contains the following information:

1. Unique identifier – supplied by Microsoft Access
2. number – datapoint number in each dataset
3. Set – the dataset associated with the data
4. X\_val – the X axis value
5. X\_SD – standard deviation of X axis value
6. Y\_val – the Y axis value
7. Y\_SD – standard deviation of the Y value

The Data Table has expanded significantly since FY19. **At present, there are 15,571 datasets included in the data table.** A summary of the data captured in the Access database is reported in detail below.

#### 4. Data Capture Process

The first step in the capture of sorption data is to digitize data included in the target references. Target references are being identified primarily through the RES<sup>3</sup>T surface complexation reference compilation. The data contained in the references are digitized using the DataThief software which allows the user to capture data reported in digital plots, *including data uncertainties*. Most sorption data are reported in the literature as percent sorbed vs. pH. However, some data are reported in terms of K<sub>d</sub> (mL/g), K<sub>a</sub> (m<sup>2</sup>/g), or simply equilibrium aqueous concentration. Regardless of the units included in the plotted data, the DataThief software captures the raw information contained in the plot and the raw data are imported into the Access database. To facilitate the data import process, a text import form was developed in Access such that digital data produced by the Datathief digitization process (included error bars) can be imported into the database automatically.

From the standpoint of data uncertainty, the data digitization is limited by the presence or absence of error bars on the figures. If error bars are included, the data uncertainties can be captured directly. If error bars are not included, an estimate of the data uncertainty must be made. This requires a rather detailed scheme to be put in place since error propagation from plots of percent sorbed, K<sub>d</sub>, or logK<sub>d</sub> will all require a different approach to estimating digitization error.

Once data are imported into the database, a series of unit conversion, uncertainty estimations, and data regularization processes are necessary. Automating this process is essential as the database continues to expand. These processes are being written external

to the Access database and scripted using the R environment. The goal of is to produce large CSV datasets with self-consistent units for all variable in the database. The most challenging aspect of this is the conversion of various type of X-Y plots into representative values of aqueous and sorbed concentrations of sorbents.

As an example, we demonstrate the equations used to convert  $K_d$ , percent sorbed, and fraction sorbed parameters into aqueous and sorbed concentrations of a sorbent. Aqueous and sorbed concentrations of a sorbent are essential values to be used in the PHREEQC/PEST optimization algorithm as well as the machine learning applications that are being pursued.

#### **4.1 Unit Conversions**

To produce a self-consistent dataset of values for use in surface complexation modeling effort, we need to export the total sorbent concentration (Sorbent\_val(mol/L)), the aqueous equilibrium concentration (Aq(mol/L)), and the sorbed concentration (either as Sorbed(mol/L) or Sorbed(mol/g)).

##### **4.1.1. Data Reported as Percent Sorbed**

To calculate concentration in the aqueous phase, Aq(mol/L), total concentration in the sample, Sorbent\_val(mol/L), and concentration on the solid phase, Sorbed(mol/L), the following calculations are necessary:

$$\text{Sorbent\_val(mol/L)} = \text{Reported in Access database}$$

$$\text{Sorbed(mol/L)} = \text{Sorbent\_val(mol/L)} * \text{Sorbed(\%)} / 100$$

$$\text{Sorbed(mol/g)} = \text{Sorbed(mol/L)} / \text{Mineral\_val(g/L)}$$

$$\text{Aq(mol/L)} = \text{Sorbent\_val(mol/L)} - \text{Sorbed(mol/L)}$$

##### **4.1.2. Data Reported as Fraction Sorbed**

To calculate concentration in the aqueous phase, Aq(mol/L), total concentration in the sample, Sorbent\_val(mol/L), and concentration on the solid phase, Sorbed(mol/L), the following calculations are necessary:

$$\text{Sorbent\_val(mol/L)} = \text{Reported in Access database.}$$

$$\text{Sorbed(mol/L)} = \text{Sorbent\_val(mol/L)} * \text{Sorbed(fraction)}$$

$$\text{Sorbed(mol/g)} = \text{Sorbed(mol/L)} / \text{Mineral\_val(g/L)}$$

$$\text{Aq(mol/L)} = \text{Sorbent\_val(mol/L)} - \text{Sorbed(mol/L)}$$

### 4.1.3. Data Reported as Kd or Rd

To calculate concentration in the aqueous phase, Aq(mol/L), total concentration in the sample, Sorbent\_val(mol/L), and concentration on the solid phase, Sorbed(mol/L), from the reporting of Kd (or Rd), the following calculations are necessary (similar calculations necessary if data reported as log(Kd) or log(Rd)):

Kd(mL/g) = Reported in Access database.

Aq(mol/L) = Reported in Access database.

*Note: Kd or Rd must be in units of mL/g.*

$$\text{Sorbent\_val(mol/L)} = \text{Kd(mL/g)} \times \text{Aq(mol/L)} \times (1/1000) \times \text{Mineral\_val(g/L)} + \text{Aq(mol/L)}$$
$$= \text{Aq(mol/L)} \times (\text{Kd(mL/g)} \times (1/1000) \times \text{Mineral\_val(g/L)} + 1)$$
$$\text{Sorbed(mol/L)} = \text{Sorbent\_val(mol/L)} - \text{Aq(mol/L)}$$
$$\text{Sorbed(mol/g)} = \text{Sorbed(mol/L)} / \text{Mineral\_val(g/L)}$$

If Aq(mol/L) is not reported in the database, alternative equations are needed but are not illustrated here for the sake of brevity.

### 4.2 Error Propagation

The more complete set of calculations required to produce a dataset with uniform variable units and their associated estimated uncertainties are reported in Table 1. These unit conversions and error estimates capture all the possible X-Y axis parameters and associated units that have been encountered as part of the data digitization effort.

Table 1. Unit conversions and uncertainty calculations contained in digitized X-Y plots.

Axis	Units	Conversion	SD Calculation
alkalinity	meq/L	= axis / 1000 = mol/L HCO <sub>3</sub> <sup>-</sup>	As with electrolytes (5% default)
aqueous	mol/L	No conversion	As with electrolytes (5% default)
aqueous	log(mol/L)	= 10 <sup>axis</sup> = mol/L aqueous	As with electrolytes (10% default)
aqueous	mmol/L	= axis / 1000 = mol/L aqueous	As with electrolytes (5% default)
aqueous	ppb	= axis / 1000000 / MM = mol/L aqueous	As with electrolytes (5% default)
aqueous	ppm	= axis / 1000 / MM = mol/L aqueous	As with electrolytes (5% default)
charge	microC/cm <sup>2</sup>	<b>No conversion</b>	As with electrolytes (5% default)
charge	meq/kg	= axis * 96485 (C/eq) / mineral_SA (m <sup>2</sup> /g) / 10000 = microC/cm <sup>2</sup>	As with electrolytes (5% default)
charge	micromol/m <sup>2</sup>	= axis * 96485 / 10000 = microC/cm <sup>2</sup>	As with electrolytes (5% default)
charge	C/g	= axis / mineral_SA (m <sup>2</sup> /g) / 10000 * 1000000 = microC/cm <sup>2</sup>	As with electrolytes (5% default)
charge	C/m <sup>2</sup>	= axis / 10000 * 1000000 = microC/cm <sup>2</sup>	As with electrolytes (5% default)
charge	microC/m <sup>2</sup>	= axis / 10000 = microC/cm <sup>2</sup>	As with electrolytes (5% default)
charge	cmol/kg	= axis / 100 / 1000 * 96485 (C/eq) / mineral_SA (m <sup>2</sup> /g) / 10000 * 1000000	As with electrolytes (5% default)
charge	eq/g	= axis * 96485 (C/eq) / mineral_SA (m <sup>2</sup> /g) / 10000 * 1000000 = microC/cm <sup>2</sup>	As with electrolytes (5% default)
H(+)	-log(mol/L)	= pH (this is not quite right but we will leave it at that for now)	As with pH (0.1 default)
		= Aq(mol/L) * (Kd(mL/g) * (1/1000) * Mineral_val(g/L) + 1) = Sorbent_val(mol/L)	(50% default Kd)
		= Sorbent_val(mol/L) / (Kd(mL/g) * (1/1000) * Mineral_val(g/L) + 1) = Aq(mol/L)	= (Sorbent_val(mol/L) / (Kd(mL/g) / 1000 * Sorbent_val(g/L) + 1)) - (Sorbent_val(mol/L) / ([Kd(mL/g) * 1.5] / 1000 * Sorbent_val(g/L) + 1)) = Aq_SD (mol/L)
		= Sorbent_val(mol/L) - Aq(mol/L) = Sorbed(mol/L)	= ((Sorbent_SD(mol/L) <sup>2</sup> + (Aq_SD (mol/L)) <sup>2</sup> ) <sup>0.5</sup> = Sorbed_SD(mol/L)
		= Sorbed(mol/L) / Mineral_val(g/L) = Sorbed(mol/g)	= ((Sorbent_SD(mol/L) <sup>2</sup> + (Aq_SD (mol/L)) <sup>2</sup> ) <sup>0.5</sup> / Sorbent_val(g/L) = Sorbed_SD(mol/g)
Kd	mL/g		

Axis	Units	Conversion	SD Calculation
		Same as above, but, remove log first	$(\pm 0.2 \text{ Default } \log K_d)$ $= (\text{Sorbent\_val}(\text{mol/L}) / (10^{\log(K_d(\text{mL/g}) / 1000 * \text{Sorbent\_val}(\text{g/L}) + 1)) - (\text{Sorbent\_val}(\text{mol/L}) / ([10^{\log(K_d(\text{mL/g}+0.2)] / 1000 * \text{Sorbent\_val}(\text{g/L}) + 1)) = \text{Aq\_SD} (\text{mol/L})$  $= ((\text{Sorbent\_SD}(\text{mol/L})^2 + (\text{Aq\_SD} (\text{mol/L}))^2)^{0.5} = \text{Sorbed\_SD}(\text{mol/L})$  $= ((\text{Sorbent\_SD}(\text{mol/L})^2 + (\text{Aq\_SD} (\text{mol/L}))^2)^{0.5} / \text{Sorbent\_val}(\text{g/L}) = \text{Sorbed\_SD}(\text{mol/g})$
Kd	log(mL/g)		
Kd	log(L/kg)	Same as above, but, remove log first (L/kg = mL/g)	
Na(+)	mol/L	No conversion	As with electrolytes (5% default)
pH	pH	No conversion	As with pH (0.1 default)
Rd	log(L/kg)	Same as above, but, remove log first (L/kg = mL/g)	
Rd	m3/kg	Same as above, but, first convert to mL/g (m3/kg * 1000 = mL/g)	
solid	g/L	No conversion	As with electrolytes (5% default)
sorbed	mol/kg	$= \text{axis} / 1000 = \text{mol/g}$ or $= \text{axis} / 1000 * \text{mineral\_val}(\text{g/L}) = \text{mol/L}$ Sorbent_val(mol/L) = this value should be reported in the table.	As with electrolytes (5% default)
		$= \text{Sorbent\_val}(\text{mol/L}) * \text{Sorbed}(\%) / 100 = \text{Sorbed}(\mathbf{mol/L})$	$= 5 / 100 * \text{Sorbent\_val} (\text{mol/L}) = \text{Sorbed\_SD}(\text{mol/L})$
		$= \text{Sorbed}(\text{mol/L}) / \text{Mineral\_val}(\text{g/L}) = \text{Sorbed}(\mathbf{mol/g})$	$= 5 / 100 * \text{Sorbent\_val} (\text{mol/L}) / \text{Mineral\_val}(\text{g/L}) = \text{Sorbed\_SD}(\text{mol/g})$
sorbed	%	$= \text{Sorbent\_val}(\text{mol/L}) - \text{Sorbed}(\mathbf{mol/L}) = \text{Aq}(\text{mol/L})$	$= 5 / 100 * \text{Sorbent\_val} (\text{mol/L}) = \text{Aq\_SD}(\text{mol/L})$
		No conversion mol/g or	As with electrolytes (5% default)
sorbed	mol/g	$= \text{axis} * \text{mineral\_val}(\text{g/L}) = \text{mol/L}$ $= 10^{\text{axis}} / 1000 = \text{mol/g}$ or	As with electrolytes (10% default)
sorbed	log(mol/kg)	$= 10^{\text{axis}} / 1000 * \text{mineral\_val}(\text{g/L}) = \text{mol/L}$	
sorbed	fraction	Sorbent_val(mol/L) = this value should be reported in the table.	(0.05 default)

Axis	Units	Conversion	SD Calculation
		= Sorbent_val(mol/L) * Sorbed(fraction) = Sorbed( <b>mol/L</b> )	= 0.05 * Sorbent_val (mol/L) = Sorbed_SD(mol/L)
		= Sorbed(mol/L) / Mineral_val(g/L) = Sorbed( <b>mol/g</b> )	= 0.05 * Sorbent_val (mol/L) / Mineral_val(g/L) = Sorbed_SD(mol/g)
		= Sorbent_val(mol/L) - Sorbed( <b>mol/L</b> ) = Aq(mol/L)	= 0.05 * Sorbent_val (mol/L) = Aq_SD (mol/L)
sorbed	mmol/kg	= axis / 1000000 = mol/g or = axis / 1000000 * mineral_val(g/L) = mol/L	As with electrolytes (5% default)
sorbed	log(mol/m2)	= 10 <sup>axis</sup> * mineral_SA(m2/g) = mol/g or = 10 <sup>axis</sup> * mineral_SA(m2/g) * mineral_val(g/L) = mol/L	As with electrolytes (10% default)
sorbed	log(mol/mol)	= 10 <sup>axis</sup> * Sorbent(mol/L) / mineral_val(g/L) = mol/g or = 10 <sup>axis</sup> * Sorbent(mol/L) = mol/L	As with electrolytes (10% default)
sorbed	mmol/g	= axis / 1000 = mol/g or = axis / 1000 * mineral_val(g/L) = mol/L	As with electrolytes (5% default)
sorbed	micromol/g	= axis / 1000000 = mol/g or = axis / 1000000 * mineral_val(g/L) = mol/L	As with electrolytes (5% default)
sorbed	log(mol/g)	= 10 <sup>axis</sup> = mol/g or = 10 <sup>axis</sup> * mineral_val(g/L) = mol/L	As with electrolytes (10% default)
total H(+)	mol/L	= axis * 96485 (C/eq) / mineral_val(g/L) / mineral_SA (m <sup>2</sup> /g) / 10000 * 1000000 = microC/cm <sup>2</sup>	As with electrolytes (5% default)
total H(+)	mmol/L	= axis / 1000 * 96485 (C/eq) / mineral_val(g/L) / mineral_SA (m <sup>2</sup> /g) / 10000 * 1000000 = microC/cm <sup>2</sup>	As with electrolytes (5% default)
total OH(-)	mol/L	= -axis * 96485 (C/eq) / mineral_val(g/L) / mineral_SA (m <sup>2</sup> /g) / 10000 * 1000000 = microC/cm <sup>2</sup>	As with electrolytes (5% default)

### 4.3. Status of Data Digitization Effort

The following is a short summary providing statistics for the data incorporated into the Access database of sorption data. Two efforts are underway. The first was the digitization of data associated with radionuclide sorption to clay with a particular focus on montmorillonite/bentonite backfill material. The second is the integration of data available from our RES<sup>3</sup>T partners. The RES<sup>3</sup>T data are centered around uranium sorption to a broad range of minerals. It also includes potentiometric titration data for a broad range of minerals, including clays. In both cases, manuscript data digitization is oriented towards references that have been identified in the RES<sup>3</sup>T database. This has significantly simplified the identification of references will appropriate sorption data in the literature.

General statistics for data included in the database are reported in Table 2. Data included in the database capture radionuclide sorption to individual minerals (i.e. binary sorption experiments). The database includes potentiometric titration for these mineral phases which are a critical component needed to simulate surface protonation behavior.

Table 2. General statistics of the LLNL sorption database.

Data Table	Count
References	158
Datasets	1,567
Data	15,571

The sorbents included in the database include radionuclides that are common to a GDSA analysis (i.e. Am, U, Np, Pu, Se, Sr, Cs, etc.). Other elements that are less relevant to GDSA (i.e. Cr, Cu, P, Rb) were captured in the database as result of the data collection process though not intentionally; these data were digitized only when they were present in manuscripts that contained GDSA-relevant data. Major cation/anion sorption data are included as they are an essential component of the ion exchange process or may contribute to competitive surface sorption processes (e.g. Ca, Mg, K, Na, S). Lastly, H(+) is included in the sorbent list and refers to the potentiometric data that were captured in the database (Table 3).

Table 3. List of sorbents included in the database and associated concentration range.

Sorbent	min	max	sorbent units
Am(+3)	5.00E-10	2.90E-07	mol/L
Ba(+2)	3.12E-08	1.00E-07	mol/L
Ca(+2)	2.00E-06	2.52E-01	mol/L



<b>Sorbent</b>	<b>min</b>	<b>max</b>	<b>sorbent units</b>
Cd(+2)	1.00E-08	3.20E-05	mol/L
Cm(+3)	2.00E-07	2.00E-07	mol/kg
Co(+2)	5.60E-09	1.00E-02	mol/L
Cr(+3)	9.62E-04	9.62E-04	mol/L
Cr(+6)	5.00E-06	5.00E-06	mol/L
Cs(+)	1.51E-09	7.95E-04	mol/L
Cu(+2)	3.10E-07	6.35E+02	mol/L
Eu(+3)	1.00E-09	1.11E-04	mol/L
H(+)			mol/L
HCO <sub>3</sub> (-)	5.50E-05	8.30E-04	mol/L
humic acid	9.00E+00	9.00E+00	mg/L
K(+)	1.24E-03	5.04E-01	mol/L
Mg(+2)	5.77E-05	3.63E-03	mol/L
Mn(+2)	1.00E-07	1.00E-02	mol/L
Ni(+2)	5.00E-09	1.00E-02	mol/L
NpO <sub>2</sub> (+)	1.00E-14	6.00E-06	mol/L
Pb(+2)	8.50E-08	2.07E+00	mol/L
PO <sub>3</sub> (-3)	1.00E-04	1.00E-04	mol/L
Pu	1.00E-14	6.00E-08	mol/L
Rb(+)	1.27E-09	7.95E-04	mol/L
SeO <sub>3</sub> (-2)	1.90E-05	1.90E-05	mol/L
SO <sub>4</sub> (-2)	1.72E-04	4.00E-03	mol/L
Sr(+2)	1.00E-08	5.00E-02	mol/L
Th(+4)	1.00E-11	3.00E-07	mol/L
UO <sub>2</sub> (+2)	1.00E-08	1.00E-03	mol/L
Yb(+3)	2.10E-05	2.10E-05	mol/L
Zn(+2)	1.00E-09	6.54E+02	mol/L

Digitized sorption data were general collected from experiments performed in simple electrolytes (e.g. NaClO<sub>4</sub>, NaCl) and across a range of ionic strength. However, data capture included unusual electrolytes in some cases (e.g. S<sub>2</sub>O<sub>4</sub>). The full list of electrolytes and the associated concentration range is listed in Table 4. The HCO<sub>3</sub>(-) electrolyte is a special case in that concentrations may be controlled either by direct addition to solution or by controlling the CO<sub>2(g)</sub> fugacity in equilibrium with solution. The concentration in solution was captured in both cases. When experiments are performed under atmospheric CO<sub>2(g)</sub> conditions, the database captures the general trends in atmospheric CO<sub>2(g)</sub> concentrations over the past century. Manuscript publication dates captured in this database range from 1952 to present.

Table 4. List of electrolytes included in the database and associated concentration range.

<b>Electrolyte</b>	<b>min</b>	<b>max</b>	<b>Units</b>
acetate	1.0E-02	1.0E-02	mol/L
Ba(+2)	2.0E-04	5.0E-04	mol/L
Ca(+2)	1.4E-05	4.0E-01	mol/L
Citrate	1.0E-02	1.0E-02	mol/L
Cl(-)	4.0E-04	6.0E+00	mol/L
ClO4(-)	1.0E-03	5.0E+00	mol/L
F(-)	1.0E-04	5.0E-04	mol/L
humic acid	9.0E+00	9.0E+00	mg/L
HCO3(-)	7.8E-06	1.0E+00	mol/L
I(-)	4.0E-03	1.0E-01	mol/L
K(+)	1.4E-05	2.0E+00	mol/L
Mg(+2)	7.4E-05	5.4E-02	mol/L
NO3(-)	1.0E-03	2.5E+00	mol/L
NH4(+)	8.7E-03	8.7E-03	mol/L
Na(+)	2.5E-04	6.0E+00	mol/L
oxalate	5.0E-04	5.0E-04	mol/L
PO4(-3)	2.0E-06	1.0E-04	mol/L
pH	2.5E+00	1.0E+01	pH
pyromellitate	5.0E-04	1.0E-03	mol/L
SO4(-2)	3.8E-05	2.8E-02	mol/L
S2O4(-2)	1.0E-03	1.0E-03	mol/L
salicylate	5.0E-04	5.0E-04	mol/L
SiO2(aq)	1.0E-04	1.0E-04	mol/L
Sr(+2)	1.5E-04	5.0E-04	mol/L
UO2(+2)	1.0E-06	1.0E-03	mol/L

The focus of our effort has been the capture of sorption to aluminosilicate clays with a particular focus on montmorillonite, which is a major component of bentonite backfill material. However, a number of other minerals were captured in the data digitization effort to date. The list of minerals included in the database are listed in Table 5. An upgrade to our database this fiscal year has been to capture the source of material used in sorption experiments. This is helping to capture and identify potential variation in data that results from characteristics of particular source materials (e.g. comparison of SWy-1 montmorillonite, SAz-1 montmorillonite, and synthetic forms of montmorillonite).

Table 5. Minerals included in the database.

<b>Mineral</b>	<b>Mineral_Formula</b>	<b>Mineral_Source</b>
Al(OH)3	gamma-Al(OH)3	synthetic
albite		natural

<b>Mineral</b>	<b>Mineral_Formula</b>	<b>Mineral_Source</b>
alumina	alpha-Al <sub>2</sub> O <sub>3</sub>	Ventron
alumina	alpha-Al <sub>2</sub> O <sub>3</sub>	Wako
alumina	gamma-Al <sub>2</sub> O <sub>3</sub>	Degussa
alumina	gamma-Al <sub>2</sub> O <sub>3</sub>	Fisher
alumina	gamma-Al <sub>2</sub> O <sub>3</sub>	synthetic
amorphous silica	SiO <sub>2</sub>	Merck
amorphous silica	SiO <sub>2</sub>	synthetic
bentonite		Fluka
bentonite		Kunippia F
bentonite		MX-80
bentonite		Jinchuan
biotite		Nihon
birnessite	delta-MnO <sub>2</sub>	synthetic
boehmite	gamma-AlOOH	BA Chemical
boehmite	gamma-AlOOH	Rare Mettalic
calcite	CaCO <sub>3</sub>	Spectrum
calcite	CaCO <sub>3</sub>	Wyandotte
calcite	CaCO <sub>3</sub>	Mexico
calcite	CaCO <sub>3</sub>	Fisher
chlorite		Grimsel
clinoptilolite		Death Valley Junction
ferrihydrate	Fe(OH) <sub>3</sub>	synthetic
gibbsite	gamma-Al(OH) <sub>3</sub>	commercial
gibbsite	gamma-Al(OH) <sub>3</sub>	Merck
gibbsite	gamma-Al(OH) <sub>3</sub>	Alcan
gibbsite	gamma-Al(OH) <sub>3</sub>	synthetic
gibbsite	gamma-Al(OH) <sub>3</sub>	Dalian Luming
gibbsite	gamma-Al(OH) <sub>3</sub>	Alcan SF-4
gibbsite	gamma-Al(OH) <sub>3</sub>	Alcoa
goethite	alpha-FeOOH	BASF
goethite	alpha-FeOOH	synthetic
goethite	alpha-FeOOH	Fe-52
goethite	alpha-FeOOH	Bayer
goethite	alpha-FeOOH	Nihon
hematite	alpha-Fe <sub>2</sub> O <sub>3</sub>	synthetic
hematite	alpha-Fe <sub>2</sub> O <sub>3</sub>	Nihon
hematite	alpha-Fe <sub>2</sub> O <sub>3</sub>	Wako
hematite	alpha-Fe <sub>2</sub> O <sub>3</sub>	natural
hematite	alpha-Fe <sub>2</sub> O <sub>3</sub>	Aldrich
hydrrous aluminum oxide		synthetic

<b>Mineral</b>	<b>Mineral_Formula</b>	<b>Mineral_Source</b>
hydrous manganese oxide		synthetic
illite		Morris illite
illite		Socodis SA
illite		Marblehead
illite		du Puy
illite		Silver Hill
kaolinite		KGa-1
kaolinite		KGa-1B
kaolinite		Aldrich
kaolinite		KGa-2
lepidocrosite	gamma-FeOOH	Rare Mettalic
magnetite	Fe <sub>3</sub> O <sub>4</sub>	Puratronic
magnetite	Fe <sub>3</sub> O <sub>4</sub>	Nihon
magnetite	Fe <sub>3</sub> O <sub>4</sub>	Wako
montmorillonite		SWy-1
montmorillonite		Aldrich, K10
montmorillonite		SAz-1
montmorillonite		SWy-2
muscovite		natural
quartz	SiO <sub>2</sub>	Merck
quartz	SiO <sub>2</sub>	Min-U-Sil 30
quartz	SiO <sub>2</sub>	BDH
quartz	SiO <sub>2</sub>	Sigma
quartz	SiO <sub>2</sub>	Wedron #510
vernadite	delta-MnO <sub>2</sub>	synthetic

The RES<sup>3</sup>T database authors (F. Bok, HZDR) have compiled a large set of data for U sorption to a number of mineral phases. In addition, these authors have also compiled potentiometric titration data for these same minerals. We are in the process of integrating these data into the Access database. Minerals associated with this data integration effort include birnessite, ferrihydrite, gibbsite, goethite, hematite, magnetite, montmorillonite, quartz, rutile, and zirconia. The total number of individual datapoints included in these datasets is on the order of 5,000-10,000 points. Importantly, this data integration effort will provide a basis for modeling the surface protonation for an important set of minerals that are relevant to the GDSA efforts.

## 5. Fitting Raw Sorption Data using PHREEQC-PEST Optimization

The goal of this effort is the development of a consistent database of surface complexation/ion exchange constants for radionuclides and mineral surfaces relevant to the GDSA effort. As such, the digitization of data is simply the first step in the

development of a surface complexation/ion exchange database for use in nuclear waste repository performance assessment. To achieve this end goal, data captured in the Access database must be fitted to a surface complexation/ion exchange models to produce reaction constants that can then be employed in performance assessment calculations. To this end, scripts were developed to extract and format the relevant data captured in the sorption database as input into a PEST parameter estimation code that is linked to the surface complexation/ion exchange code contained in the PHREEQC code. The details of the input files will not be described here. However, it should be noted that modules, macros, and queries were initially developed in the Microsoft Access to produce input files that can be directly inserted in the PEST parameter estimation code and linked to the PHREEQC software. However, this path is proving to be unsustainable as our database grows in complexity. Instead, we are moving towards a more robust approach that involves the unit conversion and data manipulation algorithms develop in R. These outputs are to be used as data for further analysis using machine learning and PHREEQC/PEST data fitting that will be performed using scripts written in Python. This transition was necessary to take advantage of machine learning. While the details of this process are still under development through a collaboration with Dr. Haruko Wainwright (UC Berkeley), these schemes are being developed during the summer of FY20 as part of a LLNL initiative and student internship program facilitating faculty-LLNL collaborations.

To perform the parameter estimation, PHREEQC required a thermodynamic database to simulate the aqueous speciation and precipitation of mineral phases at each solution condition for each sorption data point captured in the Access database. The PHREEQC package contains historical thermodynamic data based on LLNL's SUPCRT data that was supported by the US nuclear waste repository program at Yucca Mountain. This thermodynamic database is being updated as part of the Argillite and Crystalline International work packages (see individual milestone reports associated with these work packages). Furthermore, collaboration with the NEA-TDB efforts is leading to new updates to the thermodynamic data for radionuclides relevant to nuclear waste repository science. It is the intent of this effort that the surface complexation/ion exchange database take the results of these thermodynamic database development efforts as direct input into the fitting of surface complexation/ion exchange data to provide a self-consistent set of reactions both from the standpoint of radionuclide speciation and solubility and reactions at the mineral-water interface. As new thermodynamic data become available, raw sorption data capture in the Access database will be refit to provide a consistent representation of radionuclide aqueous speciation, solubility, and mineral-water interface reaction constants.

## 6. Planned FY21 Efforts

The FY20 effort has focused primarily on building out the Access database of raw sorption data and developing a framework for surface complexation/ion exchange data fitting methods and surface complexation/ion exchange database development. Effort is coordinated with international partners involved in similar database development efforts (e.g. HZRD RES<sup>3</sup>T). Here, we described the development of the sorption data capture

process. We will complete our data capture for radionuclide (Cs, Sr, U, Np, and Pu) sorption to clay minerals (with particular focus on bentonite/montmorillonite). Subsequently, a more complete methodology for development of a surface complexation/ion exchange constant database from the primary sorption data will be pursued. A key component of that effort is the automation 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 scripts needed to perform this automation were originally implemented in Access and are now being translated into R and Python scripts that are much more flexible and adaptable. Of particular interest is the expansion of our data interrogation effort by applying modern data science methods (e.g. machine learning). The combination of machine learning approaches with more traditional PEST/PHREEQC data fitting approaches will provide flexibility to GDSA efforts (e.g. use of mechanistic surface complexation/ion exchange models versus “smart Kd” lookup tables). The data analysis schemes are being developed to facilitate links to thermodynamic database development efforts (e.g. SUPCRTNE, NEA-TDB) to allow for updates to our 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 and Crystalline International work package and in support of the 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. The goal of this effort is the development of consistent models of radionuclide sorption to mineral surfaces that can be implemented in performance assessment models for the GDSA effort.

## 7. Acknowledgments

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

## 8. References

- Bradbury, M. H. and Baeyens, B., 1993. A general application of surface complexation modeling radionuclide sorption in natural systems. *J. Colloid Interface Sci.* **158**, 364-371.
- Bradbury, M. H. and Baeyens, B., 2009. Sorption modelling on illite. Part II: Actinide sorption and linear free energy relationships. *Geochim. Cosmochim. Acta* **73**, 1004-1013.
- Bradbury, M. H., Baeyens, B., and Thoenen, T., 2010. Sorption Data Bases for Generic Swiss Argillaceous Rock Systems. Nagra, Wettingen, Switzerland.

- Charlton, S. R. and Parkhurst, D. L., 2011. Modules based on the geochemical model PHREEQC for use in scripting and programming languages. *Computers & Geosciences* **37**, 1653-1663.
- Davis, J., Ochs, M., Olin, M., Payne, T., and Tweed, C., 2005. Interpretation and prediction of radionuclide sorption onto substrates relevant for radioactive waste disposal using thermodynamic sorption models. OECD/Nuclear Energy Agency, Paris.
- Doherty, J., 2003. PEST: Model-Independent Parameter Estimation. Watermark Numerical Computing.
- Dresden-Rossendorf, H.-Z., 2013. RES<sup>3</sup>T - Rossendorf Expert System for Surface and Sorption Thermodynamics. RES<sup>3</sup>T - Rossendorf Expert System for Surface and Sorption Thermodynamics, Dresden, Germany.
- Geckeis, H., Lützenkirchen, J., Polly, R., Rabung, T., and Schmidt, M., 2013. Mineral–Water Interface Reactions of Actinides. *Chemical Reviews* **113**, 1016-1062.
- Herbelin, A. L. and Westall, J. C., 1994. FITEQL, A computer program for determination of chemical equilibrium constants from experimental data. Department of Chemistry, Oregon State University.
- Ochs, M., Payne, T. E., and Brendler, V., 2012. Thermodynamic sorption modeling in support of radioactive waste disposal safety cases. A guideline document. OECD/NEA, Paris.
- Parkhurst, D. L. and Wissmeier, L., 2015. PhreeqcRM: A reaction module for transport simulators based on the geochemical model PHREEQC. *Advances in Water Resources* **83**, 176-189.
- Zavarin, M., Turner, G. D., and Westall, J. C., 2004. FIT4FD. Modification of the Program FITEQL to Facilitate Rapid Evaluation of Complex Datasets, Livermore (CA).
- Zavarin, M., Wolery, T.J., Atkins-Duffin, C. 2016. M4FT-16LL080302052-Update to Thermodynamic Database Development and Sorption Database Integration. LLNL-TR-701407, Lawrence Livermore National Laboratory.
- Zavarin, M., Balboni, E., Booth, C., Wolery, T., Atkins-Duffin, C. 2018. M4SF-18LL010302082-Thermodynamic Database Development and Identification of Actinide Sequestration in Corrosion Products, LLNL-TR-756687, Lawrence Livermore National Laboratory.
- Zavarin, M. 2019. M4SF-19LL010301082-SurfaceComplexation and Ion Exchange Database Development Phase 1: Clay Minerals, LLNL-TR-778004, Lawrence Livermore National Laboratory.