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M4SF-19LL010301082-Surface Complexation and Ion Exchange Database Development Phase 1: Clay Minerals

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1. Introduction

This progress report (Level 4 Milestone Number M4SF-19LL010301082) summarizes research conducted at Lawrence Livermore National Laboratory (LLNL) within the Argillite International Collaborations Activity Number Activity SF-19LL010301081. 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 SFWST that is aligned with the Helmholtz Zentrum Dresden Rossendorf (HZDR) sorption database development group in support of the database needs of the Spent Fuel and Waste and Science Technology (SFWST) program.

FY19 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 RES³t). Two components of database development are pursued. First, a primary sorption data capture effort is focused 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 (3/27/20 Milestone). 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. 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 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 international efforts.

2. The RES³T 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 the recent 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-Rossendorf, 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 RES³T 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 (SC 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 140 minerals, nearly 5500 surface complexation reaction constants, and nearly 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 RES³T project provides a foundation for developing a comprehensive surface complexation database but does not go so far as to provide one.

Three key issues prevent the application of the RES³T database in performance assessment and other radionuclide transport/risk assessment models. They are:

- An inability to integrate disparate data sets and surface complexation model constructs into single unified model and associated set of reaction constants
- An inability to produce self-consistent reaction constants based on a common set of aqueous speciation constants and surface properties.
- The absence of error propagation in the sorption data and/or database constants needed to assess model uncertainties.

To address these limitations, the inclusion of primary sorption data in the RES³T database is needed. This would allow for integration of all available literature data, error propagation, and database updating and ensure self-consistency between aqueous speciation, mineral solubility, and surface complexation databases.

In FY14, we developed a test-case for U(VI) sorption to quartz and demonstrated how a self-consistent set of surface complexation constants could be produced from ~400 batch sorption data digitized from the published literature (11 publications in total, Table 1). The minimization routine was performed using the software developed at LLNL (Zavarin et al., 2004) and based on the FITEQL software (Herbelin and Westall, 1994). However, this approach did not provide the flexibility needed to easily evaluate and test various surface complexation models. Thus, alternative approaches have been investigated. One promising approach that has been pursued here is to combine the reactive transport code

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PHREEQC (Charlton and Parkhurst, 2011; Parkhurst and Wissmeier, 2015) with the parameter estimation software PEST (Doherty, 2003).

Table 1. Surface complexation data reported in the RES3T database association with U(VI) sorption to quartz.

SCM	Mineral	Area	Site	pK 1	pK 2	logK	Chemical Equation	Literature
DDL	Quartz	0.2	4.81		5.62	-5.72	$\text{»Si-(OH)}_2 + \text{UO}_2\langle 2+\rangle = \text{»Si-O}_2\text{-UO}_2 + 2 \text{H}\langle 1+\rangle$	AZBN00a
DDL	Quartz	0.2	4.81		5.62	-5.51	$\text{»Si-(OH)}_2 + \text{UO}_2\langle 2+\rangle = \text{»Si-O}_2\text{-UO}_2 + 2 \text{H}\langle 1+\rangle$	AZZBN01
DDL	Quartz	10	10	-1.6	7.6	-7.259	$\text{»X-OH} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»X-O-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	JHLCH99
DDL	Quartz	10	10	-1.6	7.6	9.529	$\text{»X-OH} + \text{UO}_2\langle 2+\rangle + \text{CO}_3\langle 2-\rangle = \text{»X-O-UO}_2\text{CO}_3\langle 1-\rangle + \text{H}\langle 1+\rangle$	JHLCH99
DDL	Quartz	10	10	-1.6	7.6	-1.978	$\text{»X-OH} + \text{UO}_2\langle 2+\rangle = \text{»X-O-UO}_2\langle 1+\rangle + \text{H}\langle 1+\rangle$	JHLCH99
DDL	Quartz	0.05			-7.2	-16.75	$\text{»SiOH} + 3 \text{UO}_2\langle 2+\rangle + 5 \text{H}_2\text{O} = \text{»SiO-(UO}_2)_3(\text{OH})_5 + 6 \text{H}\langle 1+\rangle$	NB10
DDL	Quartz	0.05			-7.2	0.3	$\text{»SiOH} + \text{UO}_2\langle 2+\rangle = \text{»SiO-UO}_2\langle 1+\rangle + \text{H}\langle 1+\rangle$	NB10
DDL	Quartz	0.05			-7.2	-5.65	$\text{»SiOH} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»SiO-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	NB10
DDL	Quartz	0.31	2.3	-1.24	7.06	-0.3	$\text{»Si-OH} + \text{UO}_2\langle 2+\rangle = \text{»Si-O-UO}_2\langle 1+\rangle + \text{H}\langle 1+\rangle$	PJTP01
DDL	Quartz	0.31	2.3	-1.24	7.06	-18.7	$\text{»Si-OH} + \text{UO}_2\langle 2+\rangle + 3 \text{H}_2\text{O} = \text{»Si-O-UO}_2(\text{OH})_3\langle 2-\rangle + 4 \text{H}\langle 1+\rangle$	PJTP01
DDL	Quartz	0.03	2.3		7.2	0.3	$\text{»Si-OH} + \text{UO}_2\langle 2+\rangle = \text{»Si-O-UO}_2\langle 1+\rangle + \text{H}\langle 1+\rangle$	PTBP98
DDL	Quartz	0.03	2.3		7.2	-16.75	$\text{»Si-OH} + 3 \text{UO}_2\langle 2+\rangle + 5 \text{H}_2\text{O} = \text{»Si-O-(UO}_2)_3(\text{OH})_5 + 6 \text{H}\langle 1+\rangle$	PTBP98
DDL	Quartz	0.03	2.3		7.2	-5.65	$\text{»Si-OH} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si-O-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	PTBP98
DDL	Quartz	0.1	2.31		7.2	-8.45	$\text{»Si-OH} + \text{UO}_2\langle 2+\rangle + 2 \text{H}_2\text{O} = \text{»Si-O-UO}_2(\text{OH})_2\langle 1-\rangle + 3 \text{H}\langle 1+\rangle$	VT98
NE	Quartz	0.33	0			-4.95	$\text{»Si(w)-OH} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si(w)-O-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	DK01
NE	Quartz	0.33	0			1.06	$\text{»Si(s)-OH} + \text{UO}_2\langle 2+\rangle = \text{»Si(s)-O-UO}_2\langle 1+\rangle + \text{H}\langle 1+\rangle$	DK01
NE	Quartz	0.33	0			-3.19	$\text{»Si(s)-OH} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si(s)-O-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	DK01
NE	Quartz	0.33	0			-2.56	$\text{»Si(s)-OH} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si(s)-O-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	DK01
NE	Quartz	0.33	0			-4.98	$\text{»Si(w)-OH} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si(w)-O-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	DK01
NE	Quartz	0.33	0			1.2	$\text{»Si(s)-OH} + \text{UO}_2\langle 2+\rangle = \text{»Si(s)-O-UO}_2\langle 1+\rangle + \text{H}\langle 1+\rangle$	DK01
NE	Quartz	0.33	0			-4.64	$\text{»Si(w)-OH} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si(w)-O-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	DK01
NE	Quartz	0.33	0			-0.03	$\text{»Si(w)-OH} + \text{UO}_2\langle 2+\rangle = \text{»Si(w)-O-UO}_2\langle 1+\rangle + \text{H}\langle 1+\rangle$	DK01
NE	Quartz	0.33	0			-5.28	$\text{»Si(w)-OH} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si(w)-O-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	DK01
NE	Quartz	0.33	0			10.183	$\text{»Si(w)-OH} + \text{UO}_2\langle 2+\rangle + \text{CO}_3\langle 2-\rangle = \text{»Si(w)-O-UO}_2\text{CO}_3\langle 1-\rangle + \text{H}\langle 1+\rangle$	DK01
NE	Quartz	0.33	0			-3.28	$\text{»Si(s)-OH} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si(s)-O-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	DK01
NE	Quartz	0.33	0			-4.73	$\text{»Si-OH} + \text{UO}_2\langle 2+\rangle = \text{»Si-O-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	KCKD96
NE	Quartz	0.33	0			-5.32	$\text{»Si(w)-OH} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si(w)-O-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	KCKD96
NE	Quartz	0.33	0			-2.65	$\text{»Si(s)-OH} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si(s)-O-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	KCKD96
NE	Quartz	0.33	0			-2.56	$\text{»Si(s)-O(0.5)H} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si(s)-O(0.5)-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	K02b
NE	Quartz	0.33	0			-7.78	$\text{»Si(w)-O(0.5)H} + \text{UO}_2\langle 2+\rangle + \text{CO}_2 + \text{H}_2\text{O} = \text{»Si(w)-O(0.5)-UO}_2\text{CO}_3(\text{OH})\langle 2-\rangle + 3 \text{H}\langle 1+\rangle$	K02b
NE	Quartz	0.33	0			-6.56	$\text{»Si(w)-O(0.5)H} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si(w)-O(0.5)-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	K02b
NE	Quartz	0.33	0			-5.57	$\text{»Si(s)-O(0.5)H} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si(s)-O(0.5)-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	K02b
NE	Quartz	0.33	0			-6.5	$\text{»Si(w)-O(0.5)H} + \text{UO}_2\langle 2+\rangle + \text{CO}_2 + \text{H}_2\text{O} = \text{»Si(w)-O(0.5)-UO}_2\text{CO}_3(\text{OH})\langle 2-\rangle + 3 \text{H}\langle 1+\rangle$	K02b
NE	Quartz	0.33	0			-5.28	$\text{»Si(w)-O(0.5)H} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si(w)-O(0.5)-UO}_2(\text{OH}) + 2 \text{H}\langle 1+\rangle$	K02b
TL	Quartz	0.32	0.00184		8.4	1.98	$\text{»Si(s)-OH} + \text{UO}_2\langle 2+\rangle = \text{»Si(s)-O-UO}_2\langle 1+\rangle + \text{H}\langle 1+\rangle$	FDZ06
TL	Quartz	0.32	0.00184		8.4	-1.88	$\text{»Si(s)-OH} + \text{UO}_2\langle 2+\rangle + \text{H}_2\text{O} = \text{»Si(s)-O-UO}_2(\text{OH}) + \text{H}\langle 1+\rangle$	FDZ06

3. Digitized Database Structure

To initiate our pursuit of a comprehensive sorption database in support of the SFWST program, we returned to our original test case of U(VI) sorption to quartz. A search of the RES³T database for all surface complexation references related to U(VI) sorption to quartz and associated surface complexation constants revealed 11 references to this mineral-radionuclide pair. Importantly, it should be noted that the RES³T database does not capture sorption data reported in the literature that did not include a surface complexation model. Thus, there are a number of publications on U(VI) sorption to quartz that may not exist in the RES³T database simply because a surface complexation modeling effort was not included in the publication. This suggests that, if necessary, sorption reference reported in RES³T can be supplemented by additional sorption data in the literature. However, for this test case, we did not attempt to capture these additional datasets.

The initial database of sorption data was developed in Microsoft Access with a series of linked tables. The tables include the following:

1. Reference Table
2. Dataset Table
3. Data Table
4. Mineral Site Density Table
5. Atmospheric CO₂ Table

The reference table (Table 2) captures the following information:

1. Unique identifier – supplied by Microsoft Access
2. Reference name – Unique name for reference
3. Original manuscript – pdf of original manuscript
4. Importer – Name of person performing the data import
5. Original data – Y/N answer to whether the data appear to be original to the reference manuscript
6. In database – Y/N answer to whether the raw data are captured in the database

Table 2. Reference table in the digitized sorption database.

Reference					
ID	Reference	Field1	Imported by	Original data?	In database?
1	azbn00	1	Mavrik Zavarin	y	y
2	azbn01	1	Mavrik Zavarin	y	y
10	azbn98	1	Mavrik Zavarin	n	n
9	fdz06	1	Mavrik Zavarin	y	y
3	IAC	1	Mavrik Zavarin	n	n
4	jhlch99	1	Mavrik Zavarin	y	y
8	kckd96	1	Mavrik Zavarin	y	y
7	kd01	1	Mavrik Zavarin	y	y
5	pjtp01	1	Mavrik Zavarin	y	y
6	ptbp98	1	Mavrik Zavarin	y	y

The scheme used in the RES³T reference nomenclature is intended to provide a unique identifier for each literature reference in the database. In LLNL's thermo.com.V8.R6+ database, the reference format is the following:

89zac/kit

Zachara, J.A., Kittrick, J.A., Dake, L.S., and J.B. Harsh, 1989, Solubility and surface spectroscopy of Zinc precipitates on Calcite: *Geochim. Cosmochim. Acta*, 53, 9-19.

In the RES³T database, the reference format is based on the author name initial and year of publication such that

JHLCH99

J. Jung, S. P. Hyun, J. K. Lee, Y. H. Cho, P. S. Hahn. 1999. Adsorption of UO₂²⁺ on natural composite materials, *Journal of Radioanalytical and Nuclear Chemistry*, 242(2): 405-412

This formalism was used in our digitized sorption database.

The Dataset table (Table 3) 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 which 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. 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. ElectrolyteX – Name of electrolyte ion X
7. ElectrolyteX_val – Value for electrolyte X
8. ElectrolyteX_SD – standard deviation for electrolyte X value
9. ElectrolyteX_units – units of electrolyte X value (e.g. mol/L)
10. Sorbent – Name of sorbent
11. Sorbent_val – Value of sorbent
12. Sorbent_SD – standard deviation of sorbent value
13. Sorbent_unit – Units of sorbent value
14. Mineral_val – Value of mineral
15. Mineral_SD – standard deviation of mineral value
16. Mineral_units – Units of mineral_val (e.g. g/L)
17. MineralSA – surface area of mineral
18. MineralSA_SD – standard deviation of mineralSA
19. MineralSA_units – Units of mineralSA
20. Mineralsites – mineral reactive sites value
21. Mineralsites_SD – standard deviation of mineral reactive site value
22. Mineralsites_units – Units of Mineralsites (e.g. sites/nm²)
23. GasX – Name of gas in equilibrium with solution
24. GasX_val – Value of GasX
25. GasX_SD – standard deviation of GasX value
26. GasX_units – units of GasX value (e.g. bar)
27. X_axis – Name of X axis in figure
28. X_units – Units of X axis
29. Y_axis – Name of Y axis on figure
30. Y_units – Units of Y axis

Table 3. Example of Dataset table from sorption database (with some columns omitted).

Dataset																							
ID	Reference	Set	Field1	Mineral	Electrolyte1	Electrolyte1_val	Electrolyte1_units	Sorbent	Sorbent_val	sorbent units	Mineral_val	Mineral_units	MineralSA	MineralSA_units	Mineralsites	Mineralsites_units	Gas1	Gas1_val	Gas1_units	X_axis	X_units	Y_axis	Y_units
1	azbn00	azbn00_f1	2	quartz	Na(+1)	1.00E-01	mol/L	U(+6)	1.00E-06	mol/L	1.20E+01	g/L	2.00E-01	m ² /g	2.31E+00	sites/nm ²	N ₂ (g)	8.00E-01	bar	pH	pH	sorbed	%
2	azbn01	azbn01_f1a	2	quartz	Na(+1)	1.00E-01	mol/L	U(+6)	1.00E-06	mol/L	1.25E+01	g/L	2.00E-01	m ² /g	4.81E+00	sites/nm ²	N ₂ (g)	8.00E-01	bar	pH	pH	sorbed	%
3	jhlch99	jhlch99_f4a	2	quartz	K(+1)	1.00E-02	mol/L	U(+6)	1.00E-05	mol/L	1.20E+01	g/L	1.00E+01	m ² /g	1.00E+01	sites/nm ²	N ₂ (g)	8.00E-01	bar	pH	pH	sorbed	%
4	jhlch99	jhlch99_f4b	2	quartz	K(+1)	1.00E-02	mol/L	U(+6)	1.00E-04	mol/L	1.20E+01	g/L	1.00E+01	m ² /g	1.00E+01	sites/nm ²	N ₂ (g)	8.00E-01	bar	pH	pH	sorbed	%
5	jhlch99	jhlch99_f4c	2	quartz	K(+1)	1.00E-02	mol/L	U(+6)	1.00E-05	mol/L	1.20E+01	g/L	1.00E+01	m ² /g	1.00E+01	sites/nm ²	N ₂ (g)	8.00E-01	bar	pH	pH	sorbed	%
6	jhlch99	jhlch99_f4d	2	quartz	K(+1)	1.00E-02	mol/L	U(+6)	1.00E-04	mol/L	1.20E+01	g/L	1.00E+01	m ² /g	1.00E+01	sites/nm ²	N ₂ (g)	8.00E-01	bar	pH	pH	sorbed	%
7	pjtp01	pjtp01_f1a	2	quartz	Na(+1)	1.00E-01	mol/L	U(+6)	2.03E-07	mol/L	2.86E+01	g/L	3.10E-01	m ² /g	2.31E+00	sites/nm ²	N ₂ (g)	8.00E-01	bar	pH	pH	Kd	mL/g

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 N₂ 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 CO₂. The CO₂ 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 CO₂ in the Access Database (Table 4). This table contains the fugacity of CO₂ in the atmosphere as a function of time. Thus, for experiments performed under atmospheric conditions, the CO₂ fugacity in the experiments is based on the atmospheric CO₂ fugacity at the date of publication (which is presumed to be close to the date of the actual experiments).

Table 4. CO₂ composition of the atmosphere as a function of time (Excerpt from Atmospheric CO₂ table).

atmospheric CO2				
ID	year	CO2	Units	calculated_bar
1	1900	295.67	ppm	2.96E-04
11	1910	299.38	ppm	2.99E-04
21	1920	304.25	ppm	3.04E-04
31	1930	306.62	ppm	3.07E-04
41	1940	311.36	ppm	3.11E-04
51	1950	312.82	ppm	3.13E-04
61	1960	316.62	ppm	3.17E-04
71	1970	324.78	ppm	3.25E-04
81	1980	338.70	ppm	3.39E-04
91	1990	354.07	ppm	3.54E-04
101	2000	369.12	ppm	3.69E-04

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 (Table 5). 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.

Table 5. The mineral_site_density table. Units are in sites/nm².

mineral_site_density			
ID	Mineral	Norm_Site_Density	Norm_Site_density_SD
1	quartz	2.31E+00	N/A
2	goethite	2.31E+00	N/A

The final table contained in the database is simply called Data and captures the values contained in each Dataset entry (Table 6). 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

Table 6. Excerpt from the Data table in the database.

Data						
ID	number	Set	X_val	X_SD	Y_val	Y_SD
2	1	azbn00_f1	3.55E+00	N/A	-6.02E+00	7.83E+00
3	2	azbn00_f1	4.08E+00	N/A	-4.96E+00	8.10E+00
4	3	azbn00_f1	4.63E+00	N/A	1.32E+00	7.38E+00
5	4	azbn00_f1	5.03E+00	N/A	1.26E+01	6.56E+00
6	5	azbn00_f1	5.49E+00	N/A	1.51E+01	6.34E+00
7	6	azbn00_f1	5.93E+00	N/A	4.17E+01	4.27E+00
8	7	azbn00_f1	6.37E+00	N/A	4.97E+01	3.76E+00
9	8	azbn00_f1	6.89E+00	N/A	4.62E+01	3.98E+00
10	9	azbn00_f1	7.23E+00	N/A	3.90E+01	4.52E+00
11	10	azbn00_f1	7.61E+00	N/A	1.90E+01	6.07E+00
12	11	azbn00_f1	8.15E+00	N/A	-1.96E-01	7.58E+00
13	12	azbn00_f1	9.00E+00	N/A	-7.09E+00	8.05E+00

3. Digitized Data Capture Process – U(VI) of Quartz

The first step in the capture of sorption data is to digitize all data included in the references provided by the RES³T database (Figure 1). These data are digitized using the DataThief software which allows the user to capture data reported in digital plots included in a reference. Most sorption data are reported in the literature as percent sorbed

vs. pH. However, some data are reported in terms of K_d (mL/g) , K_a (m²/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.

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. In this example, the uncertainty was assumed to be equivalent to the larger value of two possibilities: 5% of the aqueous concentration or 1% of the total sorbent concentration, regardless of the units used in the published figure.

The uncertainty in pH was not captured in our database though it can be included in future database development efforts.

4. 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 Generic Disposal System Assessment (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 sorption database must be fitted to a surface complexation/ion exchange model 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 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.

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 raw sorption data. 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 dataset is being updated as part of the Argillite and Crystalline International 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 databases become available, raw sorption data capture in the above database will be refit to provide a consistent representation of radionuclide aqueous speciation, solubility, and mineral-water interface reaction constants.

As an example of this approach, we performed a fitting of the raw sorption data for U(VI) sorption to quartz based on the above database. While this represents only a single mineral and a single radionuclide, the methodologies developed here can be easily expanded to capture the sorption behavior of all radionuclides and minerals that may be of interest to the nuclear waste repository performance assessment.

Figure 2 presents the overall fitting result for all data digitized from 11 references cited in the RES³T database for U(VI) sorption to quartz. In this case, the surface complexation model used in the fitting was the simplest non-electrostatic model. A reasonable fit to the data was achieved by adjusting the values of four surface reactions constants. Importantly, the 95th percentile confidence intervals for each constant were

approximately 0.5 log units which provides a direct estimate of the uncertainty in U(VI) retardation behavior that is result of our use of this mineral-water interface model. This uncertainty could be propagated into simplified K_d or other radionuclide retardation approaches that may be used in GDSA performance assessment models.

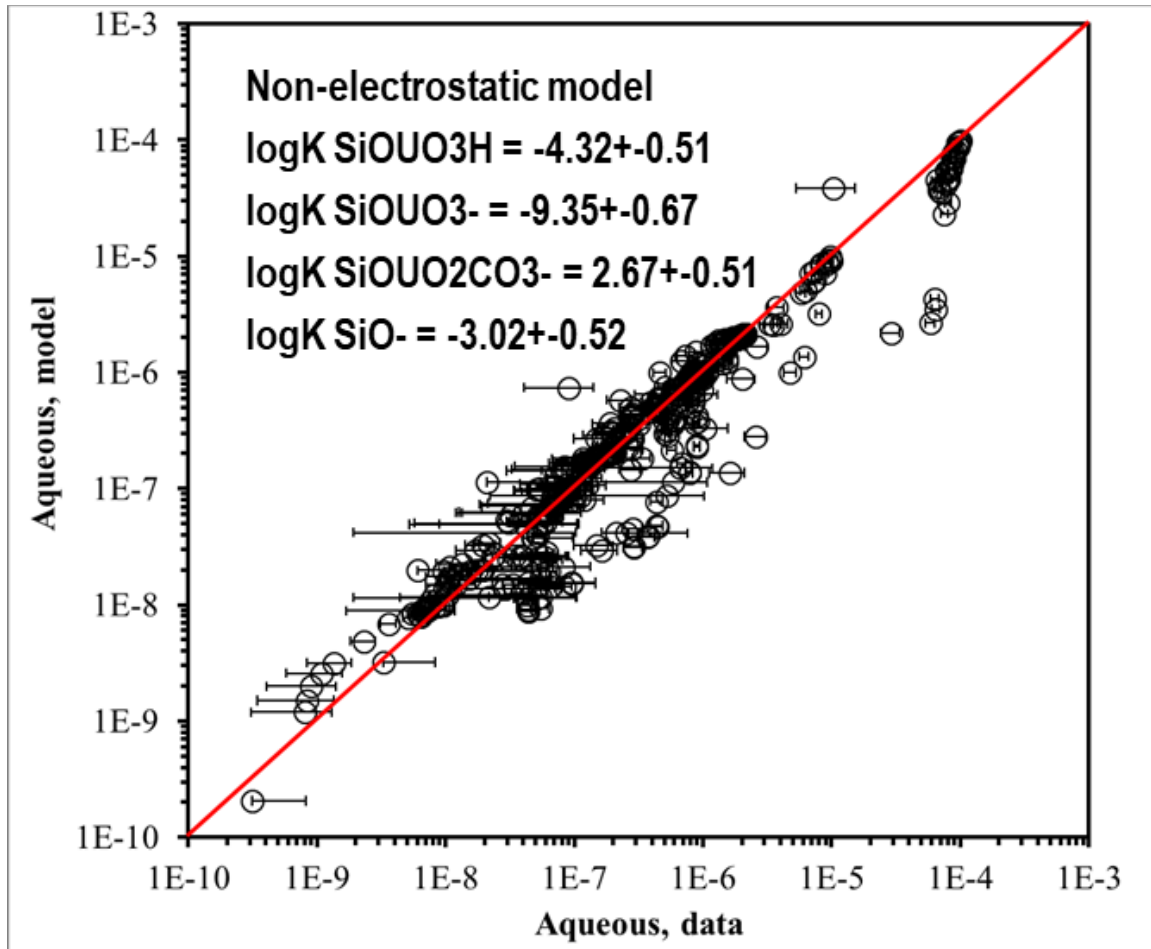


Figure 2. Simultaneous fit to all U(VI)-quartz sorption data references in the latest RES³T database using a non-electrostatic surface complexation model.

Figure 3 presents a different example of the fit to all data digitized sorption data from 11 references cited in the RES³T database for U(VI) sorption to quartz. In this case, the surface complexation model used in the fitting was the diffuse double layer model. A reasonable fit to the data was achieved by adjusting the values of three surface reactions constants (and notably the absence of a uranyl carbonate surface complex). Importantly, the 95th percentile confidence intervals for each constant were approximately 0.3 log units which suggests a significant reduction in uncertainty over the non-electrostatic model. This uncertainty could be propagated into simplified K_d or other radionuclide retardation approaches that may be used in GDSA performance assessment models. However, it suggests that the use of a diffuse double layer surface complexation model reduces the overall uncertainty in the fitted parameters and would lead to a reduced uncertainty in the performance assessment models of U(VI) migration.

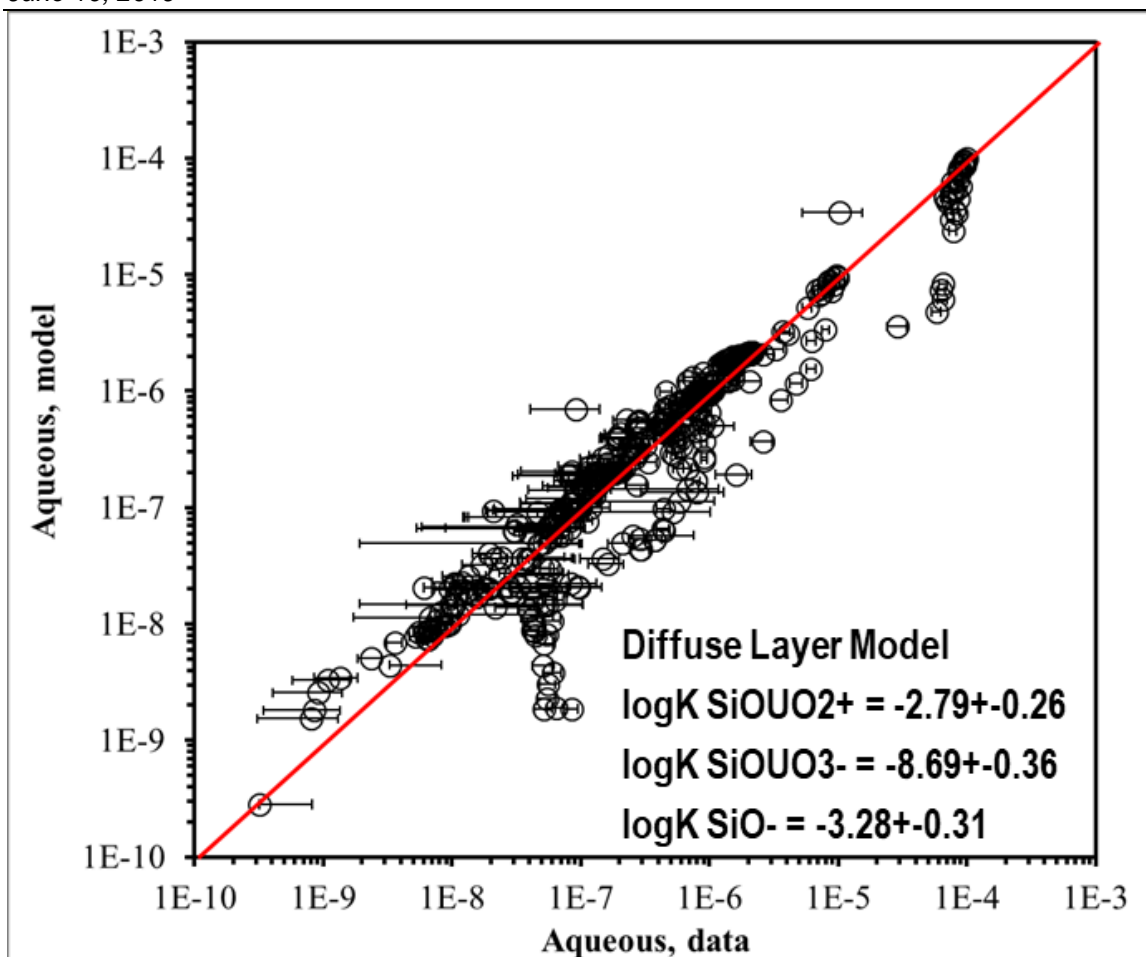


Figure 3. Simultaneous fit to all U(VI)-quartz sorption data references in the latest RES3T database using a diffuse double layer surface complexation model.

5. Planned FY19/20 Efforts

To date, the FY19 effort has focused on developing a framework for surface complexation/ion exchange database development. Effort is coordinated with international partners involved in similar database development efforts (e.g. HZRD RES³T). Here, we described the development of the sorption data capture database and its implementation for the case of U(VI) sorption to quartz. We will now focus on the primary sorption data capture for radionuclide (Cs, Sr, U, Np, and Pu) sorption to clay minerals (with particular focus on bentonite/montmorillonite). Subsequently, 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 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 are already in place. Subsequent efforts 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. 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 NE Generic Disposal System Analysis effort.

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