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M4SF-23LL010302062-NEA-TDB Management and International Sorption Model Collaboration

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Contents

1. Introduction

This progress report (Level 4 Milestone Number M4SF-23LL010302062) summarizes research conducted at Lawrence Livermore National Laboratory (LLNL) within the Crystalline International Collaborations Activity Number SF-23LL01030206. The activity is focused on our long-term commitment of engaging our partners in international nuclear waste repository research. This includes participation in the Nuclear Energy Agency Thermochemical Database (NEA-TDB) Project and development of methodologies for integrating US and international thermodynamic databases for use in SFWST Generic Disposal System Assessment (GDSA) efforts.

A continuing focus for FY23 efforts has been to support the US participation in the NEA-TDB effort (Mavrik Zavarin replaced Cindy Atkins-Duffin on the NEA-TDB Management Board (MB) and Executive Group (EG)) and developing mechanisms for integration of NEA-TDB thermochemical data with LLNL's SUPCRTNE thermodynamic database that supports the SFWST GDSA activities. This effort is coordinated with the Argillite work package SUPCRTNE database development efforts. The goal is to provide a downloadable database that will be hosted on a LLNL website which integrates NEA-TDB data into the LLNL SUPCRTNE database where appropriate.

As part of our international activities, we continue our effort to integrate international sorption databases into L-SCIE (Zavarin et al., 2022b). We presented opportunities to include sorption in the next phase of NEA-TDB efforts at the April 2023 EG meeting in Paris. FY23 efforts focused on ensuring interoperable database development across multiple international database development activities. The overall goal is to produce an open source database that can be shared and integrated with multiple nuclear waste programs internationally and harness modern data science workflows and algorithms to incorporate these new approaches into reactive transport and performance assessment models.

In collaboration with our Helmholtz Zentrum Dresden Rossendorf partners, we recently demonstrated the power of FAIR open source databases by fitting iron oxide (hydrous ferric oxide, goethite, hematite, and magnetite) protolysis constants to all available L-SCIE data. The results were submitted as a manuscript to J. Colloid Interface Science. This work will inform future metal sorption studies on a variety of iron oxides in order to discern the most appropriate acidity constants and surface complexation modeling constructs to account for pH-dependent mineral surface charge behavior. This work also explored automated surface complexation model development workflows in order to generate higher throughput model input files for a more facile incorporation into GDSA activities.

2. Nuclear Energy Agency Thermochemical Database Program

The Nuclear Energy Agency (NEA) Thermochemical Database Program (TDB) was conceived of and initiated with the goal to 1) make available a comprehensive, internally consistent, internationally recognized database of selected chemical elements; 2) meet the specialized modeling requirements for safety assessments of radioactive waste and; 3) prioritize the critical review of relevant data for inorganic compounds and complexes containing actinides. Data from other elements present in radioactive waste are also critically reviewed as well as compounds and complexes of the previously considered elements with selected organic ligands.

The objective of the Program is to produce a database that contains data for all the elements of interest in radioactive waste disposal systems; document why and how the data are selected; give recommendations based on original experimental data, rather than compilation and estimates; document the sources of experimental data; provide internally consistent thermodynamic parameters, and treat solids and aqueous species of the elements of interest for nuclear storage performance assessment calculations.

The qualification of existing data is conducted using documented Guidelines which include several components. A Technical Review is conducted by subject matter experts who critically review experimentally determined literature data; reanalyze the data as necessary; and select data for inclusion in the database. Upon completion of the Technical Review, a Peer Review is undertaken. A second, independent panel of reviewers ensure that the technical reviewers followed the review Guidelines. A Comment Resolution component ensures that the Technical Reviewers address the comments made by the Peer Reviewers. At this time, the volume is readied for final publication. Distribution of the Reviews is completed as open source material and in electronic form via the NEA TDB website.

Phases VI of the NEA-TDB program was officially started in February 2019 with all participating member parties having signed the Framework Agreement. The First Meeting of the Management Board (MB) and the Executive Group (EG) were held at the NEA in Paris February 19-20, 2019. Lena Evins (Sweden-SKB) was elected Chair of the MB and Stephane Brassinnes (ONDRAF/NIRAS- Belgium) Vice Chair. Canada and the Netherlands joined the Programme for this Phase. Elected to the Executive Group were Chair Marcus Altmaier (INE-Germany), Cindy Atkins-Duffin (DOE/LLNL-USA), Benoit Made (ANDRA-France), Pascal Reiller (CEA Saclay – France), and Kastriot Spahiu (SKB (retired)-Sweden. Som of the projects that were not completed in Phase V were brought forward to Phase 6.

The U.S. representative to the NEA TDB Management Board, Cynthia Atkins-Duffin, retired from LLNL in FY23. Mavrik Zavarin, also from LLNL, replaced her on the Management Board. The Management Board also elected Mavrik Zavarin to replace Cynthia Atkins-Duffin on the Executive Group. Mavrik Zavarin is also the point of contact to complete the Cements State of the Art Report. The Cement SOAR review will be completed in FY24.

A Management Board (MB) and Executive Group (EG) meetings were held in Paris on November 7 and 8, 2022. At this meeting Mavrik Zavarin was introduced as the new US representative to the Management Board. An EG meeting was held in Paris on April 3, 2023 where Mavrik Zavarin joined the EG. Follow-on online meetings were held by the EG on May 31, 2023 and by the MB on June 29, 2023 to discuss the path forward for a Phase 7 of the NEA-TDB project.

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

- **Iron (Part II) Volume** – Published online (NEA TDB website) in January, 2020.
- **2nd Update of the Actinides Volume** – Published online (NEA TDB website) in October, 2020
- **Ancillary Data Volume** – The volume is in the final stages of production, expected publication (NEA TDB website) in 2023. Carlos Jove-Colon (USA) served as one of the peer reviewers.
- **Molybdenum Data Volume** – This review continues to struggle with delivery of information from the team to the NEA. Several rescoping and personnel assignments were put into place. The EG has taken a more active management role in this project (Pascal Reiller is the EG liaison). To motivate the completion of this data volume, a hard deadline for the first internally reviewed draft of the volume was set for December 2023. At that point, some sections that are not complete may need to be omitted from the final volume. Final publication of the volume is anticipated in 2025.
- **Cements State of the Art Report** –The NEA Project Coordinator and the EG liaison (previously Cindy Atkins-Duffin, USA and new Mavrik Zavarin, USA) convened quarterly meetings with the review team. The SOAR is now ready for peer review and the external review team is being assembled. Thomas Matschei (Aachen University) and **Ed Matteo (SNL)** have been confirmed as reviewers. An additional reviewer is being identified. Final publication of the volume is anticipated in Q3 of 2024.
- **High Ionic Strength Solutions State of the Art Report** – Progress continues to be slow on this project. The next deliverable, a complete draft delivered to NEA, is due in September 2023. As in the Mo report, the EG has decided to make this a hard deadline. If some sections are not ready in September, 2023, they may be omitted from the SOAR rather than extending the deadline. The current planned review by the NEA TDB is planned for the fourth quarter of 2023 and external peer review to start in Q3 of 2024.
- **Organics Update** – The initiation report has been completed and the Management Board accepted the report as presented, paid, and closed out the reviewer contracts. The Management Board has prioritized the completion of the existing volumes higher than the start of new activities. While recognizing the importance of this Update, the decision was made to defer the start of this effort to a possible Phase 7 of the TDB Program.
- **Lanthanides Volume** – This activity is ongoing. Work on this volume continues with anticipated draft submission to NEA TDB by Q4 of 2024 and external peer review in 2025.
- **High Temperature State of the Art Report** – The initiation report has been completed and accepted. The Management Board has prioritized the completion of the existing volumes higher than the start of new activities. While recognizing the importance of this Update, the decision was made to defer the start of this effort to a possible Phase 7 of the TDB Program.
- **TDB course** –The 7th edition of the TDB course is being planned as an in-person event to be held in conjunction with Migration 2023, Nantes, France.

- **TDB Electronic Database** – Currently only maintenance activities such as the populations of the eTDB with the new selected values from the Ancillary and Molybdenum volumes are being undertaken. All available NEA staff resources have been focused on the management, editing, and publication of the review volumes. Thus, updates to the electronic database may not be made until the start of a proposed Phase 7.

Based on the pace of Phase 6 deliverables and the expressed interest by the NEA-TDB partners not to enter into a Phase 7 until all ongoing activities reach the peer review stage, the MB decided to extend Phase 6 into a second no-cost 1 year extension. This allows Phase 6 to be extended to Q1 of 2025. At that point, we anticipate that the Ancillary Data volume will be published and the Molybdenum Data volume, Cements SOAR, and High Ionic Strength SOAR will be in the peer review stage or completed. The Lanthanides Data volume will also be nearing the peer review stage. This will also allow for sufficient time to develop a plan forward for Phase 7 which, if approved, would begin at the end of Phase 6. The tentative schedule for preparing a Phase 7 agreement is as follows:

- Draft agreement: end of 2023
- Ready for signature: mid 2024
- Start of TDB-7: Q1 2025

Discussion of Phase 7 priority activities has already begun. The MB members were sent a TDB 7 Questionnaire entitled “Towards a future TDB Phase”. The value of the NEA TDB was acknowledged by most MB members and the value of the NEA-TBD activity was predominantly associated with the production of Data Volumes. The MB was in general agreement that Phase 7 should prioritize the Update to Organics Data volume and the High Temperatures and Pressures SOAR which already have approved initiation reports from Phase 6. Some significant interest in developing a Data Volume on iodine thermodynamics was noted. Discussion of Phase 7 priority research areas will continue as the draft agreement is put in place and identification of participating countries is established. Depending on the level of participation and the interests of the participating agencies, the scope and effort associated with Phase 7 activities will be defined.

3. International Collaboration on L-SCIE Database Development

García, D., Dagnelie, R.V.H., Zavarin, M., 2023. Editorial: Sorption Processes in Nuclear Waste Management: Data Knowledge Management and New Methodologies for Data Acquisition/Prediction. Frontiers in Nuclear Engineering.

In late FY22, we collaborated with Dr. Garcia (Amphos21) to develop a special research topic in the Frontiers in Nuclear Engineering journal entitled “Sorption processes in nuclear waste management: Data knowledge management and new methodologies for data acquisition/prediction”. In FY23, the full research topic was published and an editorial was accepted for publication as part of this special topic (García et al., 2023). In addition to this activity, we are pursuing access to a number of new data streams to support the continued development of the L-SCIE community database and we will continue to pursue international collaborations that promote interoperable design of databases and the principles of Open Science and FAIR data (Wilkinson et al., 2016).

The following is a shortened version of the editorial that was included in the special research topic "Sorption processes in nuclear waste management: Data knowledge management and new methodologies for data acquisition/prediction"

A fundamental approach to Nuclear Waste Repository research involves the collection of experimental data in a laboratory setting, development of empirical and/or mechanistic numerical models representing those observations, and application of these models into reactive transport and performance assessment models as predictive tools for informing society of impacts and risks associated with nuclear waste repository scenarios (Stevens et al., 2020). The assimilation and interpretation of experimental data must take advantage of both new data and the rich historical data available in the literature and apply novel modeling approaches to improve predictive tools, particularly from the standpoint of uncertainty quantification, for nuclear waste repository performance assessment (Zavarin et al., 2022a).

Experimental data collected in a laboratory setting is fundamentally different from large formatted sensor data that are much more amenable to "big data" approaches. New data science approaches to interrogate experimental laboratory data have been limited, in large part, by the lack of common standards and approaches to archiving these data types (i.e. findable, accessible, interoperable, reusable "FAIR" data) (Wilkinson et al., 2016). As these new approaches are applied to sorption and other data, they will fundamentally change how predictive tools quantify impacts and risks associated with siting nuclear waste repositories.

In the series of articles published as a special research topic in the Frontiers in Nuclear Engineering, authors apply novel modeling approaches to experimental data categorized as sorption data. Traditionally, these data inform empirical (e.g. Kd) or mechanistic (e.g. surface complexation) models that are subsequently used in reactive transport models at various scales as predictive tools for assessing transport behavior. These same data and/or models can also inform the development of Reduced Order Models (Garibay-Rodriguez et al., 2022; Li and Zarzycki, 2022) that can be applied more efficiently to complex large scale models (e.g. performance assessment models).

Romanchuk et al. (2022) focus on the question of self-consistent Surface Complexation Model (SCM) database development by presenting a data fitting workflow that combines new and literature-derived sorption data for three radionuclides in specific oxidation states (U(VI), Eu(III), Np(V)) and the iron(III) oxide mineral goethite fit using the PHREEQC (Parkhurst, D.L. and Appelo, C.A.J., 2013) geochemical solver linked to the MOUSE (Linge et al., 2020) optimization software with automation that relies on the Python programming language. They show that expansion of their approach to a larger set of elements (Cd(II) and Zn(II)) is relatively straightforward and suggests further expansion by adopting Linear Free Energy Relationships (LFER) across an even greater number of sorbing elements.

The application of SCMs to predict organic compounds' behavior at solid-water interfaces is particularly complicated by the large number of organic compounds present in nuclear waste repositories and the associated near- and far-fields. Organic compounds can sorb to mineral surfaces but can also form aqueous and ternary complexes with radionuclides. As a result, developing comprehensive modeling approaches for organic compounds' reactive transport remain elusive. Szabo et al. (2022) explore this topic by examining the uptake of multiple organic compounds (degradation products of polyacrylonitrile-based polymers) to cements. They use relatively simple Langmuir models to explore the relative affinity of these organic compounds and review affinity patterns of a large number of organic compounds reported in the literature. The examination of sorption behavior across a wide number of organic compounds reveals relationships between functional group type, functional group density, and surface affinity.

Hinchliff et al. (2022) examine the role of cellulosic organic compounds on Sr sorption to hydrated cements. Again, new and literature data are combined to develop a comprehensive understanding of Sr diffusivity and sorption to hydrated cements. The analysis reveals surprisingly enhanced retardation of Sr and suggests that cellulose organic degradation products impact Sr retention though the exact mechanisms have yet to be revealed. Nevertheless, the results point to the need to expand surface complexation and surrogate modeling approaches beyond simple binary radionuclide sorption models. Importantly, the increased complexity brings increased importance to the development of large FAIR sorption databases (Wilkinson et al., 2016) that capture the multidimensional sorption conditions. Development of software and workflows that can readily take advantage of the rich data sources available in the literature will greatly benefit the nuclear waste repository research community in the coming years.

An apparent roadblock in SCM database development is the apparent data paucity as it relates to development of well constrained geochemical models. However, Zavarin et al. (2022) determined that the cumulative number of peer reviewed publications referencing the topic of sorption and adsorption has already reached ~1,000,000. Thus, as several authors discuss, this apparent lack of data is, in large part, due to a lack of FAIR data rather than lack of data per se. This lack of FAIR data has severely limited the development of self-consistent SCM databases. A recent data assimilation effort at Lawrence Livermore National Laboratory and collaborators at the Helmholtz Zentrum Dresden Rossendorf, has been developing a data digitization pipeline (Zavarin et al., 2022a). To date, the manual digitization of data has yielded a LLNL SCIE database that includes 211 references and a total of 22,732 individual digitized data and associated metadata. Importantly, this approach to data mining is labor intensive and cannot be expanded beyond a set of targeted data (e.g. reactions specific to the nuclear waste performance assessment needs). Adoption of new approaches to data assimilation are clearly needed.

New modeling approaches that take advantage of FAIR database development efforts are also needed. Garibay-Rodriguez et al. (2022) describe a computational framework for radionuclide migration assessment in clay rocks that is based on OpenGeoSys6 which is linked to a number of geochemical solvers (PHREEQC, GEMS, etc.) and can be applied to both traditional surface complexation/ion exchange models as well as surrogate models. For portability, the modeling framework is built around the JupyterLab Python framework that guarantees that all the source code and its dependencies can be executed efficiently and reliably, independent of any computing environment. Importantly, the surrogate models (aka look-up tables) are explicitly tied to the mechanistic surface complexation/ion exchange models. Test cases suggest that surrogate models can yield significant computational speed-up while maintaining a similar level of precision in model output. Garibay-Rodriguez et al. (2022) argue that open source software approaches are key to continuing software development and longterm improvements in nuclear waste performance assessment models.

Li and Zarzycki (2022) describe a computational pipeline to generate synthetic SCM data and discuss approaches to transform this dataset into AI-learnable input for use in surrogate models. In their approach, available surface complexation model databases are used to produce high density sorption data across a very wide range of conditions. The generated synthetic datasets can more readily take advantage of AI algorithms that can be used in surrogate model development. The approach is tested for determination of the electrostatic properties of a prototypical oxide/electrolyte interface using the triple-layer surface complexation modeling construct. The authors provide a theoretical framework for developing surrogate models using AI and based on developing synthetic sorption data from traditional surface complexation databases.

Nuclear Waste Repository reactive transport and performance assessment modeling teams have a number of opportunities to apply modern processes, workflows, and machine learning in predictive tools for informing society of impacts and risks associated with nuclear waste repository scenarios. Both the assimilation and interpretation of experimental data can harness ML to improve predictive tools, particularly from the standpoint of uncertainty quantification. While a number of challenges are still present (e.g. automation of various component of the data assimilation and interpretation in the data stream), these approaches will provide a robust and nimble framework for evaluating nuclear waste repository performance that is adaptable to the unique timescales that repository performance, oversight, and monitoring will require.

4. Workflow development for community potentiometric titration data modeling and database development

Han, S.-C., Chang, E., Zechel, S., Bok, F., Zavarin, M., 2023. Application of community data to surface complexation modeling framework development: Iron oxide protolysis. Journal of Colloid and Interface Science 648, 1015-1024. doi.org/https://doi.org/10.1016/j.jcis.2023.06.054.

The information presented below is a summary from a manuscript published in June 2023 in the Journal of Colloid and Interface Science (Han et al., 2023). This publication describes the workflow developed, in conjunction with our L-SCIE database, to simulate community potentiometric titration data. The development of a consistent set of surface protonation reactions is an important first step in the development of self-consistent surface complexation databases. In this manuscript, we develop surface protonation constants for a series of iron oxide phases.

4.1 Introduction

Since the surface charge of the mineral affects the sorption affinity between adsorbate and adsorbent, estimating the protolysis of mineral surface is crucial for surface complexation models (SCM). For this reason, surface protolysis constants of minerals, which describe degree of the protonation and deprotonation of surface functional groups, are essential input parameter of SCMs and the selection of proper values for the constants is important in terms of reliable modeling. In various studies, however, different protolysis constants have been utilized even when the type of SCM and mineral used in their studies are identical (see Table 1). This fact leads to ambiguity in the selection of 'representative' protolysis constants and uncertainty in the further development of self-consistent surface complexation databases. In other words, there now exists an impasse in the integration of the experimental data scattered in different studies into comprehensive SCM frameworks that reconcile the full community-wide data.

In light of this challenge, our task aimed at developing potentiometric titration modeling workflow for modeling digitized community potentiometric titration data. The workflow focuses on fitting compiled community data for each individual iron oxide mineral (i.e., ferrihydrite, goethite, hematite, and magnetite) to produce representative protolysis constants that account for all potentiometric titration data collected from multiple literature sources.

Table 1. Diffuse double layer surface complexation model protolysis constants and site densities for ferrihydrite reported in the literature. Data from RES³T database (Brendler et al., 2003; Dresden-Rossendorf, 2013).

	1st protolysis constant (pK_{a1})	2nd protolysis constant (pK_{a2})	Site density (sites·nm^{-2})	Reference
1	6.09	7.38	2.2583	(Nowack et al., 1996)
2	6.51	9.13	0.0203	(Arnold et al., 1998)
3	7	9.2	7.0903	(Nomaan et al., 2021)
4	7.01	7.86	0.7300	(Veselská et al., 2016)
5	7.29	8.93	2.2553	(Eibl et al., 2019)
6	7.5	10.2	9.9966	(Landry et al., 2009)

4.2 Development of Surface Complexation Modeling Framework

As part of this effort, a community data driven surface complexation modeling framework has been developed. The framework begins with a database of community titration/sorption data, i.e., L-SCIE (Zavarin et al., 2022a), followed by a potentiometric titration modeling workflow, which is then followed by surface complexation modeling workflow (Figure 1). The L-SCIE database provides input data for both potentiometric titration modeling workflow (L-ASTM, LLNL Automated Surface Titration Model) and surface complexation modeling workflow (L-ASCM, LLNL Automated Surface Complexation Model). The protolysis constants produced by L-ASTM are used as input parameters for the surface complexation model (L-ASCM).

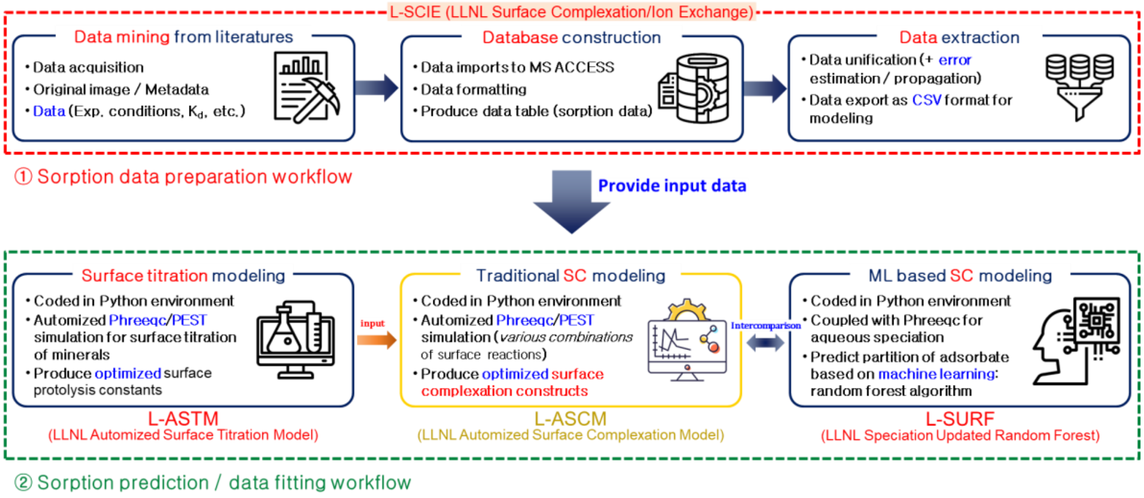

Figure 1. Workflow of community data driven surface complexation modeling framework

Data processing and workflow associated with L-ASTM was written in Python and the code was integrated with PHREEQC (Parkhurst, David L and Appelo, C.A.J., 2013) and PEST (Doherty, 2018) for data fitting. The details of the workflow of L-ASTM are shown in Figure 2. First, the code imports potentiometric titration data extracted from the L-SCIE database and categorizes the data by dataset. For example, single reference may include several experimental datasets conducted under various experimental conditions, e.g., ionic strength. For each of these datasets, the L-ASTM code generates the relevant PHREEQC/PEST input files and runs a separate PHREEQC/PEST data fitting. Once the fitting is performed for each dataset, two protolysis constants (pK_{a1} and pK_{a2}) and associated 95% confidence intervals ($\pm 2\sigma$) are generated. Finally, weighted arithmetic mean pK_{a1} and pK_{a2} values of all datasets are calculated to produce ‘representative’ average protolysis constants by using equations (1) – (3).

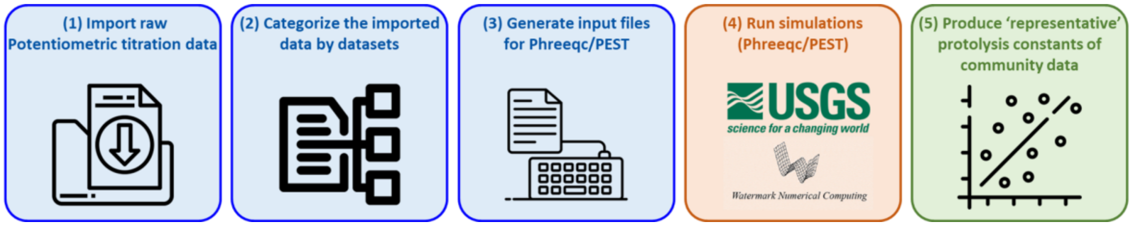

Figure 2. Surface complexation modeling workflow (L-ASTM code) for potentiometric titration data.

Weighted average (x_{wav}) is the best estimation for the true x value when there are N measurements of x with corresponding uncertainties (i.e., $x_1 \pm \sigma_1, \ldots, x_N \pm \sigma_N$), and can be calculated by the following Eqs. (1) and (2) (Heckert and Filliben, 2003; Taylor, 1997):

$$x_{wav} = \frac{\sum w_i x_i}{\sum w_i} \tag{1}$$

$$w_i = \frac{1}{\sigma_i^2} \tag{2}$$

where x_i denotes i^{th} measurement of x and w_i represents the corresponding weight which is the reciprocal square of uncertainty of i^{th} measurement (σ_i). Finally, uncertainty in the weighted average can be calculated by Eq. (3) (Heckert and Filliben, 2003):

$$\sigma_{wav} = \sqrt{\frac{\sum w_i (x_i - x_{wav})^2}{\frac{(N' - 1)\sum w_i}{N'}}} \tag{3}$$

where N' denotes the number of non-zero weights. In our case, total number of measurements, N, is equal to total number of datasets, x_i corresponds to pK_{a1} or pK_{a2} from the i^{th} dataset and σ_i is the uncertainty of pK_{a1} or pK_{a2} from the i^{th} dataset.

4.3 Case Study of Potentiometric Titration Modeling for Iron Oxides

The FY23 efforts were focused on potentiometric titration modeling for iron oxides to demonstrate a method to reconcile community data-wide potentiometric titration data using FAIR data principles to produce mineral protolysis constants. In this FY23 task, potentiometric titration data for four iron oxide minerals (i.e., ferrihydrite, goethite, hematite, and magnetite) were evaluated. It should be noted that the data used in this study (Table 2) was extracted from the L-SCIE database and may not reflect all available data in the literature. Nevertheless, since our SCM framework is based on the FAIR data principle, one can easily refit the protolysis constants as new data become available.

Table 2. Description of iron oxide potentiometric titration data used in this study.[a]

Iron oxide minerals	Data count	No. of datasets	No. of references	pH range
Ferrihydrite	1,119	40	12	2.7 – 11.7
Goethite	1,982	79	23	3.0 – 11.0
Hematite	1,702	61	16	2.7 – 11.1
Magnetite	301	14	8	2.3 – 12.0

[a] Potentiometric titration data included in the L-SCIE database and evaluated here include: 1) ferrihydrite: (Antelo et al., 2010; DAVIS III, 1978; Dyer, 2003; Ghoneimy et al., 1997; Hofmann et al., 2005; Hsi and Langmuir, 1985; Kanungo and Mahapatra, 1989; Moon and Peacock, 2013; Nagata and Fukushi, 2010; Nagata et al., 2009; Pivovarov, 2009; Trivedi and Axe, 2001), 2) goethite: (Balistrieri and Murray, 1981; BARROW and COX, 1992; Bowden et al., 1980; Fujita et al., 1994; Gunnarsson et al., 2002; Hayes et al., 1991; Hoins et al., 1993; Hsi and Langmuir, 1985; Lackovic et al., 2003; Lumsdon and Evans, 1994; Missana et al., 2003b; Müller and Sigg, 1992; Naveau et al., 2005; Peacock and Sherman, 2004; Rahnemaie et al., 2006; Robertson and Leckie, 1997, 1998; Rundberg et al., 1994; Sigg, 1980; Trivedi and Axe, 2001; van Geen et al., 1994; Villalobos and Leckie, 2000; Yates, 1975), 3) hematite: (Breeuwsma and Lyklema, 1971; Christl and Kretzschmar, 1999; Čolić et al., 1991; Estes et al., 2013; Gibb and Koopal, 1990; Gunnarsson et al., 2001; Hesleitner et al., 1987; Hesleitner et al., 1991; Hwang and Lenhart, 2008; Kohler et al., 1999; Marmier and Fromage, 1999; Murphy et al., 1999; Peacock and Sherman, 2004; Pivovarov, 1998; Romanchuk and Kalmykov, 2014; Yates, 1975), and 4) magnetite: (Blesa et al., 1984; Catalette et al., 1998; Fujita et al., 1994; Marmier et al., 1999; Mayant et al., 2008; Missana et al., 2003a; Regazzoni et al., 1983; Tamura et al., 1983).

One of the most significant improvement in the workflow compared to FY22 is that now the current workflow utilizes the surface site densities (SSDs) of iron oxides obtained using a crystallographic approach (Eibl et al., 2019; Neumann et al., 2021). The crystallographically-derived SSDs for singly coordinated groups on ferrihydrite, goethite, hematite, and magnetite are 6.53, 6.60, 5.83, and 4.56 sites·nm^{-2}, respectively (Table 3). These values were used in the estimation of protolysis constants. However, natural minerals likely include irregularities that may cause variation in SSD values. For this reason, sensitivity analysis of SSD was also conducted to examine the effect of SSD on pK_a estimation. The SSDs applied in the sensitivity analysis ranged from 3 to 10 sites·nm^{-2} (i.e., 3, 5, 7, and 10 sites·nm^{-2}). An SSD of 2.31 sites·nm^{-2}, suggested by Dzombak and Morel (1990) for hydrous ferric hydroxide, has previously been recommended for use in estimating binding constants on many types of minerals (Davis and Kent, 1990). By considering the fact that the value has been conventionally used in a number of surface complexation modeling efforts, SSD of 2.31 sites·nm^{-2} was also included in our sensitivity analysis.

Table 3. Surface site densities of ferrihydrite, goethite, hematite, and magnetite.

Iron oxide mineral	Crystallographically-Derived SSD (sites·nm^{-2})	Iron oxide mineral	Crystallographically-Derived SSD (sites·nm^{-2})
Ferrihydrite	6.53	Hematite	5.83
Goethite	6.60	Magnetite	4.56

4.4 Diffuse Double Layer Model Protolysis Constants of Ferrihydrite, Goethite, Hematite, and Magnetite

The iron oxide pK$_a$ values were estimated by fitting the community potentiometric titration data. The diffuse double layer model (DDLM) was initially adopted to describe the electrical double layer, and SSDs obtained from the crystallographic approach were used (see Table 3). The calculated iron oxide pK$_a$ values are summarized in Table 4 and Figure 3 shows a modeling example: ferrihydrite potentiometric titration data, model fits using weighted mean pK$_a$ values, and fits to individual datasets. As shown in Figure 3, protolysis constants produced by the community data-driven workflow can reproduce most of the experimental data with reasonable accuracy. In the case of some datasets, however, the fitted model did not reproduce the experimental data. The poor fit to the data is, in most cases, indicative of erroneous reporting of potentiometric titration data (e.g., afpmagl10 datasets by Antelo et al. (2010)).

Table 4. Diffuse double layer model protolysis constants for iron oxides as a function of surface site density.

Iron oxides	SSD (sites·nm^{-2})	pK_{a1}††	pK_{a2}††	R value
Ferrihydrite	2.31	6.7 ± 0.4	8.7 ± 0.6	0.916
	3	6.5 ± 0.4	8.7 ± 0.6	0.916
	5	6.2 ± 0.4	8.9 ± 0.6	0.915
	6.53†	**6.1 ± 0.4**	**9.0 ± 0.6**	**0.915**
	7	6.1 ± 0.4	9.0 ± 0.6	0.915
	10	5.9 ± 0.4	9.2 ± 0.6	0.916
Goethite	2.31	6.9 ± 0.8	9.1 ± 0.7	0.880
	3	6.7 ± 0.7	9.2 ± 0.7	0.877
	5	6.4 ± 0.7	9.4 ± 0.7	0.868
	6.60†	**6.2 ± 0.7**	**9.5 ± 0.6**	**0.867**
	7	6.2 ± 0.7	9.6 ± 0.6	0.867
	10	6.0 ± 0.7	9.7 ± 0.6	0.868
Hematite	2.31	7.6 ± 0.7	9.2 ± 0.82	0.875
	3	7.3 ± 0.7	9.3 ± 0.86	0.877
	5	6.9 ± 0.8	9.4 ± 0.79	0.874
	5.83†	**6.8 ± 0.8**	**9.4 ± 0.79**	**0.872**
	7	6.7 ± 0.8	9.5 ± 0.79	0.873
	10	6.5 ± 0.8	9.6 ± 0.77	0.872
Magnetite	2.31	6.2 ± 0.2	7.3 ± 0.2	0.922
	3	6.1 ± 0.2	7.5 ± 0.4	0.923
	4.56†	**5.9 ± 0.2**	**7.4 ± 0.6**	**0.935**
	5	5.8 ± 0.2	7.5 ± 0.6	0.934
	7	5.7 ± 0.3	7.6 ± 0.7	0.940
	10	5.5 ± 0.3	7.6 ± 0.7	0.944

†Crystallographically-derived surface site density (used as reference case).

††Reported uncertainties are mean weighted $\pm\sigma$ of the fitted pK_a values (Eq. 3).

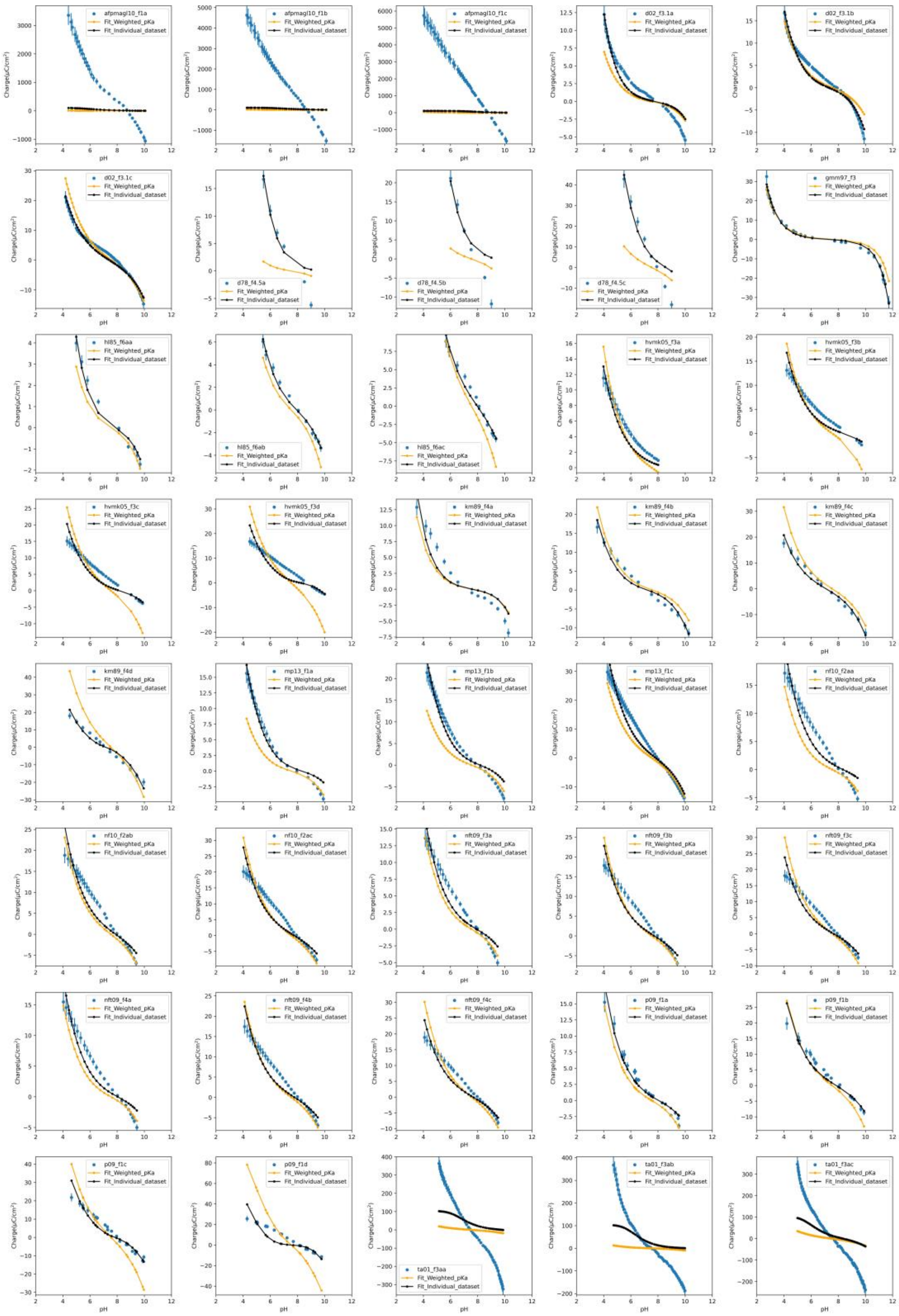

Figure 3. Potentiometric titration data of ferrihydrite (blue), modeling data using weighted mean DDLM pK_a values (orange), and DDLM fits obtained for individual datasets (black). All models used the crystallographically-derived surface site density (Table 4). Error bars represent estimated data uncertainties at one standard deviation.

4.5 Effect of Type of Electrical Double Layer

In order to build a self-consistent SCM reaction database, protolysis constants should be estimated using a consistent SCM type (e.g., non-electrostatic model (NEM), DDLM, or constant capacitance model (CCM)) which, in turn, is identical to that used for downstream sorption modeling. In this task, we examined how the SCM type affects the protolysis constants and evaluated how well each SCM type reproduces the potentiometric titration data. The modeling was conducted for four iron oxides (i.e., ferrihydrite, goethite, hematite, and magnetite) and three types of SCM: NEM, DDLM, and CCM (Table 5). As summarized in Table 5, estimated pK_a values were different according to the type of SCM. For example, pK_{a1} of the NEM is lower than that of the DDLM, while pK_{a2} of the NEM is higher than that of the DDLM.

Table 5. Estimated protolysis constants of iron oxide minerals with different surface complexation models using crystallographically estimated surface site densities (Table 3).

Iron oxides	SCM type	pK_{a1}	pK_{a2}	$(pK_{a1} + pK_{a2})/2$	Capacitance
Ferrihydrite	**NEM**	**3.51 ± 0.65**	**11.03 ± 0.57**	**7.27 ± 0.43**	**-**
	DDLM	**6.09 ± 0.40**	**9.00 ± 0.56**	**7.55 ± 0.34**	**-**
	CCM	**6.41 ± 0.38**	**9.78 ± 0.39**	**8.10 ± 0.27**	**1.11 ± 0.52**
Goethite	**NEM**	**5.06 ± 1.08**	**9.96 ± 1.10**	**7.51 ± 0.77**	**-**
	DDLM	**6.23 ± 0.69**	**9.54 ± 0.63**	**7.89 ± 0.47**	**-**
	CCM	**6.93 ± 0.37**	**10.90 ± 0.33**	**8.92 ± 0.25**	**0.90 ± 0.18**
Hematite	**NEM**	**3.99 ± 0.61**	**10.83 ± 0.61**	**7.41 ± 0.43**	**-**
	DDLM	**6.84 ± 0.75**	**9.42 ± 0.79**	**8.13 ± 0.54**	**-**
	CCM	**7.25 ± 0.39**	**10.94 ± 0.44**	**9.10 ± 0.29**	**1.07 ± 0.22**
Magnetite	**NEM**	**4.17 ± 0.70**	**8.73 ± 1.46**	**6.45 ± 0.81**	**-**
	DDLM	**5.85 ± 0.22**	**7.44 ± 0.60**	**6.65 ± 0.32**	**-**
	CCM	**6.06 ± 0.37**	**6.07 ± 0.36**	**6.07 ± 0.26**	**2.08 ± 1.46**

The type of SCM also significantly affects the quality of fit. Figure 4 illustrates the fit quality for each SCM type and mineral phase in the form of normalized histograms as a percent difference between the experimental and modeled surface charge. The interquartile ranges (IQRs) of weighted residual data obtained from the models using each SCM type are also reported. The histograms exclude outliers where the data points fall below Q1 (first quartile of the data) – 1.5×IQR or above Q3 (third quartile of the data) + 1.5×IQR. As shown in Figure 4, the IQR of the NEM is always greater than the IQR of the DDLM and CCM. This implies that the fit quality of DDLM and CCM is overall better than that of the NEM.

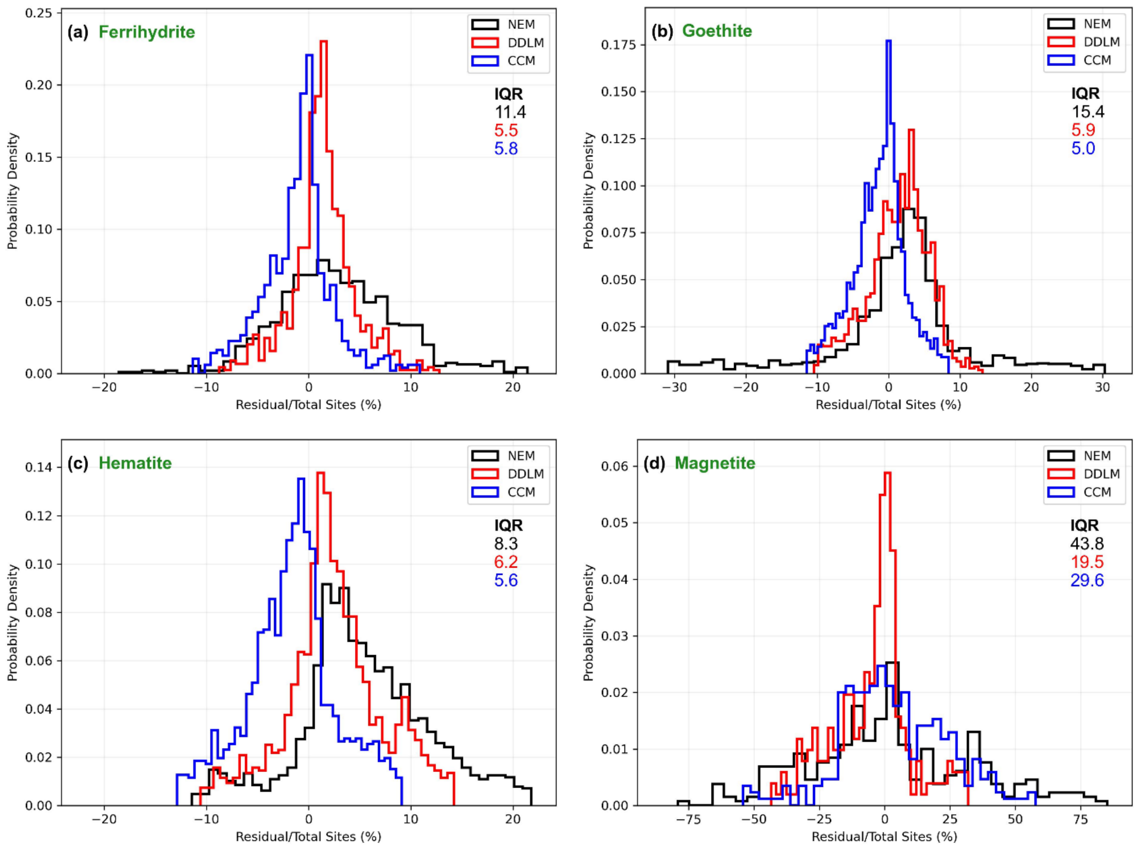

Figure 4. Normalized histograms as a percent difference between the experimental and modeled surface charge for NEM, DDLM, and CCM models of (a) ferrihydrite, (b) goethite, (c) hematite, and (d) magnetite. The bin size of each histogram is equivalent to one tenth of IQR.

4.6 Effect of Surface Site Density on Protolysis Constants

As summarized in Table 4 and Figure 5, the value chosen for SSD significantly affects the modeled pK_a values for iron oxides. The most remarkable observation was that pK_{a1} decreased with increasing SSD, while pK_{a2} increased with increasing SSD. This systematic tendency was consistent regardless of the type of iron oxide mineral and is in good agreement with other studies (Christl and Kretzschmar, 1999; Hayes et al., 1991; Hwang and Lenhart, 2008).

The quality of DDLM fit, i.e., R value which is equivalent to a weighted Pearson correlation coefficient and calculated excluding outliers, derived based on each SSD value is given in Table 4. As evident in Table 4, no clear correlation was found between R value and SSD, and no obvious maximum was obtained for R value. The observed sensitivity of SSD to quality of data fitting is in good agreement with other studies by Christl and Kretzschmar (1999) and Hwang and Lenhart (2008). Since the data fitting quality is insensitive to SSD while modeled pK_a values are not, fitting the potentiometric titration data by optimizing arbitrary SSD might impede the accuracy in determining pKa values. In similar, Christl and Kretzschmar (1999) noted that fitting the surface titration data would not be recommended for determining SSD.

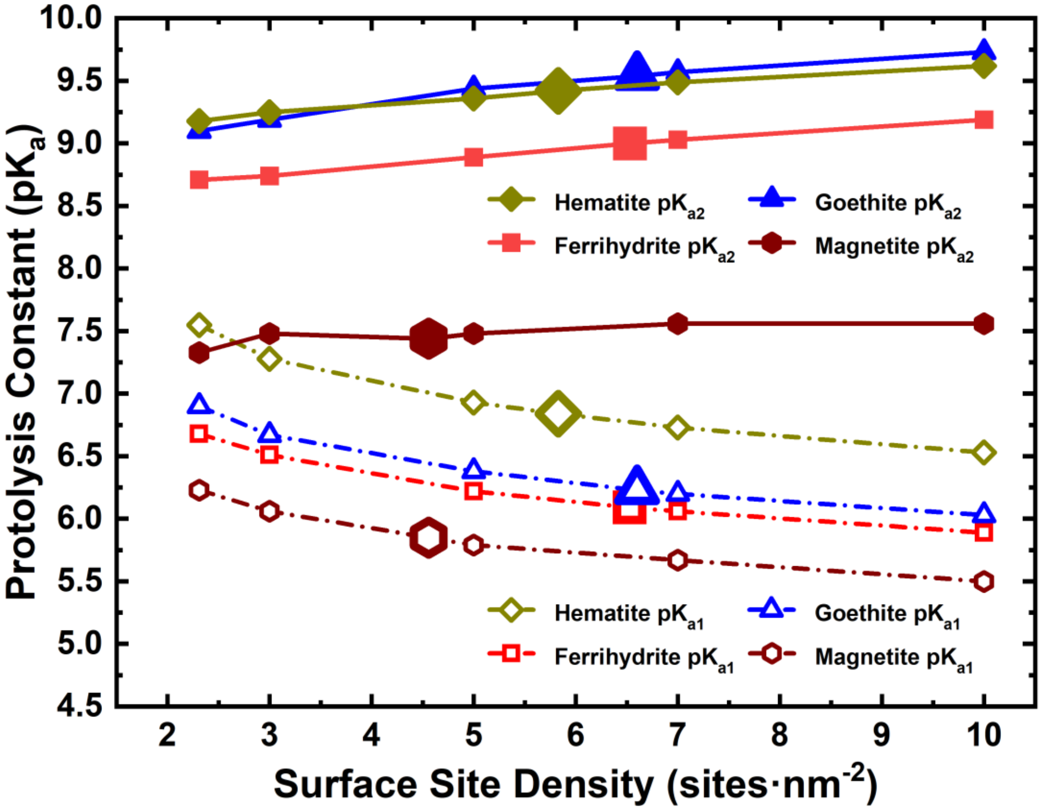

Figure 5. Diffuse double layer model protolysis constants for iron oxides as a function of surface site density. Large symbols represent the protolysis constants obtained with crystallographically-derived surface site density.

4.7 Concluding Remarks

In the FY23 study, the community data-based surface complexation modeling framework was successfully developed and was utilized for iron oxide potentiometric titration systems to produce ‘representative’ protolysis constants that account for all potentiometric titration data collected from multiple literature sources. In addition, the influence of SCM type and effect of SSD on potentiometric titration modeling were examined.

Simulation results showed that the protolysis constants produced by the potentiometric titration data workflow can reproduce most of the experimental data with reasonable accuracy. In addition, the present study shows that the application of community data-driven modeling can additionally identify erroneous datapoints. This feature can be investigated to increase the robustness and reliability of databases and/or surface complexation models.

Importantly, our current modeling results emphasize the need for consistency in SSD, pK_a values, and SCM type in any self-consistent SCM database. The framework developed through this task provides an approach to developing such a self-consistent database using the principles of FAIR community data. Furthermore, since this framework is readily expandable (as community data increase) and extensible (as the number of minerals increase), the framework can be easily applied to other minerals of interest.

5. Planned FY24 Efforts

A continuing focus for FY24 efforts will be to support the US participation in the NEA-TDB effort. The focus of FY24 activities will be the development of an agreement for a Phase 7 activity that will start in Q1 of 2025.

In FY24, we will use our position on the NEA-TDB MB and EG to facilitate the integration of NEA-TDB thermochemical data with LLNL's SUPCRTNE thermodynamic database that supports the SFWST GDSA activities. This effort is coordinated with the Argillite work package SUPCRTNE database development efforts. The goal is to provide a downloadable database that will be hosted on LLNL's thermodynamics website which incorporates NEA-TDB data into the LLNL database where appropriate.

Finally, we will continue our effort to integrate international sorption databases into the L-SCIE database. FY24 efforts will focus on incorporating the PSI clay dataset into L-SCIE, as described in the Argillite international activity milestone report. We will also actively pursue opportunities to engage in the EURAD program that will be initiated in FY24 by our European collaborators at the Karlsruhe Institute of Technology (KIT), Germany.

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