Used Fuel Disposition Campaign

Comprehensive Approaches to Developing Ion Exchange and Surface Complexation Databases for Nuclear Waste Repository Modeling and PA

Mavrik Zavarin

Glenn T. Seaborg Institute, LLNL

(V. Brendler, Frank Bok, HZDR, RES^{3}T contact)

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The most appropriate path forward for development of sorption models/databases for PA remains an open question

- **We need to develop self-consistent surface complexation/ion exchange models, in concert with thermodynamic models, for nuclear waste repository performance assessment**
- **This issue was expressly identified in the recent NEA Sorption project reports**

Example: RES^{3}T database

- **RES^{3}T is a digital open source thermodynamic sorption database**
  - mineral-specific surface complexation constants
  - Used in additive models
  - Data records comprise metadata and surface complexation reactions
    - *Non-Electrostatic, Diffuse Double Layer, Constant Capacitance, Triple Layer, Basic Stern, and the 1-pK Model as extended to CD-MUSIC.*
  - Comprehensive database of publications

RES^{3}T database development

Neptunium Adsorption on Synthetic Amorphous Iron Oxyhydroxide

DON C. GIRVIN,[1] LLOYD L. AMES, ALLEN P. SCHWAB, AND JEFF E. MCGARRAH

Environmental Sciences Department, Pacific Northwest Laboratory, Richland, Washington 99352

Received January 4, 1988; accepted April 19, 1990

Neptunium adsorption on synthetic amorphous iron oxyhydroxide ($Fe_2O_3 \cdot H_2O(a)$) was investigated at 25°C for initial Np(V) concentrations between 4.5×10^{-11} and 4.5×10^{-13} *M* in 0.1 *M* $NaNO_3$ electrolyte solutions undersaturated with atmospheric CO_2 for pH > 7. The surface properties of the $Fe_2O_3 \cdot H_2O(a)$ were determined by CO_2-free acid-base titration (pH(PZC) acidity and electrolyte complexation constants were determined using the triple-layer model (TLM). The aqueous speciation of Np(V) is oxycation, NpO_2^+, in the region of the adsorption edges (5 < pH < 8). At the ated, the adsorption data are consistent with the hypotheses that (1) $Fe_2O_3 \cdot$ "ideal" single-site ligand, (2) no deprotonation of surface sites need be invoked to describe Np(V) adsorption, and (3) $NpO_2(OH)^0$ is the dominant Np surface species. A single surface-coordination reaction, $XOH + (NpO_2^+)_s + H_2O = (XOH{-}NpO_2(OH))^0 + H_s^+$ (log $K = -3.2$), described all adsorption data and is independent of the surface-coordination model. Surface hydrolysis of NpO_2^+ occurs 2.4 pH units below NpO_2^+ hydrolysis in bulk solution ($pK_{HY1} = 8.85$).

example

Information captured in database:

1. Reference
2. Mineral
3. Mineral characteristics
4. Solution conditions
5. Surface complexation model
6. Protonation constants
7. Surface complexation constants

131	minerals
1529	specific surface area measurements
1474	surface site data records
4636	surface complexation reactions
2642	literature references

Information NOT captured in database:

1. **Primary sorption data**
2. **Aqueous speciation model**

Application of RES^{3}T in the present configuration is difficult

- ***No ability to integrate disparate data sets and model fits***
- ***No ability to update surface complexation constants when new aqueous speciation data are available***
- ***No comprehensive error propagation in data or database constants***

Enhancements to RES³T can lead to a database amenable to PA

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example

Information captured in database:

1. Reference
2. Mineral
3. Mineral characteristics
4. Solution conditions
5. Surface complexation model
6. Protonation constants
7. Surface complexation constants
8. **Primary sorption data**

131	minerals
1529	specific surface area measurements
1474	surface site data records
4636	surface complexation reactions
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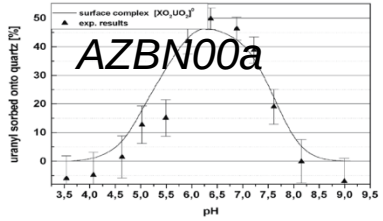
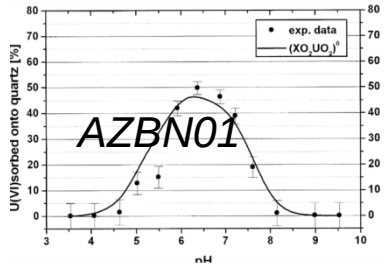
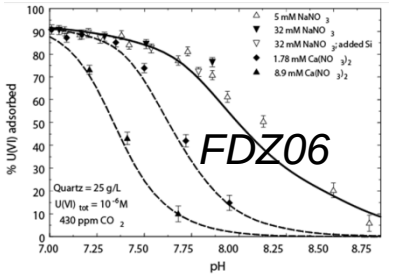
Addition of primary sorption data allows for integration of all available literature data, error propagation, and database updating to ensure self-consistent aqueous speciation, solubility, and sorption models

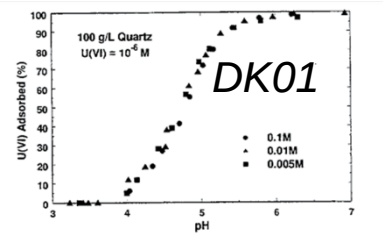
Used Fuel Disposition

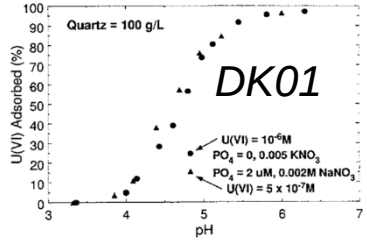
Example: Comprehensive Evaluation of U(VI) sorption to quartz

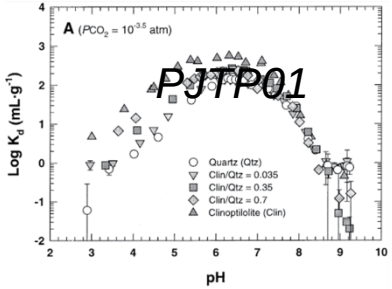


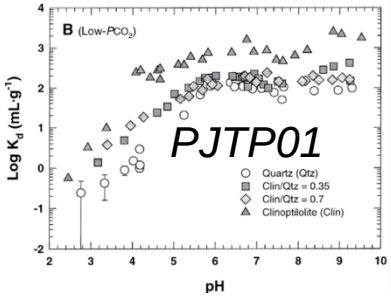


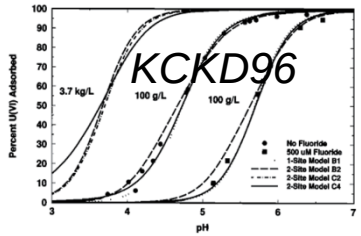


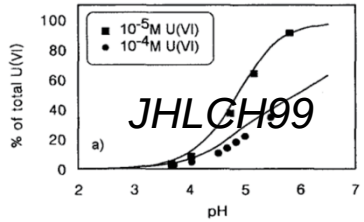


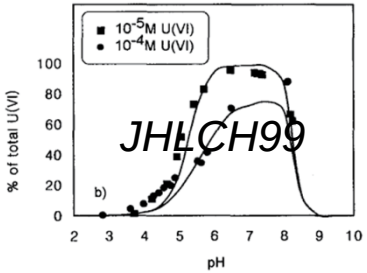


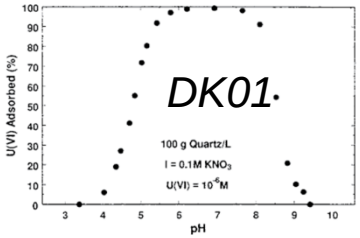


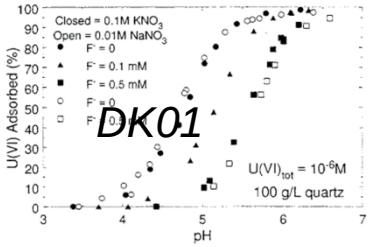


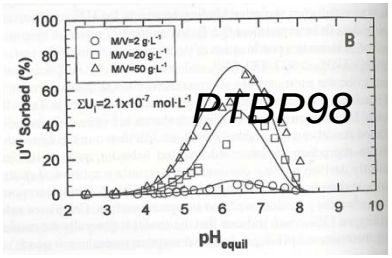


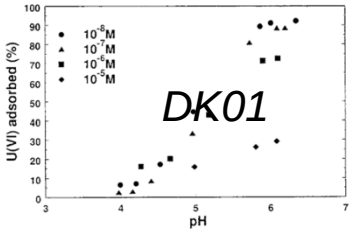


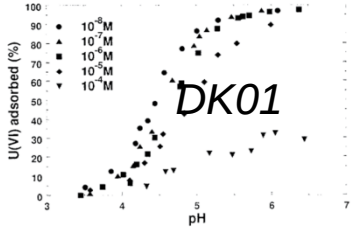


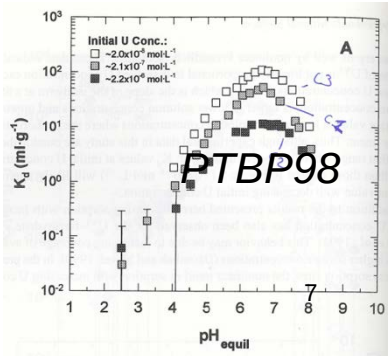








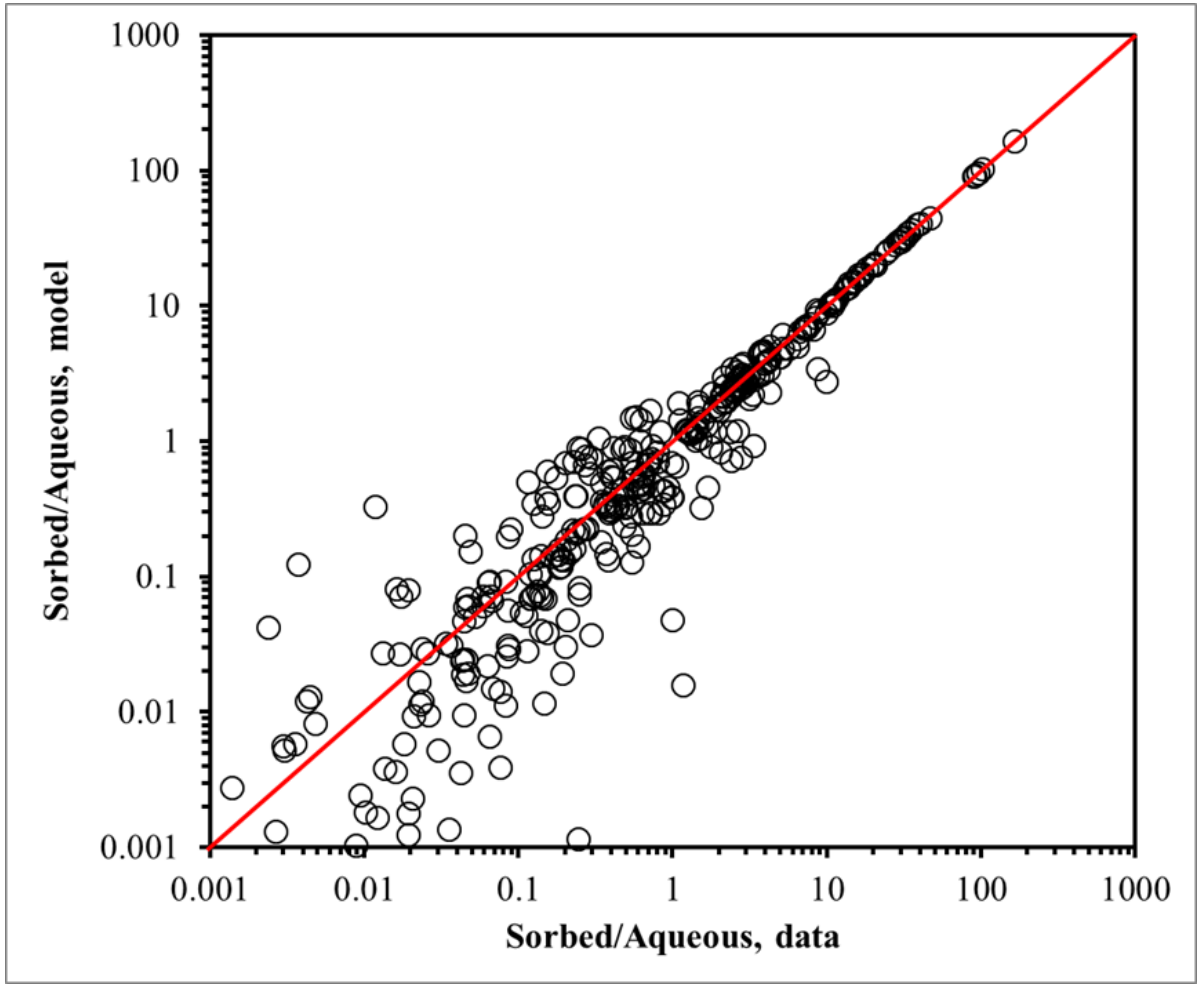




U(VI)-quartz surface complexation model development

- ***Aqueous speciation data from NEA databases***
- ***Sorption references from RES^{3}T database***
- ***Metadata from RES^{3}T database***
- ***Literature data digitized with DataThief software***
- ***Surface complexation model fitting using the FIT4FD software (derivative of FITEQL model)***
- ***Data uncertainty propagated through to fitted reaction constants***

U(VI)-quartz Non-Electrostatic surface complexation model fitting



Comparison of data and model fits of the ratio of sorbed to aqueous concentrations for all batch sorption data contained in references identified by the RES^{3}T database for U(VI) sorption to quartz. Increasing scatter at low sorbed/aqueous ratios is a result of inherent uncertainties associated with samples with little to no U(VI) sorption. One-site non-electrostatic surface complexation model

FY16 Effort

- **FY16 effort:**
  - Employ more robust fitting codes
    - *PEST optimization*
    - *PhreeqC*
  - Test a variety of surface complexation models
    - *DLM, TLM, MUSIC, GEM (Kulik)*

A Phreeqc-PEST optimization model

- **Meta-data from RES^{3}T**
- **Raw data digitized from literature**
- **TDB from NEA**

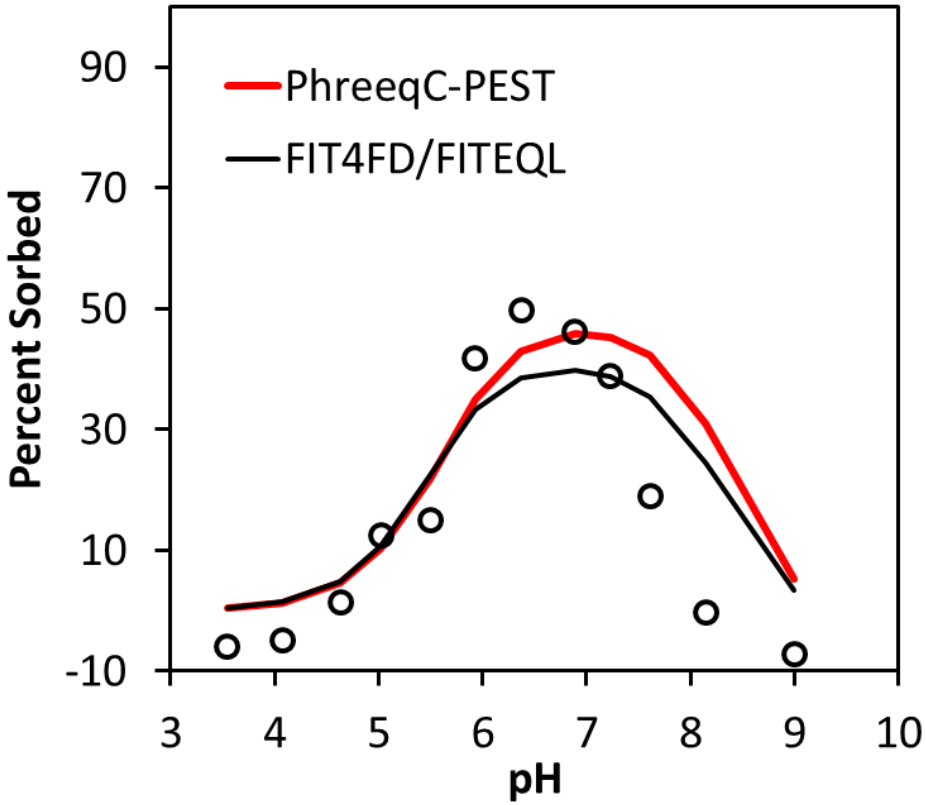
PHREEQC (PRESENTLY) PHREEQCRM (MORE EFFICIENT?)

PEST parameter estimation

- **Fitted SC constants**
  - Compare DLM, NEM, MUSIC model
- **Fitted ion exchange constants**
- **Parameter uncertainties**

Test Case: AZBN00a

- Good fit comparison between FIT4FD/FITEQL and PhreeqC-PEST optimization
- PhreeqC-PEST is an effective optimization framework



U(VI)-SiO_2 sorption
12.5 g/L, 0.2 m^2/g, 4.8 sites/nm^2

REFERENCE:
Arnold T, Zorn T, Bernhard G, Nitsche H (2000): Applying the DDLM to model the sorption of uranium onto quartz and muscovite. in: Annual report 1999; Forschungszentrum Rossendorf e.V., Institute of Radiochemistry; Dresden (Germany)

FY16-FY17 NEXT STEPS

- Expansion to all available U(VI)-SiO_2 sorption data
  - Testing different SC models
  - DLM, MUSIC, NEM, ETC.
- Expand SC model to test a range of RN-mineral pairs
- Link efforts with RES^3T and NIST*
  - *NIST ACS Spring meeting highlighted interest in developing comprehensive SC/IE databases for UFD and other contaminant transport research.
- **Provide an approach to produce a comprehensive SC/IE database that is easily updateable and consistent with NEA TDB**