

## CAPABILITY OF SURFACE COMPLEXATION MODELS AND DATABASES FOR PREDICTING RADIONUCLIDE SORPTION

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### ABSTRACT

The paper presents examples illustrating the current blind predictive capabilities of surface complexation models (SCM) and respective databases. High-quality experimental sorption data sets were used as provided by Phase II of the Nuclear Energy Agency (NEA) Sorption Project for its fitting assessment efforts. The systems covered are Np(V) sorption onto hematite, U(VI) sorption onto quartz and Se sorption onto goethite. To keep the number of parameters at a minimum, the Diffuse Double Layer model was selected to account for electrostatics. All calculations were performed with the FITEQL code, version 3.2 [1]. Based on the information in the sorption database RES<sup>3</sup>T [2] for the above minerals and chemically similar phases, first a set of relevant species was formed. Then respective surface complexation parameters were taken from RES<sup>3</sup>T: the binding site density for the minerals, the surface protolysis constants, and the brutto stability constants for all relevant surface complexes. To be able to compare and average thermodynamic constants originating from different sources, the normalization concept as introduced by Kulik [3] was applied. Lacking data was substituted by estimates exploiting chemical analogy. The only system-specific parameters directly going into the computations were the solid-liquid ratio and the specific surface area.

The model prediction almost always represented the experimental values for the sorbed amount of Np, U and Se within one order of magnitude or better, provided an adequate chemical system was assumed. There, sorption was expressed as conventional distribution coefficients  $K_D$  as required by most performance assessment (PA) software. Further improvements may arise from a broader data base eliminating the need for data estimations through chemical analogies.

### INTRODUCTION

World-wide activities focus on the remediation of radioactively contaminated sites. One common aim is to deliver a more profound chemical base for risk assessment, namely all those physico-chemical phenomena governing the contamination plume development in time and space. Coupled transport codes able to tackle this challenge have to simplify the resulting very complex reaction pattern. To do so in an adequate way requires to extend the knowledge about retardation and mobilization phenomena and the underlying basic processes and interactions, such as physisorption, chemisorption, co-precipitation, inclusion, diffusion, surface-precipitation, or the formation of solid solutions. Whereas the simplest (and older) sorption models do not distinguish between the various processes contributing to the overall sorption, newer model approaches try to address all relevant processes separately.

Sorption models in a strict sense are usually grouped into two classes, the phenomenological models, and the surface complexation models. Phenomenological adsorption models comprise different variants of the equilibrium distribution coefficient ( $K_D$ ) model. The  $K_D$  framework is built on the concept of distribution (or retardation) coefficients. This is defined as the experimentally determined ratio of the sorbed (fixed, immobilized) and unsorbed (free, truly dissolved) fraction of a component (chemical element) under equilibrium conditions.

The subsuming of many physico-chemical processes into one parameter is a severe weakness of the  $K_D$  principle [4,5,6]. Distribution coefficients are difficult to measure with a good precision and accuracy. Even slight changes in one system parameter (say the  $E_H$  or the content of a major cation, or the occurrence of a new mineral phase, etc.) can drastically change them. To measure the effect of all combinations of these parameters is impossible. That means, all  $K_D$  values used nowadays in risk assessment or other prognostic studies are just snapshots for specific locations of the site valid only for the geochemical conditions at the time of the measurement. This in turn assigns them very large uncertainties.

A much better strategy is the decomposition of the  $K_D$  value into the main basic processes defining it. Such an approach will unfold the single distribution coefficient into a vector of parameters, such as  $E_H$ , pH, concentrations of the various components, binding site densities, surface areas, and temperature. Apparently this is a step backwards. But it has the great advantage that all these parameters can be measured with more reliability and precision. Knowing the functional relationships between these processes and how they contribute to the  $K_D$  allows a computation of latter rather than a measurement. Moreover, simulations with variable parameter values, even for hypothetical conditions, may easily yield a  $K_D$  surface as a function of the "primary" parameter vector:  $K_D = f(E_H, \text{pH}, p_{\text{CO}_2}, T, \dots)$ . Usually, the function  $f$  can not be expressed as an explicit function but contains implicit formulations only accessible through numeric iterations. Also, some long-term effects that may render conventional distribution coefficients meaningless (co-precipitation, diffusion of trace elements into crystal lattices) can be accounted for in a better way. Another application is expressing  $K_D$  as a function of time, related to better-defined time dependencies of other basic parameters. Furthermore, it becomes possible to identify those parameters affecting the  $K_D$  strongest. Consequently, extra measurements can be designed efficiently to reduce its uncertainty. And last but not least the formal keeping of the used  $K_D$  paradigm renders it easy to couple a "smart  $K_D$ " framework with already existing contaminant transport and risk assessment codes, enhancing its acceptance.

The unfolding of  $K_D$  values leads to modern concepts that treat surface reactions as complex formations analogous to such reactions in homogeneous aqueous solutions. Therefore these models are called Surface Complexation Models (SCM), for details refer to, e.g., [7]. The SCM concept combined with a powerful sorption database allows a straightforward extension towards rocks and soils composed of several minerals. Their sorption behavior should be predicted from the weighted superposition of the sorption processes for all constituting minerals. The number of important rock-forming minerals is limited, more than 95 % of the known rocks in the earth's crust consist of only about 20 minerals and mineral groups [8]. Thus we hypothesized that the sorption behavior of contaminants onto rocks can be described in a competitive fashion based on the simultaneous sorption onto its mineralogical components and also onto possibly forming secondary minerals. Applications of simple variants of such an approach have already been proven successfully [9,10].

To support the above approach a digital thermodynamic database for surface complexation equilibria is essential. Therefore, a digitized version of a thermodynamic sorption database has been implemented recently as a relational database implemented with the Microsoft Access software: "RES<sup>3</sup>T - Rossendorf Expert System for Surface and Sorption Thermodynamics" [2]. One of its major goals is providing a sound foundation for the use of SCM in risk assessment studies. The RES<sup>3</sup>T database should finally be able to deliver recommended data sets for such SCM applications.

## MODELING

Over the last decades, tremendous progress has been achieved with regard to surface complexation models, concerning both theoretical, experimental, and modeling aspects. Now it seems time to transfer

the gathered knowledge to those requiring it in the field of performance assessment (PA). However, this transfer appears to be rather slow. Many people consider SCM to be too complex to handle, and not really trustworthy, in part because there are too few data available. To overcome this bias and the resulting hesitation, and to pave the way for a broader application in PA, we found it essential to check the general predictive capabilities of SCM before. This must include:

- Check the ability to predict  $K_D$  values
- Develop robust modeling strategies including data supply
- Verify modeling tools
- International exchange of expertise and ideas

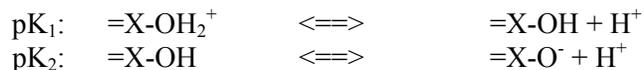
Similar targets are pursued by the Nuclear Energy Agency (NEA) Sorption Project Phase II [11]. It started a comparative application assessment for the present fitting and predictive capabilities of SCM. Based on strict quality criteria, experimental sorption data sets were selected for seven test cases. These sets included experimental data for the sorption of neptunium(V) onto hematite, uranium(VI) sorption onto quartz and selenium sorption onto goethite, which are in the focus of the present study serving as comparison counterparts for blind prediction exercises.

We decided to also apply the NEA Sorption Project criteria for the model quality assessment. Namely, the deviation in  $K_D$  should be below one order of magnitude to label a blind prediction result as acceptable.

### General Prediction Strategy

For all three cases, a general stepwise methodology was utilized:

- S In a first step, a literature survey mainly based on the RES<sup>3</sup>T database helped to define the chemical system, i.e. the mineral properties and the set of surface species.
- S The value for the specific surface area is strongly dependent on the sample history and grain size fraction. It can not be generalized, so the respective experimentally determined value was used for the computations.
- S All reaction constants were converted to infinite dilution (when necessary) by assigning activity coefficients based on the Davies-Equation [12] to all dissolved species.
- S Because the reported reaction constants are related to different site densities, it was necessary to convert the values to a reference state to enable comparison and averaging. Here, the procedure according to Kulik [3] was followed, based on a reference surface site density of 12.05 sites/nm<sup>2</sup>. This value of course was then also used for all subsequent predictive modelings.
- S To keep the system as simple as possible, in no case was a distinction between strong and weak binding sites applied. The values of  $pK_1$  and  $pK_2$  for the two successive protolysis steps always refer to the following deprotonation reactions, with  $=X-OH$  denoting a generic neutral surface binding site:



- S When the data situation was too sparse, various approximations were utilized to derive a sensible chemical model, namely the estimations based on crystallography and thermodynamics as published, e.g., by Sverjensky and co-workers [13] or the extrapolation from chemically similar systems (with regard to both mineral and sorbent) by applying the Linear Free Energy Relationships (LFER) as, e.g., described by Dzombak and Morel [14]. If such approaches failed, a simple transfer of data from chemically similar systems (with identical charge) was accepted. There, as a last resort, parameters based on electrostatic terms different from the chosen SCM were also taken into account. Preliminary uncertainty analysis showed for most cases that the sorption

modeling error imposed by omitting a surface reaction totally is much larger than assigning an respective surface complex formation constant with large uncertainties. Of course, if time, manpower and the availability of experimental raw data allows, a re-fitting of these data to a presumably correct chemical surface model is the best way.

- S After normalization, the data records applying to the same reaction (mineral surface protolysis and surface complex formation) were compared and judged to identify and exclude outliers and doubtful data points. The remaining sets were then averaged to obtain respective model parameters and also an estimation of their uncertainty.

The Diffuse Double Layer (DDL) [14,15] model was chosen as a rather straightforward SCM variant, again to keep the number of parameters at a minimum, but also because many published data sets are based on that SCM type.

### Parametrization of Np(V) Sorption onto Hematite

Concerning hematite, the parameters derived from the very data set being the foundation of the predictions reported here had to be excluded - otherwise it would not have been a proper blind prediction exercise. This left us with four independent DDL data records for the hematite surface protolysis [16,17,18,19]. After normalization, none of them showed obvious errors or differed significantly enough from the rest to become suspicious. Hence an averaging seemed to be adequate leading to the values  $pK_1^n = 6.46 \pm 0.89$  and  $pK_2^n = 10.00 \pm 0.87$ .

There are only very few SCM investigations reported for Np sorption on hematite, so also data for Np sorption on similar iron (hydr)oxide phases were utilized to obtain information about a realistic surface species set and its DDL parameters. Some experiments in the comparison data set were performed under gas atmospheres containing CO<sub>2</sub>, therefore carbonate surface species had to be considered too besides Np(V) ones. The following surface species have been reported so far independent from the SCM sub-model (in parentheses: number of publications): =FeO-NpO<sub>2</sub> (5), =FeOH-NpO<sub>2</sub><sup>+</sup> (1), =FeOH-NpO<sub>2</sub>OH (1), =FeO-NpO<sub>2</sub>OH<sup>-</sup> (2), =FeO-HCO<sub>2</sub> (7), =FeO-CO<sub>2</sub><sup>-</sup> (7), =FeOH-H<sub>2</sub>CO<sub>3</sub> (5), =FeOH-HCO<sub>3</sub><sup>-</sup> (4), and =FeO-NpO<sub>2</sub>(HCO<sub>3</sub>)<sub>2</sub><sup>2-</sup> (2). Based on this list, and considering that FITEQL is not able to distinguish between species differing only in their water content, the following species were selected: =FeO-HCO<sub>2</sub>, =FeO-CO<sub>2</sub><sup>-</sup>, =FeO-NpO<sub>2</sub>, and =FeO-NpO<sub>2</sub>(HCO<sub>3</sub>)<sub>2</sub><sup>2-</sup>. There was no independent DDL-based information about a ternary Np(V)-carbonate surface complex available. Hence the only way to account for the clear spectroscopic evidence for that species was to apply data from the respective goethite system [20], based on the Triple Layer SCM, however. But with omitting the ternary complex being the only alternative, we decided to use this electrostatically inconsistent value nevertheless.

Below the selected species are given, with their normalized DDL reaction constants  $\log K^n$ , taken from literature included in the RES<sup>3</sup>T database. The reaction constants refer to equations based on H<sub>2</sub>CO<sub>3</sub>(aq) as master species for carbonate.

= FeO-HCO <sub>2</sub>	$\log K^n =$	-4.75±0.41	[21,22,23]
= FeO-CO <sub>2</sub> <sup>-</sup>	$\log K^n =$	3.10±0.29	[21,22]
= FeO-NpO <sub>2</sub>	$\log K^n =$	-3.31	[24]
= FeO-NpO <sub>2</sub> (HCO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	$\log K^n =$	11.25	[20]

The aqueous speciation of neptunium(V), as well as auxiliary data for the carbonate equilibria, were based on the thermodynamic data recommended by the NEA [25].

The experimental data sets by Kohler et al. [20] used for evaluating the predictions are comprised of 52 data points for the Np(V) sorption at varied pH, ionic strength, solid/liquid ratio, Np content, and carbonate partial pressure in the atmosphere in contact with the solution.

The experimental value for the specific surface area of hematite, also used for the modeling, was 14.4 m<sup>2</sup>/g.

### Parametrization of U(VI) Sorption onto Quartz

There are several parameter sets available derived from potentiometric titrations of SiO<sub>2</sub> surfaces, mainly quartz and amorphous silica. The ones selected for this work are from eight different papers [26,27,28, 29,30,31,32,33], giving (after normalization)  $pK_2^n = 7.83 \pm 0.18$ . The first protolysis step was not considered here, because it occurs only in the extreme acidic region not covered by the raw data used for this blind prediction exercise. Moreover, papers differentiating between strong and weak binding sites have not been taken into account because all silanol sites on SiO<sub>2</sub> surfaces have very similar chemical environments as can be derived from crystallographic considerations. There is also no spectroscopic evidence for such distinctions so far.

The U(VI) surface species for iron (oxy)hydroxides proposed in the literature so far can generally be grouped into two categories: mono- and bi-dentate surface complexes. Here, the simpler approach based on the assumption of mono-dentate binding is followed. As with the previous case, the comparison data set covers different levels of CO<sub>2</sub> content in the atmosphere, thus carbonate surface speciation has to be considered, too. The initial list of mono-dentate surface complexes extracted from the literature covering all SCM submodels (in parentheses: number of publications) includes: =SiO-UO<sub>2</sub><sup>+</sup> (6), =SiO-UO<sub>2</sub>OH (5), =SiO-(UO<sub>2</sub>)<sub>3</sub>(OH)<sub>5</sub> (4), =SiO-UO<sub>2</sub>(OH)<sub>3</sub><sup>2-</sup> (1), =SiOH<sub>2</sub>-UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>-</sup> (1), and =SiOH<sub>2</sub>-UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>3-</sup> (1). There is no information available for pure carbonate complexes on SiO<sub>2</sub> surfaces so far. The first three uranyl surface species most often are postulated simultaneously, so they were selected. From the two possible ternary species, the one with higher carbonate content was excluded because it is only relevant at rather high carbonate content and pH. After normalization and averaging (if applicable), the following set of SCM parameters remained:

= SiO-UO <sub>2</sub> <sup>+</sup>	log K <sup>n</sup> =	-1.03±0.94	[32,33,34,35,36]
= SiO-UO <sub>2</sub> OH	log K <sup>n</sup> =	-6.56±0.41	[33,36,37]
= SiO-(UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>5</sub>	log K <sup>n</sup> =	-17.50±0.23	[33,34,36]
= SiOH <sub>2</sub> -UO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup>	log K <sup>n</sup> =	-5.86	[38]

The aqueous speciation of U(VI) was based on the NEA thermodynamic data [39].

The experimental data used to validate the blind predictions (106 experimental data points were used excluding the data for fluoride-containing subsystems) originate from unpublished results by Kohler, M. and Davis, J.A., U. S. Geological Survey, with part of the data set published in [40]. The total uranium concentration ranges from 10<sup>-8</sup> M to 10<sup>-5</sup> M, pH was varied between 3.5 and 9.1, and the ionic strength was held at 0.01 M with NaNO<sub>3</sub> as background electrolyte. Most of the experiments were performed in air, but with some runs under a nitrogen atmosphere with 7.5 % CO<sub>2</sub>.

The experimental value for the specific surface area of quartz, also used for the modeling, was 0.33 m<sup>2</sup>/g.

### Parametrization of Se(IV)/Se(VI) Sorption onto Goethite

Goethite as a well defined mineral often used as model substrate has been thoroughly characterized in previous studies. There were 13 independent publications of surface protolysis data records based on the

DDL model available [4,18,22,23,29,41,42,43,44,45,46,47,48]. From that pool averages for the first and second hydrolysis step were derived after normalization of the original values, yielding  $\text{pK}_1^n = 6.59 \pm 0.60$  and  $\text{pK}_2^n = 10.41 \pm 0.80$ .

The selection of species started from a survey over all iron (hydr)oxides. For the sake of simplicity, we did not consider bi-dentate surface complexes. This led to the species listed below (in parentheses: number of publications):

- a) Selenate:  $=\text{Fe}-\text{SeO}_4^-(1)$ ,  $=\text{FeOH}-\text{SeO}_4^{2-}(1)$ ,  $=\text{FeOH}_2-\text{SeO}_4^-(3)$ , and  $=\text{FeOH}_2-\text{HSeO}_4(1)$
- b) Selenite:  $=\text{Fe}-\text{SeO}_3^-(3)$ ,  $=\text{Fe}-\text{HSeO}_3(1)$ , and  $=\text{FeOH}-\text{SeO}_3^{2-}(1)$

The first and third selenate species are indistinguishable for FITEQL for reasons explained above. In addition, DDL parameters were only available from Dzombak and Morel [14], so the species and SCM parameters listed below are all from the same source, at least guaranteeing a high degree of consistency.

= $\text{Fe}-\text{SeO}_4^-$	$\log K^n = 7.00$
= $\text{FeOH}-\text{SeO}_4^{2-}$	$\log K^n = 0.07$
= $\text{Fe}-\text{SeO}_3^-$	$\log K^n = 11.96$
= $\text{FeOH}-\text{SeO}_3^{2-}$	$\log K^n = 4.44$

The aqueous speciation of selenate and selenite (basically the hydrolysis steps of  $\text{H}_2\text{SeO}_4$  and  $\text{H}_2\text{SeO}_3$ ), as well as the respective data for the carbonate system, were based on the NEA thermodynamic data [39].

The experimental data stem from work performed by Hayes [49]. 70 data points for selenate sorption and 22 data points for selenite sorption were used for the prediction test. This system is the most challenging one due to a very sparse parameter matrix and really high pH values for some data points. Further experimental data at an ionic strength of 1 molar were not used because FITEQL can not handle such solutions properly. Ionic strength, solid/liquid ratio and pH were varied. The experiments were carried out under air atmosphere, but the gas phase size in the closed experimental set-up was so small that the carbonate equilibria in solution and on the surface can be neglected.

The experimental value for the specific surface area of goethite, also used for the modeling, was  $52 \text{ m}^2/\text{g}$ .

## Modeling Tool

All predictive modeling was performed with the FITEQL software, version 3.2 [1]. Some well known problems rendered the work difficult, however. FITEQL is cumbersome with regard to data input and processing of results. More serious was the fact, that the code is not able to handle ionic strengths larger than 0.5 M because only the Davies-Equation [12] is implemented to compute activity coefficients. In addition, FITEQL does not store internally the stoichiometric coefficient of water in a reaction, thus it can not discriminate species differing only in their water content.

## RESULTS AND DISCUSSION

### Np(V) Sorption onto Hematite

Fig. 1 illustrates the prediction quality for selected sorption subsets, based on the relative amount of neptunium(V) bound to the surface. The best matching is obtained for the lowest surface loading (solid / liquid ratio of 1 g hematite / L and at  $1.2 \times 10^{-7} \text{ M Np}$ ). The largest deviations are observed for the experiments at the highest loading (solid / liquid ratio of 1 g / L and at  $1.2 \times 10^{-6} \text{ M Np}$ ), where the prediction

generally overestimates the sorption. Fig. 2 shows that the simulation congruence for all data subsets is within one order of magnitude when focusing on the conventional distribution coefficient  $K_D$ .

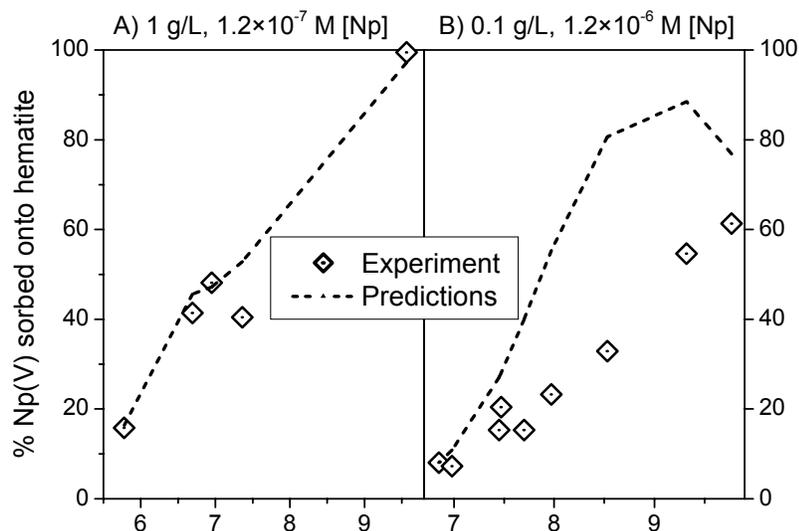


Fig. 1 Example for Best and Worst Predictions for Subsets of the Experiments of Np(V) Sorption onto Hematite, Comparing Measured and Predicted Percentage of Sorbed Np(V)

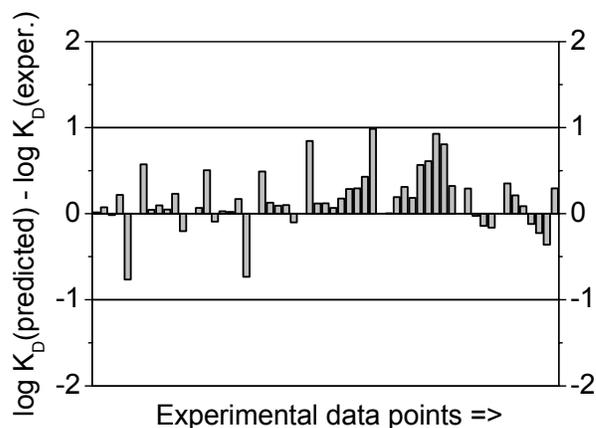


Fig. 2 Differences in Log(KD) between predicted and measured Np(V) sorption onto hematite

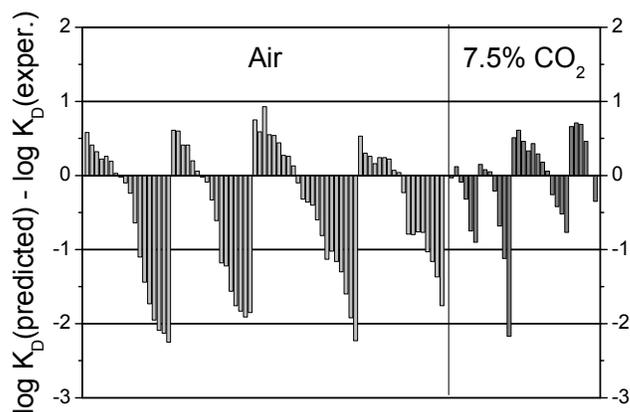


Fig. 3 Differences in  $\log(K_D)$  between predicted and measured U(VI) sorption onto quartz.

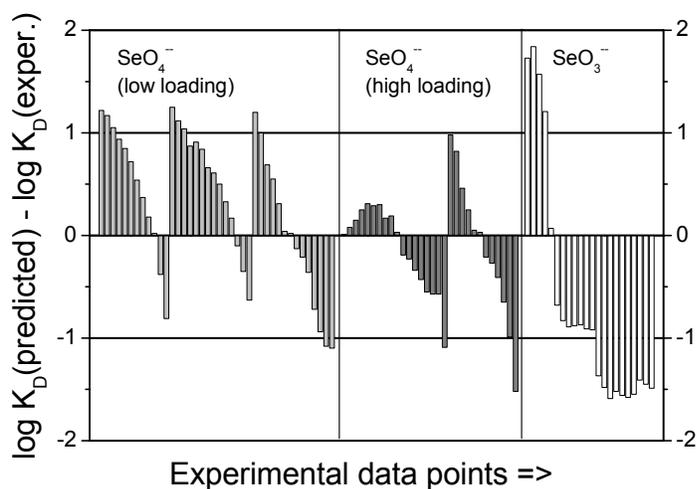


Fig. 4 Differences in  $\log(K_D)$  between predicted and measured selenium sorption onto goethite

### U(VI) Sorption onto Quartz

As can be seen in Fig. 3, the prediction quality is not as good as it was for the Np(V) case. Significant underestimations of the uranyl sorption occur in regions at  $\text{pH} > 7$ , the reasons for being not clear so far. Maybe the introduction of further carbonate and/or hydroxo surfaces complexes of uranyl can resolve this issue. Another alternative would be the switch from a mono-dentate model to a bi-dentate model. This sacrifices simplicity, but there is some spectroscopic evidence for the respective bi-dentate surface species, see e.g. [50,51].

## Se(IV)/Se(VI) Sorption onto Goethite

The quality of the blind prediction of Se(IV)/Se(VI) sorption onto goethite is illustrated by Fig. 4. For selenate sorption, there are differences in the acidic range at very high loadings. This is not really worrying because also the experimental error expressed in  $K_D$  is highest there, when more than 99% of the selenium is bound to the surface. More serious are the underestimations in the basic region beyond pH 9 (and thus above the point-of-zero-charge of goethite) indicating the possible existence of another surface species. There are general difficulties with the selenite sorption, suggesting the supporting reaction constants are based on too few experiments.

## CONCLUSIONS

It can be concluded, that the application of SCM can indeed be very valuable for estimating distribution coefficients for contaminants in some well defined mineral systems. The SCM database so far assembled within the RES<sup>3</sup>T project is able to provide the respective parameter sets following the stepwise strategy of species selection, data collection, normalization and averaging extended to chemically similar mineral surfaces and tolerating inconsistencies in the electrostatics rather than omitting surface species. Still, incomplete chemical system setup is the main reason for deviations between the model prediction and measured sorption distribution coefficients. For some systems important for radioactive waste management it is necessary to start additional sorption experiments, especially at higher pH ranges in combination with increased carbonate content, to obtain reliable SCM parameters.

Here it should also be mentioned that the high-quality data sets used in this work as reference data for comparison with the blind predictions, of course have also been processed by the experimenters to derive SCM parameter sets. Thus, the data base to tackle real-world application cases for Np(V) sorption onto hematite, U(VI) sorption onto quartz, or Se(IV)/Se(VI) sorption onto goethite actually is broader and of higher confidence than the subsets that could be used for the purpose of this work.

The goal to provide reliable SCM parameter sets will be striven for further, not only by a steady extension of the sorption database RES<sup>3</sup>T, but also by international efforts to derive commonly accepted guidelines for tackling sorption from the data generation to the data processing and modeling. Finally this should enable the establishment of recommended data sets for surface complexation models. Such efforts have to be accompanied by the development of better modeling tools to overcome the shortcomings of the FITEQL code.

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