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# Development of Mechanistic Sorption Model and Treatment of Uncertainties for Ni Sorption on Montmorillonite/Bentonite

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Geological Isolation Research Unit
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Sorption and diffusion of radionuclides in buffer materials (bentonite) are the key processes in the safe geological disposal of radioactive waste, because migration of radionuclides in this barrier is expected to be diffusion-controlled and retarded by sorption processes. It is therefore necessary to understand the detailed/coupled processes of sorption and diffusion in compacted bentonite and develop mechanistic /predictive models, so that reliable parameters can be set under a variety of geochemical conditions relevant to performance assessment (PA).

For this purpose, JAEA has developed the integrated sorption and diffusion (ISD) model/database in montmorillonite/bentonite systems. The main goal of the mechanistic model/database development is to provide a tool for a consistent explanation, prediction, and uncertainty assessment of $K_d$ as well as diffusion parameters needed for the quantification of radionuclide transport.

The present report focuses on developing the thermodynamic sorption model (TSM) and on the quantification and handling of model uncertainties in applications, based on illustrating by example of Ni sorption on montmorillonite/bentonite. This includes i) a summary of the present state of the art of thermodynamic sorption modeling, ii) a discussion of the selection of surface species and model design appropriate for the present purpose, iii) possible sources and representations of TSM uncertainties, and iv) details of modeling, testing and uncertainty evaluation for Ni sorption.

Two fundamentally different approaches are presented and compared for representing TSM uncertainties: i) TSM parameter uncertainties calculated by FITEQL optimization routines and some statistical procedure, ii) overall error estimated by direct comparison of modeled and experimental $K_d$ values. The overall error in $K_d$ is viewed as the best representation of model uncertainty in ISD model/database development.

Keywords: Radionuclide Migration, Sorption, Ni, Montmorillonite, Bentonite, Mechanistic Model, Database, Uncertainty, Geological Disposal

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# モンモリロナイト/ベントナイトへのNiの収着に関する現象論的収着モデルの開発と不確実性の取り扱い

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地層処分基盤研究開発ユニット

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（2010年12月2日受理）

放射性廃棄物地層処分の安全評価において，放射性核種の緩衝材/ベントナイト中での収着・拡散現象は，その移行遅延を支配する重要な現象である。実際の処分環境で考慮すべき圧縮ベントナイトでの収着・拡散複合現象の理解とそれを反映した現象論的モデル/評価手法の開発が，安全評価において，様々な地球化学条件を考慮して信頼性の高い核種移行パラメータ設定を行ううえで重要となる。

この目的のために，日本原子力研究開発機構では，ベントナイトとその主成分であるモンモリロナイトを対象として，統合された収着・拡散(ISD)モデル及びデータベースの開発を進めている。この現象論的モデル/データベース開発の主要な目的は，核種移行の定量的評価に必要な収着分配係数や拡散係数の整合的な説明と予測，不確実性評価のためのツールを提供することである。

本報告は，Niのモンモリロナイト/ベントナイトへの収着を例として，熱力学的収着モデルの開発と不確実性の取り扱いに焦点をあてる。具体的には，1) 熱力学的収着モデル開発の現状の要約，2) ここでの目的に適した表面化学種とモデル概念の選定に関する議論，3) 熱力学的収着モデルの不確実性に関する可能性のある要因と定量化，4) Niの収着のモデル化，適用性確認及び不確実性評価の詳細，について報告する。

熱力学的収着モデルの不確実性の定量化のため，1) FITEQLコードの最適化手法と統計的手法から計算される熱力学収着モデルパラメータの不確実性，2) 収着分配係数のモデル化結果と実測データとの直接的な比較により評価される包括的な誤差の２つの異なった手法を検討，両者の比較を行った。ISDモデル/データベース開発におけるモデルの不確実性の定量化法としては，後者の包括的誤差評価が，現時点での最良の手法と評価された。

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# 1. Introduction

Sorption and diffusion of radionuclides in buffer materials (bentonite) and host rocks (rock matrix) are the key processes in the safe geological disposal of radioactive waste, because migration of radionuclides in these barrier materials is expected to be diffusion-controlled and retarded by sorption processes. It is therefore necessary to understand the detailed/coupled processes of diffusion and sorption in compacted bentonite/intact rock and develop mechanistic/predictive models, so that reliable parameters can be set under a variety of geochemical conditions relevant to performance assessment (PA).

JAEA has developed the mechanistic (thermodynamic) sorption and diffusion database in combination with an integrated sorption/diffusion (ISD) model, and published first prototype model and database in FY2009 (Tachi et al., 2010). As shown in Figure 1.1, the ISD model (Ochs et al., 2001, 2003) allows to calculate (1) the composition of bentonite porewaters and the surface speciation of the bentonite, as a function of groundwater and bentonite composition, (2) the speciation of radionuclides in these porewaters, (3) the sorption of major ions and radionuclides to bentonite surfaces based on ion exchange and surface complexation processes and (4) the electrostatic interaction of diffusing radionuclide species with pore surfaces in compacted bentonite. The combination of the different models into the ISD model/database scheme allows to simultaneously calculate $K_d$, $D_e$ and $D_a$, ensuring internal consistency between these parameters.

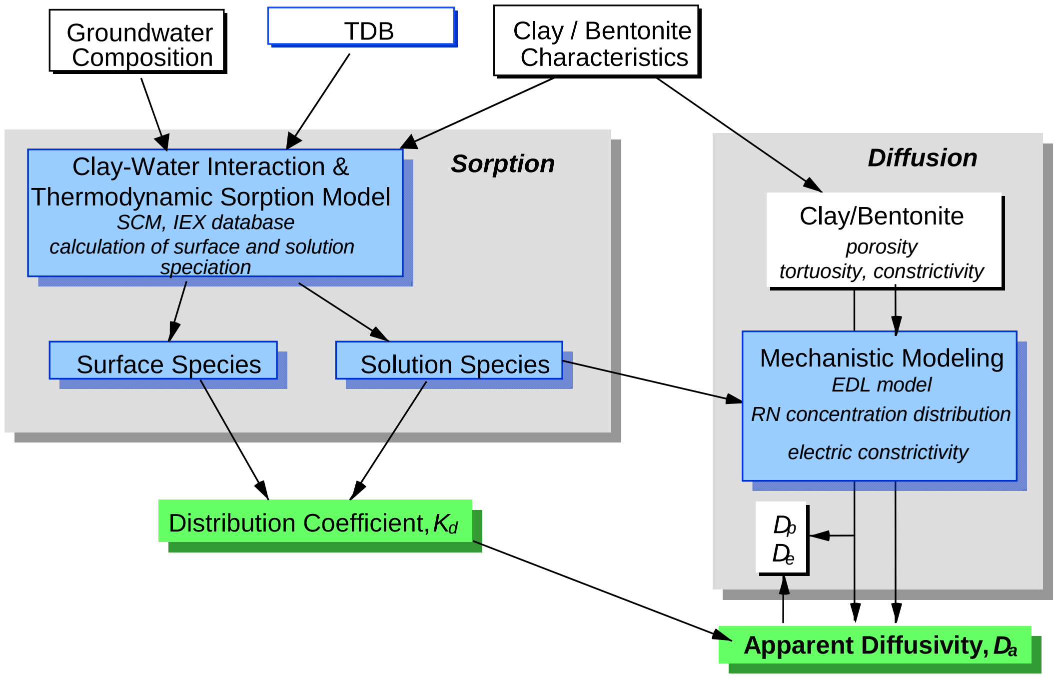


Figure 1.1 Schematic overview of the integrated sorption and diffusion (ISD) model / database (Ochs et al., 2001, 2003).

The main goal of the mechanistic model/database development is to provide a tool for a consistent explanation, prediction, and uncertainty assessment of $K_d$ as well as diffusion parameters needed for the quantification of radionuclide transport.

The present report focuses on developing the thermodynamic sorption model (TSM) and on the quantification and handling of model uncertainties in applications, based on illustrating by example of Ni sorption on montmorillonite / bentonite. This includes a summary of the present state of the art of thermodynamic sorption modeling (Chapter 2), a discussion of the selection of surface species and model design appropriate for the present purpose (Chapter 3), possible sources and representations of TSM uncertainties (Chapter 4), and details of modeling, testing and uncertainty evaluation for Ni sorption (Chapter 5).

# 2. State of the art of thermodynamic sorption models (TSMs) for clays

## 2.1 Background for sorption model for clays

### 2.1.1 Clay structures and sorption mechanisms

The principal mineral in bentonite is montmorillonite which is also important in clay rocks, mudstones etc. This clay mineral is composed of octahedral alumina sheets sandwiched between tetrahedral silica sheets (2:1 clay) as shown in Figure 2.1. Such clay minerals feature two distinctly different types of surfaces, where two main types of sorption take place (e.g., Sposito, 1984; Stumm and Morgan, 1996).

- The planar siloxane (‘layer’) surfaces of clay minerals are permanent charge surfaces. These charges can derive from isomorphous substitutions, which result in a constant negative surface charge. A macroscopically electrically neutral surface involves charge-compensating cations, and sorption takes place when compensating ions are exchanged. Ion exchange models have been used in soil science since the first quarter of the 20th century. Several formalisms have been developed to correct for activity changes of the exchanger as a function of the composition of the charge-compensating ions. The most common are the equivalent fraction (Gaines-Thomas, GT) and mole fraction (Vanselow) models.
- The edge surfaces of clay minerals are variable charge surfaces. They carry a net positive or negative surface charge depending on the species sorbed to their surfaces (potential-determining ions), often involving surface-bound OH$^-$ groups. Surface complexation and ligand exchange models were established by Stumm, Schindler and co-workers in the 1970s by extending proton-binding and metal coordination chemistry in a rigorous fashion to surface chemistry. To account for the electrostatic field, the mass laws for surface equilibria often include an electrostatic correction term. The scientific basis for these corrections is derived from electrical double layer (EDL) theory.

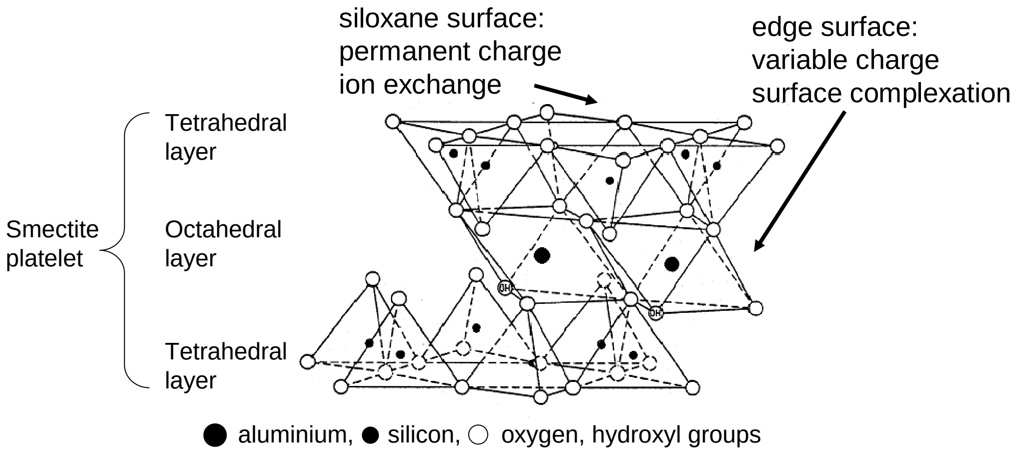


Figure 2.1 : Illustration of the structure, surface types, and corresponding sorption processes on 2:1 clay minerals (modified after Grim and Kulbicki, 1961).

Ion exchange is the typical sorption mechanism for alkali and alkaline-earth elements, as well as for transition metals at low pH values where positive species are predominant. Surface complexation is generally the more relevant process for all reactive elements (transition metals, actinides, lanthanides, reactive anions such as carbonate). Both ion exchange and surface complexation take place simultaneously, but at different surfaces.

### 2.1.2 Themodynamic sorption model for clays and consistency of model parameters

**Ion exchange:** The description of ion exchange by site-binding models is relatively simple. In many cases it only requires selectivity coefficients (or the corresponding ion exchange constants) to successfully model the competitive sorption of cations by clay layer surfaces.

It has been observed early on in the study of ion exchange processes that selectivity coefficients are dependent on the composition (more specifically, the activity) of the exchanger phase. Several formalisms, including the Gaines-Thomas (equivalent fraction) and Vanselow (mole fraction) approach have been developed to take this into account (Sposito, 1984). Ion exchange constants corresponding to these formalisms are independent of the exchanger phase and can thus be applied to any clay.

Because ion exchange is relevant mostly for simple cations only, and/or because selectivity coefficients are normally determined in the acidic pH-range where hydrolysis of cations is not important, it is typically perceived that there is often no (or no important) dependency of selectivity coefficients on underlying aqueous thermodynamic data. However, if the sorption of a given divalent element M(II) onto the siloxane surface (surface species $X^-$) would be modeled using both the $M^{2+}$ as well as e.g. the $MOH^+$ ion (i.e., using the surface species $X_2M$ and XMOH), then the determination and resulting value of the corresponding selectivity coefficient would of course be dependent on the equilibrium constant for the aqueous reaction

$$M^{2+} + H_2O = MOH^+ + H^+$$

**Surface complexation:** It is sometimes assumed by users of surface complexation models (SCMs) that model parameters can also be applied in a straightforward manner to other chemical systems; i.e., that a model developed for a given clay or Fe-oxide can be applied to a different sample of the same mineral. This assumption is based on analogy with aqueous chemistry, where thermodynamic constants for aqueous complex formation and mineral equilibria can be applied in any system (at the same temperature and pressure). However, many of the parameter values used in SCMs represent conditional, model-dependent values rather than true thermodynamic properties (see Sverjensky, 2003).

Surface complexation stability constants have many qualifying conditions, i.e., are dependent on total site density, surface area, EDL model used, etc., in addition to the qualifying conditions (T, p, zero ionic strength) for aqueous complex formation. To illustrate, the value of an edge surface protonation/ deprotonation constant determined from acid/base titration data of montmorillonite is dependent on a range of parameters that are determined or assumed for the model parameterization (in addition to p, T):

- the total site density of the clay edge surface;
- the specific surface area of the clay edge;
- the model chosen, including types of different sites and EDL correction term (if any).

In case of surface complexation reactions involving reactive radionuclides (RN), the value of the equilibrium constant will further depend on the underlying TDB.

**Combined ion exchange/surface complexation models:** In case of RN sorption on clays, it is often necessary to simultaneously consider ion exchange of the non- or weakly hydrolyzed metal cation species as well as subsurface complexation reactions. This is typically observed with most transition metal and lanthanide/actinide elements (for illustration, see examples in NEA, 2005).

In such cases, the fitted values for ion exchange and surface complexation constants are mutually dependent on each other. When such models are applied to other systems, they need to be applied as a whole (in addition to meeting the conditions discussed above). It is therefore not possible to use the surface complexation model in combination with different ion exchange constants.

### 2.1.3 Sorption data and other evidence for radionuclide-clay interactions

During the last 10-15 years, new and more systematic experimental sorption data on clays have become available for several relevant radionuclides. Many of the earlier sorption studies conducted with clay materials in the context of radioactive waste disposal were aimed at determining $K_d$ for one or a few sets of, often complex, conditions that were thought to be of direct relevance for PA. In contrast, the more recent studies typically were aimed at developing sorption datasets valid for a more extensive parameter space, to allow an interpretation of RN sorption behavior and an extension to various conditions. For these purposes, the experimental data are often interpreted by thermodynamic (mechanistic) sorption models (TSMs). The corresponding experimental studies often include one or several of the following approaches:

- Instead of complex clays and clay rocks, single clay mineral phases, such as montmorillonite are used. These minerals are often purified to remove impurities, especially traces of calcite/dolomite, in order to allow the performance of surface-acid/base titrations. The purified clays are typically converted to a mono-ionic (typically Na) form (e.g., Bertetti et al., 1998; Baeyens and Bradbury, 1997).
- Many data sets include the classical sorption edges and isotherms. In some cases, several sorption edges and isotherms are measured as a function of conditions (e.g., electrolyte concentration). In many cases, the available datasets are more restricted and include, for example, only 1-2 sorption edges but no isotherm (e.g., Gorgeon, 1994).
- Most studies are done in simplified systems. Even in cases where a wide range of conditions are covered in terms of pH and ionic strength, the solution chemistry is typically restricted to different concentrations of a simple electrolyte, such as $NaNO_3$, with pH adjustments by NaOH and $HNO_3$ (e.g., Baeyens and Bradbury, 1997).
- Only few studies are available where the influence of typical groundwater components (such as alkali-earth elements, carbonate, sulfate) on sorption has been investigated (e.g., Turner et al., 1996, 1998)
- On the other hand, more information regarding the properties of relevant mineral surfaces and the identity of radionuclide surface species has become available through spectroscopic investigations.

  - Such studies suggest that at a mechanistic level, the description of clay edge surfaces by generic ">SOH" surface sites is a simplification, and that the explicit distinction between >SiOH (silanol) and >AlOH (aluminol) surface sites may be a closer representation of reality (Dähn et al., 2003).
  - Spectroscopy also supports or confirms the existence of various surface species assumed in surface complexation models, such as inner- and outer-sphere surface complexes or ternary surface-RN-carbonato complexes (e.g., Chisholm-Brause et al., 2004).

## 2.2 Strategies and key model components for TSM development

### 2.2.1 Categories of TSM and evidence from the NEA Sorption Project

When the state of the art of thermodynamic sorption models (TSMs) is being discussed, it needs to be made clear from the beginning what purpose the respective models are supposed to serve. Remember that any model is always connected to a purpose. In case of TSMs, the purpose varies over a very wide range and may include purposes as divergent as

- research tools to aid in the investigation of the surface chemistry of well-characterized, pure mineral phases;
- pragmatic engineering tools to support the quantification of radionuclide sorption in complex mineral/groundwater environments.

Based on these two examples, it is easy to imagine that the state of the art in TSMs will vary considerably among the different scientific and technical fields.

Despite this variety, the TSMs developed to date by a variety of research groups for many different substrates and purposes can be roughly organized into the following three categories (Table 2.1, cf. NEA, 2005):

Table 2.1 Overview of categories for thermodynamic sorption models (TSMs)

**(1) Chemically most accurate & detailed models**

Purpose: prediction of sorption based on structural and surface chemical information

- surface species confirmed by spectroscopy / most accurate EDL models
- require detailed surface chemical data → difficult to develop/parameterize
- e.g. CD-MUSIC[*1] approach. Example: Tournassat et al. (2004) used 27 types of sorption sites to model proton, Na- and Ca-exchange on montmorillonite, based on structural and morphological data

**(2) Traditional or standard TSMs**

Purpose: prediction of sorption based on empirical fits to well-defined sorption data (single minerals) supplemented by structural and surface chemical information

- simpler than CD-MUSIC models, but more chemical detail than top-down models
- compromise between chemical accuracy and empirical fitting
- e.g. 1- or 2-site surface complexation models with (CCM[*2], DLM[*3], TLM[*4]…) or sometimes without EDL-correction term . Examples: the models by Bradbury and Baeyens (2005) or Ochs et al. (2003) used only a generic SOH site for the clay edge; Zachara and McKinley (1993) used SiOH- and AlOH-sites

**(3) Top-down models**

Purpose: prediction (only interpolation) of sorption based on empirical fits to sorption data on whole substrates (e.g. whole mudrock)

- focus on good fit (possibly at cost of chemical accracy)
- substrate is treated as one solid with generic sites, not as a mixture of minerals (mudrock as one component, not ad the sum of smectite and illite)
- e.g. empirical surface complexation models without EDL-term (NEM[*5]) for complex substrates where component additivity is not given (Davis et al., 2002).

[*1] CD-MUSIC ; carge-distribution multi-site ion complexation, [*2] CCM ; constant capacitance,
[*3] DLM ; diffuse layer model, [*4] TLM ; triple layer model, [*5] NEM ; non-electrostatic model

The following brief discussion will be oriented towards the situation for clays as relevant in the context of radioactive waste disposal.

An extensive illustration of the state of the art of sorption modeling for substrates relevant for radioactive waste disposal is provided by the modeling exercise carried out within phase II of the NEA Sorption Project (NEA, 2005). The task in this exercise was clearly to develop TSMs for the sorption of different radionuclides on simple and complex substrates, within a limited framework regarding time and effort. The outcome of this very extensive study was that nearly all of the developed models belong to categories 2 and 3 above. While the modelers were free to build on chemically more sophisticated models available in the literature and recent spectroscopic information, it became evident that the amount of detailed information required to develop and actually parameterize a category-1 model is available for very few and well-characterized systems only.

### 2.2.2 Empirical vs. structural models

From a purely chemical point of view, the MUSIC models are clearly the most accurate representation of surface reactions. These models are not based on fits to sorption data, but try to predict sorption on the basis of independent information on mineral composition, structure, and surface morphology. For many solids, this information is not sufficiently known.

In case of pure clay minerals, Tournassat et al. (2004) and Bourg et al. (2007) could show that MUSIC-type models are able to predict the behavior of simple ions ($H^+$, $Na^+$, $Ca^{2+}$) at the clay-water interface. In order to do this, Tournassat et al. (2004) explicitly considered the heterogeneity of the octahedral alumina layer with various isomorphic substitutions. Bourg et al. (2007), on the other hand, took into account the spillover of electric charge form the planar to the edge surface.

With regard to the application to radionuclide sorption on bentonite and clay rocks, the application of MUSIC-type models is largely prevented for the following reasons:

- The detail of information mentioned above is typically not available for whole substrates. It is also not clear to which degree detailed processes such as charge spillover can be transferred from a pure clay mineral to a system containing other charged minerals (quartz…) in addition.
- At the same time, this type of detailed information on surface structure is not available at all in case of compacted systems, which makes any justification of a MUSIC-type model difficult.
- The aqueous chemistry of most relevant radionuclides is more complex than that of simple alkaline or alkaline earth elements. Accordingly, their surface chemistry is also more complex and the details of their binding to the surface and accumulation in the EDL above clay surfaces are not available at present.
- Isolated spectroscopic evidence is available for radionuclide binding to clays. While this is sufficient for providing arguments for the inclusion of certain species in traditional TSMs (e.g. ternary carbonate species), it is not sufficient for providing the comprehensive information on surface structure needed for MUSIC modeling.
- Even for the most simple reactions, such as surface protolysis, not enough information on clay edge structure and reactivity is currently available to allow the development of a MUSIC-type model without empirically fitted parameters (see Bourg et al., 2007).

Thus, practically all models available to date for the description of radionuclide sorption on clays and clay substrates are empirical models. This means that they are based on measured radionuclide sorption data.

Within these models, there is some variation in terms of the level of detail, but overall, the models presently used for radionuclide sorption on clays are relatively similar. They are all relatively simple surface complexation/ion exchange models developed for specific clay minerals such as montmorillonite or illite (category-2 models in the scheme shown in Table 2.1). Modeling of sorption in more complex clays such as bentonite or clay rocks can be done using these models directly and accounting for the weight fraction of clay minerals in the respective substrates. It can further be shown (e.g., Tachi et al., 2009) that the sorption by individual clay components in clay-dominated rocks can be treated in an additive way (component additivity, see NEA, 2005).

Differences between the models used by different researchers and waste management organizations are mainly related to details of treating surface complexation at the edge sites:

- Representation of surface sites: The clay edge consists of silanol and aluminol groups. Spectroscopy suggests that mainly the latter are involved in radionuclide binding, whereas silanol groups react mainly with $H^+$ (Dähn et al., 2003).
    - It is clearly established (see examples in NEA, 2005) that acid-base reactions and radionuclide sorption can be modeled using a simplified representation of the clay edge based on generic surface sites (">SOH"). Most models are based on this concept.
    - A smaller group of TSMs uses silanol and aluminol groups. Most of these models, however, approximate edge site behavior by taking protolysis constants directly from silica and aluminum oxides. This may introduce large errors, as shown in e.g. NEA (2005). The modeling of actual silanol and aluminol behavior would need spectroscopic information that is not available for most systems.
- Type of EDL correction term (if any) for the edge surface reactions (see section 2.2.3 below)

Because sorption in clay-rich substrates is normally dominated completely by different clay minerals (metal oxides, organic coatings, etc. are usually not important), the purely empirical top-down (GC, see NEA, 2005) models are practically never used for clays.

In summary, the experience gathered by various groups during the last 1-2 decades suggests that relatively simple (traditional) surface complexation/ion exchange models are best suited for modeling radionuclide sorption on different clays and clay rocks. Where required, these models can be combined in a component additivity approach. MUSIC-type models are emerging as valuable tools for elucidating details of the interaction of simple ions with clay surfaces, but the available database does not allow to parameterize such complex models for most of the relevant applications. They also do not necessarily offer a better performance when the calculation of $K_d$ is the main concern.

### 2.2.3 EDL models

The surface complexation models for clay edge site reactions are often combined with an EDL correction model (this needs to be distinguished from EDL models used to calculate electrostatic effects caused by the permanent layer charge).

In a surface complexation model, the EDL term is a correction factor applied to the respective surface equilibrium constants, it is in that sense similar to an activity correction model for aqueous equilibria. The most common EDL models are listed below (details are given in many surface or aquatic chemistry textbooks, such as Stumm and Morgan, 1996; see also Westall and Hohl, 1980; NEA, 2005):

1. DLM (Diffuse Layer Model)
2. CCM (Constant Capacitance Model)
3. TLM (Triple Layer Model), including BSM variant (Basic Stern Model)
4. CD (Charge Distribution, typically combined with MUSIC-model)
5. NEM (Non-Electrostatic Model)

Models 1-3 represent variations of the same Gouy-Chapman model which describes the decrease of an electric potential and the associated concentration profiles of ions from a charged surface to the bulk solution. Somewhat special cases are the charge distribution model, where the charge of a species can be distributed over different water layers (taking into account the coordinative environment of different ions and the water structure) and the so-called non-electrostatic model. The latter does not consider any correction factor for the surface equilibrium constants (roughly equivalent to neglecting activity corrections in aqueous chemistry).

Nearly all of the radionuclide sorption models for clays developed so far are based on the simpler types of EDL-terms (DLM and to a lesser degree CCM) or on the NEM approach. The TLM and BSM have the disadvantage that they are specific to a given background electrolyte which requires re-calibration in cases of model applications to systems with a background electrolyte different from that used for model parameterization.

## 3. Selection of TSM design for the ISD model/database development

The selection of the basic model design for the development of TSMs for different RNs within the ISD model/database development is linked with the foreseen model application. The final goal for the TSMs is their application to relevant substrates (which may be directly relevant for HLW disposal but also for related research activities). Based on the presently foreseen strategy for future HLW disposal in Japan, different clay-rich materials are included as relevant substrates in the ISD database development:

- compacted bentonite as buffer and backfill material, and
- various argillaceous rock types as potential host formations for waste as well as for URLs engaged in related research.

The final goal of TSM applications to disposal-relevant substrates can include several specific objectives:

- Interpretation and planning of
    - laboratory, batch-type sorption experiments to determine radionuclide $K_d$,
    - diffusion experiments,
    - migration experiments at a larger scale (e.g., in a URL).
- Prediction and support of radionuclide $K_d$ values for PA-specific conditions, which may include
    - interpolation in case of radionuclides with a good base of sorption data,
    - but also extrapolations and "blind" predictions in case of little researched elements.

### 3.1 Selection of surface species

At a very general level, the selection of surface species was oriented along the expected speciation of a given radionuclide in solution. In the earlier stages of the present modeling program, surface reactions were typically formulated assuming initially only the most simple surface reaction (which may be viewed as a simple exchange of $H^+$ vs. $M^+$ or $M^{2+}$, see Dzombak and Morel, 1990; NEA, 2005):

$$>SOH + M^{2+} = >SOM^{+} + H^{+} \quad (3.1)$$

and adding more species only if required due to an unsatisfactory fit to the data.

Subsequently, the modeling procedure was changed to initially assuming a full suite of surface hydrolytic species (e.g., $>SOHM^{2+}$, $>SOM^{+}$, $>SOMOH$, $>SOM(OH)_2^{-}$ in case of a divalent metal ion), which can be interpreted as sorption of the metal ion as formulated in eq. (3.1), followed by protonation or deprotonation of the surface complex as a function of pH. After an initial model run fit using FITEQL, the less important surface species were then deleted for further fitting calculations to make the model as simple as possible.

This change in modeling strategy was based on the observation that 1-species models do in nearly every case not allow to achieve a reasonable fit to the experimental data. This observation is perfectly consistent with past model experience (Dzombak and Morel, 1990; Bradbury and Baeyens, 1997, 2005) which shows that sorption edges that do not have a sharp slope (as in case of a simple oxide) but extend over a relatively wide pH-range (as in case of clay minerals) can often only be modeled by use of either several surface species or several surface sites. As discussed above, the present modeling is based on only one type of surface site.

It should be noted that possible choices of surface species were further restricted by limiting stoichiometries to the formation of one-to-one (1:1), monodentate and mononuclear surface complexes. While it is possible that better models could be developed by also considering 1:2 or 2:1 stoichiometries, this was not tested, for the following reasons:

- Bi- or multinuclear surface complexes are only expected to be relevant at fairly high surface loading, in analogy to aqueous complex formation. Considering that radionuclides will typically be present at trace concentrations, this type of complexes seems not to be relevant.
- Bidentate surface complexes are thermodynamically not well defined (they are highly conditional, their value is dependent on the S/W ratio, see Sverjensky, 2003).
- In the absence of clear experimental evidence, the introduction of more complex stoichiometries seems not to be warranted.

## 3.2 Selection of TSM design

The basic clay-water interaction model as well as all radionuclide sorption models considered in the ISD model/database development so far correspond to the same basic TSM design. This choice was made initially in the sense of a working hypothesis, and was retained up to now on the basis of the on-going parameterization of radionuclide sorption models.

The basic selected design considers ion exchange at the siloxane surface and edge surface protolysis and complexation. The SC-model is a 1-site, 2-pK model, including a diffuse layer (DL) correction term.

This choice is to a large degree based on the goals of the ISD model/database development and on the properties of clay-rich substrates briefly discussed above. Each choice regarding model design and general approach is briefly discussed below.

- **Use of an identical TSM structure for both clay-water interaction and radionuclide sorption models:** The initial choice to use an identical TSM structure for both clay-water interaction and radionuclide sorption models follows directly from the need to calculate both porewater composition and radionuclide $K_d$, especially in case of bentonite. Only the present approach allows a simultaneous calculation of both (which would not be possible in case of different model designs for clay-water interaction and sorption). This approach would further allow to calculate $K_d$ for several radionuclides (and main elements) simultaneously and thus also the treatment of competitive effects.
- **Combination of ion exchange and surface complexation:** This is a common approach for clay minerals; it is required to address both types of processes.
- **Use of generalized edge surface groups:** A simple model using generalized edge surface groups (">SOH") was preferred over a possibly more mechanistic model using silanol and aluminol sites for the following reasons (see also section 2.2.2):

  - There is isolated spectroscopic evidence (e.g., Dähn et al., 2003) that Ni and Th are bound only to the aluminol groups, and that the silanol groups are only involved in the binding of $H^+$. However, this is not universally established and not reflected in most of the published models for clay minerals. Further, a much more complex model (including a total of 27 site types, cf. Tournassat et al., 2004) would need to be constructed when the detailed atomic structure of the edge surface is considered (including the different possibilities of isomorphous substitution).
  - On the other hand, several (empirical) models (e.g. Zachara and McKinley, 1993; Turner et al., 1998) postulate the binding of radionuclides to both silanol and aluminol sites, using silica and Al-oxide as analogs. However, the acid-base characteristics of these oxides do not appear to be a good representation of the clay edge surface (NEA, 2005).
  - In particular the electrostatic effects in narrow pores, and possibly also the presence of other charged mineral surfaces (mainly silica), is likely to influence the acid-base behavior of individual edge surface groups to some degree. Considering further the uncertainties regarding mechanistic details and the general uncertainties of TSM applications to compacted clay, a distinction of structurally different edge surface sites does not seem to be meaningful.
- **Use of only one type of generalized edge surface groups (simple 1-site SCM):** Similar to the previous point, an initial decision was made to try and avoid the introduction of more than one type of generic sites (such as the weak/strong sites used by e.g. Dzombak and Morel, 1990, Bradbury and Baeyens, 1997). This preference for a simple 1-site model is based on the anticipated use of TSMs at high S/W ratios. Strong/weak site models may include a small fraction of high-affinity sites to define the sorption maximum in a pH-edge, while the slope of the curve is fitted by adjusting the affinity of the RN to the weak site (at a lower value). See section 3.3.1 for further details.
- **Use of a diffuse layer model (DLM) as electrostatic correction term:** The choice of a simple EDL correction term was made for several reasons:
  - The contribution of a pH-dependent edge charge to the overall clay charge is well established and can be seen in e.g. electrophoresis experiments (cf. Bolt, 1979). Since such a charge behavior influences the binding of metals and other species, the use of a surface complexation model with EDL-correction was preferred over the use of a non-electrostatic model.
  - At the same time, the use of complex EDL-terms was avoided. TLM/BSM are specific to a given electrolyte, which makes the application of a calibrated model to a system with a different or mixed electrolyte difficult or impossible. The CD-type models are too complex, and too much based on detailed information on surface structures, to justify their use for compacted materials.
  - Of the remaining choices (CCM and DLM), the DLM model was preferred because it does not introduce any additional adjustable TSM parameters.

- Finally, for very pragmatic reasons, the chosen EDL-correction term should be easy to handle with common speciation codes.

**In terms of overall model characteristics**, the selected TSM design should be suitable for

- applications to different clays in contact with different groundwaters;
- applications to compacted systems.

Because of the geochemical uncertainties that are characteristic for these systems and the required approximations (especially for compacted systems), this means that the selected TSM

- should not be very sensitive with regard to approximations in the clay surface structure;
- should be based on macroscopic information, such as titration and radionuclide sorption data rather than on microscopic data and detailed information on surface structure.

Both of these requirements logically lead to simplified models rather than a very detailed and mechanistic approach. The selected TSM is therefore a compromise between empirical simplicity and robustness vs. chemical detail.

**In terms of model performance**, the choice of

- using the same model design for all applications (clay-water interaction, sorption of several radionuclides);
- using a 1-site model (rather than an empirically fitted strong/weak site model, see section 3.3.1)

means that in some cases the mathematical goodness of the model fit to a specific set of radionuclide sorption data may receive 2nd priority in comparison to overall consistency and simplicity.

## 3.3 Example: Ni sorption

This section serves to illustrate the general concepts discussed in previous sections:

(a) First, the choice of a simple 1-site model is illustrated using the strong/weak site model of Bradbury and Baeyens (2005).

(b) Second, the selection of surface species is illustrated in the case of the Ni model developed.

### 3.3.1 Choice of 1-site model

For the reasons explained above (section 3.2), the use of generic SOH sites was preferred over the use of silanol/aluminol sites or the multi-site model by Tournassat et al. (2004).

Bradbury and Baeyens (1997, 2005) developed a flexible and successful model using

(c) a simplified picture of the clay edge with generic SOH sites, on one hand,

(d) but using three types of empirically fitted sites: 1 strong and 2 weak sites

For the present model, a simple 1-site model was chosen initially, for the following reasons:

1. Weak/strong or other empirically fitted SOH types are not based on any independently determined or confirmed surface characteristics.
2. Once the approach of using a simplified empirical model is selected, it seems illogical to go back and complicate the model by introducing different types of SOH sites.
3. For radionuclide sorption in the presence of trace concentrations, only the strong sites are relevant anyway; this is illustrated below (Figure 3.1). In the Bradbury and Baeyens (2005) model, the weak sites are only needed to describe Ni sorption at high surface loading (i.e. at high Ni and low solid concentrations).

Figure 3.1 shows the distribution of sorbed Ni on the strong and weak sites used by the model of Bradbury and Baeyens (2005) in the presence of 1 g/L of montmorillonite. It can be seen that a relatively small change in total Ni concentration leads to a significant change in the distribution of Ni sorbed to the strong and weak sites:

(a) At low total Ni ($1.3 \times 10^{-7}$ M), the concentration of Ni sorbed to the weak site is at least an order of magnitude less than the concentration of Ni sorbed to the strong site. Under these conditions, a total of $2.2 \times 10^{-6}$ moles/L of strong sites is present, which is significantly higher than the total Ni concentration. The distribution of Ni between strong and weak sites is therefore given by the equilibrium constants for the surface species and is not limited by the amount of sites available. If extrapolated to higher S/W ratios, including compacted conditions, the distribution of Ni surface species will stay approximately constant.

(b) At a concentration of total Ni ($5.0 \times 10^{-6}$ M) that is slightly higher than the concentration of strong sites, the availability of the strong site becomes limiting, and the weak site becomes important for Ni sorption in the pH region of about pH 8-9. With higher Ni concentrations, this effect would increase.

This comparison of conditions (a) and (b) shows that a generic 2-site model using strong/weak sites can be sensitive with respect to the ratio of strong site and radionuclide concentration (in detail, this dependency will depend on the ratio of strong to weak sites). With regard to the present application, the following considerations are relevant:

- If the weak sites are actually needed for model parameterization, care must be taken when applying the model to different S/W ratios and radionuclide concentrations. A model where the sorbed radionuclide is distributed over strong/weak sites at low solid concentrations (as are typical for batch experiments) will effectively turn into a 1-site model at high solids concentrations (there will be a high enough amount of strong sites available to render the weak sites irrelevant).
- On the other hand, if the weak site is not relevant during model parameterization, it will have no effect on the goodness of it and will be irrelevant from the beginning.

**In summary**, the weak site is either important to describe radionuclide sorption and makes the model performance dependent on S/W ratio and radionuclide concentration, or it is not important and may then be abandoned. The latter case corresponds to low surface loading, which is the relevant situation for radionuclide sorption under PA conditions.

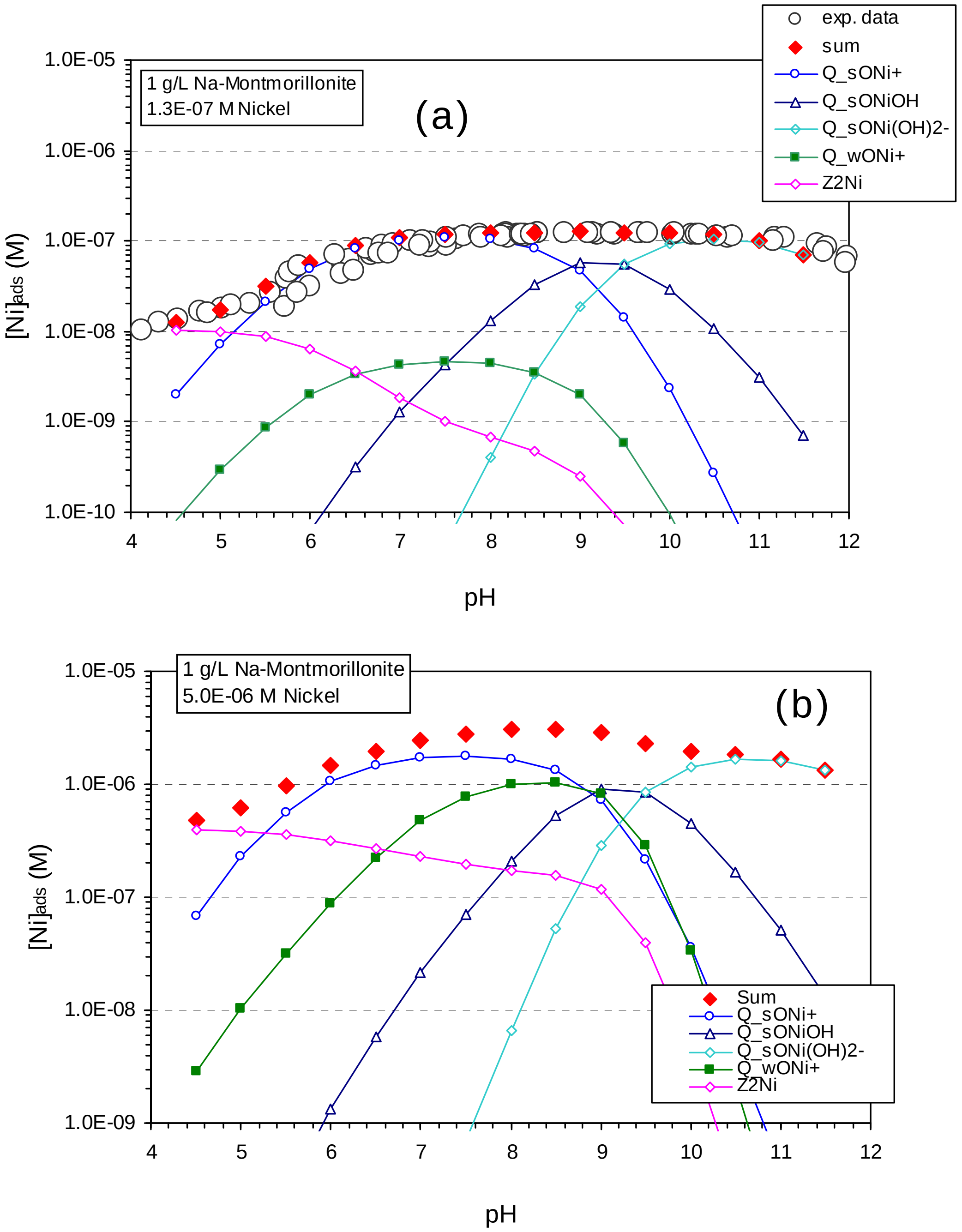


Figure 3.1: Distribution of Ni surface species using the model of Bradbury and Baeyens (2005). (a) corresponds to the experimental conditions of Baeyens and Bradbury (1997), (b) to hypothetical conditions with higher Ni concentration. The species distribution in compacted clay corresponds approximately to (a).

### 3.3.2 Surface species

As pointed out in section 3.1, the selection of surface species is typically a matter of decision. To evaluate the plausibility of the surface species chosen in the example discussed below, the acid-base speciation of the clay surface as well as the aqueous speciation of Ni is illustrated first.

The edge surface speciation according to the basic clay-water interaction model JAEA09/a, developed in Tachi et al. (2010), is shown in Figure 3.2 for the conditions of the H12 titration experiments (Shibutani et al., 1999) and in Figures 3.3 and 3.4 for the three different NaCl conditions of the titration experiments by Bradbury and Baeyens (1997), i.e., in the absence of Ni. At I = 0.1 M, the chemical conditions in both systems are nearly identical, and the only difference lies in the S/W ratio. The edge surface properties of the SWy-1 montmorillonite used by Bradbury and Baeyens (1997) are assumed to be identical to those of the purified Tsukinuno montmorillonite used by Shibutani et al. (1999).

The speciation of dissolved Ni in the sorption experiment at I = 0.1 M by Bradbury and Baeyens (1997) is shown in Figure 3.5. Note that this species distribution corresponds to the use of the thermodynamic data by Hummel et al. (2002, Nagra/PSI TDB). Use of another set of thermodynamic data, such as the NEA-TDB (Gamsjäger et al., 2005) would lead to a different calculated distribution of Ni species.

It can be seen from these figures that in the absence of sorbing radionuclides, the clay surface tends to be largely protonated below pH ~ 5, and to be deprotonated (hydrolyzed) above pH ~9. This is relatively similar to the protolysis behavior of the strong and weak-1 site in the model of Bradbury and Baeyens (1997, 2005).

On the other hand, Ni forms positively charged (protonated) aquo ions up to pH ~9 in the absence of complexing ligands (other than $H_2O$), whereas negatively charged species (hydrolytic species or deprotonated aquo ions) become dominant only at pH > 11.5.

This comparison between surface protolysis and Ni hydrolysis in solution shows that the tendency of Ni to form positively charges species even at elevated pH cannot be transferred directly to surface complexation according to the JAEA09/a model, where a negatively charged surface starts to prevail above pH 9 or so. Therefore, there is a wide pH range where positively charged, neutral, or negatively charged Ni surface species are possible. This is a rather typical situation for the selection of surface species.

In such a case, surface species can be selected on the basis of their importance for sorption (e.g., based on FITEQL results using a range of surface species and omitting the less important species). This is especially true when a simplified model design is used, as in the present approach. If possible, this should be followed by a check of the reasonableness of the selected species.

As can be seen from the surface speciation as calculated by the JAEA09/a_Ni1 model (Figure 3.6), the predominance region of the finally selected Ni surface species agree approximately with their corresponding aqueous species:

- the neutral surface complex >SONiOH corresponds to the uncharged aqueous species $Ni(OH)_2$;
- the single positively charged surface complex $>SONi^+$ is omitted, it is also not very important in the hydrolysis of Ni;

- the peak of the double positively charged surface complex $>SOHNi^{2+}$ corresponds to the high-pH end of the predominance region of the $Ni^{2+}$ ion; at lower pH, ion exchange is becoming more important.

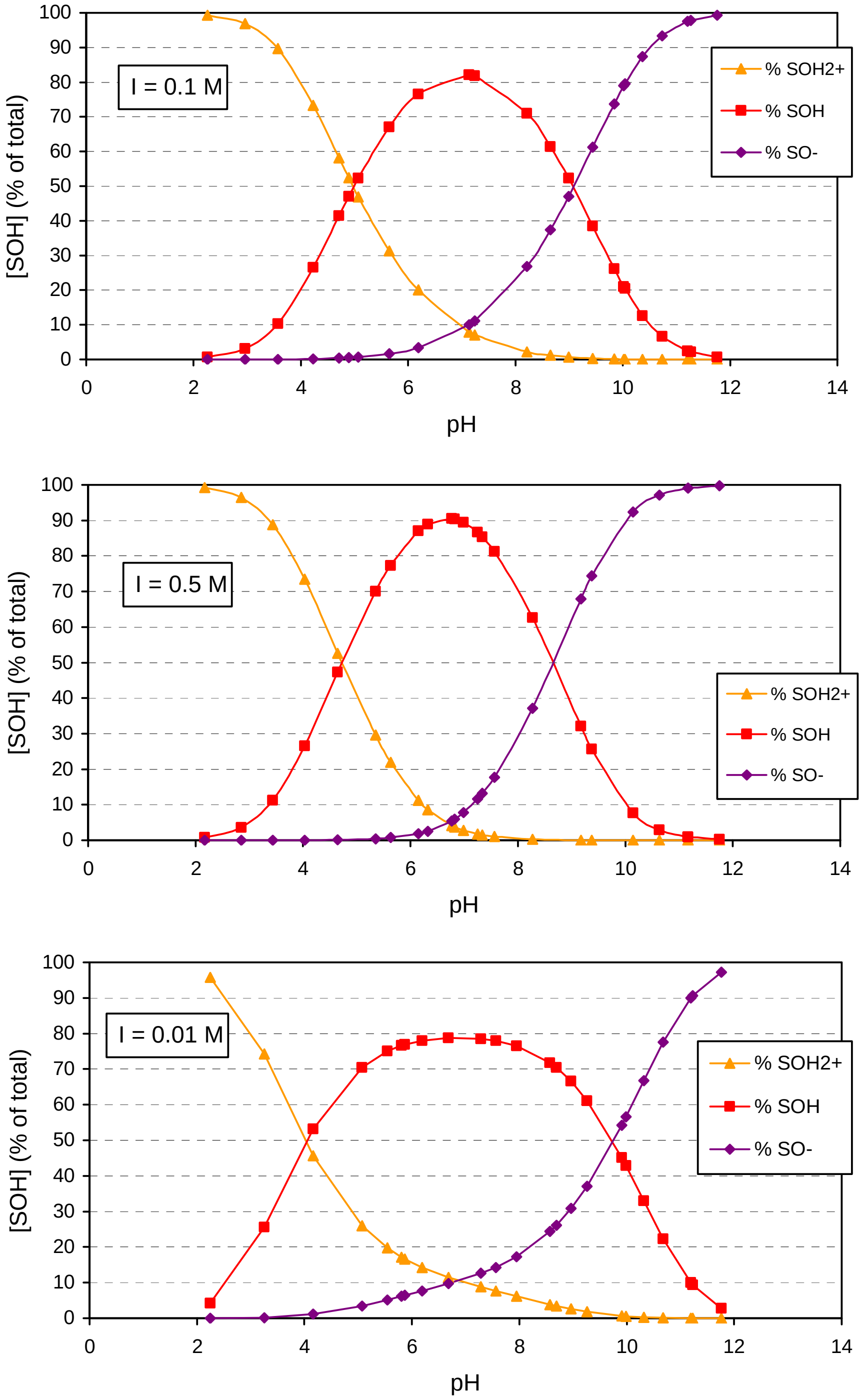


Figure 3.2: Acid-base speciation of the edge surface of montmorillonite under the three different NaCl conditions of the H12 titration experiments (S/W = 6.3 g/L, Shibutani et al., 1999), according to the basic clay-water interaction model JAEA09/a (Tachi et al., 2010).

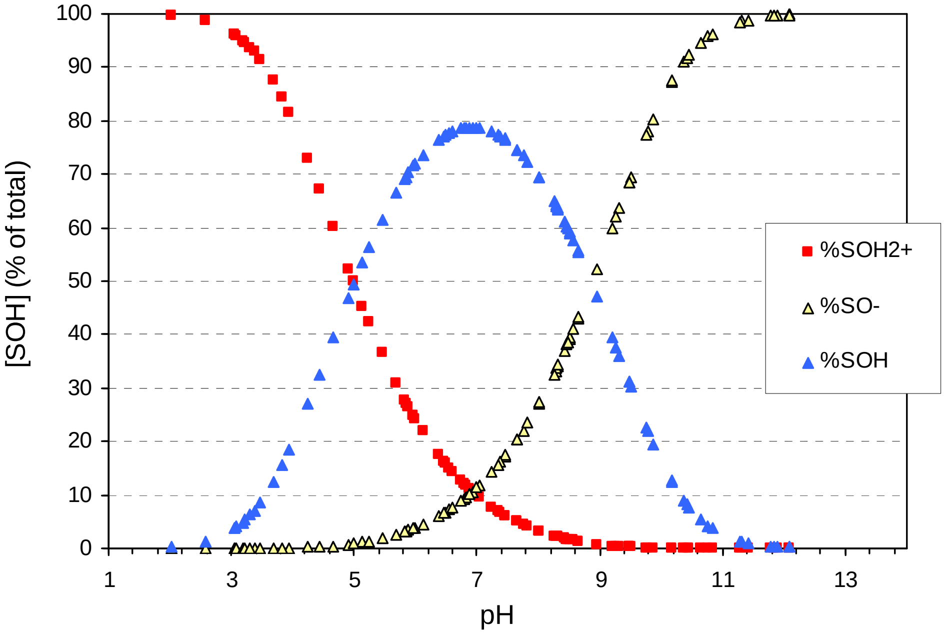


Figure 3.3: Acid-base speciation of the edge surface of montmorillonite under the conditions of the titration experiments by Bradbury and Baeyens (1997, S/W = ca. 1 g/L, 0.1 M $NaClO_4$), according to the basic clay-water interaction model JAEA09/a.

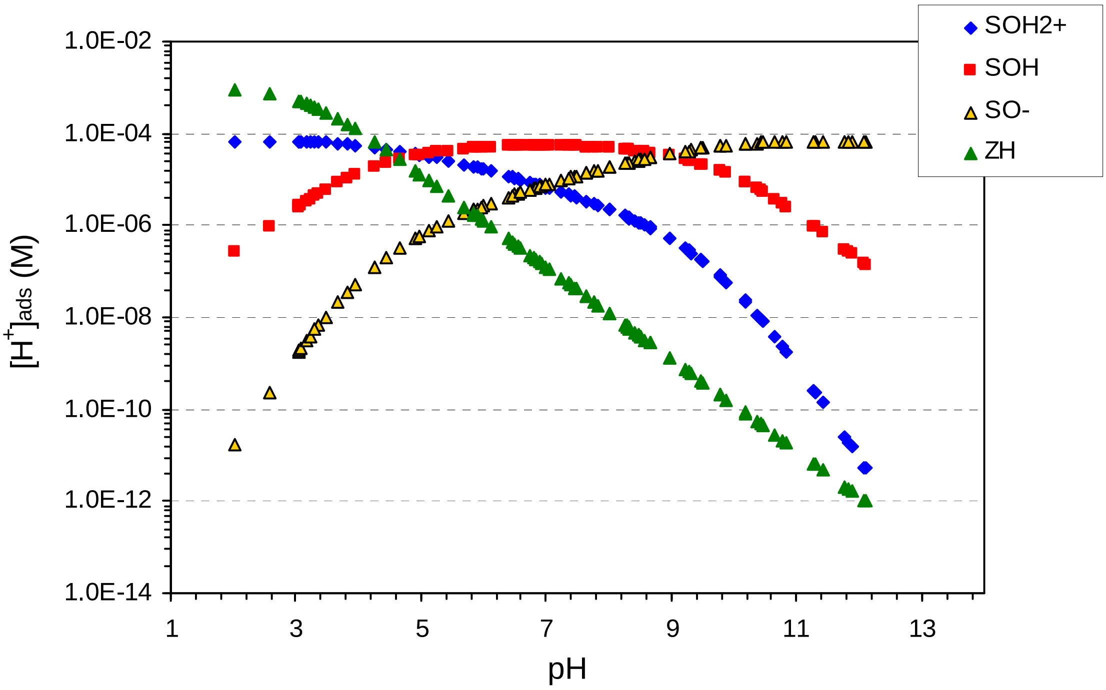


Figure 3.4: $H^+$ distribution on the edge and siloxane surface of montmorillonite under the conditions of the titration experiments by Bradbury and Baeyens (1997, S/W = ca. 1 g/L, 0.1 M $NaClO_4$), according to the basic clay-water interaction model JAEA09/a.

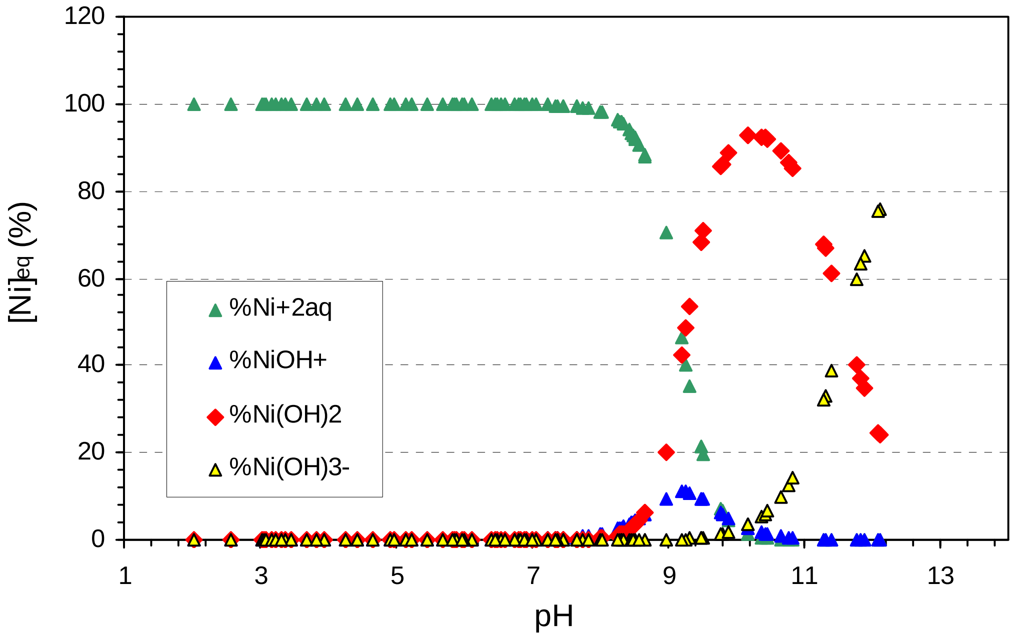


Figure 3.5: Speciation of dissolved Ni under the conditions of the sorption experiment by Bradbury and Baeyens (1997; S/W = ca. 1 g/L, [Ni] = 1.3E-07 M, 0.1 M $NaClO_4$), according to the thermodynamic data in Hummel et al. (2002).

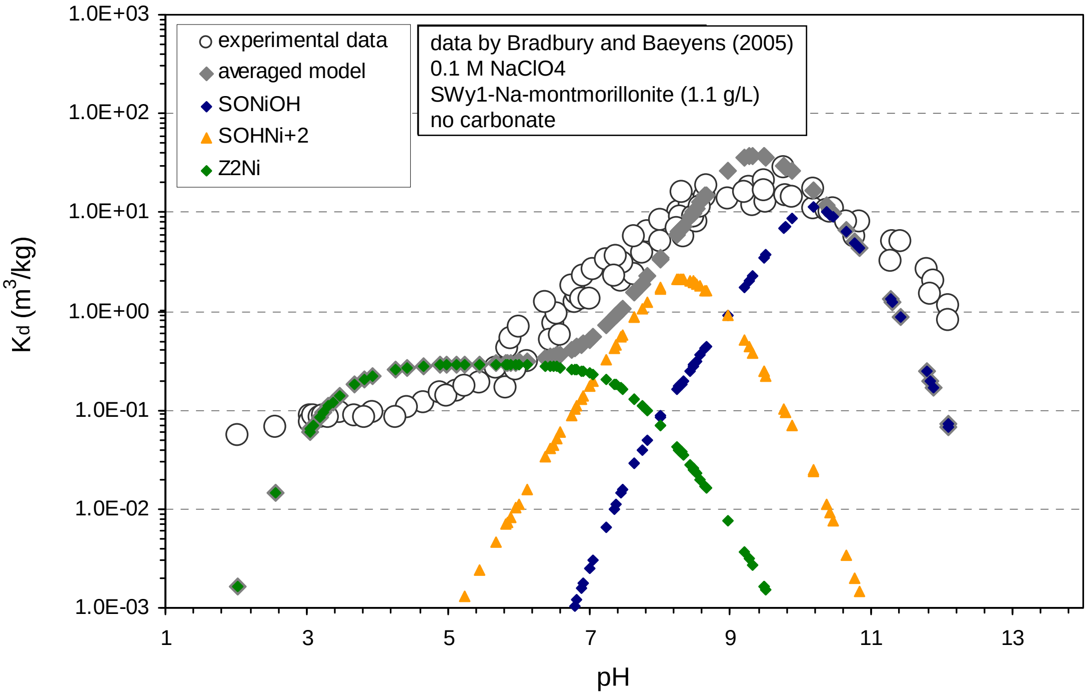


Figure 3.6: Result of the sorption model for Ni (JAEA09/a_Ni1). See section 5.2 on Ni model for model description.

## 4. Uncertainties relevant in TSM applications

When TSMs are being used for the derivation of $K_d$ values for radionuclides (or in case of any other model application), it is important for the user (including implementers and regulators) to be informed with regard to the uncertainties associated with the calculated values. In case of the present application, uncertainties of calculated $K_d$ values can originate from two fundamentally different sources (see NEA, 2005; Ochs et al., 2006):

- uncertainties associated with the sorption model itself (including conceptual uncertainties as well as uncertainties of surface complexation constants and other TSM parameters);
- uncertainties in the application conditions (such as the groundwater composition).

This is schematically shown in Figure 4.1. This illustration shows further that the overall error associated with the result of a TSM calculation can be influenced by a large number of factors.

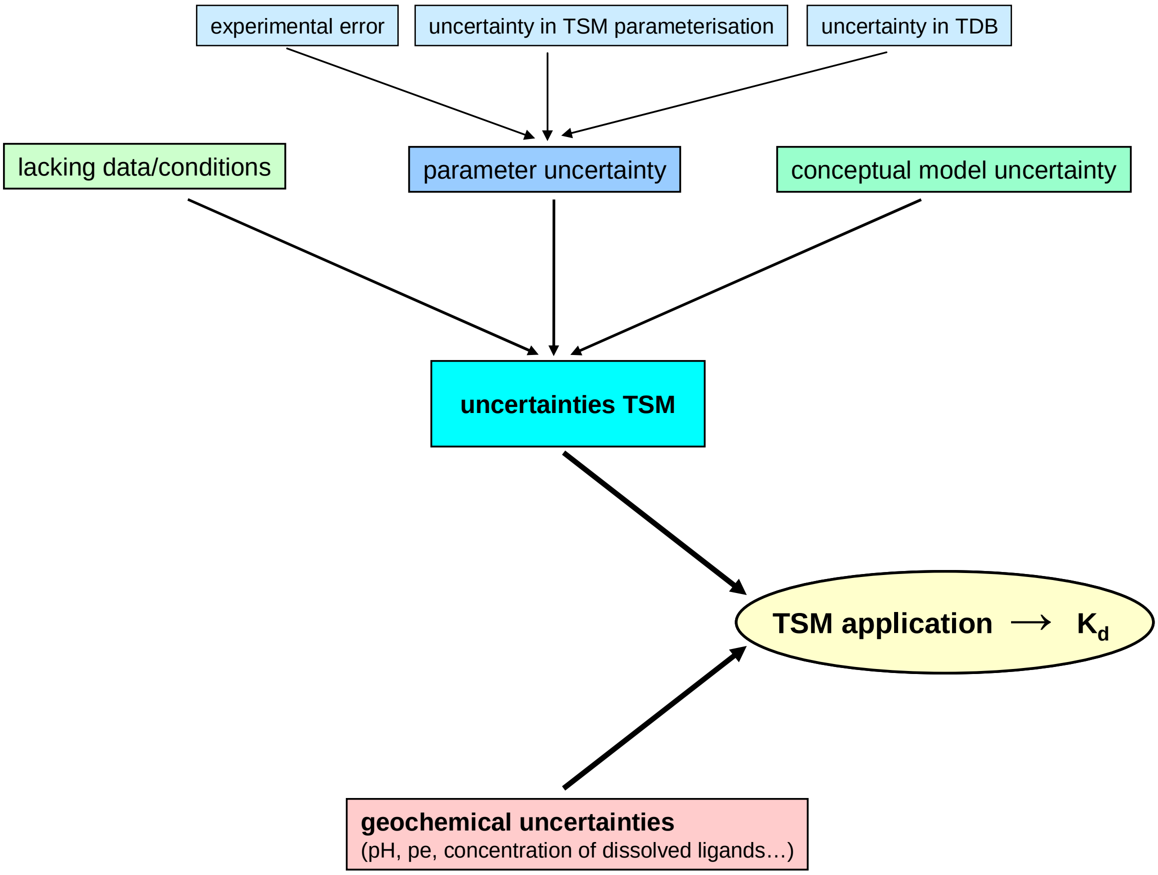


Figure 4.1: Illustration of uncertainties flowing into the total uncertainty of a calculated $K_d$ value. For simplicity, the geochemical uncertainties are not listed in detail.

The assessment of model uncertainties is further complicated by the fact that not all model uncertainties are quantitative in nature. In addition, the meaning of the term "model uncertainties" is not always clearly defined. Therefore, section 4.1 gives an overview of uncertainties associated with TSMs and methods of taking them into account.

## 4.1 TSM uncertainties: general aspects

### 4.1.1 Overview, types of TSM uncertainties

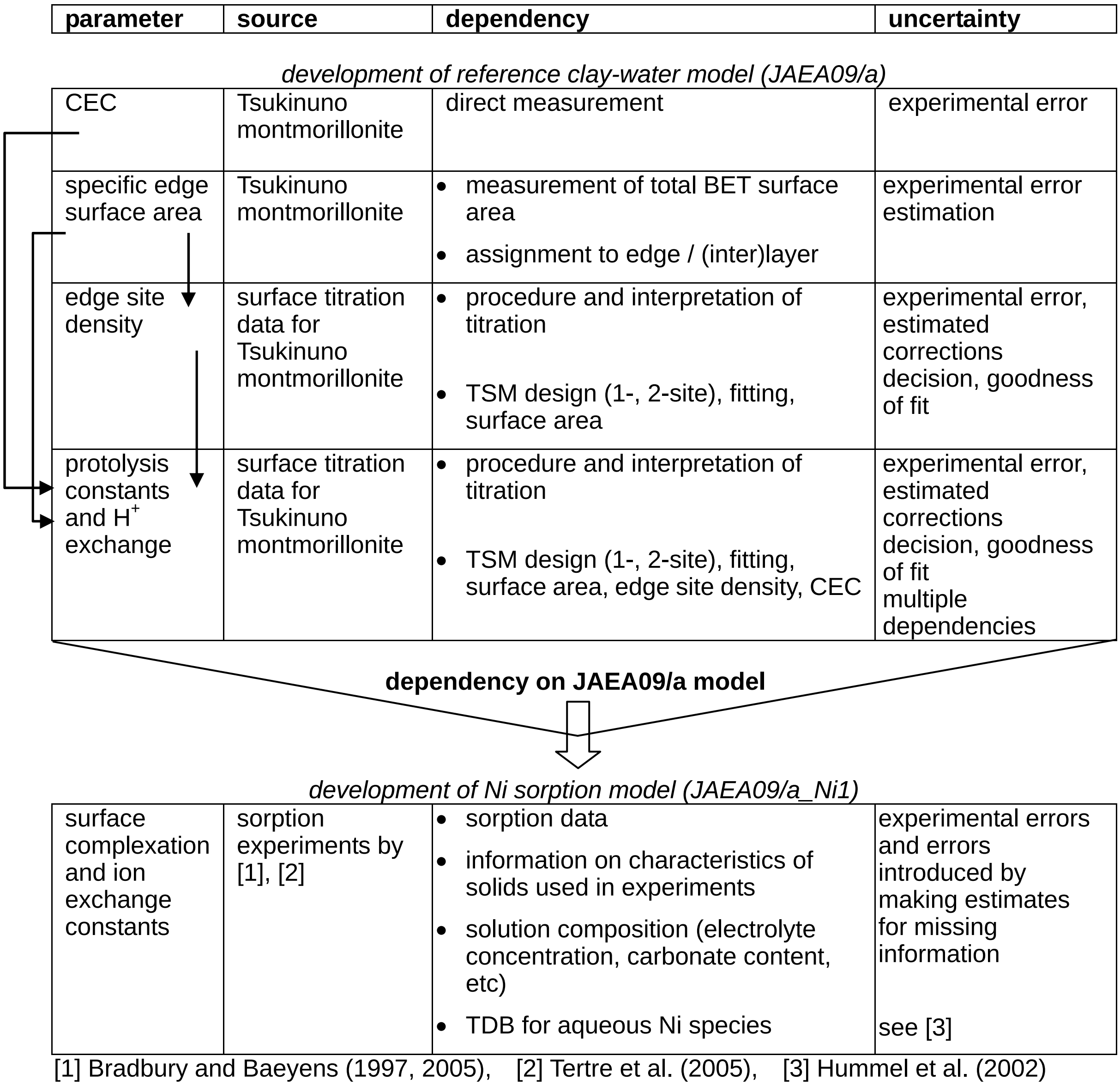
When considering the meaning of the global uncertainty associated with a TSM that is used in support of PA, it becomes clear that this uncertainty should represent the overall degree of confidence with regard to the calculated results representing the true values. This includes a much wider range of information than, for example, simple measures for the goodness of fit of a model calculation to a particular dataset. At a fundamental level, the following sources contributing to overall TSM uncertainties can be distinguished (see also Figure 4.1), conceptual model uncertainty and uncertainties in the actual TSM parameters:

- ***Conceptual model uncertainty*** refers to any uncertainty as to whether the chosen TSM design represents an appropriate formulation of the chemical equilibrium problem to be solved. This uncertainty therefore includes questions (or lack of confidence) regarding the choice of number and types of surface sites, surface species, and EDL terms. This type of uncertainty is not quantitative (numerical), but possible numerical effects can be evaluated by applying several model designs to a given problem.
- ***Parameter uncertainty*** refers to the numerical uncertainty of TSM parameters, including
    - CEC
    - specific surface area
    - density of clay edge sites (>SOH)
    - edge site protolysis and $H^+$ ion exchange constant
    - surface complexation and ion exchange constants for any given RN

  An overview of the sources for uncertainties in these parameters and their interdependencies is illustrated in Figure 4.2. Parameter uncertainties may originate from two types of errors:
    - Type 1: errors in the underlying data, including
        - measurement errors regarding mineralogical and surface properties of the substrate (CEC, surface area);
        - experimental errors of surface titration and RN sorption data;
        - underlying TDB for aqueous species.
    - Type 2: errors introduced in the numerical fitting of TSM parameters to original experimental data (goodness of fit).
- ***Uncertainty due to lacking data (incomplete calibration)*** refers to two possible aspects:
    - Within a narrowly defined set of conditions (for example, Ni sorption on pure montmorillonite at pH 2-12 and in the presence of 0.01-0.1 M $NaClO_4$), data may be

missing that would be needed for a complete parameterization of the model, such sorption edges at higher ionic strength, different S/W ratios and Ni concentrations.

- When a wider set of conditions (e.g. bentonite in contact with groundwater) is of concern, data are typically missing for a range of relevant conditions, such as sorption in the presence of carbonate, sulfate, etc.



*development of reference clay-water model (JAEA09/a)*

| **parameter** | **source** | **dependency** | **uncertainty** |
|---|---|---|---|
| CEC | Tsukinuno montmorillonite | direct measurement | experimental error |
| specific edge surface area | Tsukinuno montmorillonite | • measurement of total BET surface area<br>• assignment to edge / (inter)layer | experimental error estimation |
| edge site density | surface titration data for Tsukinuno montmorillonite | • procedure and interpretation of titration<br>• TSM design (1-, 2-site), fitting, surface area | experimental error, estimated corrections decision, goodness of fit |
| protolysis constants and $H^+$ exchange | surface titration data for Tsukinuno montmorillonite | • procedure and interpretation of titration<br>• TSM design (1-, 2-site), fitting, surface area, edge site density, CEC | experimental error, estimated corrections decision, goodness of fit<br>multiple dependencies |

**dependency on JAEA09/a model**

*development of Ni sorption model (JAEA09/a_Ni1)*

| **parameter** | **source** | **dependency** | **uncertainty** |
|---|---|---|---|
| surface complexation and ion exchange constants | sorption experiments by [1], [2] | • sorption data<br>• information on characteristics of solids used in experiments<br>• solution composition (electrolyte concentration, carbonate content, etc)<br>• TDB for aqueous Ni species | experimental errors and errors introduced by making estimates for missing information<br>see [3] |

[1] Bradbury and Baeyens (1997, 2005), [2] Tertre et al. (2005), [3] Hummel et al. (2002)

Figure 4.2: Overview of the various uncertainties in clay-water model (example JAEA09/a) and radionuclide sorption model (JAEA09/a-Ni1) and their sources and inter-dependencies.

Before the various sources of uncertainties in TSM parameters are discussed in section 4.1.3, a brief overview of published approaches to the definition of TSM uncertainties is given below.

### 4.1.2 State of the art in addressing uncertainties

Despite its importance for confidence in sorption modeling, very little information on the treatment of TSM uncertainties is available in the literature. It also has to be admitted that very little is known with regard to the interrelations of the various uncertainties and how, for example, a given uncertainty in the surface site density of a mineral may influence the uncertainty in equilibrium constants. Similarly, it is not well established how uncertainties in model parameters translate into uncertainties in $K_d$. Accordingly, both of these issues are an important subject of the on-going Phase III of the NEA Sorption Project (NEA, 2011).

Even though the amount of available literature and information is very limited, it is possible to distinguish two completely different approaches:

***Approach (a)*** This approach is focused on uncertainties of TSM parameters with respect to the modeling of one particular dataset (or in some cases several sets of data corresponding to identical conditions). In these cases, typically some type of representation for the statistical uncertainty resulting from the fitting procedure (e.g., standard deviations of equilibrium constants calculated by FITEQL, or confidence intervals based on these values, etc.) is used as uncertainty estimate. This approach is typically used by researches interested in obtaining the best possible fit with a pre-selected model design; examples are Westall and Hohl (1980), Goldberg (1991), Dzombak and Morel (1990).

***Approach (b)*** A completely different approach is used when the goal is an evaluation of the overall usefulness of a TSM with regard to the prediction of sorption in a variety of systems.

- In these cases, the direct comparison of predicted vs. calculated $K_d$ is used for model evaluation, whereas statistical measures (such as goodness of fit or uncertainty of individual surface equilibrium constants) are not considered to be very relevant. Examples are Bradbury and Baeyens (1995) and NEA (2005).
- While not stated explicitly, the neglect of statistical measures is possibly based on the assumption that the models are applied to systems whose conditions are qualitatively different from those of model calibration (i.e., different clay minerals, different solution composition). The uncertainty introduced by this type of extrapolation is not well reflected by statistical measures that are derived from model calibration.

The first quantitative comparison of different TSMs was done by Westall and Hohl (1980): their modeling shows that different TSMs may describe a given set of experimental data equally well (i.e., TSMs are non-unique, as pointed out again by NEA, 2005). Westall and Hohl (1980) also pointed out that the parameters derived for the different models cannot be compared directly (even though the experimental data may be equally well described by different models), i.e., the constants are model-dependent.

Goldberg (1991) investigated and illustrated some of the interdependencies between model parameters indicated in Figure 4.2. She observed that different values for surface site density result in different choices of surface species for the adsorption of $MoO_4^{2-}$ when these are selected according to the goodness of fit parameter given by FITEQL (overall variance); i.e., different suites of surface species give the best fit depending on the accepted value for surface site density. It is also acknowledged that tests of the goodness of fit can only be compared among models when the number of optimized parameters is the same.

Dzombak and Morel (1990) conducted an extensive TSM development for the sorption of a number of elements on hydrous ferric oxide by re-fitting original experimental data. They describe in detail how the uncertainty information supplied by FITEQL may be used to derive some kind of uncertainty measure for final equilibrium constants and also illustrate the effect of the number of experimental data and their (assumed) uncertainty on the error calculated by FITEQL.

An extensive comparison of TSMs was performed in the NEA Sorption Project II modeling exercise (NEA, 2005). Because of the many factors influencing overall model performance (see Figure 4.1) and the fact that statistical measures of model parameters cannot be directly compared between different TSM designs, a simple (non-weighted), averaged comparison of predicted and experimental $K_d$ values was used

$$\text{overall TSM error} \quad = \quad \sum \left| \log \left(K_d \text{ predicted} / K_d \text{ measured}\right) \right| \times n^{-1} \qquad \text{(eq. 4.1)}$$

This allowed further to quantitatively compare TSMs that had been developed by using optimizations codes like FITEQL and models developed by fitting sorption curves by trial and error (using e.g. PHREEQC).

Bradbury and Baeyens (1997, more detail is given in their 1995 report) compared the suitability of different model designs for fitting their Ni sorption data on montmorillonite. Rather than relying on any statistical measure for the goodness of fit, they did the fitting by trial and error; i.e., compared calculated and experimental $K_d$ values. As fit criterion, they tried to optimize the ability of their model to describe multiple datasets. They further state that this ability of a model would be its ultimate measure of usefulness, because of the additional constraint exerted by requiring the model to fit several datasets. Models build only on one set of data even cannot be evaluated in this regard (because the model was fitted to only one dataset without further constraint).

### 4.1.3 Sources of uncertainties and relevance for TSM applications

As outlined in Figure 4.2, there are a number of adjustable TSM parameters, whose uncertainty is based on different sources of errors in each case, and whose numerical values (and thus, uncertainty) are interdependent. This makes a comprehensive discussion nearly impossible, and is the reason behind the fact that to date, no comprehensive error analysis on TSM parameters is available. A first step in this direction will be contained in the guideline book that will be the main deliverable of Phase III of the NEA Sorption Project (NEA, 2011). Figure 4.1 illustrates that the uncertainty of TSMs may arise from different sources (see also section 4.1.1):

The uncertainty of the actual TSM parameters is influenced by external (errors associated with experimental data and underlying thermodynamic data) and internal (numerical errors made in the fitting process) factors. When a numerical code is used for model parameterization, information on the uncertainty of TSM parameters can often be obtained. In the case of the well-known code FITEQL v.4 (Herbelin and Westall, 1999), the error reported for optimized equilibrium constants takes into account

- experimental error, if known;
- numerical error made in the fitting process (goodness of fit).

On the other hand, the uncertainty of the underlying thermodynamic data for aqueous species is not considered. Note that this uncertainty may be relevant, especially in the case of strongly hydrolyzing elements. Further, it is typically thought of as an uncertainty of the formation constants of aqueous species. However, more relevant may be the basic selection of species considered in a TDB (for example, the consideration - or not - of mixed hydroxo-carbonato complexes).

These uncertainties mainly flow into parameter uncertainty; i.e., are represented by the numerical error of a TSM parameter. They are of direct relevance and their interpretation is straightforward when a TSM is being applied under conditions that were included in the fitting process.

On the other hand, when a TSM is being applied to conditions that lie outside the range of model calibration, the question arises as to which type of uncertainties would be dominating the overall model performance:

- the parameter uncertainties as discussed above,
- the uncertainties originating from extrapolation; i.e., from the application of a TSM to conditions that were not considered in the model development.

This question is very difficult to address, for the following reasons:

- First, no detailed investigation has been conducted to date on this topic. The few studies available in the literature are concerned with limited aspects only (see section 4.1.2).
- Second, the uncertainties that may arise due to lacking experimental data and insufficient model parameterization are difficult to estimate (they cannot be directly quantified, as the experimental database is not available in the first place). The following, very general guidelines can be given:
    - This type of uncertainty will become more dominant as the degree of extrapolation increases. For example, consider a TSM that has been calibrated on the basis of sorption experiments performed in a simple Na-electrolyte in the absence of carbonate and in the pH-range 4-8. When this model is being applied to calculate $K_d$ at pH 9, but under otherwise identical conditions, it can be assumed that all governing sorption processes (competitive binding of RN to dissolved and surface-bound $OH^-$) are still included and that the error due to incomplete calibration will be small. On the other hand, if the same model is applied to pH 9 in a saline solution that also contains Ca and carbonate, several important processes may be missing and the error due to incomplete calibration may be dominating the overall error.
    - It can further be expected that a significant influence of this type of uncertainty is likely to increase with increasing complexity of the sorbing element's chemistry. Consider again the above situation. It can be easily imagined that in the extrapolative model application, more important sorption processes would be neglected in the case of actinides than in the case of Ni.

## 4.2 Possible representation of TSM uncertainties in the ISD model/database development

Following the above discussion, the question is how uncertainties in the present modeling context could be represented in the most useful way. It may be helpful to approach this question by first considering

- the available experimental database and the expected use of the models
- the actual methods available for model calibration.

Both of these issues are addressed in the following two sections, the approaches (a) and (b) for error representation introduced in section 4.1.2 are then re-considered and illustrated further below in section 4.2.3.

### 4.2.1 Experimental database and expected use of TSMs

The available database for the elements of concern in the ISD model/database development consists in most cases of only a few studies which had been in part obtained under different conditions and are therefore not entirely compatible. For example, in the case of some actinides, only one dataset might be available. Further, most of the available datasets were obtained on montmorillonite in the Na-form, in the presence of simple electrolyte solutions.

Based on the available data it is therefore not possible to calibrate the models directly with respect to the conditions relevant for their application; i.e., with respect to the sorption reactions that may be relevant in the presence of typical groundwater cations and anions.

There are also several inconsistencies in the experimental database. Relevant examples are the different datasets for Ni by Bradbury and Baeyens (1997, 2005) and Tertre et al. (2005). While both datasets appear to be of good quality, they are not compatible with each other: they show a different behavior in terms of sorption as function of pH (slope) and ionic strength (position of sorption plateau), see datasets A and C in Figure 4.3.

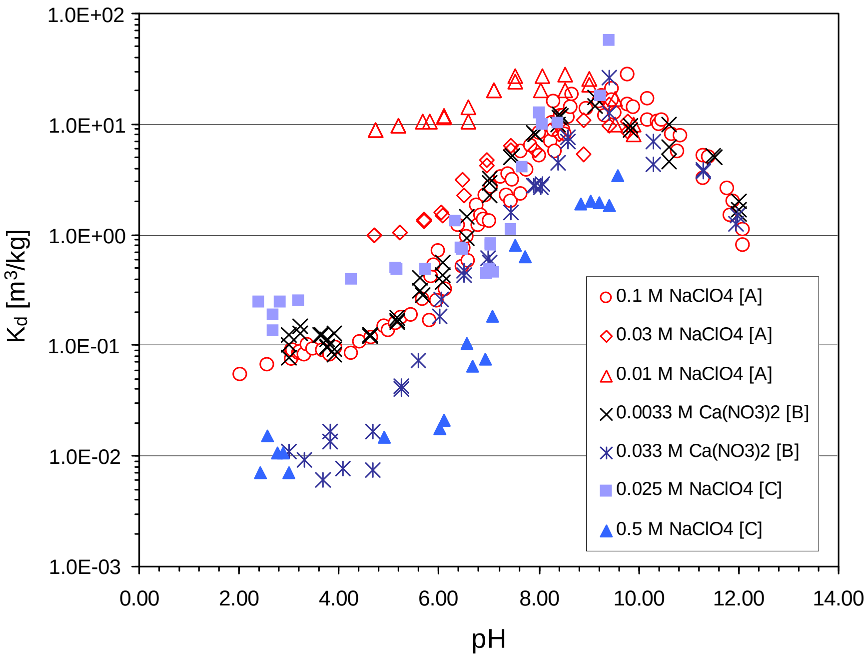


Figure 4.3: Overview of Ni sorption data on montmorillonite. [A]: Bradbury and Baeyens (2005); [B]: Bradbury and Baeyens (1999); [C]: Tertre et al. (2005).

This example shows that a model cannot describe both Ni datasets well. The uncertainty of TSM parameters (standard deviation, SD) calculated by FITEQL only represents an error estimate for model calibration by either one of these datasets, but FITEQL cannot take into account the overall uncertainty of Ni sorption as illustrated by both datasets.

### 4.2.2 Model calibration

#### 4.2.2.1 Overview of options

Basically, two different methods are available to optimize TSM parameters on the basis of original experimental data:

- use of a computer optimization routine;
- optimization of parameters through trial and error calculations.

Both types of approaches were utilized by a number of modelers in the NEA Sorption Project modeling exercise (NEA, 2005). The models developed so far for the ISD model/database development (Tachi et al., 2010) were parameterized using both methods where they appeared most appropriate. For automatic fitting, the code FITEQL, version 4 (Herbelin and Westall, 1999) was used. Both approaches are compared below in terms of their respective advantages and drawbacks, focusing on FITEQL in terms of computer codes:

***Computer optimization routine (example FITEQL):***

- These are typically based on a non-linear least squares error minimization method linked to a speciation program. The most well-known example for this type of code is FITEQL (cf. Herbelin and Westall, 1999). The use of FITEQL for the development of a sorption database (for hydrous ferric oxide) was promoted by Dzombak and Morel (1990).
- Such codes allow to optimize several parameters simultaneously (at least in theory). In practice, this is often not possible due to the numerical restrictions of this code. This requires the user to make subjective choices on the selection of parameters to be optimized, or on the data ranges to be considered, etc., which significantly impairs the objectiveness of fitting that FITEQL could theoretically offer.
- The optimization by FITEQL is less objective than one would expect, however, because fitting results are dependent on the error for the experimental data that has to be entered or assumed by the user (see also Dzombak and Morel, 1990; Altmaier et al., 2004). This is illustrated in Figure 4.4.
- FITEQL provides a quantitative measure for the goodness of fit and an estimated error (standard deviation, SD) for the optimized model parameters. However, the calculation of these values by FITEQL is highly dependent on the error estimates for the experimental data which have to be provided by the user. Unfortunately, these are often not available, and FITEQL only allows to define an error for a data type, not for individual data points.
- In cases where several datasets (e.g. at different ionic strengths) are available for fitting, the results of the individual optimization runs need to be consolidated into one best parameter, by

averaging or similar procedures. As noted by Dzombak and Morel (1990), this is not straightforward.

- FITEQL does not allow optimizing directly on the basis of the final target parameter, $K_d$. Instead, optimization has to be done on dissolved or sorbed RN concentration.

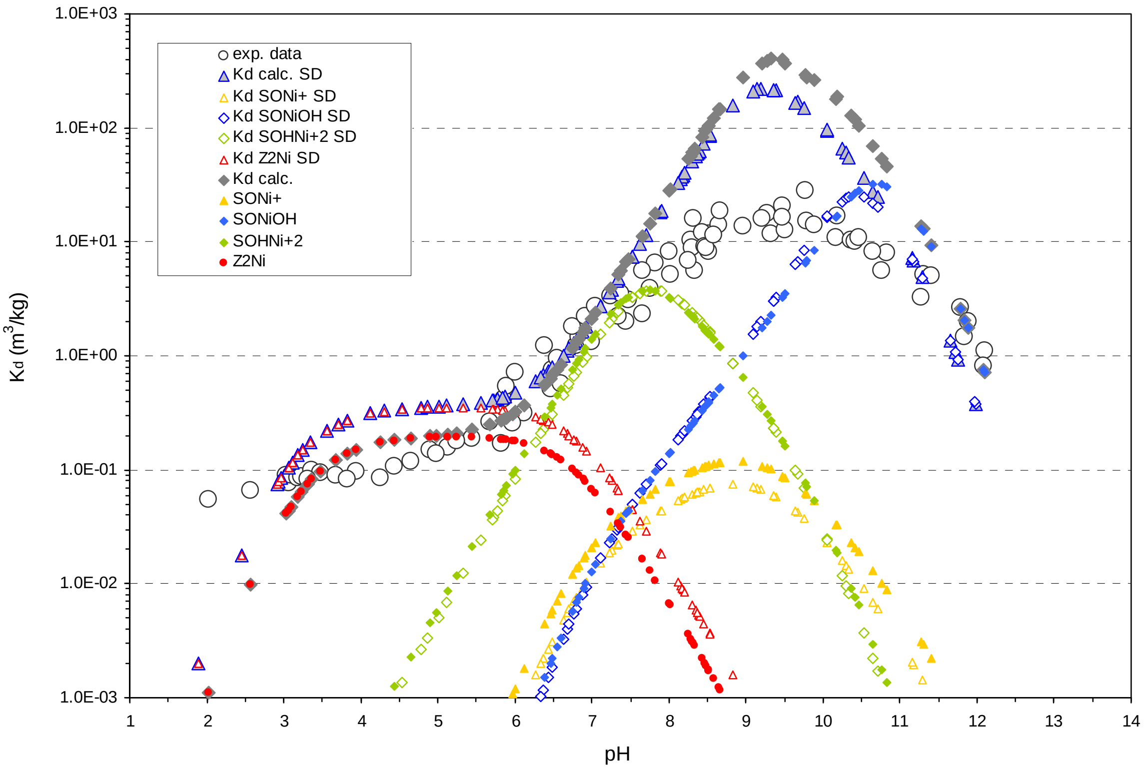


Figure 4.4: Illustration of optimization result by FITEQL using the sorption data by Bradbury and Baeyens (2005) on Na-SWy-1 (S/W = ca. 1 g/L, [Ni] = 1.3E-07 M, 0.1 M $NaClO_4$). Underlying surface chemical model: JAEA09/a, aqueous thermodynamic data for Ni are from Hummel et al. (2002). Relative error of $[Ni]_{ads}$ = 0.35 (curves marked "SD"). Results correspond to modeling trials 2 and 4 in the development of the JAEA09/a_Ni1 model (see section 5.2).

### *Trial and error calculations:*

- Trial and error calculations can be done with any speciation code capable of handling surface complexation.
- Optimization of parameters can realistically only be done one parameter at a time. In practice, this is often not a serious drawback, due to the restrictions imposed by FITEQL (see above).
- The nature of the optimization process is more subjective than in case of a computer code:
    - Therefore, this method may be perceived as less scientific or less established than automatic optimization: But with the publication of the Ni sorption papers by

Bradbury and Baeyens (1997), trial and error has been established as an accepted method in the literature. Further, trial and error was accepted as a valid and useful method in the NEA Sorption Project modeling exercise (NEA, 2005).

  - This method may also be perceived as purely qualitative: However, it is no problem to compare the results of different trials in a quantitative way (using e.g. the approach of NEA, 2005, see eq. 4.1).

- Trial and error fitting allows to select any representation of sorption (including $K_d$) as basis for optimization.

#### 4.2.2.2 Summary of our experience in sorption modeling in the ISD model/database development

In order to parameterize the basic clay-water model on the basis of sorption data for the selected radionuclides, we performed many calculations with FITEQL using various suites of surface species. However, the results were very mixed: in some cases, the optimization routine of FITEQL was able to converge, in others not. Based on the calculations performed so far, it is difficult to detect a system behind the cases where FITEQL is converging and where not. Altmaier et al. (2004) note that the optimization routine of FITEQL is kept numerically simple and that the simultaneous optimization of more than one parameter is often not possible because of numerical problems in the code.

For selected cases of Ni sorption, the experimental data used for parameterization were also varied, testing dissolved RN concentrations in addition to adsorbed concentrations. However, this did actually not improve the situation at all. The reason why convergence can be achieved in some cases but not in others is not entirely clear, but presumably the dissolved or adsorbed concentrations are so similar over a wide pH-range that it is difficult to handle for the numerical optimization routine of FITEQL. In the case of parameterizing the Ni model, many modeling trials could only be run when the experimental error was included (see section 5.2).

In summary, the use of FITEQL very much restricts the modeling options. This was the reason why we had used fitting by trial and error in many cases in our previous modeling efforts (see Tachi et al., 2010).

### 4.2.3 Illustration of methods for representing uncertainties: Ni example

As indicated in section 4.1, two fundamentally different approaches are available for representing TSM uncertainties:

Option 1: Errors can be assigned to the TSM parameters, in particular with the equilibrium constants, based on some statistical procedure.

Option 2: The uncertainties may be provided directly as an error estimate for the calculated results, based on experience in the model performance.

#### 4.2.3.1 Option 1: errors assigned to TSM parameters

**Modeling individual datasets:** Option 1 is straightforward when the description of one particular set of sorption data is concerned, and when uncertainty information on the experimental data is available.

In such a case, error estimates for surface equilibrium constants can be obtained directly by FITEQL and have a clear statistical meaning. The values obtained for the JAEA09/a_Ni1 model are given in Table 5.1. Two possible problems are evident:

- The standard deviation (SD) calculated by FITEQL for the 0.1 M dataset is so small that the log$K$ values obtained for the 0.03 and 0.01 M datasets are outside the error range for the 0.1 M dataset.
- This shows that the error propagation method of FITEQL (based on the experimental errors given in Bradbury and Baeyens, 1995) is not adequately reflecting uncertainties. This can only be detected if several datasets are available that can be used in the same fitting procedure.
- It can be seen that the SD calculated by FITEQL is strongly influenced by the number of datapoints (SD is smaller for 0.1 M than for the other datasets), although this does not necessarily reflect quality.

Note that the SD values for each dataset are dependent on the assigned experimental error, which is not reported in case of most experimental studies. The SD values for individual datasets are based on the assumption that the experimental data used for model calibration constitute a representative sample of all possible outcomes. In a statistical sense, this gives another open question:

- For conditions outside of the range covered in the experiments, the meaning of the SD values is not clearly defined.

**Illustration of effect of SD values for individual datasets:** This is illustrated in Figure 4.5 for the Ni sorption edge at I = 0.1 M by Bradbury and Baeyens (2005), for both $K_d$ and the residual (dissolved) Ni concentration.

- This illustrates that the provided SD values reflect primarily the (assumed) experimental uncertainty.
- The deviation of model results from experimental data is not represented by the calculated SD values.

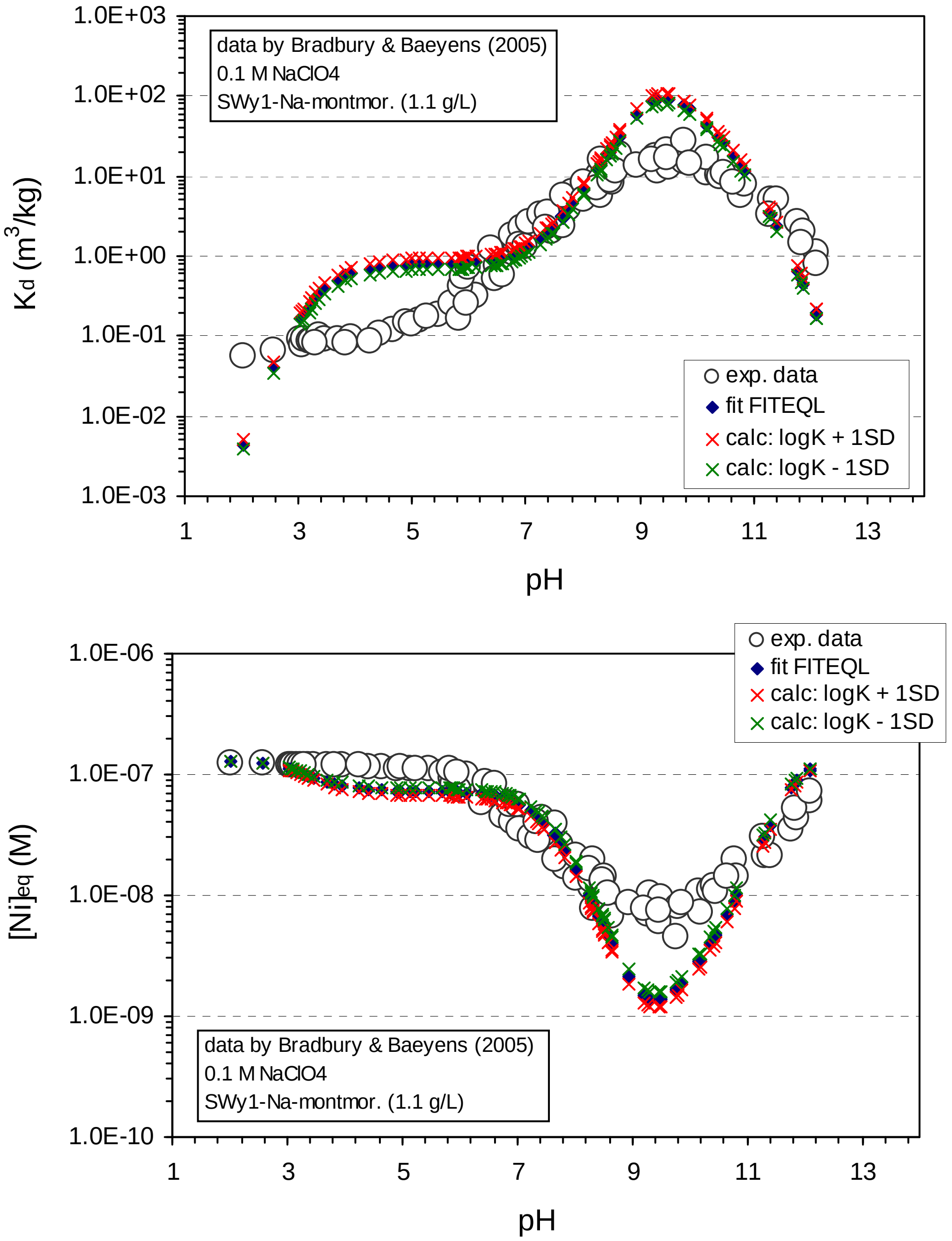


Figure 4.5: Fitting of Ni sorption edge at I = 0.1 M by Bradbury and Baeyens (2005) using FITEQL (modeling trial 6, see section 5.2.7), plotted as $K_d$ and as $[Ni]_{eq}$. This represents the fit to the 0.1 M dataset, not the final model with averaged constants. Shown are also errors corresponding to ± 1 SD of the fitted log*K* values (see Table 5.1).

**Use of several datasets:** In order to be robust (i.e., in order to be applicable to many conditions), it is of advantage when several different datasets can be considered in model development, such as the three datasets by Bradbury and Baeyens (2005) at I = 0.1, 0.03 and 0.01 M (used for the JAEA09/a_Ni1 model, see section 5.2).

However, FITEQL only can handle one dataset at a time (or datasets under identical conditions that are grouped). Typically, this will result in several optimum estimates for a given parameter (where each estimate corresponds to one experimental dataset, see Table 5.1). These individual estimates then have to be consolidated into one best estimate (e.g. by averaging).

The best procedure to follow for selecting the final best estimate is not established, and the transfer of the error estimates from the individual model runs to the finally selected data is not straightforward (see Dzombak and Morel, 1990):

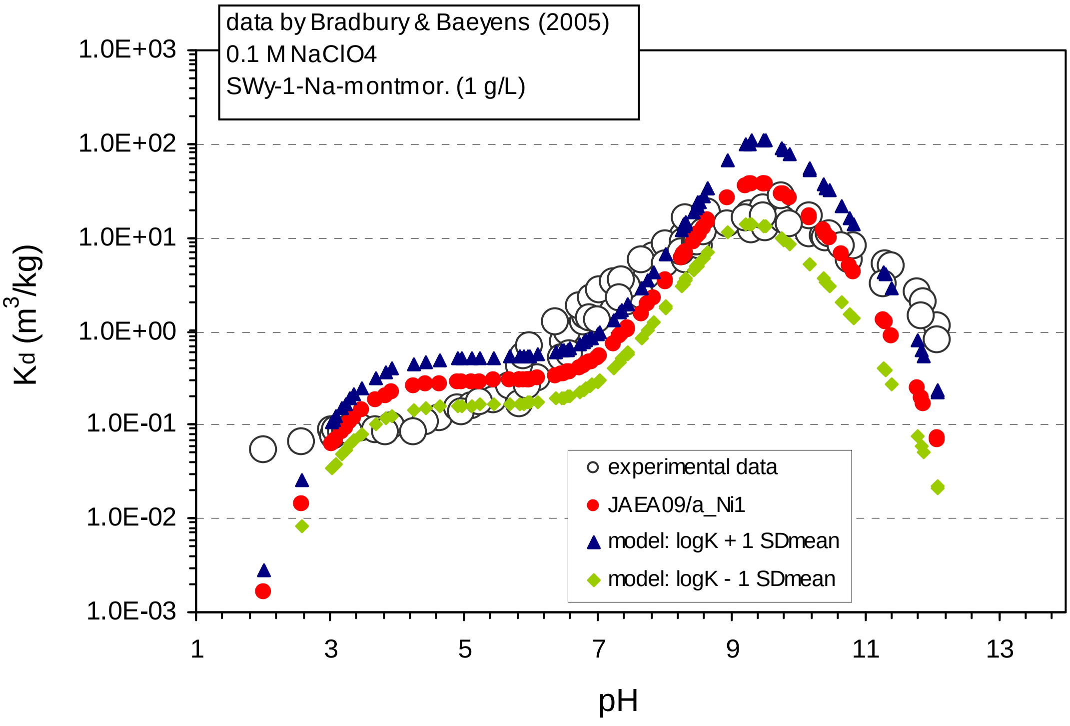
- When uncertainties for the individual estimates are available (based on reliable estimates for experimental error), an error-weighted average (using e.g. 1/SD as weighing factor) can be calculated.
- In all other cases, the calculation of a simple mean (without any weighing factor) may be the simplest solution.

**Error estimates for averaged log*K* values:** Once the averaged best estimate log*K* values are determined, the question is how to calculate the corresponding (average) error estimates.

- In the development of the JAEA09/a_Ni1 model (see Table 5.2), the $SD_{mean}$ for the final (best estimate) log*K* values have been calculated based on a statistical procedure for error estimates of weighted averages.
- As can be seen from Table 5.2, these $SD_{mean}$ values lie in between simply averaged (weighted) SDs based on the SDs provided by FITEQL for each dataset and SD values for (hypothetical) non-weighted average log*K* values.

The effect of the $SD_{mean}$ on $K_d$ values calculated by the JAEA09/a_Ni1 model are shown in Figure 4.6:

- It can be seen that the $SD_{mean}$ of the final model leads to a significantly larger spread of $K_d$ than the SD for the fit of an individual dataset.
- Considering the uncertainty of the experimental datapoints, it appears that $SD_{mean}$ is a reasonable representation of model uncertainties.



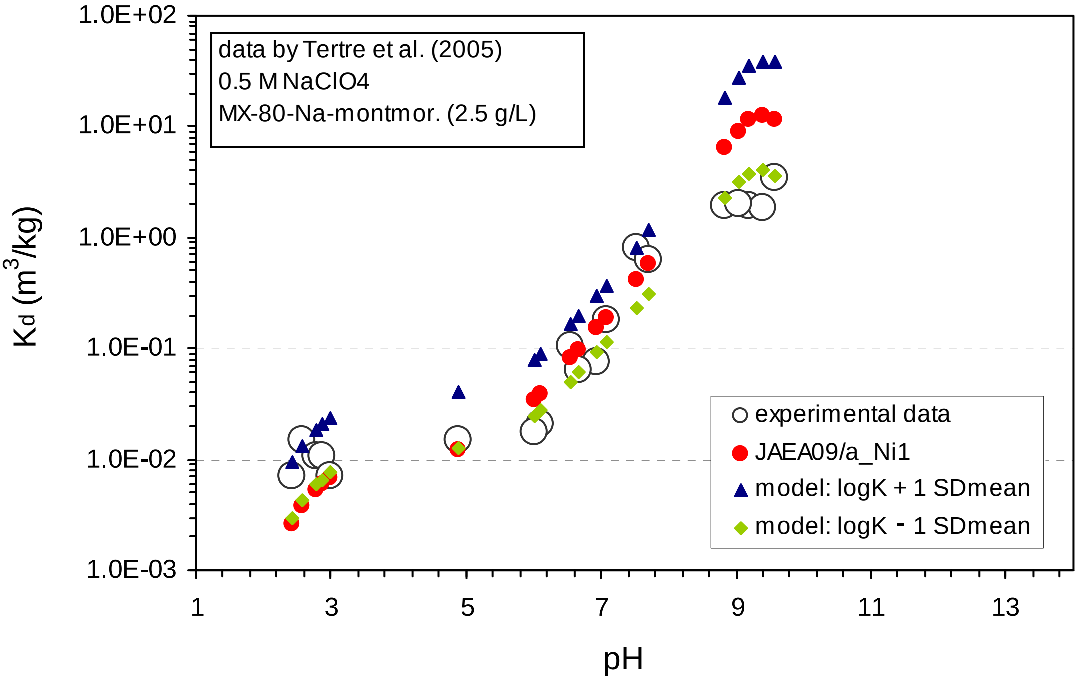


Figure 4.6: Recalculation of Ni sorption edges at I = 0.1 M by Bradbury and Baeyens (2005) and at I = 0.5 M (Tertre et al., 2005) using the final, averaged JAEA09/a_Ni1 model. Shown are also errors corresponds to ± 1 best estimate standard deviation ($SD_{mean}$) of the averaged log*K* values (see Table 5.2).

#### 4.2.3.2 Option 2: direct error estimates for calculated $K_d$

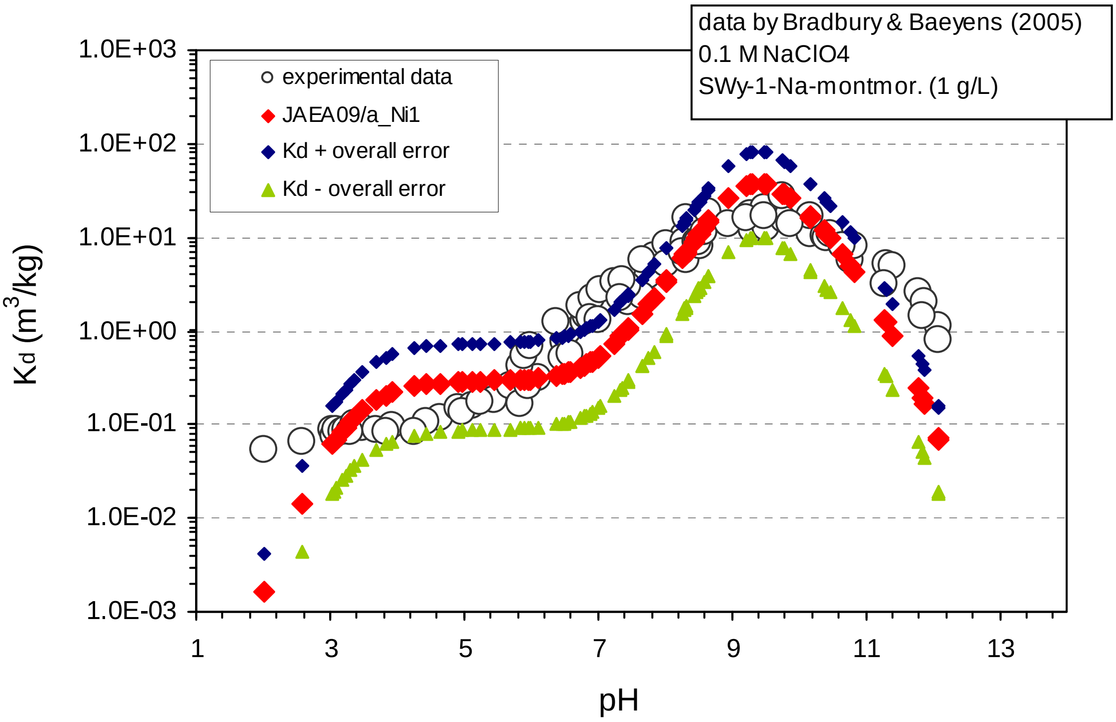
According to eq. (4.1), an overall uncertainty for $K_d$ is obtained as follows for the JAEA09/a_Ni1 model (see section 5.2):

**overall uncertainty = log $K_d$ ± 0.46**

This uncertainty is directly applied to calculated $K_d$ values. An illustration is given in Figure 4.7, using again the 0.1 M dataset for Na-SWy-1 montmorillonite by Bradbury and Baeyens (2005) and the data obtained at I = 0.5 M by Tertre et al. (2005).

### 4.2.4 Conclusions for uncertainty assessment

- Uncertainties associated with TSM parameters (log*K* values) appear to be reasonable descriptors of model uncertainty only in cases where several datasets can be fitted and the SD of the averaged model constants can be calculated.
- In case of individual datasets, SD by FITEQL is likely to underestimate model uncertainty.
- The validity of the SD values provided by FITEQL is dependent on the availability of realistic error estimates for the experimental data.
- From a pragmatic point of view, the determination of SD values for log*K* is dependent on fitting with a code like FITEQL, which is not possible in all cases. In case of trial-and-error fitting, the determination of SD values is very questionable.
- The use of the overall error in $K_d$ (see eq. 4.1) as a representation of model uncertainty
    - is a more direct representation of overall model uncertainty,
    - takes into all account implicitly all factors that lead to a discrepancy between modeled and experimental data
    - is not dependent on a particular fitting method or code.
- The overall error in $K_d$ (see eq. 4.1) is viewed as the best representation of model uncertainty.



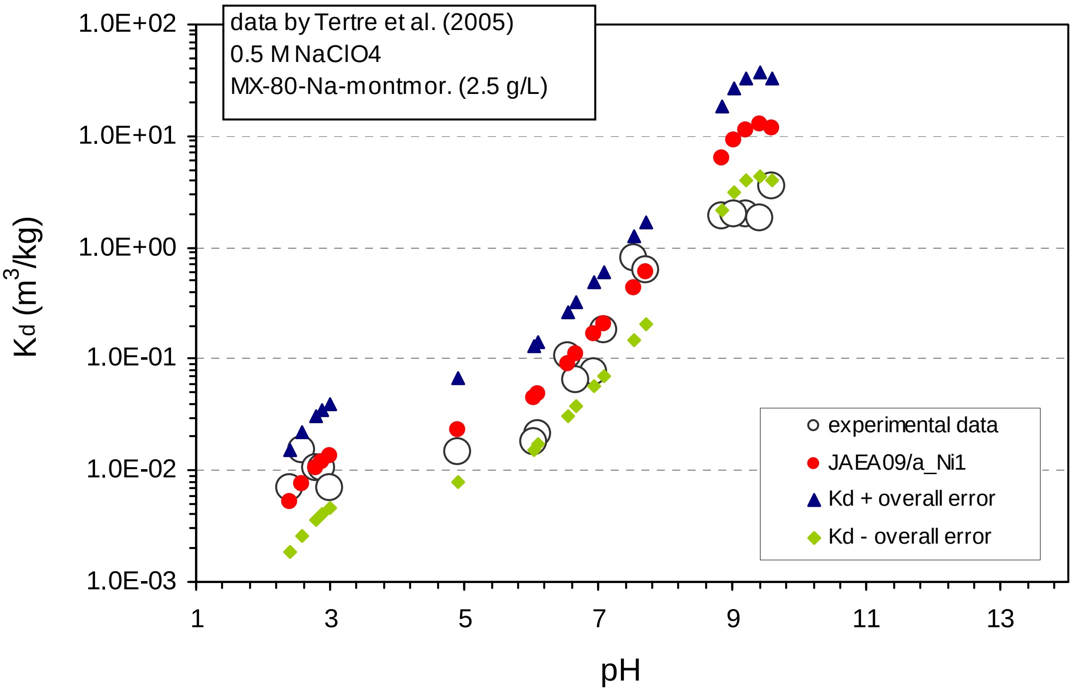


Figure 4.7: Recalculation of Ni sorption edge at I = 0.1 M by Bradbury and Baeyens (2005) using the final, averaged JAEA09/a_Ni1 model. Shown are the overall errors in $K_d$ calculated according to eq. (4.1): overall uncertainty = log $K_d \pm 0.46$.

# 5. Development of Ni sorption model and uncertainty assessment

The model for Ni sorption presented in Tachi et al. (2010) had been developed largely on the basis of trial and error fitting. To illustrate and compare different approaches for model parameterization and handling of uncertainties, it was attempted to parameterize a sorption model for Ni by the use of FITEQL. In this chapter, Ni sorption model development and uncertainty assessment are presented in detail.

## 5.1 Choice of residual Ni concentration for model optimization

First, the actual modeling process was re-evaluated. In our earlier modeling (Tachi et al., 2010), modeling with FITEQL was attempted using $[Ni]_{ads}$ as basis for optimization. This was not very successful in terms of reproducing experimental $K_d$ values (and therefore abandoned in favor of trial and error), and the fact that nearly all Ni is adsorbed over a relatively wide pH-range was identified as a probable reason. Comparisons of experimental data vs. model results expressed as $[Ni]_{ads}$ and as $K_d$ illustrate this (Figure 5.1).

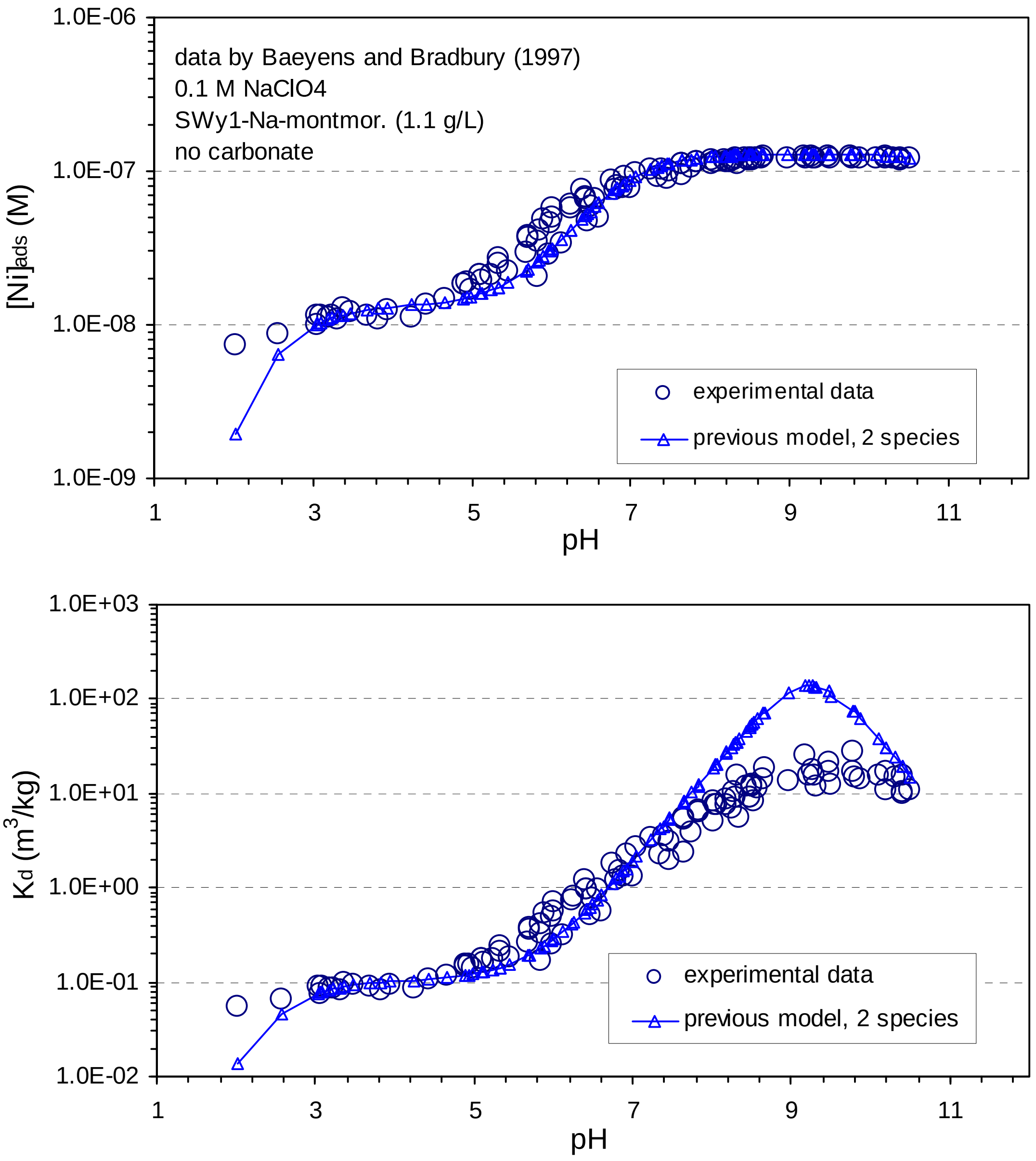


Figure 5.1: Fitting of experimental dataset A using two Ni surface complexes (>SONiOH, >SOHNi$^{+2}$) and one ion exchange species ($Z_2Ni$). Shown on top is the concentration of sorbed Ni in molar units, $[Ni]_{ads}$; $K_d$ is plotted in the bottom panel. Fitting was done by trial and error.

Therefore, use of the residual, dissolved Ni concentration $[Ni]_{eq}$ as basis for optimization by FITEQL was evaluated. The data plotted in Figure 5.2 suggest that $[Ni]_{eq}$ may be a better representation of $K_d$ in terms of resolution as a function of pH.

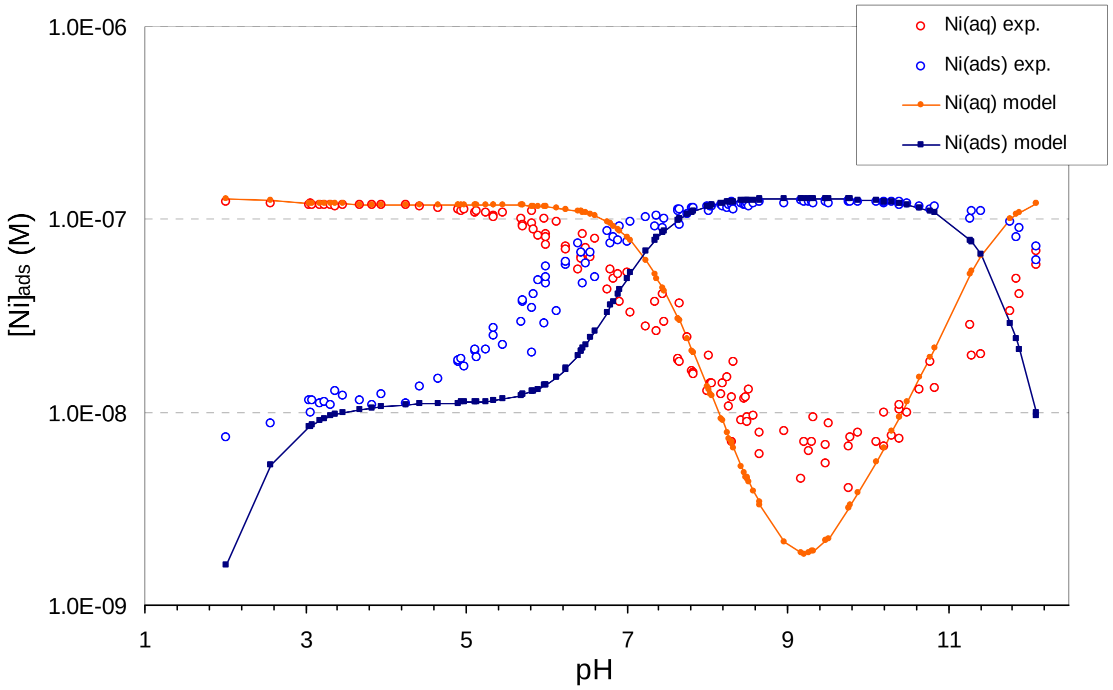


Figure 5.2: Comparison of adsorbed and residual Ni concentrations in the experiments by Bradbury and Baeyens (1997). The model curves are calculated with the previous model.

## 5.2 Development of Ni sorption model

### 5.2.1 Model summary

- Label: JAEA09/a_Ni1
- Underlying clay-water model: JAEA09/a
- Experimental data: Baeyens and Bradbury (1997), Ni sorption edges on SWy-1 montmorillonite (Na-form), $[Ni]_{tot} = 1.3 \times 10^{-7}$ M, S/W ratio is about 1.1 g/L, background electrolyte: 0.1 M, 0.03 M and 0.01 M $NaClO_4$. Note that data are as given in Bradbury and Baeyens (2005, includes a wider pH range than their 1997 publication). More information is given in Baeyens and Bradbury (1995).
- Basis for optimization are the residual dissolved Ni concentrations calculated from the reported log $K_d$ data.
- Fitting procedure for final model: automatic optimization by FITEQL 4, including experimental errors (see modeling trial 6)
- Thermodynamic data for aqueous Ni species are from Hummel et al. (2002)
- All modeling trials leading to the final model parameterization are documented below, including unsuccessful approaches. Note that modeling started by using the experimental

data without assigning experimental uncertainties; this applies to modeling trials 1 - 3. In trials 4 - 6, experimental errors were accounted for.

### 5.2.2 Modeling trial 1: 4 surface complexes, 1 ion exchange species (data at 0.1 M)

- As pointed out in section 3.3.2, it is not possible to decide on surface species a priori based on separately evaluating >SOH and aqueous Ni speciation.
- Therefore, it was initially attempted to include all Ni surface complexes corresponding to the hydrolytic sequence in aqueous solution (i.e., the sequence from doubly positive $>SOHNi^{2+}$ to negative $>SONi(OH)_2^-$, see section 3.1) and to simplify the model based on the importance of species according to FITEQL results.
- Experimental data were used without specifying uncertainties. Optimization was based on residual (dissolved) as well as adsorbed experimental Ni-concentrations.
- FITEQL did not converge (presumably due to overdetermination) using the above surface complexes.
- While not useful for further modeling, these trials suggested that convergence problems may be smaller using residual experimental Ni-concentrations.

### 5.2.3 Modeling trial 2: 3 surface complexes, 1 ion exchange species (data at 0.1 M)

- As discussed in section 3.3.2, the 3 surface species ($>SONi^+$, $>SONiOH$, $>SOHNi^{2+}$) and the ion exchange species $Z_2Ni$ were considered most relevant.
- The model was optimized using again both adsorbed and residual experimental Ni-concentrations, without consideration of experimental errors.
- Better results were achieved using the residual experimental Ni-concentrations. Additionally, this approach showed fewer problems with FITEQL (Figure 5.3).

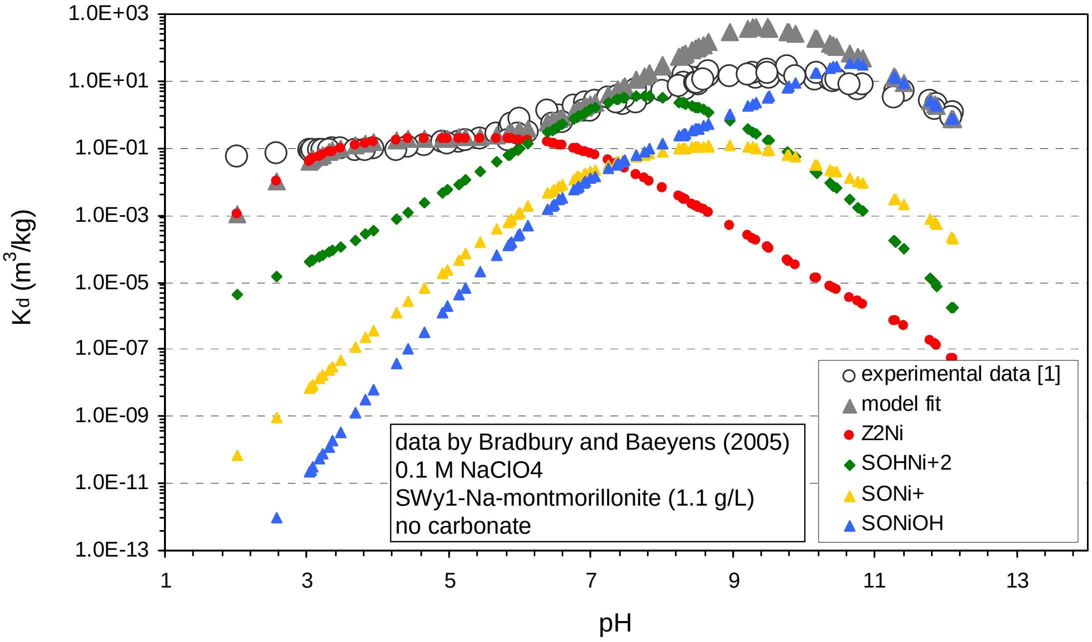


Figure 5.3: Fitting of the experimental data by [1] Bradbury and Baeyens (2005) in 0.1M $NaClO_4$ background solution using 3 surface complexes (>$SONi^+$, >SONiOH, >$SOHNi^{2+}$) and one ion exchange species ($Z_2Ni$)

### 5.2.4 Modeling trial 3: 2 surface complexes, 1 ion exchange species (data at 0.1 M)

- Following trial 2, the model was re-fitted using 2 surface complexes (>SONiOH, >$SOHNi^{2+}$) and one ion exchange species $Z_2Ni$.
- The least important surface complex from trial 2 (>$SONi^+$) was omitted.
- Omitting this species allows for a simpler model with the same goodness of fit
- As in trial 2, there is an overestimation of the $K_d$ values in the pH range between pH 8 and 12 (Figure 5.4).

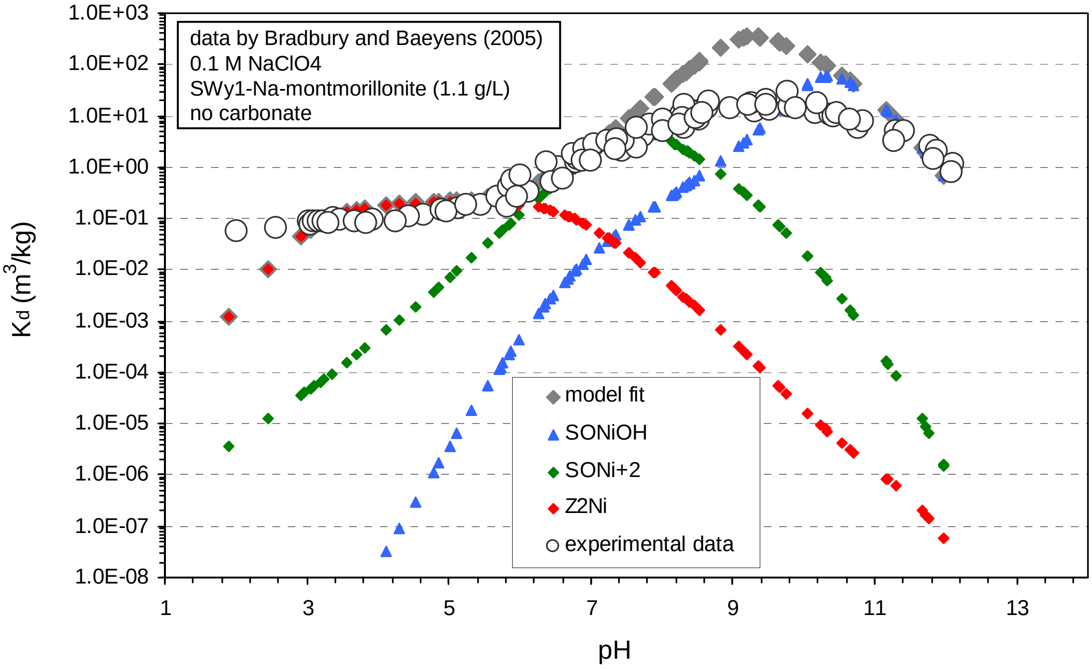


Figure 5.4: Fitting of the experimental data by Bradbury and Baeyens (2005) in 0.1M $NaClO_4$ background solution using 2 surface complexes (>SONiOH, $>SOHNi^{2+}$) and one ion exchange species ($Z_2Ni$)

### 5.2.5 Modeling trial 4: 3 surface complexes, 1 ion exchange species (data at 0.1 M)

- Modeling trials 2 and 3 were repeated taking into account experimental uncertainty
- As input for FITEQL, the relative error of the residual Ni concentrations has been calculated using an error in $K_d$ cited in Baeyens and Bradbury (1995): log $K_d \pm 0.15$. The corresponding error in $[Ni]_{eq}$ depends on the magnitude of $K_d$; an average value of 35% has been taken for all values of $[Ni]_{eq}$.
- The same surface complexes ($>SONi^+$, >SONiOH, $>SOHNi^{2+}$) and ion exchange species ($Z_2Ni$) as in trial 2 were used.
- Consideration of the experimental error in the optimization process improves the model fit and the overestimation of the $K_d$ values in the pH region 8-12 is reduced (Figure 5.5).

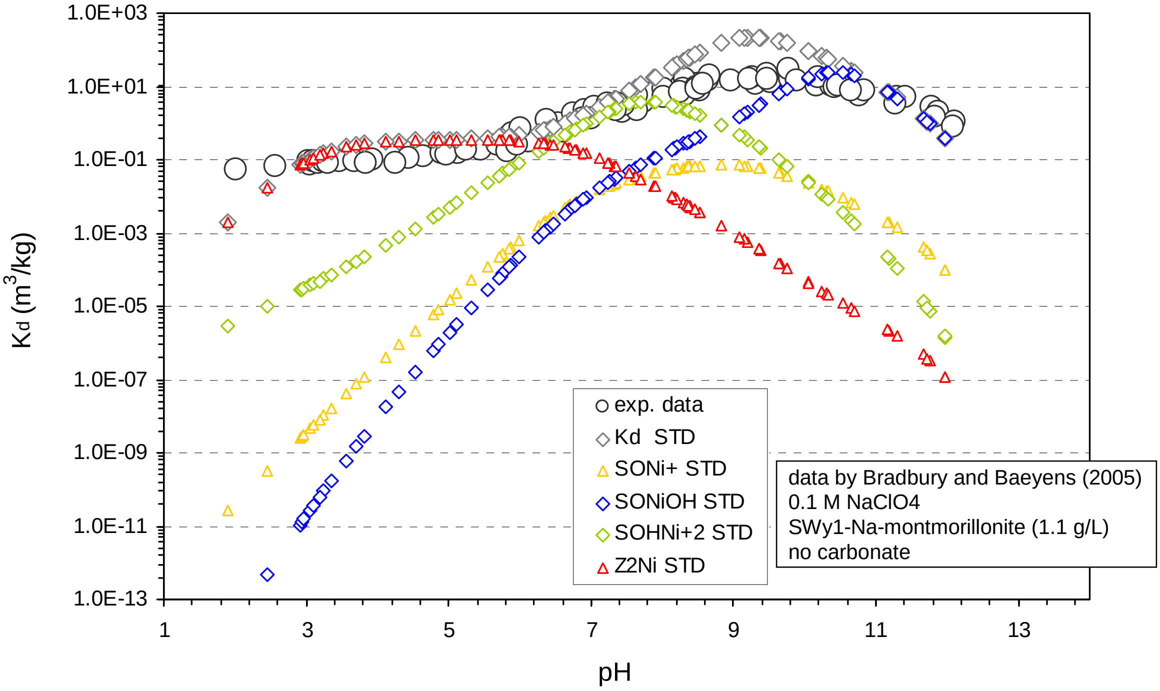


Figure 5.5: Fitting of the experimental data by Bradbury and Baeyens (2005) with 0.1 M $NaClO_4$ background solution using 3 surface species ($>SONi^+$, >SONiOH, $>SOHNi^{2+}$) and one ion exchange species ($Z_2Ni$) and a relative error of 35%.

### 5.2.6 Modeling trial 5: 3 surface complexes, 1 ion exchange species (data at 0.01 & 0.03 M)

- Following trial 4, the same approach (using the relative error of the experimental data) was applied to datasets with different ionic strengths (0.01 M, 0.03 M).
- However, FITEQL was not able to converge in all cases
- Therefore, it was decided to neglect again the least significant surface complex $>SONi^+$.

### 5.2.7 Modeling trial 6: 2 surface complexes, 1 ion exchange species (three pH-edges for differenet NaCl conditions)

- The least important surface complex from the previous trial $>SONi^+$ was omitted.
- This is equivalent to trial 3, except that experimental uncertainties are considered
- The result for I = 0.1 M is shown in Figure 5.6. To compensate for the missing $>SONi^+$ species in the pH-range 6-7, ion exchange is made stronger which leads to an overprediction of sorption at low pH.
- On the other hand, omission of the surface species $>SONi^+$ allows FITEQL to fit all the Ni datasets. As will be seen below, the averaged constants allow a good fit to many datasets, which seems to be more important than optimizing the fit to one particular set of data.

- The same optimization approach was applied to the experimental datasets of Bradbury and Baeyens (2005) at I = 0.01 M and 0.03 M. The results are shown in Figure 5.7 and Figure 5.8, respectively. Both fits are able to fit the experimental data well, only the fit for 0.03 M overestimates slightly the experimental data in the lower pH range.
- The resulting optimum constants for each dataset are given in Table 5.1, together with their respective uncertainties.

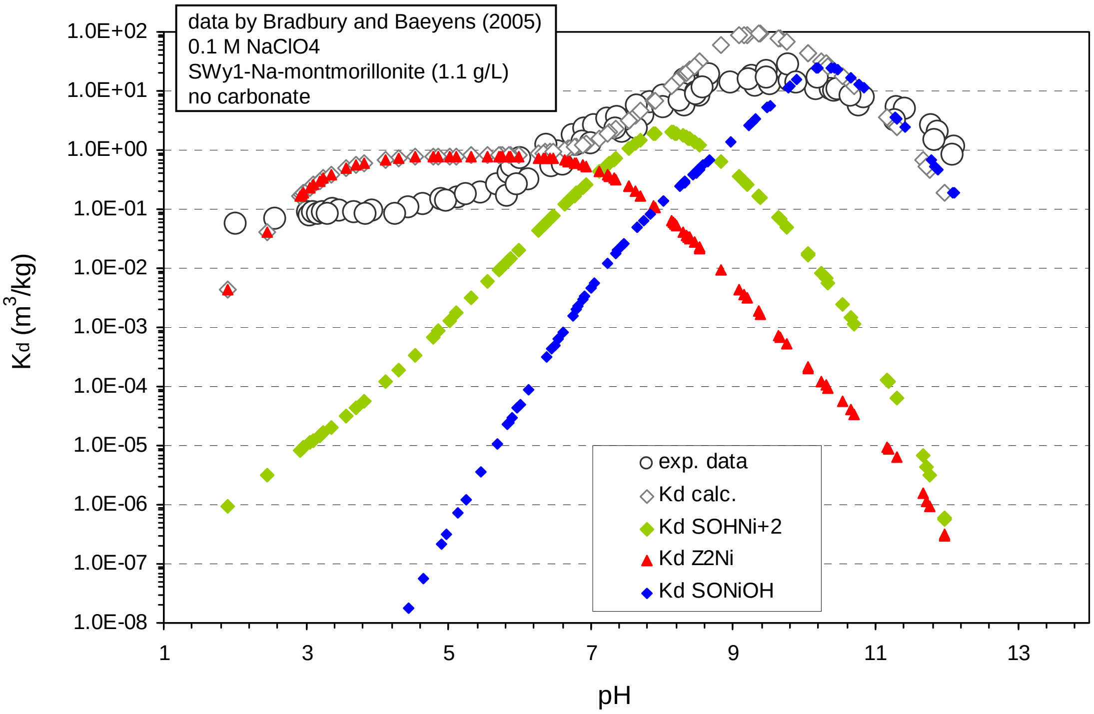


Figure 5.6: Fitting of the experimental data by Bradbury and Baeyens (2005) in 0.1M $NaClO_4$ background solution using 2 surface complexes (>SONiOH, $>SOHNi^{2+}$) and one ion exchange species ($Z_2Ni$) and a relative error of 35%.

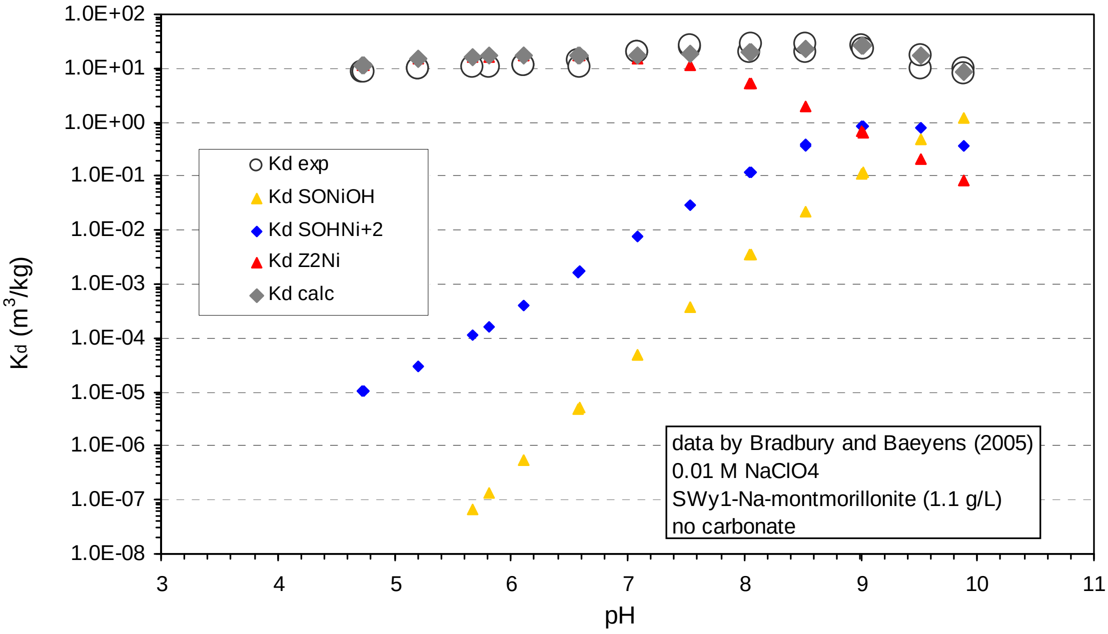


Figure 5.7: Fitting of the experimental data by Bradbury and Baeyens (2005) in 0.01 M $NaClO_4$ background solution using 2 surface complexes (>SONiOH, $>SOHNi^{2+}$) and one ion exchange species ($Z_2Ni$) and a relative error of 35%.

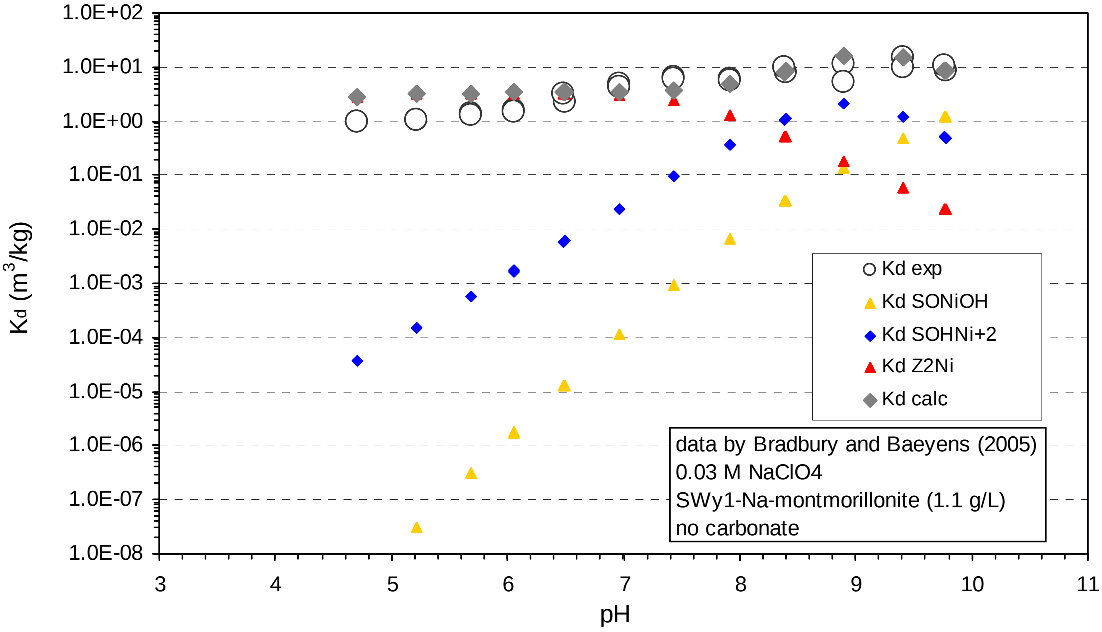


Figure 5.8 Fitting of the experimental data by Bradbury and Baeyens (2005) in 0.03 M $NaClO_4$ background solution, 2 surface complexes (>SONiOH, $>SOHNi^{2+}$), one ion exchange species ($Z_2Ni$) and a relative error of 35%.

Table 5.1: Summary of optimum constants for each dataset (sorption edges at I = 0.1 / 0.03 / 0.01M by Bradbury and Baeyens, 2005) and of their uncertainties (standard deviations, SD) as obtained by FITEQL (modeling trial 6). All constants refer to the formation of the surface species indicated.

| **dataset (sorption edge)** | **surface species** | **log*K*** | **SD** | **overall error $K_d$ 1)** |
|---|---|---|---|---|
| 0.1 M | >SONiOH | -11.26 | 0.06 | 0.53 |
| | $>SOHNi^{+2}$ | 4.24 | 0.07 | |
| | $Z_2Ni$ | 44.16 | 0.07 | |
| 0.03 M | >SONiOH | -12.52 | 0.21 | 0.22 |
| | $>SOHN^{i+2}$ | 3.64 | 0.16 | |
| | $Z_2Ni$ | 43.71 | 0.06 | |
| 0.01 M | >SONiOH | -12.53 | 0.23 | 0.12 |
| | $>SOHNi^{+2}$ | 3.58 | 0.23 | |
| | $Z_2Ni$ | 43.46 | 0.05 | |

1) calculated for each dataset according to

$$\text{overall TSM error} = \sum \left| \log (K_d \text{ predicted} / K_d \text{ measured}) \right| \times n^{-1} \qquad \text{(eq. 4.1)}$$

### 5.2.8 Calculation of mean surface complexation and ion exchange constants and their uncertainties

- All calculations are based on the results of modeling trial 6
- Following the successful optimization of the model for the 3 sorption edges (I = 0.01 / 0.03 / 0.1 M) by Bradbury and Baeyens (2005) and the determination of optimum constants for each dataset, overall best estimates need to be selected. As noted by Dzombak and Morel (1990), this is not straightforward and there is no clear way established in the literature of how this should be done.
- Basically, any of the following options is possible:
  - simple averaging of constants, without weighing
  - calculations of weighted averages, using e.g. the following weighing factors:
    - the reciprocal of a statistical uncertainty (such as 1/SD, see Table 5.1) obtained for each constant and dataset
    - 1/(absolute error in $K_d$), which can be calculated for each dataset by using eq. (4.1)
    - number of datapoints for each dataset
  - selection by expert judgment
- A comparison of model predictions using non-weighted average constants as well as weighted average constants with 1/SD and 1/(absolute error in $K_d$) as factors is given in Figure 5.9 for the dataset at I = 0.1 M.

- Based on the comparison of the results obtained by the different average constants, and because it reflects both the goodness of fit as well as the number of datapoints in each dataset, 1/SD was chosen as weighing factor for the calculation of weighted average constants.
- The resulting best estimates are given in Table 5.2 together with their corresponding standard deviations (SD). Only for comparison, further measures of uncertainty are provided:

  (1) the SD of the best estimate log*K* values ($SD_{mean}$) is calculated from the SD estimates given in the FITEQL output using the following equation for SD of weighted means of experimental data:

$$SD_{mean} = \sqrt{\frac{1}{\sum_{i=1}^{n} 1/\sigma_i{}^2} \times \frac{1}{(n-1)} \sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{\sigma_i^2}} \qquad \text{(eq. 5.1)}$$

  (2) is a simple averaged (weighted) standard deviation for each constant;

  (3) the standard error of non-weighted means is calculated by common statistical procedures for of each group of optimum constants without considering the uncertainties provided by FITEQL (simply averaging the constants, then calculating the SD for that average).

- Based on a comparison of all calculated and experimental data for the sorption edges at I = 0.1, 0.03, 0.01 M by Baeyens and Bradbury (1997), an overall error for predicted $K_d$ of log $K_d$ ± 0.45 is calculated according to eq. (4.1).

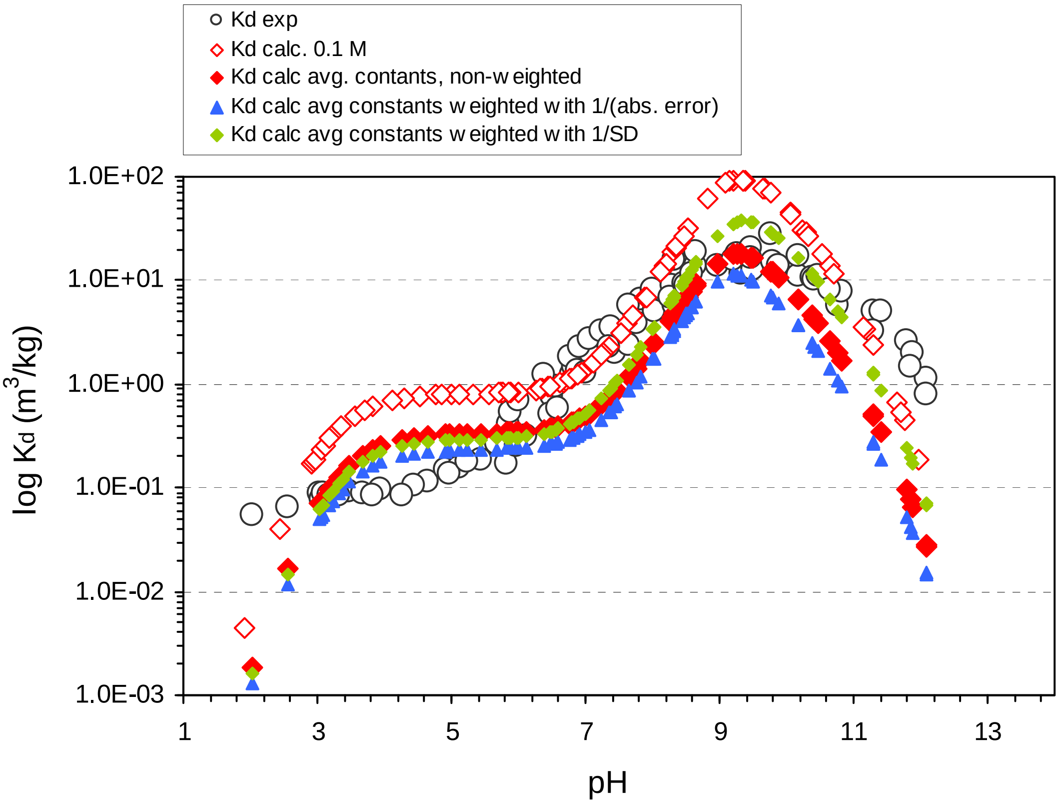


Figure 5.9: Comparison of model predictions using non-weighted average constants as well as weighted average constants with 1/SD and 1/(absolute error in $K_d$) as factors. Modeling trial 6, data by Bradbury and Baeyens (2005), I = 0.1 M.

Table 5.2: Summary of final, constants (averaged best estimates) for the JAEA09/a_Ni1 model and their uncertainties ($SD_{mean}$). Averaged constants are based on the optimized values obtained for each dataset in modeling trial 6 (sorption edges at I = 0.01 / 0.03 / 0.1 M by Bradbury and Baeyens, 2005), see Table 5.1. All constants refer to the formation of the surface species indicated.

| surface species | best estimate log*K* (weighted average) | (1) SD of best estimate log*K* values ($SD_{mean}$) | (2) weighted average of SD for each dataset | (3) standard error of non-weighted means |
|---|---|---|---|---|
| >SONiOH | -11.70 | 0.35 | 0.11 | 0.51 |
| $>SOHNi^{+2}$ | 3.97 | 0.20 | 0.12 | 0.26 |
| $Z_2Ni$ | 41.00 [1)] | 0.19 | 0.06 | 0.25 |

1) converted to Gaines-Thomas formalism

## 5.3 Application and testing of the JAEA09/a_Ni1 model

After the average best estimate constants are obtained, the final model needs to be tested to the degree possible:

- **Overview of model applications**
    - First, the finalized model with averaged constants is re-applied to the three datasets used in the fitting process (sorption edges at I = 0.01 / 0.03 / 0.1 M by Bradbury and Baeyens, 2005) to see whether the averaged constants are still suitable for describing each individual dataset.
    - Second, the model is applied in a predictive fashion to independent data by Tertre et al. (2005).
    - Third, the model is again applied primitively, but this time in the presence of Ca on Ca-montmorillonite (Bradbury and Baeyens, 1999)
- **Approach for model applications to different clay systems**
    - The JAEA09/a_Ni1 model contains various parameters (log*K* values, CEC, edge surface site density and specific surface area). For the present model testing, these need to be applied to
        - → a different clay sample
        - → a Ca-clay
        - → different solid/water ratios
    - Concentration of ion exchange sites:
        - → Calculated for each case by using the CEC and S/W ratio
        - → For each application case, the measured CEC of the sample is accepted (and expressed as CEC of the montmorillonite phase)
    - Concentration of surface complexation sites:
        - → This is treated as a fixed property of the JAEA09/a_Ni1 model (i.e., SOH site density is regarded as being independent of CEC).
        - → The value of $6.24\times10^{-5}$ moles/g montmorillonite is used throughout. Concentration of SOH sites for each case is calculated based on the S/W ratio.
    - Specific edge surface area:
        - → This is also treated as a fixed property of the JAEA09/a_Ni1 model.
        - → The value of 50 $m^2$/ g montmorillonite (BET, from Shibutani et al., 1999) is used throughout.
        - → It is acknowledged that different values (up to factor 2) are measured for different montmorillonite samples. Considering the uncertainties of measuring and assigning the total surface area to planar and edge surfaces, it is preferred

to always use the value of 50 $m^2$/ g which is consistent with the other TSM parameters.

- Equilibrium constants:
  - → Surface complexation and protolysis constants are only dependent on the specific surface area and SOH site density; they are used for all cases without any adjustment and always in connection with a DL correction term.
  - → Ion exchange constants: They are implemented as half-reactions, always with a log*K* of 20 for the formation of ZNa as reference. The constant for $Z_2Ni$ is recalculated for the CEC (in M) in each case using the Gaines-Thomas convention. Further constants needed (such as for the competition between Ni and Ca) are taken from the literature (again as half reactions).
  - → The TDB for aqueous Ni species is from Hummel et al. (2002). This is consistent with CODATA auxiliary data for main elements.

### 5.3.1 Re-application to the data by Bradbury and Baeyens (2005)

- The final model is re-applied to the three datasets used in the fitting process (sorption edges at I = 0.01 / 0.03 / 0.1 M by Bradbury and Baeyens, 2005)
- Figure 5.10 shows the model calculation using weighted average constants with 1/SD for 0.1M. The models for 0.01 M and 0.03 M are shown in Figure 5.11 and Figure 5.12.
- The final averaged model JAEA09/a_Ni1 is able to reproduce the experimental data at all ionic strengths satisfactorily.

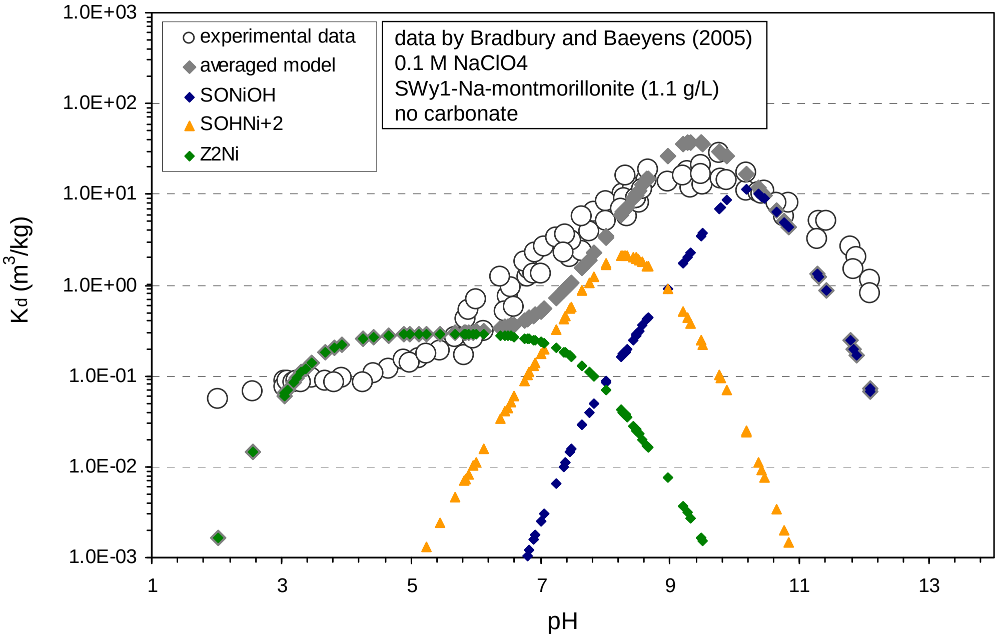


Figure 5.10: Re-calculation of the experimental data in 0.1 M $NaClO_4$ background solution by Bradbury and Baeyens (2005) using the JAEA09/a_Ni1 model.

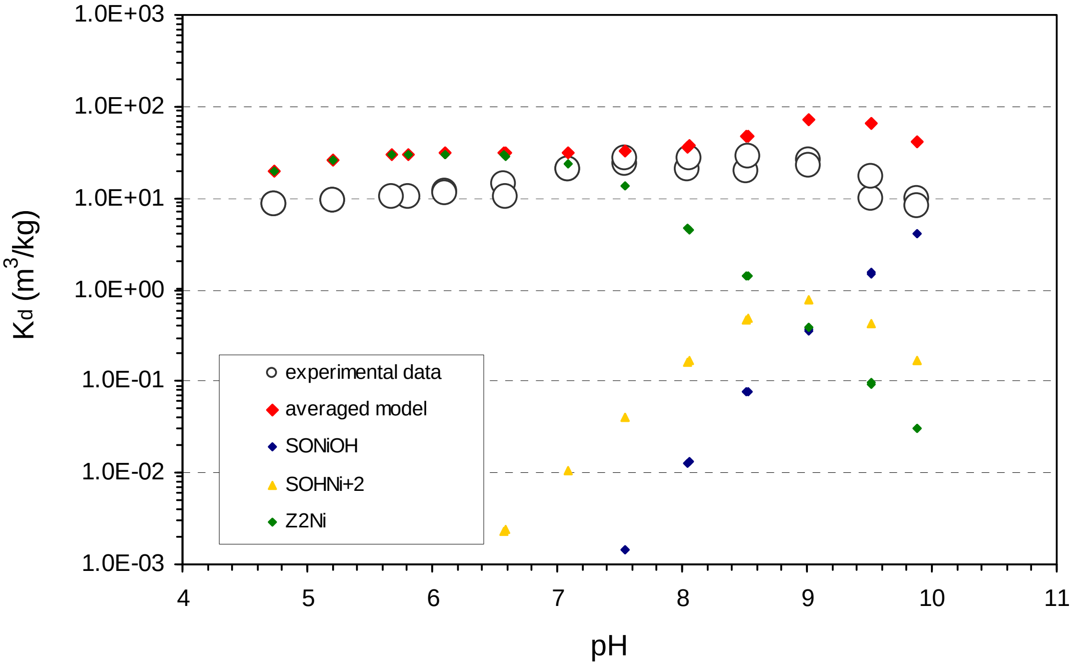


Figure 5.11: Re-calculation of the experimental data in 0.01 M $NaClO_4$ background solution by Bradbury and Baeyens (2005) using the JAEA09/a_Ni1 model.

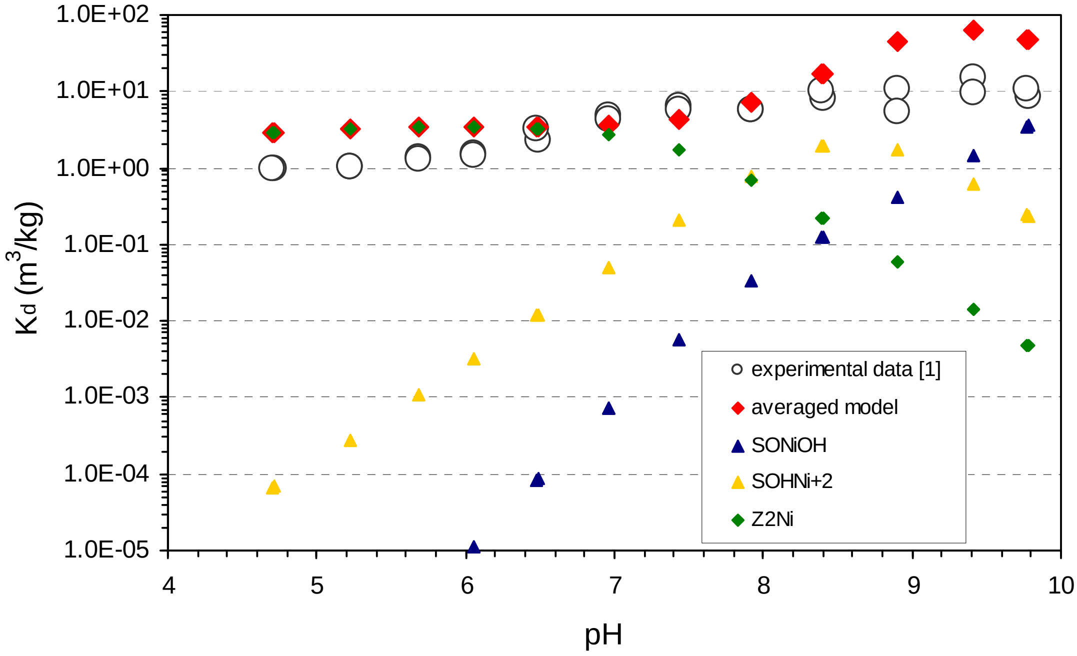


Figure 5.12: Re-calculation of the experimental data in 0.03 M $NaClO_4$ background solution by Bradbury and Baeyens (2005) using the JAEA09/a_Ni1 model.

### 5.3.2 Application to the data by Tertre et al. (2005)

- This is a predictive test using independent Ni sorption data obtained on the Na-form of MX-80. S/W ratio, initial Ni as well as $NaClO_4$ concentrations are also different from those of Bradbury and Baeyens (2005).
- Figure 5.13 shows that the JAEA09/a_Ni1 model is able to predict the data by Tertre et al. (2005) well.
- The model predictions show a smaller dependency of sorption on ionic strength than the experimental data. Note that this is a direct consequence of the difference in experimental results between Tertre et al. (2005) and Bradbury and Baeyens (2005) and cannot be reconciled by any modeling.

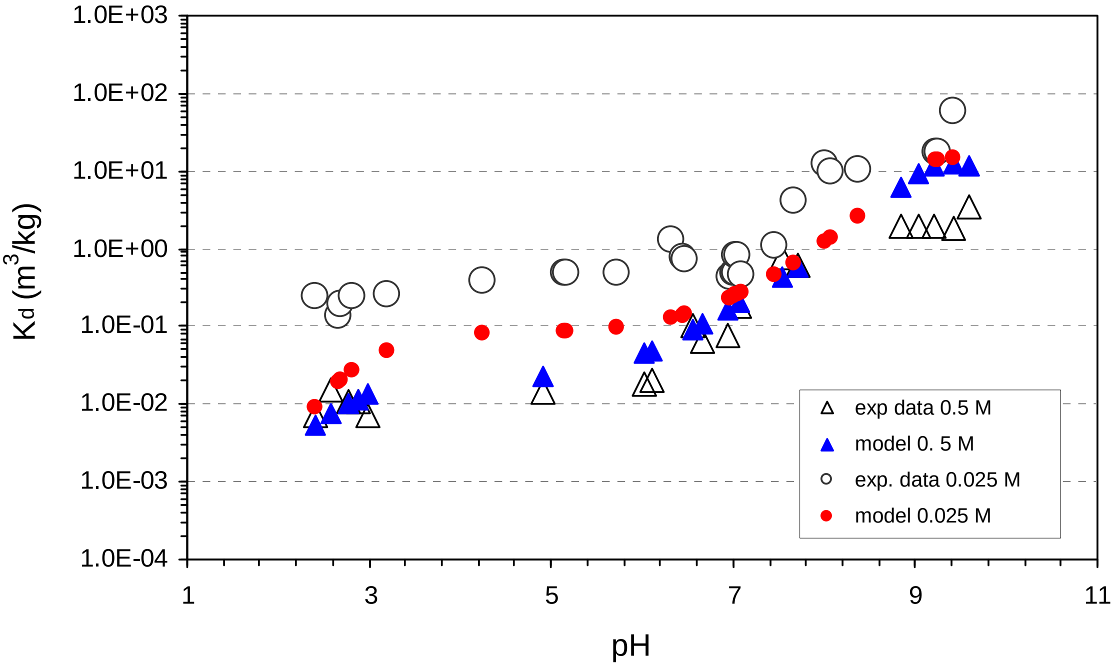


Figure 5.13: Comparison of experimental Ni sorption data by Tertre (2005) in 0.025 M and 0.5 M $NaClO_4$ background solution with predictions by the JAEA09/a_Ni1 model

### 5.3.3 Application to the data by Bradbury and Baeyens (1999) on Ca-montmorillonite

- In a further predictive application, the JAEA09/a_Ni1 model was applied to the data obtained by Bradbury and Baeyens (1999) on Ca-SWy-1 in different $Ca(NO_3)_2$ solutions.
- For this application, a Ca-Na ion exchange constant is needed in addition to the parameters contained in the JAEA09/a_Ni1 model. This was taken directly from Oda and Shibata (1999), without any further fitting.
- Figure 5.14 and Figure 5.15 show that the model is also able to predict Ni sorption well in a Ca-system.

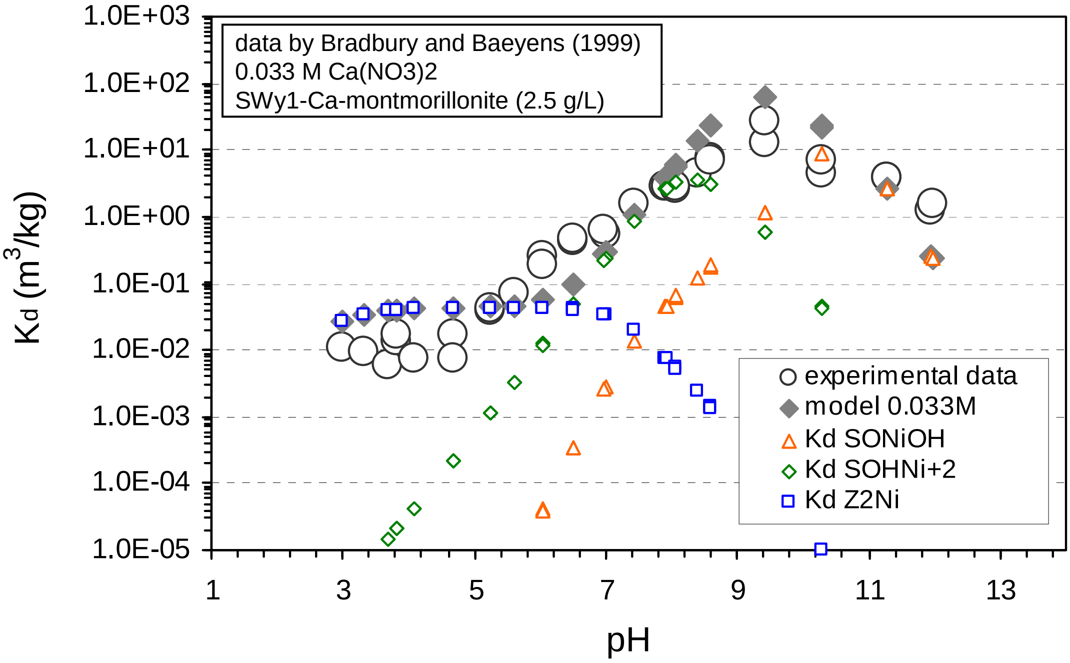


Figure 5.14: Comparison of experimental Ni sorption data by Bradbury and Baeyens (1999) in 0.033 M $Ca(NO_3)_2$ background solution with predictions by the JAEA09/a_Ni1 model.

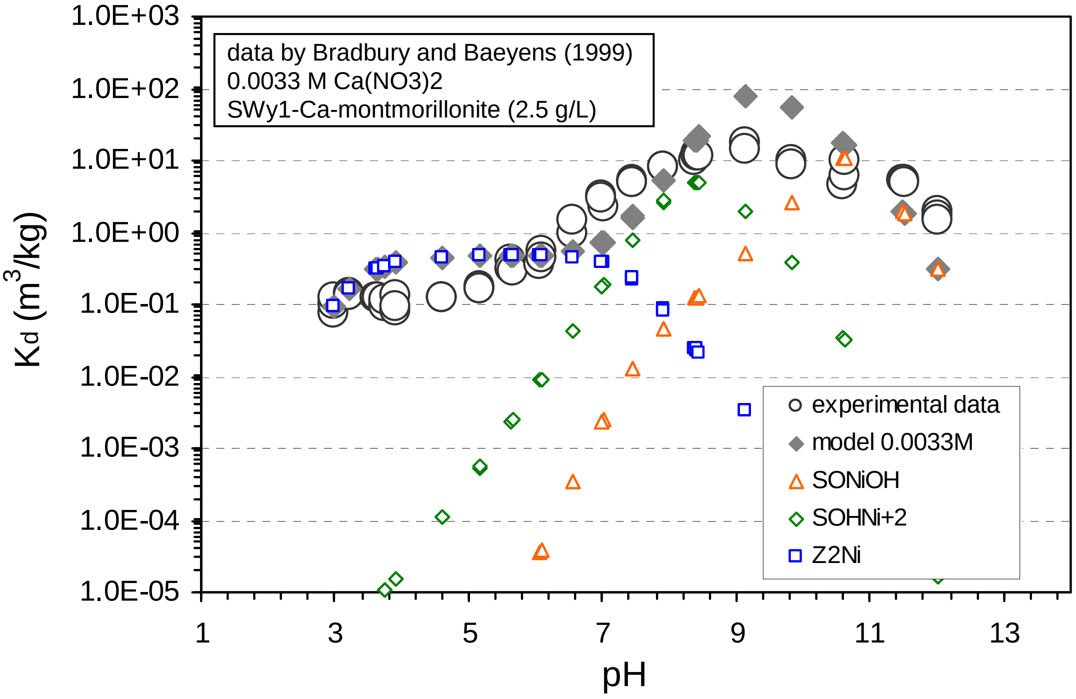


Figure 5.15: Comparison of experimental Ni sorption data by Bradbury and Baeyens (1999) in 0.0033 M $Ca(NO_3)_2$ background solution with predictions by the JAEA09/a_Ni1 model.

### 5.3.4 Overall uncertainty of $K_d$

- According to eq. (4.1), an overall uncertainty for $K_d$ is obtained as follows for the JAEA09/a_Ni1 model:

  **overall uncertainty = log $K_d$ ± 0.45**

  This value takes into account a direct comparison of calculated and experimental $K_d$ values for the following datasets:

  - Ni sorption on Na-SWy1 in 0.1 M, 0.03 M, and 0.01 M $NaClO_4$ (Bradbury and Baeyens, 2005)
  - Ni sorption on Na-MX-80 in 0.5 M and 0.025 M $NaClO_4$ (Tertre et al., 2005)
  - Ni sorption on Ca-SWy1 in 0.033 M and 0.0033 M $Ca(NO_3)_2$ (Bradbury and Baeyens, 1999)

  Note that the consideration of the additional datasets by Tertre et al. (2005) and Bradbury and Baeyens (1999) does not increase the estimate for the overall error of $K_d$.

### 5.3.5 Calculation of $K_d$ in compacted bentonite in contact with groundwater

As a first illustration of applying different error estimates, $K_d$ is calculated for compacted Kunigel-V1 bentonite in equilibrium with different groundwaters:

- two hypothetical groundwaters defined for the H-12 assessment (FRHP, SRHP, see Ochs et al., 1999);
- a groundwater from the Horonobe URL site (JAEA, 2007)

It was assumed that the bentonite was closed with respect to $CO_2$, all calculations were carried out with PHREEQC using the Ni model JAEA09/a_Ni1.

The results for the three calculation cases are shown in Figure 5.16. As expected, sorption is increasing with increasing pH and is approximately in the same range as Ni sorption in the presence of simple electrolyte solutions. The relatively small differences in salinity/ionic strength and carbonate concentration among the solutions are of less importance. Figure 5.17 illustrates the calculated error in $K_d$ when

- the uncertainties in logK values of the Ni model
- the direct error in predicted $K_d$

are considered for error derivation.

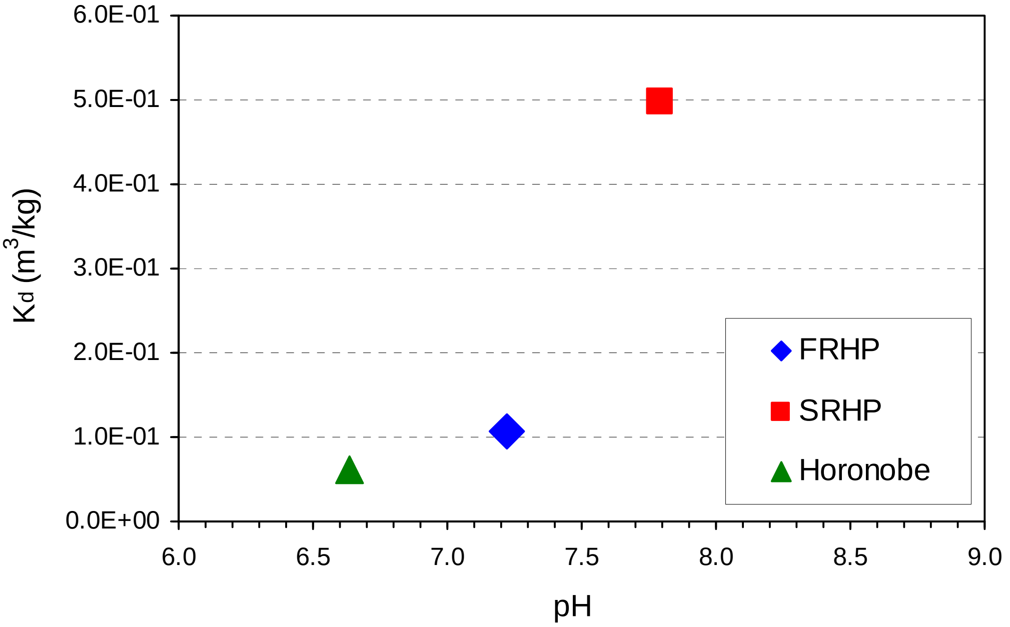
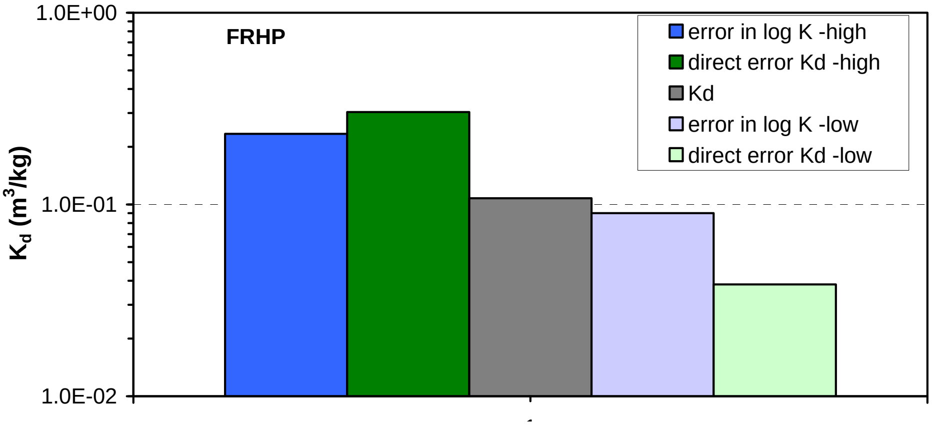
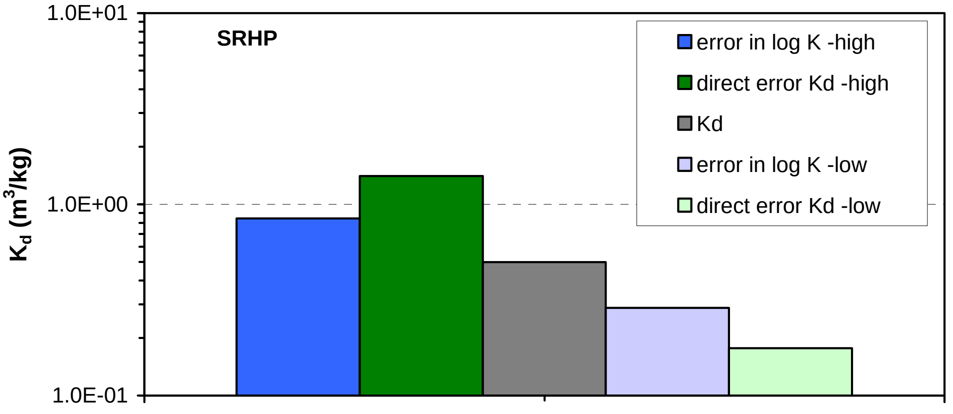


Figure 5.16: Calculation of $K_d$ for compacted Kunigel-V1 bentonite in equilibrium with FRHP, SRHP, and Horonobe-type groundwater (Ni model JAEA09/a_Ni1).

### 5.3.6 Summary for Ni sorption model and its applications

- Using the given combination of surface species, the JAEA09/a clay-water model can be parameterized on the basis of the sorption edge data by Bradbury and Baeyens (2005) using FITEQL.
- This allows to derive uncertainties of the constants for the individual model fits. The transfer to the final, average best estimates is not straightforward (different possibilities).
- The resulting Ni model JAEA09/a_Ni1 allows satisfactory fits to the data by Bradbury and Baeyens (2005).
- It also satisfactorily predicts independent data by Tertre et al. (2005) and Bradbury and Baeyens (1999), which demonstrates its robustness.
- An illustration of applying different error estimates is given.





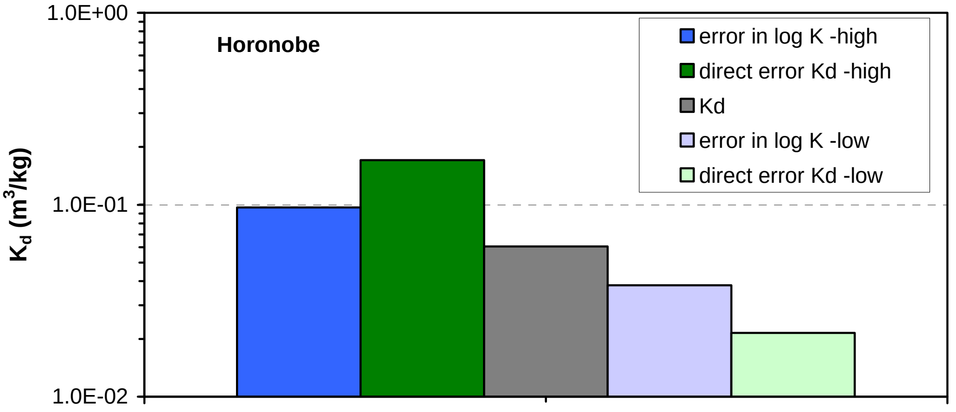


Figure 5.17: Calculated $K_d$ for compacted Kunigel-V1 bentonite in equilibrium with FRHP, SRHP, and Horonobe-type groundwater (Ni model JAEA09/a_Ni1). Errors derived by considering the uncertainties in logK values of the Ni model (blue) and by considering directly the error in predicted $K_d$ (green) are shown.

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# 国際単位系（SI）

表１．SI 基本単位

| 基本量 | SI 基本単位 | |
|---|---|---|
| | 名称 | 記号 |
| 長さ | メートル | m |
| 質量 | キログラム | kg |
| 時間 | 秒 | s |
| 電流 | アンペア | A |
| 熱力学温度 | ケルビン | K |
| 物質量 | モル | mol |
| 光度 | カンデラ | cd |

表２．基本単位を用いて表されるSI組立単位の例

| 組立量 | SI 基本単位 | |
|---|---|---|
| | 名称 | 記号 |
| 面積 | 平方メートル | $\mathrm{m^2}$ |
| 体積 | 立法メートル | $\mathrm{m^3}$ |
| 速さ，速度 | メートル毎秒 | m/s |
| 加速度 | メートル毎秒毎秒 | $\mathrm{m/s^2}$ |
| 波数 | 毎メートル | $\mathrm{m^{-1}}$ |
| 密度，質量密度 | キログラム毎立方メートル | $\mathrm{kg/m^3}$ |
| 面積密度 | キログラム毎平方メートル | $\mathrm{kg/m^2}$ |
| 比体積 | 立方メートル毎キログラム | $\mathrm{m^3/kg}$ |
| 電流密度 | アンペア毎平方メートル | $\mathrm{A/m^2}$ |
| 磁界の強さ | アンペア毎メートル | A/m |
| 量濃度(a)，濃度 | モル毎立方メートル | $\mathrm{mol/m^3}$ |
| 質量濃度 | キログラム毎立法メートル | $\mathrm{kg/m^3}$ |
| 輝度 | カンデラ毎平方メートル | $\mathrm{cd/m^2}$ |
| 屈折率(b) | （数字の）　1 | 1 |
| 比透磁率(b) | （数字の）　1 | 1 |

(a)　量濃度（amount concentration）は臨床化学の分野では物質濃度（substance concentration）ともよばれる。

(b)　これらは無次元量あるいは次元１をもつ量であるが、そのことを表す単位記号である数字の１は通常は表記しない。

表３．固有の名称と記号で表されるSI組立単位

| 組立量 | SI 組立単位 | | | |
|---|---|---|---|---|
| | 名称 | 記号 | 他のSI単位による表し方 | SI基本単位による表し方 |
| 平面角 | ラジアン(b) | rad | 1 (b) | m/m |
| 立体角 | ステラジアン(b) | sr(c) | 1 (b) | $\mathrm{m^{2/}m^2}$ |
| 周波数 | ヘルツ (d) | Hz | | $\mathrm{s^{-1}}$ |
| 力 | ニュートン | N | | $\mathrm{m\ kg\ s^{-2}}$ |
| 圧力，応力 | パスカル | Pa | $\mathrm{N/m^2}$ | $\mathrm{m^{-1}\ kg\ s^{-2}}$ |
| エネルギー，仕事，熱量 | ジュール | J | N m | $\mathrm{m^2\ kg\ s^{-2}}$ |
| 仕事率，工率，放射束 | ワット | W | J/s | $\mathrm{m^2\ kg\ s^{-3}}$ |
| 電荷，電気量 | クーロン | C | | s A |
| 電位差（電圧），起電力 | ボルト | V | W/A | $\mathrm{m^2\ kg\ s^{-3}\ A^{-1}}$ |
| 静電容量 | ファラド | F | C/V | $\mathrm{m^{-2}\ kg^{-1}\ s^4\ A^2}$ |
| 電気抵抗 | オーム | Ω | V/A | $\mathrm{m^2\ kg\ s^{-3}\ A^{-2}}$ |
| コンダクタンス | ジーメンス | S | A/V | $\mathrm{m^{-2}\ kg^{-1}\ s^3\ A^2}$ |
| 磁束 | ウエーバ | Wb | Vs | $\mathrm{m^2\ kg\ s^{-2}\ A^{-1}}$ |
| 磁束密度 | テスラ | T | $\mathrm{Wb/m^2}$ | $\mathrm{kg\ s^{-2}\ A^{-1}}$ |
| インダクタンス | ヘンリー | H | Wb/A | $\mathrm{m^2\ kg\ s^{-2}\ A^{-2}}$ |
| セルシウス温度 | セルシウス度(e) | ℃ | | K |
| 光束 | ルーメン | lm | cd sr(c) | cd |
| 照度 | ルクス | lx | $\mathrm{lm/m^2}$ | $\mathrm{m^{-2}\ cd}$ |
| 放射性核種の放射能 (f) | ベクレル (d) | Bq | | $\mathrm{s^{-1}}$ |
| 吸収線量, 比エネルギー分与, カーマ | グレイ | Gy | J/kg | $\mathrm{m^2\ s^{-2}}$ |
| 線量当量, 周辺線量当量, 方向性線量当量, 個人線量当量 | シーベルト (g) | Sv | J/kg | $\mathrm{m^2\ s^{-2}}$ |
| 酸素活性 | カタール | kat | | $\mathrm{s^{-1}\ mol}$ |

(a)SI接頭語は固有の名称と記号を持つ組立単位と組み合わせても使用できる。しかし接頭語を付した単位はもはやコヒーレントではない。

(b)ラジアンとステラジアンは数字の１に対する単位の特別な名称で、量についての情報をつたえるために使われる。実際には、使用する時には記号rad及びsrが用いられるが、習慣として組立単位としての記号である数字の１は明示されない。

(c)測光学ではステラジアンという名称と記号srを単位の表し方の中に、そのまま維持している。

(d)ヘルツは周期現象についてのみ、ベクレルは放射性核種の統計的過程についてのみ使用される。

(e)セルシウス度はケルビンの特別な名称で、セルシウス温度を表すために使用される。セルシウス度とケルビンの単位の大きさは同一である。したがって、温度差や温度間隔を表す数値はどちらの単位で表しても同じである。

(f)放射性核種の放射能（activity referred to a radionuclide）は、しばしば誤った用語で”radioactivity”と記される。

(g)単位シーベルト（PV,2002,70,205）についてはCIPM勧告2（CI-2002）を参照。

表４．単位の中に固有の名称と記号を含むSI組立単位の例

| 組立量 | SI 組立単位 | | |
|---|---|---|---|
| | 名称 | 記号 | SI 基本単位による表し方 |
| 粘度 | パスカル秒 | Pa s | $\mathrm{m^{-1}\ kg\ s^{-1}}$ |
| 力のモーメント | ニュートンメートル | N m | $\mathrm{m^2\ kg\ s^{-2}}$ |
| 表面張力 | ニュートン毎メートル | N/m | $\mathrm{kg\ s^{-2}}$ |
| 角速度 | ラジアン毎秒 | rad/s | $\mathrm{m\ m^{-1}\ s^{-1}=s^{-1}}$ |
| 角加速度 | ラジアン毎秒毎秒 | $\mathrm{rad/s^2}$ | $\mathrm{m\ m^{-1}\ s^{-2}=s^{-2}}$ |
| 熱流密度，放射照度 | ワット毎平方メートル | $\mathrm{W/m^2}$ | $\mathrm{kg\ s^{-3}}$ |
| 熱容量，エントロピー | ジュール毎ケルビン | J/K | $\mathrm{m^2\ kg\ s^{-2}\ K^{-1}}$ |
| 比熱容量，比エントロピー | ジュール毎キログラム毎ケルビン | J/(kg K) | $\mathrm{m^2\ s^{-2}\ K^{-1}}$ |
| 比エネルギー | ジュール毎キログラム | J/kg | $\mathrm{m^2\ s^{-2}}$ |
| 熱伝導率 | ワット毎メートル毎ケルビン | W/(m K) | $\mathrm{m\ kg\ s^{-3}\ K^{-1}}$ |
| 体積エネルギー | ジュール毎立方メートル | $\mathrm{J/m^3}$ | $\mathrm{m^{-1}\ kg\ s^{-2}}$ |
| 電界の強さ | ボルト毎メートル | V/m | $\mathrm{m\ kg\ s^{-3}\ A^{-1}}$ |
| 電荷密度 | クーロン毎立方メートル | $\mathrm{C/m^3}$ | $\mathrm{m^{-3}\ sA}$ |
| 表面電荷 | クーロン毎平方メートル | $\mathrm{C/m^2}$ | $\mathrm{m^{-2}\ sA}$ |
| 電束密度，電気変位 | クーロン毎平方メートル | $\mathrm{C/m^2}$ | $\mathrm{m^{-2}\ sA}$ |
| 誘電率 | ファラド毎メートル | F/m | $\mathrm{m^{-3}\ kg^{-1}\ s^4\ A^2}$ |
| 透磁率 | ヘンリー毎メートル | H/m | $\mathrm{m\ kg\ s^{-2}\ A^{-2}}$ |
| モルエネルギー | ジュール毎モル | J/mol | $\mathrm{m^2\ kg\ s^{-2}\ mol^{-1}}$ |
| モルエントロピー, モル熱容量 | ジュール毎モル毎ケルビン | J/(mol K) | $\mathrm{m^2\ kg\ s^{-2}\ K^{-1}\ mol^{-1}}$ |
| 照射線量（Ｘ線及びγ線） | クーロン毎キログラム | C/kg | $\mathrm{kg^{-1}\ sA}$ |
| 吸収線量率 | グレイ毎秒 | Gy/s | $\mathrm{m^2\ s^{-3}}$ |
| 放射強度 | ワット毎ステラジアン | W/sr | $\mathrm{m^4\ m^{-2}\ kg\ s^{-3}=m^2\ kg\ s^{-3}}$ |
| 放射輝度 | ワット毎平方メートル毎ステラジアン | $\mathrm{W/(m^2\ sr)}$ | $\mathrm{m^2\ m^{-2}\ kg\ s^{-3}=kg\ s^{-3}}$ |
| 酵素活性濃度 | カタール毎立方メートル | $\mathrm{kat/m^3}$ | $\mathrm{m^{-3}\ s^{-1}\ mol}$ |

表５．SI 接頭語

| 乗数 | 接頭語 | 記号 | 乗数 | 接頭語 | 記号 |
|---|---|---|---|---|---|
| $10^{24}$ | ヨタ | Y | $10^{-1}$ | デシ | d |
| $10^{21}$ | ゼタ | Z | $10^{-2}$ | センチ | c |
| $10^{18}$ | エクサ | E | $10^{-3}$ | ミリ | m |
| $10^{15}$ | ペタ | P | $10^{-6}$ | マイクロ | µ |
| $10^{12}$ | テラ | T | $10^{-9}$ | ナノ | n |
| $10^{9}$ | ギガ | G | $10^{-12}$ | ピコ | p |
| $10^{6}$ | メガ | M | $10^{-15}$ | フェムト | f |
| $10^{3}$ | キロ | k | $10^{-18}$ | アト | a |
| $10^{2}$ | ヘクト | h | $10^{-21}$ | ゼプト | z |
| $10^{1}$ | デカ | da | $10^{-24}$ | ヨクト | y |

表６．SIに属さないが、SIと併用される単位

| 名称 | 記号 | SI 単位による値 |
|---|---|---|
| 分 | min | 1 min=60s |
| 時 | h | 1h =60 min=3600 s |
| 日 | d | 1 d=24 h=86 400 s |
| 度 | ° | 1°=(π/180) rad |
| 分 | ’ | 1’=(1/60)°=(π/10800) rad |
| 秒 | ” | 1”=(1/60)’=(π/648000) rad |
| ヘクタール | ha | $\mathrm{1ha=1hm^2=10^4m^2}$ |
| リットル | L，l | $\mathrm{1L=11=1dm^3=10^3cm^3=10^{-3}m^3}$ |
| トン | t | $\mathrm{1t=10^3\ kg}$ |

表７．SIに属さないが、SIと併用される単位で、SI単位で表される数値が実験的に得られるもの

| 名称 | 記号 | SI 単位で表される数値 |
|---|---|---|
| 電子ボルト | eV | $\mathrm{1eV=1.602\ 176\ 53(14)\times10^{-19}J}$ |
| ダルトン | Da | $\mathrm{1Da=1.660\ 538\ 86(28)\times10^{-27}kg}$ |
| 統一原子質量単位 | u | 1u=1 Da |
| 天文単位 | ua | $\mathrm{1ua=1.495\ 978\ 706\ 91(6)\times10^{11}m}$ |

表８．SIに属さないが、SIと併用されるその他の単位

| 名称 | 記号 | SI 単位で表される数値 |
|---|---|---|
| バール | bar | $\mathrm{1\ bar=0.1MPa=100kPa=10^5Pa}$ |
| 水銀柱ミリメートル | mmHg | 1mmHg=133.322Pa |
| オングストローム | Å | $\mathrm{1\ Å=0.1nm=100pm=10^{-10}m}$ |
| 海里 | M | 1 M=1852m |
| バーン | b | $\mathrm{1\ b=100fm^2=(10^{-12}cm)2=10^{-28}m^2}$ |
| ノット | kn | 1 kn=(1852/3600)m/s |
| ネーパ | Np | SI単位との数値的な関係は、対数量の定義に依存。 |
| ベル | B | |
| デジベル | dB | |

表９．固有の名称をもつCGS組立単位

| 名称 | 記号 | SI 単位で表される数値 |
|---|---|---|
| エルグ | erg | $\mathrm{1\ erg=10^{-7}\ J}$ |
| ダイン | dyn | $\mathrm{1\ dyn=10^{-5}N}$ |
| ポアズ | P | $\mathrm{1\ P=1\ dyn\ s\ cm^{-2}=0.1Pa\ s}$ |
| ストークス | St | $\mathrm{1\ St=1cm^2\ s^{-1}=10^{-4}m^2\ s^{-1}}$ |
| スチルブ | sb | $\mathrm{1\ sb=1cd\ cm^{-2}=10^4cd\ m^{-2}}$ |
| フォト | ph | $\mathrm{1\ ph=1cd\ sr\ cm^{-2}\ 10^4lx}$ |
| ガル | Gal | $\mathrm{1\ Gal=1cm\ s^{-2}=10^{-2}ms^{-2}}$ |
| マクスウェル | Mx | $\mathrm{1\ Mx=1G\ cm^2=10^{-8}Wb}$ |
| ガウス | G | $\mathrm{1\ G=1Mx\ cm^{-2}=10^{-4}T}$ |
| エルステッド (c) | Oe | $\mathrm{1\ Oe\triangleq(10^3/4\pi)A\ m^{-1}}$ |

(c)　３元系のCGS単位系とSIでは直接比較できないため、等号「 ≙ 」は対応関係を示すものである。

表10．SIに属さないその他の単位の例

| 名称 | 記号 | SI 単位で表される数値 |
|---|---|---|
| キュリー | Ci | $\mathrm{1\ Ci=3.7\times10^{10}Bq}$ |
| レントゲン | R | $\mathrm{1\ R=2.58\times10^{-4}C/kg}$ |
| ラド | rad | $\mathrm{1\ rad=1cGy=10^{-2}Gy}$ |
| レム | rem | $\mathrm{1\ rem=1\ cSv=10^{-2}Sv}$ |
| ガンマ | γ | 1γ=1 nT=10-9T |
| フェルミ | | 1フェルミ=1 fm=10-15m |
| メートル系カラット | | 1メートル系カラット = 200 mg = 2×10-4kg |
| トル | Torr | 1 Torr = (101 325/760) Pa |
| 標準大気圧 | atm | 1 atm = 101 325 Pa |
| カロリー | cal | 1cal=4.1858J（「15℃」カロリー），4.1868J（「IT」カロリー）4.184J（「熱化学」カロリー） |
| ミクロン | µ | $\mathrm{1\ \mu=1\mu m=10^{-6}m}$ |

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