

# **NEA Sorption Project Phase II**

Interpretation and Prediction  
of Radionuclide Sorption  
onto Substrates Relevant for  
Radioactive Waste Disposal  
Using Thermodynamic  
Sorption Models



Radioactive Waste Management

## **NEA Sorption Project Phase II**

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A report produced for the Management Board of the NEA Sorption Project  
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NUCLEAR ENERGY AGENCY  
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

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## **FOREWORD FROM THE CHAIRMAN OF THE NEA SORPTION PROJECT PHASE II**

This report presents the results of Phase II of the NEA Sorption Project conducted as a co-operative project under the auspices of the Integration Group for the Safety Case (IGSC) of the OECD/NEA Radioactive Waste Management Committee (RWMC). The modelling of the key process of radionuclide sorption is of great importance in assessing the performance or safety of deep and near-surface repositories for radioactive waste. Phase I of the Project was conducted between 1997 and 1998, and was centred on a workshop held in Oxford, United Kingdom. Presentations at this workshop illustrated not only the advances that had been made in the field of thermodynamic sorption models, but also the diversity in the details of the thermodynamic descriptions of sorption processes.

Eighteen funding organisations from thirteen countries participated in Phase II of the Sorption Project. This reflects the value placed on the contribution this project was designed to make to demonstrating the applicability and consistency of thermodynamic models to support the modelling and parameterisation of sorption in assessments.

The funding organisations were represented on a management board that took responsibility for the direction and scope of Phase II Project, reporting progress to the annual meetings of the IGSC and, through it, to the RWMC. A beneficial feature of the Project was the close collaboration between regulators and implementers in a number of countries, reflecting the shared interest in achieving robust sorption modelling.

The Management Board appointed a Technical Direction Team (TDT) of qualified, experienced scientists, and delegated to them the responsibility of developing test cases for modelling by one or more of the 20 groups drawn from the participating countries. The TDT was also responsible for the subsequent analysis and reporting, in this publication, of the modelling outcomes.

This report has been divided into three parts. Part 1 is designed as a complete status report on the Project, in order to make the synthesis of its results and interpretations, the conclusions and the recommendations accessible to the widest possible readership. Part 2 contains a more detailed description of the modelling approaches, results and interpretations. Part 3 contains the data summaries that provided the basis of the model assessment and the overall report.

In the view of the Management Board, this report reflects a realistic view of the current capabilities of thermodynamic sorption modelling, and how these capabilities could be developed in the future. It is hoped that the report will be widely read and used by all those who have an interest in assessing the contribution of sorption to the safe, long-term management of radioactive waste.

The successful outcome of Phase II of the NEA Sorption Project could not have been achieved without the scientific contributions of the TDT and the modelling groups; it also owes a great deal to the constructive review and discussion that has taken place between the different participants.

The Management Board would like to acknowledge these contributions, as well as the essential support for the Project provided by participating organisations in the form of direct funding and the provision of expert modelling groups.

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GRS/FZK/FZR	Germany
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JNC	Japan
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## **ORGANISATION OF THE REPORT**

This entire project report is organised into three parts, as detailed below.

- Part 1: This part forms the core of the project report. It contains the actual status report of the project, summaries of the main results and interpretations of test cases presented in Part 2 and all conclusions and recommendations.
- Part 2: This part contains a detailed description, assessment and interpretation of the modelling approaches and results of all test cases.
- Part 3: This part contains additional data plots that form the basis for Parts 1 and 2. In particular, graphical comparisons of experimentally determined and model-derived  $K_d$  values as well as the corresponding quantitative assessments of fits (error plots) are contained herein.

## **Acknowledgements**

The authors would particularly like to acknowledge the effort on part of the various modelling teams, without whom the whole project would not have been possible. Very gratefully acknowledged are further the support by and critical discussions with the Management Board. A thank you is also extended to the NEA staff and management board members who were of much help with regard to logistical aspects.



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\* Each participating organisation selected its modelling teams based on its own criteria.



## GLOSSARY

### Acronyms

BET	Brunauer-Emmett-Teller (a type of isotherm that forms the basis for determining surface area via adsorption of an inert gas)
BSM	basic Stern model
CA	component additivity
CCM	constant capacitance model
CEC	cation exchange capacity
DCB	dithionite-citrate-bicarbonate reagent (extracts crystalline iron phases)
DLM	diffuse layer model
EBS	engineered barrier system
EDL	electrical double layer
EGME	ethylene glycol monoethyl ether
EXAFS	extended X-ray absorption fine structure
GC	generalised composite
GT	Gaines-Thomas or equivalent fraction formalism
IE	ion exchange
IEM	ion exchange model
$K_d$	distribution coefficient (see equation 2.1)
NEM	non-electrostatic model
PA	performance assessment
RN	radionuclide
SC	surface complexation
SCM	surface complexation model
SOH	SOH stands for a surface complexation site; i.e. a hydroxo group (OH <sup>-</sup> ) bound to a metal atom (e.g. Al or Fe) on a solid surface (denoted > or S)
TAO	Tamms acid oxalate (a reagent that extracts non-crystalline iron phases such as ferrihydrite)
TDB	thermodynamic database
TDT	technical direction team

TLM	triple layer model
TSM	thermodynamic sorption model
X	stands for an ion exchange site

### **Notation**

extension:	“extension” is used for the application of a model to a system different from that used for calibration in a situation where the two systems differ only in terms of substrate, but not in terms of chemical conditions
extrapolation:	“extrapolation” is used for the application of a model to a system different from that used for calibration in a situation where the two systems differ in terms of chemical conditions (and substrate in some cases)
fitted parameter:	see Appendix 2 in Part 2 for details
substrate:	any sorbing solid; encompasses single minerals as well as complex mineral assemblages

## EXTENDED SUMMARY

### Introduction and project set-up

Deep or near-surface underground repositories are considered worldwide for the safe long-term storage and/or final disposal of radioactive wastes. A central safety feature is the prevention, or sufficient retardation of radionuclide (RN) migration to the biosphere. Radionuclide sorption is one of the most important processes which provide this safety feature; for performance assessment (PA) sorption is generally characterised by equilibrium distribution coefficients ( $K_d$  values). The NEA Sorption Project was established to address the propositions that:

- (1) the uncertainty associated with  $K_d$  values used for PA arises to a large part from the necessity to transfer  $K_d$  values experimentally determined in the laboratory to the expected *in situ* conditions corresponding to different PA scenarios;
- (2) thermodynamic sorption models (TSMs) are uniquely suited for accomplishing this transfer in a fully quantitative and traceable fashion, because of their potential ability to describe sorption under variable geochemical conditions and to integrate geochemical and sorption equilibria in a single coherent model.

This document presents the results of Phase II of the NEA Sorption Project, whose major focus was on testing and demonstrating the ability of various TSM approaches to describe radionuclide sorption over a range of geochemical conditions; i.e. to reduce uncertainty in  $K_d$  and to increase confidence in PA. The first phase of the project ran from 1997 to 1998 and illustrated not only the advances that had been made in the field of thermodynamic sorption models, but also the diversity in the details of the thermodynamic descriptions of sorption processes. Accordingly, Phase II of the NEA Sorption Project was initiated as a major international contribution towards demonstrating the consistency and applicability of different TSM approaches to support the selection of  $K_d$  values for safety assessments. To allow an evaluation of the respective merits and limitations of different TSMs, the project was implemented in the form of a comparative modelling exercise based on selected datasets for radionuclide sorption by both simple and complex materials. These were organised into seven Test Cases (TC 1-7) that were prepared and distributed to participating organisations:

- Group 1 – Simple substrates: Single oxide minerals:
  - TC1: Neptunium(V) sorption on hematite under the influence of carbonate.
  - TC2: Selenium(VI) and selenium(IV) sorption on goethite.
  - TC3: Uranium(VI) sorption on quartz under the influence of carbonate (two studies).
- Group 2 – Substrates of intermediate complexity: Clay minerals and bentonite:
  - TC4: Nickel sorption on montmorillonite and natural bentonite under varying conditions (four studies).
  - TC5: Neptunium(V) sorption on montmorillonite under the influence of carbonate (two studies).



- Group 3 – Complex substrates: Soils and sediments

TC6: Uranium sorption on weathered schist materials from the Koongarra deposit in Northern Australia.

TC7: Cobalt sorption on subsurface materials including separated mineral components from South Carolina, USA, including the effects of humic substances.

A technical direction team (TDT) was appointed to evaluate the existing database, develop test cases for sorption modelling, and carry out the subsequent analysis and interpretation of modelling outcomes. In December 2001, the selected datasets were delivered to the modelling teams in the form of standardised Excel<sup>R</sup> spreadsheets, which contained radionuclide sorption data as a function of experimental conditions as well as a range of auxiliary data. In total, 20 modelling teams participated in the exercise, allowing conclusions of the project to be based on a broad range of experience and expertise. In analysing the modelling outcomes, model fits as well as predictions were quantitatively compared with the respective experimental data. Particular attention was paid to elucidating the effects of certain model components (type of sites, electric double layer structure, etc.) and of decisions process was a 3-day participants' workshop held in October 2002 in San Lorenzo de El Escorial, Spain involving modelling teams related to all participating organisations. The material presented at this workshop forms Part 3 of the project report. Based on the feedback and additional information gained from the workshop, the TDT further interpreted and synthesised the project outcomes. The outcome of that assessment is contained in Parts 1 and 2 of the present report.

This project seeks to address the stakeholders of Phase II of the NEA Sorption Project, in particular radioactive waste management organisations and regulators, as well as modellers and experimentalists who are involved in PA.

### **Framework for the use of TSMs for performance assessment**

In PA, a large number of parameters is used to represent the relevant processes along a given migration path. Ultimately, movement and fate of radionuclides is determined by i) their maximum solubility in the respective aqueous solutions, and ii) the partitioning of their dissolved forms between the solutions and the surfaces that they encounter along their migration path.

Particularly critical in this regard is the assessment and management of uncertainty in  $K_d$  as a function of geochemical conditions, which can have a major influence on the assessment of repository performance. This means that confidence in PA may rely strongly upon confidence in  $K_d$ , and a reduction of uncertainty in  $K_d$  allows the use of excessively conservative safety factors to be avoided.

RN sorption along the migration path is significantly influenced by the variability of the geochemical composition. Because of the highly conditional nature of  $K_d$ , different estimates of  $K_d$  values for each relevant RN are required for each environmental compartment along the migration path. In addition, two additional sources of variability or uncertainty of geochemical conditions, and thus of  $K_d$ , usually have to be addressed within each compartment. First, both groundwater and solid phase composition for a given compartment can often be determined only within a certain range. In particular the *in situ* water or solid phase composition can often be estimated only through geochemical models. Secondly, where very long timeframes need to be considered (e.g. for the disposal of high-level and many intermediate-level wastes), it is necessary to estimate possible future conditions, for example by coupled geochemical/mass-transfer models. Irrespective of whether a deterministic or probabilistic approach to PA is pursued, these sources of geochemical variability, and

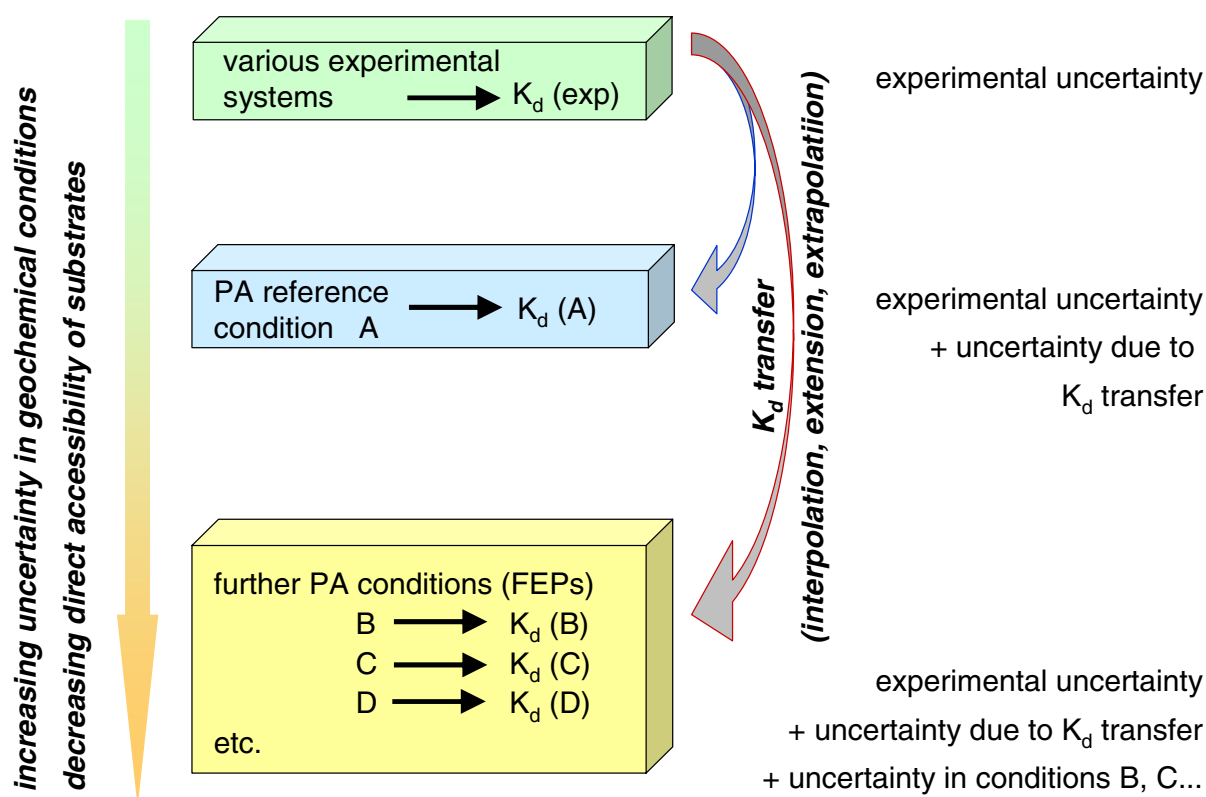
their effect on  $K_d$ , usually have to be taken into account for a reference scenario as well as for alternative scenarios.

It is obvious that it is not feasible to determine  $K_d$  for every system and condition experimentally, and many of the relevant systems are difficult to reproduce in the laboratory. Therefore, selected  $K_d$  values for PA are typically based on:

- a limited set of experimental sorption data for solid substrate samples obtained directly from a given site or chosen material; and/or
- a larger set of sorption data for approximated, simplified, or generic systems.

The relations between data obtained in approximated and/or simplified experimental systems and the derivation of  $K_d$  for conditions being modelled in performance assessments, as well as the associated principal uncertainties, are schematically illustrated in Figure 1. The resulting overall uncertainty of the selected  $K_d$  is composed of the experimental errors and any uncertainties introduced in making the transfer from approximated, experimental conditions to the actual or predicted geochemical conditions.

Figure 1: **A schematic and simplified illustration of the derivation of  $K_d$  values for performance assessment based on sorption data from approximated experimental systems and of the associated uncertainties.  $K_d$  data transfer includes any procedures (TSM approaches, expert judgment, etc.) to take into account differences in mineralogy and solution composition. Uncertainties in data transfer are almost unavoidable; their magnitude is critically dependent on how well the relations between  $K_d$  and the key geochemical parameters are constrained**



The datasets modelled in this project illustrate the variability of  $K_d$  as a function of key geochemical parameters. Therefore, the following critical issues with regard to the overall uncertainty of selected  $K_d$  values can be identified:

- In all cases where a direct measurement of  $K_d$  under PA-specific conditions is not possible, a transfer of sorption data from one set of conditions to another will invariably be required. This must take into account any differences in mineralogy as well as surface and solution speciation. This transfer can be made in the following ways:
  - i) fully quantitatively through the use of TSMs, using their unique capability to directly couple sorption and geochemistry in a single thermodynamic model;
  - ii) in a semi-quantitative way, by taking into account differences in e.g. CEC, RN speciation, etc.; or,
  - iii) by qualitative “expert judgement”.
- The larger the difference between the experimentally investigated systems and the conditions being modelled in a PA, the more the overall uncertainty will be determined by uncertainties in transferring sorption data from one set of conditions to another. Note that this will apply regardless of the method used for  $K_d$  data transfer (TSM, expert judgement, etc.).
- Uncertainties in the selected  $K_d$  will be compounded by any uncertainties in the expected geochemical conditions.

Based on these points, the following general recommendations can be made:

- Uncertainties will be smaller where data transfer to the conditions being modelled in a PA can be done through interpolation, rather than through extension or extrapolation. Therefore, the conditions being modelled in a PA should be approximated as much as possible in experiments.
- Even if extrapolation becomes necessary, it is a significant advantage if several source datasets are available, as this will allow one to perform tests of internal consistency.
- The likely requirement of having to transfer  $K_d$  from one set of conditions to another underscores the importance of understanding the influence of key geochemical parameters. Independent of the method used for data transfer, this requires the systematic variation of such parameters in experimental investigations. However, only TSMs are capable of directly coupling sorption reactions and all relevant geochemical *equilibria* in a single coherent model.

It follows from this discussion that the utility of TSMs for PA is based on their unique ability to provide a thermodynamic framework for integrating quantitatively the influence of all relevant geochemical parameters on  $K_d$  in a single equilibrium model.

While differences exist concerning the specific formulation of TSMs, they are clearly accepted as scientifically sound. That this position has been reached is largely due to the fact that for single sorbents, the key parameters defining a TSM (in particular the number and nature of sorption sites) are well constrained through independent methods, and many studies on similar materials have demonstrated reproducibility and overall consistency.

In contrast, the materials of interest to PA are more complex in nature (many of them contain several sorption-active mineral phases), and for many of these materials this same level of (scientific) credibility is not given to date, for two reasons: first, neither the analytical nor the modelling tools available allow an unambiguous characterisation of the key parameter values for a TSM. Secondly,

there clearly is a limitation of RN sorption datasets with sufficient variation of key geochemical parameters. Together these two factors loosen the constraints on modelling sorption on complex materials, and in direct consequence, allow several non-unique TSM approaches to be applied to a given dataset with the same degree of success. Therefore, a key underlying question of Phase II of the NEA Sorption Project is how to model the overall sorption behaviour ( $K_d$ ) of RNs under the given uncertainty.

### **Status of TSMs for radionuclide sorption modelling**

The inter-comparison carried out in Phase II of the NEA Sorption Project provides a unique opportunity to test and compare different thermodynamic sorption modelling approaches for several datasets. The analysis of the very large number of modelling results presented in Part 2 represents a substantial body of evidence to underpin the conclusions and recommendations given in Chapter 7, Part 1. Major outcomes of this project are discussed in the following paragraphs.

The value of TSMs in quantifying the geochemical factors that determine  $K_d$  was demonstrated in a variety of systems. The thermodynamic sorption models tested in this project were able to reproduce the trends, and in most cases the magnitude, of  $K_d$  in experimental data, over a very wide range of simple to complex mineral substrates and aqueous chemical conditions (pH, carbonate concentration, etc). The ability of the TSMs to simulate radionuclide sorption data under various chemical conditions is a significant attribute of the approach, and represents a major advantage in comparison to constant  $K_d$  or isotherm models.

Average absolute errors of model predictions in comparison to experimental data were in the range of 0.5-1 log  $K_d$  units or less for a number of cases. This capability demonstrates significant system understanding and the utility of TSMs for the selection of  $K_d$  values for PA.

It also has to be pointed out, however, that modelling personnel and their decisions and preferences have a major influence on model design and performance. In several cases, this influence became clear only after a detailed analysis by the TDT. This is important to keep in mind, and an important issue brought up in Phase I of the NEA Sorption Project needs to be re-stated: much of the usefulness and credibility of TSMs will depend on an internally consistent and transparent decision-making process during model development. Many components of a final model can be justified on the basis that some possible options were evaluated at each point and a reasonable one was chosen. In the end, the various models applied within this exercise indicate a significant diversity of approaches. This is consistent with the basic project setup, which emphasised a comparative evaluation of the best models typically in use, rather than the development of truly optimised models.

Further important outcomes of the modelling inter-comparison are summarised below:

- The consideration of multiple datasets in the fitting procedure tends to increase model complexity, but clearly improves model performance.
- Data-requirements for modelling should be considered during experimental programmes, which should ideally involve modellers' input. In particular, component additivity (CA) models should be built from single mineral models which are based on a similar range of parameter variation that is foreseen in the CA model application.
- Ternary surface complexes appear to be an important model feature in test cases involving actinides with variable partial pressure of carbon dioxide ( $p\text{CO}_2$ ).
- The site-density estimates are a particularly important part of the modelling, but were subject to considerable uncertainty. The modelling results for TC6 indicate that this

represents a major potential source of discrepancy, suggesting that further work may be required to gain a consensus and develop agreed methods of estimating site densities.

- At the present time, generalised composite (GC) approaches for complex materials appear to lead to simpler models that perform better than CA models in achieving a good description of sorption data as a function of chemical conditions. It should be noted, however, that the GC approach requires the collection of sorption data on the complex material, and thus, the material must be available for study.
- Sorption modelling for complex materials is far from being standardised, and a range of fitting and modelling approaches was used in this exercise. The transfer of models from one substrate to another is not in every case readily accomplished in the CA approach, and is not recommended for dissimilar substrates in the GC approach.
- The single mineral component models presently available are not yet adequate for a full evaluation of CA modelling for complex materials. In particular, the influence of several major groundwater anions and cations on radionuclide sorption has not been investigated sufficiently to date.
- In applying TSMs, model parameter values taken from the literature should be used with great care. For example, stability constants for surface complexation (SC) parameters cannot be used directly from the literature, even for the same mineral surface, if a different total site density is utilised in the extrapolated model. In particular the GC modelling approach is semi-empirical, and surface stability constants for such models are valid only for the particular assemblage of solid phases being studied. A partial solution to the problem of conditional surface complexation model (SCM) parameters would be the establishment of appropriate reference states.

### **Contribution to building confidence in $K_d$ for performance assessment**

The overall objective of the NEA Sorption Project is to clarify and demonstrate how the use of *thermodynamic sorption models* (TSMs) can serve to improve confidence in the  $K_d$  values used to represent radionuclide sorption in most performance assessment (PA) models. In order to see clearly how the results of Phase II of the Sorption Project have helped in this regard it is useful to identify the main foundation blocks upon which  $K_d$  confidence is built.

Nearly all PA models are based on a multi-barrier system representing a specific repository concept, including engineered barriers, host rock and surrounding geosphere system in terms of discrete compartments containing specific *solid materials* (e.g. bentonite, porous host-rock mineral assemblage, fracture lining and infilling minerals) and contacting aqueous *solutions* (porewater). In PA, radionuclide transport models generally require a  $K_d$  value for each radioelement, in each of these compartments, in order to calculate the effect of sorption on radionuclide migration. Because  $K_d$  for most radioelements is sensitive to geochemical conditions (solution composition, the nature and amount of the mineral and organic solid phases making up the solid material's wetted surface) it may vary significantly from one compartment to another if there are significant differences (spatial heterogeneity) in solid or solution composition or, for a given compartment, if the composition evolves over time because of repository-induced perturbations.

Given the foregoing, confidence in  $K_d$  values provided to PA will be improved if:

1. it can be shown that the major physical-chemical mechanisms underlying the sorption of a radioelement on different types of solid materials and how sorption intensity is affected by changes in geochemical conditions are understood;

2. it can be demonstrated that, using models which reflect this understanding, it is possible to represent changes in  $K_d$  with reasonable accuracy as a function of variations in relevant system parameters [pH, ionic strength,  $\text{CO}_2$  partial pressure ( $p\text{CO}_2$ ), etc.].

The results of the NEA Sorption Project's Phase II contribute substantially to both of these aspects.

The seven test case datasets used in the Phase II inter-comparison modelling exemplify how  $K_d$  can vary over several orders of magnitude as a function of key chemical parameters, for a diverse variety of solid materials and radioelement types. The overriding conclusion that can be drawn from the modelling results is that, *for all of these example systems, multiple teams using different model development strategies were able to represent the  $K_d$  variation over the full parameter space with good accuracy (generally within 0.5 log unit)*. Although the modelling strategies differed among the teams, *all were guided by a single principle, representation of sorption in terms of mass action and mass balance laws (i.e. TSM)*. The results also showed that model accuracy improved substantially when modellers were provided with datasets richer in sorption-pertinent information.

From a purely practical (engineering) standpoint, these highly satisfying results demonstrate that TSM-type models are an efficient and flexible means of representing existing and predicting experimental data regarding  $K_d$  dependence on potentially variable chemical parameters. If a geochemical model, coupled or not with a transport model, is available for calculating the potential chemical compositions for a given repository volume, incorporation of an appropriate TSM will allow direct calculation of the corresponding  $K_d$ .

The reasons why the Phase II results should also serve to increase confidence in the scientific credibility of TSM representations of  $K_d$  are more subtle, in part because they are woven into the nature of the exercise itself.

First consider the datasets. One of the main reasons for their selection was that they included wide variations in parameters strongly influencing  $K_d$  for different adsorbing elements. This is not fortuitous – the experimentalists who made the measurements chose their experimental parameters (e.g. pH,  $p\text{CO}_2$ , ionic strength, complexing ligand concentration) based on their knowledge of plausible reactions between the radioelement, dissolved components and the types of “sorption sites” expected to be on the surfaces of the minerals and organic substances present in the synthetic or complex solid materials they were investigating. The great amount of existing knowledge supporting the TSM “paradigm”, in particular that regarding sorption of many different types of elements onto relatively simple solid phases, allowed these experimentalists to make hypotheses about how different parameters would affect  $K_d$ ; the seven test case datasets measurements are but a few examples among many of these hypotheses being verified, at least qualitatively.

Secondly, the Phase II modelling results demonstrated that different approaches can be used in constructing a self-consistent TSM model for any given dataset, giving in many cases similar qualities of fit. While this non uniqueness might be interpreted as indicating that TSM models are an effective  $K_d$  data-fitting method, the real message is quite another and should also promote confidence. The essential characteristics of TSM descriptions that make them more scientifically credible than empirical fits to data are that they require the modeller to choose, and defend, based upon experimental data, values for the essential chemical characteristics known to govern adsorption in all systems: the number of sorption sites and corresponding total concentrations, stoichiometries for the adsorbed species and the corresponding thermodynamic equilibrium constants. The possible choices for each characteristic may be constrained in certain cases (e.g. sorption on synthetic minerals with spectroscopic data regarding surface species composition and configuration) or be much wider in

others (e.g. complex mineral assemblages having a heterogeneous mixture of sorption site types). The fact that the Phase II results showed that different choices can lead to comparable results (in the latter case) should be seen as a demonstration that the TSM approach offers a robust and scientifically defensible method of quantifying the essential characteristics of  $K_d$  of interest to PA (i.e. calculation of  $K_d$  values for potentially variable system conditions), in a rigorous, widely accepted conceptual framework.

Last but not least, the results of the Phase II modelling tend to show on one hand that predicting  $K_d$  behaviour for materials of moderate complexity (bentonite, some clay host rocks) can be based on sorption properties of the single minerals that are mainly contained in such substrates. This allows using sorption measurements on the entire substrate as an independent check. On the other hand predicting  $K_d$  behaviour for complex materials based solely on data concerning the major minerals present and sorption parameter values presented in the literature for pure, single mineral systems is difficult and subject to greater error than modelling sorption data on single mineral phases. For complex materials a dedicated experimental programme is needed to generate sufficient amounts of appropriate data in order to sufficiently constrain a TSM model. However the data requirements of a well-guided experimental programme aimed at PA purposes may be less than typically used in detailed scientific studies of sorption on single mineral phases; e.g. solid phase characterisation may be reduced. The TSM approach will, on the other hand, generally allow identification of many of the key parameters likely to strongly affect a given radioelement's  $K_d$  value, and may be used for planning and optimising such programmes.

To conclude, the results of the NEA Sorption Project Phase II show that:

- the conceptual and methodological tools needed for characterising, interpreting and justifying the  $K_d$  values provided for PA needs are largely available;
- with regard to complex materials, what is mainly needed are good quality and more complete sets of pertinent sorption data.

Future efforts of the Sorption Project should therefore be focused on development and demonstration of an “optimised”, TSM-guided approach to experimental characterisation and interpretation of radioelement adsorption on complex materials.

# **PART 1**





## 1. INTRODUCTION AND OBJECTIVES

### 1.1 Overview

Agencies worldwide with responsibility for a variety of radioactive wastes are considering deep or near-surface underground repositories for the safe long-term storage and/or final disposal of these materials. A central issue is the prevention, or sufficient retardation of, radionuclide (RN) migration to the biosphere. Radionuclide sorption is one of the most important processes which provide this safety feature (NEA, 2001). Phase II of the NEA Sorption Project was initiated as a major international contribution towards demonstrating the applicability of different thermodynamic sorption modelling (TSM) approaches to support the selection of  $K_d$  values for safety assessments of radioactive waste disposal. The project was implemented in the form of a comparative exercise with the specific aim to interpret selected well-characterised datasets for radionuclide sorption by both simple and complex materials using different modelling approaches. The systematic application of various TSMs to identical datasets allows an evaluation of the respective merits and limitations and the formulation of recommendations on the use of these models.

Agencies and individuals that share an interest in modelling sorption processes within the framework of radioactive waste disposal constitute the stakeholders of Phase II of the NEA Sorption Project. In particular, this project seeks to address the following audiences:

- Radioactive waste management or nuclear power industry organisations, as well as government organisations and regulators who are involved in evaluating sorption parameters (such as  $K_d$  values) to be used in performance assessment (PA).
- Members of the above organisations who are making decisions related to radioactive waste disposal or management.
- Modellers who are involved in the derivation or evaluation of sorption parameters within the framework of radioactive waste disposal.
- Experimentalists who design and carry out experimental programs aimed at the generation of PA-relevant sorption data.

The present Part 1 constitutes a complete status report on the project, aimed at making its results and interpretations, as well as conclusions and recommendations accessible to the above audiences in a synthesised form.

- Chapters 1 and 2 provide introductory and background information on the project and on aspects of thermodynamic sorption modelling approaches most relevant to performance assessment.
- Chapters 3 and 4 outline the project methodology and implementation.
- In Chapter 5, the main modelling results are presented and interpreted; and a more detailed discussion of key issues in the application of thermodynamic sorption models to radionuclide migration is given in Chapter 6.
- Conclusions and recommendations are presented in Chapter 7.

### **1.1.1 Relation of sorption ( $K_d$ ) to performance assessment (PA)**

In developing an understanding of the safety implications of underground repositories for radioactive waste, it is necessary to consider the likely mechanisms that could lead to a release of radioactivity from such a facility. In the majority of potential scenarios, the most critical pathway for release is the migration of RN from the waste via groundwater to the biosphere.

In any PA study, a large number of parameters is used to represent the relevant processes along this migration path. Movement and fate of RNs is dependent on the following two parameters (cf. NEA, 2001):

- The maximum solubility of the particular RN in the relevant solutions.
- The partitioning of dissolved RNs between the solution and the surfaces that they encounter on their migration path from the repository, generally characterised by equilibrium distribution coefficients ( $K_d$  values).

The estimation of  $K_d$  values for PA will rely on a relatively small amount of site-specific  $K_d$  data, supplemented by a much larger amount of information on sorption in simplified and/or similar systems. Particularly critical in this regard is the assessment and handling of parameter uncertainty. As pointed out in NEA (2001) uncertainty in  $K_d$  as a function of geochemical conditions can have a major influence on assessment of repository performance. This means that confidence in PA may rely strongly upon confidence in  $K_d$ , and a reduction of uncertainty in  $K_d$  enables avoidance of excessively conservative safety factors.

### **1.1.2 Motivation for a thermodynamic sorption modelling project**

Sorption of radionuclides on a range of surfaces encountered in multi-barrier systems is often established as one of the main processes for repository safety in either deterministic or probabilistic PA. As outlined in NEA (2001), RN sorption along the migration path is significantly influenced by the variability of the geochemical composition of the system. TSMs (see Section 2.2) are uniquely suited for relating the magnitude of  $K_d$  to governing factors such as pH and  $p\text{CO}_2$  in the host rock, because they explicitly integrate sorption reactions with overall geochemistry in a single coherent, thermodynamic model. Therefore, these models have great potential to support the selection of the values and associated uncertainties of radionuclide  $K_d$  values.

The ability of TSMs to integrate the geochemical variability of the system and its influence on the radionuclide sorption properties in a common framework potentially enables robust estimates of uncertainty, provides scientific credibility, and ultimately increases confidence in PA.

### **1.1.3 Relation to Phase I of the NEA Sorption Project**

This document presents the results of Phase II of the NEA Sorption Project. The first phase of the project ran from 1997 to 1998 and was centred around a workshop held in Oxford, UK. Presentations at this workshop illustrated the advances that had been made in the field of TSM with many successful models of RN sorption onto simple minerals and natural samples (NEA, 2001). It was recognised that there is already significant consensus in the modelling approaches, which were based on mass action laws for chemical species in solution and sorbed to the surface sites on the solid. However, there was a great diversity in the details of the thermodynamic descriptions of sorption processes. There was no clear consensus regarding whether or not a single type of TSM is applicable for modelling sorption in natural systems. In particular, the necessity and the choice of electrostatic correction terms were not resolved. The multiplicity of Electrical Double Layer (EDL) models

appeared to limit the credibility of TSMs as a whole. This is despite the fact that a similar degree of freedom is common in other fields: e.g. different methods for ionic strength correction in solution chemistry and porosity models in hydrology.

Accordingly, it was concluded (NEA, 2001) and recognised in the proposal for Phase II of the NEA Sorption Project that a systematic, critical evaluation of the various sorption modelling approaches must be carried out. A consistency of approach appropriate for different PA applications would ultimately be required to gain wider use of TSMs within PA.

## **1.2 Scope and key features of the Phase II benchmarking project**

Phase II of the NEA Sorption Project aimed to demonstrate the applicability of TSM approaches to support the selection of  $K_d$  values for PA. It took the form of a benchmarking exercise using different modelling approaches to simulate selected well-characterised datasets for RN sorption by simple and complex geologic materials.

In addition to surface chemical interactions, there is a number of additional (and often ill-defined) factors that can play an important role in retardation. These include physical factors (such as flow-wetted surface, accessibility of pores and matrix diffusion) as well as chemical factors (solid-solution formation, co-precipitation, RN oxidation-reduction on solids, etc.). It can be argued as to whether such factors need to be clearly separated or may be lumped together with sorption in PA applications. Clearly, distinction between these processes at the conceptual level is essential to reduce parameter uncertainty. Accordingly, the present report is restricted to the consideration of the surface chemical interaction; i.e. sorption. The term “ $K_d$ ” is used exclusively in this sense.

Phase II of the NEA Sorption Project was a step towards demonstrating the capability of TSMs for describing, and in some cases predicting,  $K_d$  in PA-relevant systems. While the project was implemented in the form of a “benchmarking” exercise for different TSM approaches in use at the participating organisations, it needs to be clearly distinguished from the earlier CHEMVAL benchmarking projects. The present project was not concerned with a “validation” of computer codes through the use of prescribed, identical input parameters. Instead, the goal was to interpret and/or predict selected datasets for sorption onto simple and complex materials using the TSM of choice. By applying the various TSMs in a systematic way to the same experimental data, an evaluation of the merits and limitations of the approaches became possible and recommendations on the use of these modelling approaches for PA could be made.



## **2. THERMODYNAMIC SORPTION MODELLING OF SUBSTRATES RELEVANT TO RADIOACTIVE WASTE DISPOSAL**

### **2.1 Relation of various geological substrates to PA tasks**

Despite the widespread use of TSMs for simple laboratory systems, they have had limited applications to predicting pollutant migration in the environment. This may be associated with the complexity (and associated data needs) of environmental substrates. At the same time, the importance of applying TSMs to complex environmental substrates has been recognised only in recent years, and a lower priority has been given to this challenge. However, PA requires that natural systems be modelled, regardless of their complexity.

The selection of suitable test cases for the NEA Sorption Project (Phase II) reflected the requirement to extend TSMs from simplified to complex substrates. As will be shown in the forthcoming chapters and in Part 2 of this report, the results obtained in this project for weathered rock (TC6), soils (TC7) and bentonite (TC4) show that relevant substrates are not so complex as to render sorption modelling impossible, and that the data needs can be kept at a reasonable level. To provide a PA context for the various test cases, a brief discussion of relevant simple and complex substrates for different PA situations is given below.

#### **2.1.1 Engineered barrier system (EBS)**

The EBS of radioactive waste repositories for the deep geological disposal of HLW below the groundwater table is expected to consist mainly of bentonite. Bentonite is formed through the weathering of tuff and volcanic glass, the active ingredient being 2:1 smectite clays (which usually make up  $\geq 50\%$  by weight). The relative proportions of montmorillonite, nontronite and beidellite depend on the source material. In addition to clay minerals, natural bentonite may contain silica, carbonate minerals, gypsum and halides; and possibly traces of pyrite. While natural bentonite is a complex mixture of many minerals, it appears that sorption is largely controlled by smectite, whereas the accessory minerals mainly determine the chemistry of the contacting solution or groundwater. Thus, sorption on bentonite can in principle be addressed by TSMs similar to those for pure montmorillonite.

Cement-based materials (possibly in combination with bentonite) are expected to be utilised for wastes with lower levels of radioactivity. These materials will have various applications in repository concepts, either as structural components or as part of the EBS or waste-form itself. Depending on the repository design, cement may play an important role as a chemical barrier to migration. Hardened cement paste consists of amorphous calcium-silicate-hydrates (CSH), portlandite and crystalline calcium-aluminate-phases, such as ettringite. Because of the reactivity of these mineral phases and the resulting importance of incorporation reactions, TSMs are not considered to be an adequate tool for cement-based materials.

### 2.1.2 *Repository host rocks (deep and shallow geological disposal)*

The consolidated rock formations considered as candidate hosts for deep repositories in most countries consist of crystalline rocks (e.g. granite) or clay formations.

Clay formations may contain 1:1 clays (kaolinite) and illitic clays in addition to smectites. In principle, sorption on these minerals can be handled by similar TSMs to those for montmorillonite. Some clay formations (e.g. Belgium's Boom Clay) contain substantial amounts of organic matter, which increases the complexity of the system.

In the case of granitic rock, a fresh mineral surface (such as used in experiments with machined or crushed rock) is unlikely to be representative of the surfaces involved in RN retention. The secondary minerals that form in water-containing fractures and fissures will play a much greater role. Fracture infill material containing a high proportion of clay minerals and other sheet silicates (e.g. Meyer *et al.*, 1989) may be treated analogously to natural clays. Depending on the rock composition and redox conditions, ferrous/ferric (hydr)oxides and other amorphous mineral phases may also be present. In many cases, the complexity of the system would start to approach that of surface soils or sediments (see the following section).

### 2.1.3 *Near-surface substrates (contaminated sites, surface disposal)*

This category comprises weathered rocks, unconsolidated sediments and soils. In such complex substrates, a number of RN sorbing minerals will be present simultaneously. In addition to clay minerals, ill-defined sorbents such as amorphous iron-(hydr)oxides, amorphous silica and complex natural organic matter may play important roles. Because of this mix of reactive minerals, a full characterisation of the component sorbing phases is problematic. For example, it is often impossible to carry out basic investigations such as surface acid-base titrations. This is because a substantial fraction of the substrate may dissolve in the process, and also because the resulting titration curves are composite data for a mixture of titrable phases. Although the identification of active sorbing surfaces by chemical extraction methods has been attempted (e.g. Tessier *et al.*, 1979) this usually results in ambiguous data and the usefulness of these extractions remains the subject of controversy.

For these materials, basic surface charge data are likely to be lacking, and a non-electrostatic model (NEM) for sorption may be chosen, given that there is no basis for parameterising the EDL term (see Section 2.2). Choices of EDL models and parameters are discussed in Sections 5.1.2.3 and 6.1.2, respectively.

## 2.2 **Thermodynamic sorption models and $K_d$ estimation for PA**

As noted before, an important input parameter in modelling RN mobility in the environment is the solid/liquid partitioning coefficient ( $K_d$  value). In addition to deriving the best possible  $K_d$  estimate for each specific situation, an essential underlying goal of a TSM is (has to be) chemical plausibility (see Section 2.2.1 for further details). Following the classical approach of solution coordination chemistry, surface chemical reactions are based on mass laws for dissolved and surface-bound components. Once the mass-laws for all solution and surface reactions are implemented within a TSM, the distribution of a RN between surface and solution can be computed. The derivation of  $K_d$  is then straightforward, as shown in equation 2.1:

$$K_d = \frac{\text{amount of element X sorbed per unit mass of substrate}}{\text{amount of element X dissolved per unit volume of solution}} \quad (2.1)$$

where the amount of element X sorbed per unit mass of substrate represents the stoichiometric sum of surface species of element X (moles of surface species of X/unit mass of substrate) and the amount of element X dissolved per unit volume of solution represents the stoichiometric sum of aqueous species of element X (moles of aqueous species of X/unit volume of solution).  $K_d$  values are typically reported in units of L/kg or mL/g.

The widespread use of TSMs to estimate  $K_d$  values would require surface complexation models to have a broad level of acceptance from those responsible for PA development. However, TSMs for RN sorption are less accepted than the thermodynamic models that support solubility calculations. There are probably two reasons for this (NEA, 2001):

- The perception that different sets of RN-surface *equilibria* will adequately describe a given set of experimental adsorption data; i.e. TSMs are not unique solutions. An important way to incorporate realistic surface species for TSMs is the continued acquisition of surface spectroscopic data identifying the surface species formed during adsorption reactions. For some systems, this is now possible, and maintaining consistency between spectroscopic results and surface complexation models can eliminate alternative solutions. In the meantime, the choice between non-unique solutions in simple systems is driven by the chemical plausibility of the proposed surface reactions and the goodness-of-fit to experimental data. If experimental data are obtained for a sufficiently wide range of experimental conditions (e.g. RN concentrations,  $p\text{CO}_2$ ), the possible choices in modelling can be reduced. In some cases surface species can be excluded because of poor simulation of specific datasets. The property of non-unique surface complexation model solutions is not necessarily due to a lack of thermodynamic rigor, but rather to a degree of freedom that requires additional data collection (spectroscopic or other) to be constrained and resolved. It is pointed out that non-uniqueness is by no means restricted to TSMs, but is also a common feature of solution chemical equilibria involving more than two reactants (see, for example, the actinide- $\text{CO}_2$ - $\text{H}_2\text{O}$  system; cf. Grenthe *et al.*, 1992 and Lemire *et al.*, 2001).
- The perception that the possible selection of different EDL models in surface complexation modelling (see Section 2.2.1), implies that surface complexation models will inevitably lead to non-unique solutions. Here, a comparison with activity correction methods in solution chemistry (e.g. Davies, SIT, Pitzer; see Grenthe *et al.*, 1997) or in traditional ion exchange formulations (e.g. Gaines-Thomas, Vanselow; see Sposito, 1981) can be made. As long as the SCM is self-consistent with the chosen EDL in its calibration of model parameter values, any SCM can be employed with thermodynamic rigor within a TSM. As with activity correction methods in solution chemistry, the choice of EDL model depends on the complexity of the application in which the SCM will be used and the availability of requisite model parameters.

The issue of chemical plausibility of TSMs is further discussed below, paying special attention to the treatment of surface charge. Section 2.2.2 proceeds to give an overview of the different modelling strategies available for complex natural mineral assemblages.

## **2.2.1 Chemical plausibility and treatment of surface charge**

### **2.2.1.1 Chemical plausibility of surface chemical reactions**

Radionuclide solubilities used in PA are underpinned by critically reviewed thermodynamic data for equilibrium water chemistry (e.g. Grenthe *et al.*, 1992; Silva *et al.*, 1995). These data are then



used in well-established speciation models that follow the classical mass action laws of aqueous coordination chemistry and mineral solubility (cf. Stumm and Morgan, 1996; Grenthe *et al.*, 1997).

A TSM is based on and consistent with exactly this fundamental knowledge and extends these well-established thermodynamic models to include reactions with solid surfaces (see e.g. Sposito, 1981; Davis and Kent, 1990; Stumm, 1992). To apply a TSM, the mass laws for surface reactions are combined with solution chemical and mineral solubility *equilibria*. In this sense, a TSM is chemically as reasonable as solution chemical models. Non-uniqueness in the choice of surface species has been addressed above. In the absence of spectroscopic proof regarding the existence of a particular surface species, the chemically most plausible models are based on surface species which are consistent with all our knowledge on the coordination chemistry of aqueous complexes and mineral surfaces. It is pointed out again that a sufficient variation of key parameters (pH, carbonate concentration, etc.) can be very important for constraining the choice of surface species.

Because surfaces in contact with aqueous solutions may be charged and the electrical potential at the mineral-water interface may alter surface reaction *equilibria*, a fundamental new variable is introduced when the thermodynamics of surface reactions are considered. Different correction terms have been developed to account for the effects of this electrical potential on adsorption and ion exchange. As pointed out above, these corrections may be viewed analogously to activity correction methods in solution chemistry. Because it appears (see above and NEA, 2001) that the perception of chemical plausibility is in no small part connected to the choice of electrostatic correction model, if any, this issue is discussed below in some detail (see also NEA, 2001).

#### 2.2.1.2 *Electric charge properties of natural surfaces and treatment in TSMs*

Based on their fundamental physicochemical behaviour, two types of (natural) mineral surfaces can be distinguished:

- **Variable charge surfaces** are typical of (hydr)oxides, edge surfaces of clay or mica minerals, carbonates, and solid organic matter. 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<sup>-</sup> groups. **Surface complexation 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, originally developed to describe electrokinetic phenomena. Dzombak and Morel (1990) and Davis and Kent (1990) presented discussions on the use of EDL models in SCM. Several EDL models are in common use, reflecting different model approximations of EDL structure. Three common models are the constant capacitance model (CCM), the diffuse layer model (DLM) and the triple layer model (TLM).
- **Permanent charge surfaces** are typical for the siloxane (“layer”) surfaces of clay or mica minerals. 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 20<sup>th</sup> 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.

### 2.2.1.3 *Non-electrostatic models (NEMs)*

The introduction of EDL correction terms introduces additional fitting parameters to the SCMs and increases model complexity. While this approach is chemically superior in describing adsorption data for single minerals suspended in simple electrolyte solutions, its application to more complex solid materials suspended in natural waters can be difficult to achieve without numerous assumptions.

For this reason, an alternative approach using surface complexation *equilibria* without electrostatic correction terms has been used by some modellers to describe adsorption on complex materials (Davis *et al.*, 2002; Kent *et al.*, 2000; Davis *et al.*, 1998; Westall *et al.*, 1998; van Benschoten *et al.*, 1998). In this simpler approach, referred to as non-electrostatic model (NEM), the number and stoichiometry of surface reactions is changed to achieve the best mathematical description of adsorption data. This approach may achieve a good fit to experimental data by eliminating a variable (electrostatic potential) that may be poorly understood in complex materials. The “cost” of this strategy is that the chosen surface species and the stoichiometry of the surface reactions become more empirical in nature and less thermodynamically rigorous. Nonetheless, the semi-empirical surface *equilibria* in an NEM can still be part of a self-consistent TSM, allowing adsorption to be calculated as a function of chemical conditions.

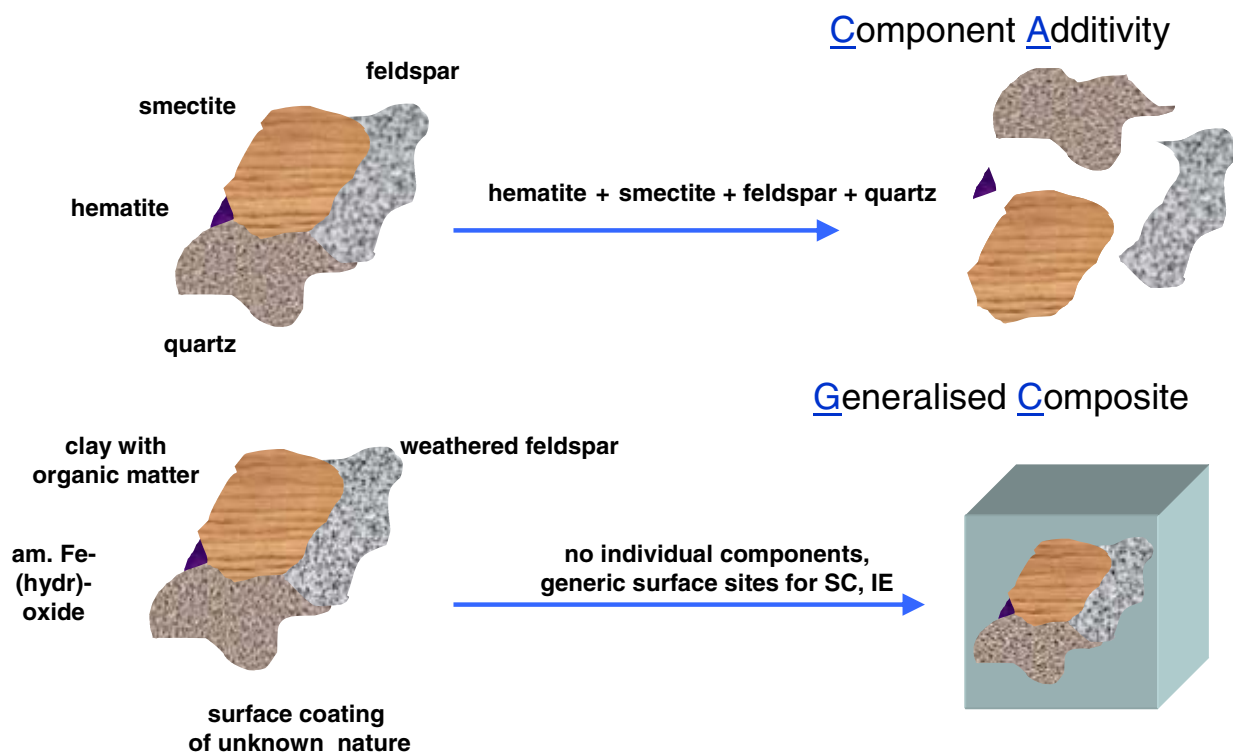
The use of an NEM can be justified when a mixture of minerals is sufficiently complex that it is not practical to determine EDL properties of its components. For example, the acidity constants of pure, insoluble mineral phases are often determined by acid-base titration. This is possible because the primary reactions that consume acid or base during the titration involve only the surface hydroxyl groups of the mineral surface. However, for a complex mineral assemblage, possibly containing adsorbed organic acids, carbonate minerals or other easily dissolved solid phases (e.g. feldspars or poorly crystalline aluminosilicate phases); the acidity constants (and EDL properties) of the mixture of phases cannot be assessed experimentally by acid-base titration. This is because the consumption of acid/base caused by the dissolution of minerals or titration of organic acid functional groups overwhelms the surface hydroxyl titration, making the experimental results very difficult to interpret.

An alternative strategy is that the EDL properties of the complex mixture can be inferred or predicted from knowledge of the EDL properties and surface areas of its mineral components. This approach assumes that non-idealities, such as overlapping EDLs and mineral coatings, are unimportant to EDL properties. Thus, in dealing with complex mixtures of minerals, the modeller can choose to estimate EDL parameters for the mixture using the available solid phase characterization, or utilise an NEM modelling approach.

### 2.2.2 *Modelling strategies for complex materials*

During model development for complex materials, many decisions are similar to those for “simple” substrates (e.g. choice of EDL model, selection of optimisation code, method of computing aqueous speciation, see Figure 7 in NEA, 2001). However, a major division of modelling strategies has emerged when modelling complex natural geological materials, between modelling strategies based on “bottom-up” (component additive-CA) and “top-down” (generalised composite-GC) approaches. These concepts are described in NEA (2001) and other literature. The CA-GC terminology was introduced in a comparative model evaluation by Davis *et al.* (1998). A schematic representation is given in Figure 2.1.

Figure 2.1: **Schematic representation of Component Additivity (CA) and Generalised Composite (GC) modelling approaches to complex substrates. The CA- and GC-terminology is taken from Davis *et al.* (1998).**



### 2.2.2.1 Component additivity approach (“bottom-up”)

The CA approach is, in principle, a predictive approach. In using this approach, one assumes that each sorbent in a complex assemblage has unique surface sites with particular sorption properties. The sorption behaviour of the complex material is derived by combining the contribution of the individual components. In broad terms, the conceptual steps required are:

1. Accurately determine the mineralogical composition.
2. Identify all of the component mineral phases that exert a significant influence on the adsorption of the radionuclide.
3. Quantify the relative contributions of different sites i.e. estimate the effective site densities by characterisation of the sorbent mixture.
4. Collect experimental data for adsorption of the radionuclide on the component phases (from the literature or from new experiments).
5. Develop individual models for the adsorption of the radionuclide on each component phase (by fitting the measured data, or by re-fitting literature data).
6. Combine the contributions of all the individual components of the material to form a model for the mineral assemblage.

#### 2.2.2.2 *Generalised composite approach (“top down”)*

The GC approach is an approach derived to fit mathematically the observed adsorptive properties of the environmental sorbent (inverse modelling). It is based on the assumption that it is not practicable to model the mineral assemblage by additivity of individual components. This may be justified for a variety of reasons, including the complexity of the material, lack of sufficient component mineral sorption data, or the inherently non-additive nature of sorption properties.

In principle the GC approach requires:

1. Systematic sorption experiments with the complex substrate and RN of interest for a wide range of conditions.
2. Assumption of generic surface functional groups.
3. Assignment of a surface site density. This can be used as a fitting parameter, although it is also possible to adopt a “recommended” literature value (such as the value of 2.31 sites/nm<sup>2</sup> recommended for hydrous ferric oxide by Dzombak and Morel, 1991).
4. Use of surface reactions that best simulate the sorption data are assumed or fitted, usually starting with a simple stoichiometry.
5. The number of site types and surface reactions can be increased in order to broaden the applicability of the model or reduce discrepancy between model outcomes and experimental measurements.

Although a mathematical fitting procedure (without pre-conceived model components) is sometimes invoked, the GC approach is commonly based on chemical reactions and concepts formulated from prior experience.



### 3. PROJECT METHODOLOGY AND APPROACH

#### 3.1 Development of test cases

The project was based upon a series of seven test cases that were prepared and distributed to participating organisations. A technical direction team (TDT) was appointed to evaluate the existing database, develop test cases for sorption modelling, and carry out the subsequent analysis and interpretation of modelling outcomes.

All test cases included a range of experimental data for model parameterisation. In some cases, the modellers were required to apply their models in a predictive mode to simulate sorption in similar systems. Details on individual test cases are provided in Part 2 of this report.

In order to select and develop the final set of test cases, the TDT undertook an extensive process of compilation and review of reported experimental sorption studies. As a basis for designing and selecting test cases, a list of desired applications of TSMs was developed. These applications included:

- Interpreting measured datasets and so provide support for selected  $K_d$  values.
- Interpolating over a narrow range of chemistry where a significant body of experimental data bounding the anticipated conditions is available.
- Interpolating over a wider range of chemical conditions (e.g. pH or ionic strength).
- Evaluating the possibility of extending models to other substrates and of extrapolation beyond the limits of the experimental data.
- Modelling the effects of ligands on sorption.
- Modelling competition effects.

A list of possible substrates for RN sorption test cases was then established, which covered a range of materials potentially of relevance to PA. This list comprised:

- Iron oxides.
- Other oxide phases, such as quartz and alumina.
- Clay single minerals, such as montmorillonite.
- Natural or complex clays, including bentonite.
- Complex mineral assemblages, such as soils, weathered rock or hard rock including fracture infill.
- Cementitious materials.

Within this framework of modelling objectives together with the target substrates, a thorough literature search was carried out to identify suitable datasets. This included an evaluation of several extensive unpublished datasets that had been made available by the participants.

The candidate datasets were then assessed according to the quantity and perceived quality of the data, as well as on the relevance of the sorbing element for PA. The main exclusion criterion for datasets proved to be a lack of sufficient parameter variation (pH, radionuclide concentration, ionic strength, etc.). A wide range of experimental conditions is essential for model development and calibration.

Hard rocks, fracture infill and cementitious materials were also excluded from the final set of test cases for those same reasons. The main exclusion criterion for datasets on these substrates proved to be a lack of sufficient parameter (pH, radionuclide concentration, ionic strength, etc.) variation for the purpose of model development. This decision to exclude cementitious materials was further based on the following reasoning:

- The majority of the available data comprised single  $K_d$  values on various hydrated cements, cement blends, mortars and concrete. Although many of these data were of good quality, the relatively high solubility of cement minerals often did not allow sufficient variation of key parameters such as pH.
- Significant uncertainties or gaps in thermodynamic data for the speciation of key RNs in hyper-alkaline solutions.
- Due to the amorphous nature and reactivity of cement minerals, uptake of radionuclides usually involves solid solution formation or even non-stoichiometric incorporation into mineral phases. Therefore, surface chemical sorption models are probably not appropriate to describe sorption in these systems.

Despite the multiplicity of sorption studies which have been reported in the literature, there is a surprisingly limited number that contain sufficient detail and provide adequate data for modelling purposes. Again, the most significant shortcoming in most cases is a lack of sufficient variation of key parameters. The final set of test cases comprised the following systems:

- |             |  |
|-------------|--|
| Test Case 1 | Neptunium sorption onto iron oxides.   |
| Test Case 2 | Selenium sorption onto iron oxides.  |
| Test Case 3 | Uranium sorption onto quartz.  |
| Test Case 4 | Nickel sorption onto montmorillonite.  |
| Test Case 5 | Neptunium sorption onto montmorillonite.   |
| Test Case 6 | Uranium sorption onto Koongarra weathered schist and component minerals.                   |
| Test Case 7 | Cobalt sorption onto a number of specific soil types, including the effect of humic acids. |

The selection was considered to provide a reasonable coverage of simple and complex substrates as well as a variety of RNs. Considerable effort was expended in preparing the test cases to ensure that they were complete, self-contained and that the modelling requirements were adequately explained. In addition, the modelling teams were provided with assistance and access to additional clarification as required during the course of the modelling phase.

## 3.2 Implementation

### 3.2.1 Modelling

In December 2001, the selected datasets were delivered to the modelling teams in the form of standardised spreadsheets. These contained sorption data as a function of experimental conditions ( $K_d$  and % sorbed values, RN concentrations for each data point, etc.) as well as auxiliary data such as surface titration curves, sorption of ligands or competing ions, etc. In addition, standard sets of solution thermochemical data [largely taken from the NEA Thermodynamic Data Base (TDB) project] were provided.

Although the modelling arrangements were the responsibility of individual participants, a total effort of about 1.5 person-months within a 6-month period was anticipated for each modelling team to carry out all chosen test cases. Output modelling results ( $K_d$  values, concentrations, speciation) were requested in the form of standard worksheets that were provided to the modellers. Modellers were also requested to provide a written description of the modelling approach including the rationale for their modelling decisions. Within the general rules and test case-specific constraints set by the TDT, the modelling teams were free either to use their standard approaches or to optimise their models as they saw fit. The TDT did not require that modelling approaches had to be optimised to achieve the best fit possible.

In total, 20 modelling teams participated in the exercise, allowing the conclusions of this project to be based on a broad range of experience and expertise.

### 3.2.2 Analysis and interpretation phase

In analysing the modelling outcomes, model fits as well as predictions were quantitatively compared with the respective experimental data. The objective of the model evaluations was to elucidate the effects of certain model characteristics (type of sites, EDL structure, etc.) on model performance. Particular attention was also paid to the decisions implicit in the development of preferred models to unravel the modelling teams' motivation for favouring a particular model design.

The selected measure for model accuracy was chosen to be:

$$\text{error} = |\text{Log}(K_d \text{ predicted}/K_d \text{ measured})| \quad (3.1)$$

The ratio of predicted/measured  $K_d$  values was chosen to avoid domination of the fitting criterion by discrepancies in the region where sorption is high. The absolute value is used to avoid sign changes associated with under- or over-estimation in the model. The above parameter was calculated for each measured data point in the test cases. In general, all points were given equal weighting, i.e. the average error was calculated as the mean absolute error for a given set of data.

Partition coefficients ( $K_d$ ) were preferred over % adsorbed for comparing quality of fit because the water/solid ratio is factored out, and because  $K_d$  is the representation used by the majority of the organisations involved in radioactive waste disposal.

Analysis and interpretation of the results of the modelling exercise considered the following criteria:

- Quality of fit (Equation 3.1).
- Model plausibility and justification.
- Model complexity (data requirements).



- Range of applicability.

This assessment was carried out in several stages:

- After the modelling results had been submitted, the TDT performed a first stage comprehensive analysis of experimental vs. calculated  $K_d$  values and related information (RN speciation etc.) for each test case and model output.
- A pivotal part in the analysis process was a 3-day participants' workshop held in October 2002 in San Lorenzo de El Escorial, Spain. This involved modelling teams related to all participating organisations, several members of the project Management Board and the TDT. This workshop offered a unique opportunity to present the preliminary analysis and discuss the implications with regard to the suitability of different TSM approaches. The material presented at this workshop forms Part 3 of the project report.
- Based on the feedback and additional information gained from the workshop, the TDT further interpreted and synthesised the project outcomes. This enabled specific conclusions regarding the effects of model design and modeller's decisions on the suitability of different TSM approaches for PA tasks. The outcome of that assessment is contained in the present report.

## 4. THE TEST CASES

This chapter provides a brief summary of the test cases that formed the basis for phase II of the NEA Sorption Project. Detailed descriptions of each test case can be found in Appendix 2, Part 2.

### 4.1 Group 1 – Simple substrates: Single oxide minerals (Test Cases 1-3)

#### 4.1.1 *Concept and purpose*

Test cases with single minerals were included in Phase II of the NEA Sorption Project for several reasons:

- Single mineral solids have been the subject of several systematic experimental investigations of adsorption phenomena, which resulted in the availability of extensive datasets that systematically address effects of key parameters on  $K_d$ .
- Due to their relative simplicity in terms of composition and types of surface sites, the experimental data are more readily interpreted in terms of the governing sorption processes.
- Some single minerals, in particular iron-(hydr)oxides, constitute important, and sometimes dominant, sorbents in natural substrates.
- Single minerals may be used as building blocks in CA models (see Section 2.2).

As a consequence of these considerations, it was decided to include at least one test case on single iron-(hydr)oxides and one on other single minerals.

#### 4.1.2 *Database, selected studies, goals*

There are many published datasets for the sorption of a range of elements (including relevant RNs) on both amorphous and crystalline iron (hydr)oxides. In addition, sorption has been extensively modelled and there are detailed supporting studies such as EXAFS measurements for some oxide minerals. Reports on several other sorbents, including aluminium-(hydr)oxides, titanium oxide, quartz, and amorphous silica, are also available in the literature and were considered for inclusion.

Although the datasets for the non-iron minerals are less comprehensive than those for the iron oxide group, several studies have been undertaken in which important aqueous chemical parameters have been varied systematically over a wide range.

In making the final selection, particular consideration was given to the range of chemical conditions studied, and the number of parameters varied. Another important consideration was the availability of data to test an issue not covered by other test cases. The following test cases were selected:

- **Neptunium(V) sorption on hematite under the influence of carbonate (TC1).**

- **Selenium(VI, IV) sorption on goethite (TC2).**
- **Uranium(VI) sorption on quartz under the influence of carbonate (two studies were combined to give TC3).**

This selection of test cases satisfied the following criteria:

- To include at least one test case with an anionic RN (TC2).
- To offer test cases where spectroscopic evidence of surface species was available either directly (TC2) or in a closely related study (TC1).
- To allow extrapolation under well-controlled conditions. (In TC3, the calibrated model was extended to a different quartz sample at a lower  $p\text{CO}_2$ ).

The datasets for these three test cases showed several important dependencies of RN sorption on geochemical parameters:

- The  $K_d$  values for the various RNs were significantly dependent on pH.
- The sorption of neptunium(V) on hematite and of uranium(VI) on quartz was measured as a function of  $p\text{CO}_2$ .
- The sorption of selenate, but not of selenite, was influenced by ionic strength.

The ability of the models to reproduce these dependencies was expected to be an important test of model performance. In particular, the datasets and modelling instructions of this group of test cases were aimed at:

- comparing model capabilities and data needs of SCMs in the absence and presence of an EDL term;
- testing the ability of different models to simulate the influence of pH on  $K_d$  values for both anions and cations; and
- demonstrating and simulating the importance of  $p\text{CO}_2$  as a geochemical boundary condition.

## **4.2 Group 2 – Substrates of intermediate complexity: Clay minerals and bentonite (Test Cases 4 and 5)**

### **4.2.1 Concept and purpose**

Clays were included because of their relevance to radioactive waste disposal. In the form of bentonite, they are almost universally proposed as part of the engineered barrier systems for high-level radioactive waste (HLW) repositories, and are being considered for the disposal of other radioactive wastes types as well. Clays are relevant as potential repository host formations, and clay minerals may be important components of natural substrates such as soils and fracture infill materials (see Section 2.1). Thus, clays are likely to be encountered on the potential migration paths of RNs from a repository to the biosphere. At the same time, the selected examples provide a good transition from “simple” systems (Test Cases 1-3) to multi-sorbent, complex mineral assemblages (Test Cases 6-7).

### **4.2.2 Database, selected studies, goals**

Numerous studies of RN sorption have been undertaken on various clays, including smectite/montmorillonite, kaolinite, bentonite and samples extracted from natural clay rock formations

(such as Boom Clay or Opalinus Clay). In view of the importance of bentonite for engineered barrier systems, particular effort was expended to find datasets that enabled model extrapolations from single clay minerals to natural bentonite.

While a large number of studies was available, various limitations reduced the suitability of many datasets:

- many studies involved alkali and alkaline earth elements or heavy metals, which are either of little relevance to PA (Cu, Cd...) or not particularly well suited for a thermodynamic sorption modelling exercise, because of the dominance of ion exchange/absence of surface complexation reactions (Cs, Sr, Ra...), and
- comparatively few studies were carried out with systematic parameter variation over a wide enough range to permit satisfactory model calibration and testing.

Consequently, the final choice comprised two test cases developed from several datasets:

- **Nickel sorption on montmorillonite and natural bentonite under varying conditions (four studies were combined to define TC4).** This test case utilised an extensive sorption database taken from four coherent studies, together with a comprehensive set of supporting data (solid characterisation, titration, sorption of additional trace elements). The substrates included a range from pure sodium-montmorillonite to natural bentonite.
- **Neptunium(V) sorption on montmorillonite under the influence of carbonate (two studies were combined to define TC5).** This test case was developed from two studies offering systematic sorption data. Although supporting data (such as solid characterisation) were limited, the modellers were given the option to obtain this information from the available literature.

The datasets for these two test cases exhibited important dependencies on geochemical parameters:

- The  $K_d$  values for the two RNs on the different minerals were significantly dependent on pH and ionic strength.
- $K_d$  values for nickel (TC4) were measured as a function of composition of exchangeable cations, competing elements and solution composition (including carbonate). The combination of competing sorption reactions and complexing ligands provided a range of experimental conditions not present in the other test cases.

The main goals of this group of test cases were:

- to demonstrate the applicability of TSMs combining surface complexation and ion exchange adsorption mechanisms to clay minerals; and
- to test the predictive capability of models calibrated for clean sodium-montmorillonite and simple electrolyte solutions in the more complex systems: (i) calcium-montmorillonite and raw bentonite and (ii) aqueous solutions including carbonate and competing major cations.

Further specific goals within these test cases were to:

- test the effect of a clay's natural inventory of Zn and Mn (potentially competing cations) on nickel sorption; and
- test the influence of carbonate complexation on neptunium sorption by a clay.

### 4.3 Group 3 – Complex substrates: Soils and sediments (Test Cases 6 and 7)

#### 4.3.1 *Concept and purpose*

From the commencement of Phase II of the NEA Sorption Project, participant organisations were particularly interested in the inclusion of complex substrates, to test and demonstrate the applicability of TSMs on such materials. Soils and sediments are significantly more complex than model minerals, having a variety of constituents, each with particular site densities, acid-base chemistry and coordinative properties for solution species. While experimental and computational investigations of trace ion adsorption to single mineral surfaces have been invaluable in model development, a successful demonstration of TSM application to natural substrates would greatly increase the acceptance of the TSM approach.

#### 4.3.2 *Database, selected studies, goals*

The datasets considered included river, bay and aquifer sediments, loamy and sandy soils, weathered and crushed rock, natural clays, and fracture infill material. The data coverage was particularly strong for uranium (about 25% of all studies in the final group concerned uranium) and also for soils (about 40% of studies were on various soils).

A weakness in many reports was the omission of experiments that systematically investigated the effects of RN concentration on sorption. Shortcomings also included inadequate characterisation of mineral components and limited information on complexing substances such as humic acids.

The datasets for rock materials tended to be particularly weak in terms of variables considered (e.g. range of pH) and questions surrounded the sample preparation. A further complication in considering sorption modelling for this group was the relationship between sorption measured on crushed rock in the laboratory and the whole rock as issues of groundwater flow and accessibility of sites become important. Therefore sorption on rocks was not included in the present project.

It was also considered desirable to include a reasonable range of radionuclides in the final selection of datasets. For this reason, only one uranium case was selected although there are several good datasets for uranium sorption on natural materials. Instead, the second test case in this group concerned adsorption of a transition metal. The selected datasets were:

- **Uranium sorption on weathered schist materials from the Koongarra deposit in Northern Australia (TC6).**
- **Cobalt sorption on subsurface materials including separated mineral components from South Carolina, USA, including the effects of humic substances (TC7).**

The main goal was to evaluate the present capabilities and limitations of TSMs to represent sorption by complex geologic materials. In particular, the test cases included a comparative evaluation of the CA and GC approaches for modelling RN sorption on complex substrates. Specific aims were:

- to determine whether the dependence of  $K_d$  on several chemical variables can be described with TSMs for complex materials;
- to evaluate the types of modelling assumptions being adopted by different modellers (for example, assuming that particular phases dominate sorption);

- to determine whether the consideration of either a limited or full sorption dataset makes an important difference (TC6), this aspect was included to facilitate conclusions on data needs;
- to evaluate model transferability to similar substrates, and the model features which facilitated such transferability;
- to determine the level of complexity required for adequate models;
- to evaluate whether the presence of humic acids can be taken into account adequately by TSMs (TC7).



## 5. PRINCIPAL RESULTS AND ASSESSMENT OF SORPTION MODELS

In this chapter, the modelling approaches used in this project are discussed and assessed. The focus is on deriving lessons relevant to the application of TSMs for describing RN sorption. The conclusions are limited to those that can be derived from the responses to the individual test cases considered in Phase II of the NEA Sorption Project. In the Chapter 6, some specific observations about the key issues in applying TSM to geochemical modelling of radioactive waste disposal are presented, and the modelling undertaken in the NEA Sorption Project Phase II is considered within a wider context.

Although some relevant conclusions regarding PA can be derived from the discussion in this chapter, it is not intended as a general analysis on the potential of TSMs for PA. Instead, it is a summary of the actual results of the modelling exercise. The conclusions are supported by an exceptionally large and comparatively well-focused database. The reader should consult Part 2 and Part 3 of this report to examine the volume and quality of the underlying data.

### 5.1 Model development and capabilities

#### 5.1.1 *Modelling strategy and modellers' decisions*

The approaches selected by the different teams in each test case encompassed a diverse range of model designs, including:

- one- and two-site SCMs;
- various EDL models;
- different conceptual site types, particularly in the test cases involving more complex materials (where various clays, iron-oxides, etc, were chosen as sorbing surfaces);
- a range of total site densities and methods for determining this parameter; and
- various RN surface species (for example, some models incorporated ternary surface species; e.g. in systems that included carbonate).

In most cases, modelling teams apparently followed a predetermined modelling strategy, rather than evaluating a range of modelling approaches for each test case in order to develop a model that would allow a team to achieve the best mathematical fit to the experimental data. The initial decisions regarding how to approach the modelling task, and the type of model desired, appeared to be the most important factor in determining the final model design. As such, some model features, which may include type of EDL model or NEM, site types and density, and number and type of surface species, clearly resulted from subjective decisions rather than from objective model optimisation. This is important, as in most cases it will not be feasible to investigate all possible decisions on model design in a systematic and truly objective fashion.

Because of the number of individual decisions, the final models for each test case usually differed significantly from each other in numerous respects. The underlying causes for differences in



modelling outcomes could not always be traced to a single modelling decision, although this was possible in the analysis of some models. However, the decision-making process used by each modelling team is the key for determining the final model structure and, ultimately, its capability (as previously observed in NEA, 2001). The development procedures for individual models are documented in detail in Part 2 of this report.

Modelling approaches also differed from each other in other important ways. One example is the choice of datasets utilised for model development. In several cases, modelling teams chose to limit calibration procedures to a particular sorption data sub-set for model development, whereas in other cases, the entire sorption dataset was used for model calibration (see Section 5.1.3).

Another source of variation was the computer code selected for optimisation and predictive computations. The reason for this is less related to numerical data treatment, but more to certain general features of different codes. It is recognised that many codes use the same (or very similar), well-tested optimisation algorithms. However, there are several codes that include certain options of thermodynamic sorption modelling as standard choices, e.g. a surface complexation-diffuse layer model as the only choice of a SC-EDL model. In several cases, such built-in features were cited by modelling teams as basis for deciding on a certain TSM approach.

### **5.1.2 Key model components**

The forthcoming sections focus on surface complexation models. Sorption on the siloxane (layer) surfaces was handled through conventional ion exchange formalisms by nearly all modelling teams participating in this exercise (with the exception of Team h, TC4, see Part 2), and there was very little variation regarding ion exchange model design.

#### *5.1.2.1 Surface sites and their properties*

Experimental datasets for RN sorption can sometimes be simulated by a single-site SCM. However, in most cases, multi-site models are required to explain sorption adequately as a function of RN adsorption density. This became evident in all test cases that included a sufficient variation of initial RN concentration. Typically, there were insufficient data to justify more than two sites, and this was a common choice in the test case responses. While one-site models could often model most of the experimental data, they invariably produced relatively large errors for parts of the datasets.

Most modelling teams who used two-site models distinguished between generic weak and strong binding sites. The non-linearity of adsorption isotherms supports the inclusion of stronger binding sites, but they often constitute only a small fraction of the total site density and there are no independent measurement techniques to quantify their population. Therefore, the strong binding site density was often fitted to the sorption data, even when the total site density was pre-selected (e.g. fitted to acid-base titration data, or taken from the literature). The population of strong binding sites obtained was generally small (1% or less of the total site density). The postulation of generic strong and weak sites and the optimisation of the respective site densities for fitting a model to the sorption data can be considered as a GC modelling philosophy, albeit applied to a single mineral surface. This should be remembered when assembling a CA model for a complex substrate. Such a model is likely to have some generic, fitted (GC-like) elements within the submodels for the individual component minerals.

It is noteworthy in this respect that three teams attempted to model the Group 2 (clays) datasets with a more mechanistic approach, in which the clay surface was viewed as being composed of silanol and aluminol groups (rather than generic weak and strong sites). Two of these teams used

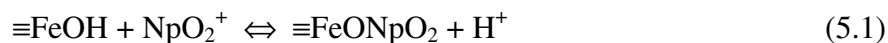
analogy considerations with single Si- and Al-oxides and assembled the clay edge surface in a CA-like fashion. These approaches were not very successful, but that may be due to their model parameterisation strategies (for a detailed analysis, the reader is referred to the analyses of TC4 and TC5 in Part 2). One successful model used silanol and aluminol group populations and densities derived from crystallographic and EXAFS data. This latter approach is also considered to be chemically more plausible than the analogy with oxides.

Total site densities were usually fitted from titration and/or sorption data, or taken from the literature. There was little consensus among the modelling teams regarding the method for estimating the total surface site density.

In TC6 (which concerned a complex natural material), the estimation of the total site density was an important factor in determining the overall performance of the models. The GC modellers tended to fit the site density, consistent with the basic philosophy of the GC approach (i.e. to fit experimental sorption data). In contrast, the CA modelling teams usually calculated the total site density either from the bulk properties of the materials (e.g. BET surface area or iron-oxide content) or by an additive method from the mineralogical components. In either case, site density was therefore a fixed parameter in the CA models. This difference became a major source of divergence between GC and CA models for these materials, as is shown in Section 5.2 below.

#### 5.1.2.2 *Surface reactions and species*

Most teams used a simple surface reaction of the type illustrated in eq. (5.1) for neptunium(V) sorption on an iron-oxide. This simple cation-binding/proton-release reaction is a simple and chemically plausible surface reaction, and is commonly used in the literature.



In cases where a second RN surface species was required, there was a range of reactions chosen. Little justification was provided by the modelling teams for the selection of these additional surface species. In many cases, the choice was based on best-fit to the data after a number of other decisions on model design had already been made. Thus, it was difficult to isolate the effects of these second surface species on model performance.

In Test Cases 1, 3 and 6, most models included a ternary neptunium- or uranium-carbonato complex to model RN sorption in the presence of carbonate. In TC5, the only model that was able to describe the data at pH > 8.5 in the presence of carbonate also included a ternary neptunium-carbonato complex. Based on the results of these test cases, it appears that the inclusion of a ternary carbonato surface complex significantly improves the model simulations for the neptunium(V) and uranium(VI) sorption data in the presence of carbonate.

#### 5.1.2.3 *EDL models*

In most test cases, several TSMs were developed that used a surface complexation model without an EDL term (SC-NEM). In a SC-NEM, it is not necessary to explicitly use surface acid-base reactions. Thus, comparatively simple models with fewer fitting parameters (relative to those with EDL terms) can be produced. However, most teams still considered the acid-base titration data and derived acidity constants without EDL correction terms to describe these data.

The outcomes of this project suggest that the choice of EDL (or use of an NEM) has a limited influence on the fitting capabilities of TSMs. In the test cases that involved a direct

comparison between models with and without EDL terms (TC1 and TC3), most modelling teams achieved a slightly better fit to the experimental data with the EDL models. Within the EDL models, the TLM approach (including the BSM variant) appeared to be the most successful over all systems considered. However, the difference was marginal. The overall variation in model performance was greater among the different modelling teams than between the SC-EDL and SC-NEM groups. At the same time, the number of fitting parameters in the SC-NEM models was similar to the number for the SC-EDL models, because the majority of the modelling teams retained acid-base reactions (which are not required in a SC-NEM).

### 5.1.3 Calibration procedures

For several test cases, the fitting procedure and optimisation method used by the various modelling teams exerted a significant influence on the final capabilities of the model. For the present purpose, fitting procedure and optimisation method are distinguished as follows:

- Fitting procedure refers to the way in which multiple datasets (e.g. sorption edges at different ionic strengths or values of  $p\text{CO}_2$ , isotherms at different pH values, or combinations of isotherms and pH edges) were used for model calibration.
- Optimisation method refers to:
  - (i) the form in which the sorption data were used (i.e.  $K_d$  or %-sorbed, logarithmic or linear scales), and
  - (ii) the method of optimising the difference between experimental and calculated values (through a computer code or fitting by eye, with or without subsequent quantitative error analysis).

In test cases where multiple datasets were available, the fitting procedure differed substantially among the various teams. The following methods were used:

- Many teams fully utilised multiple datasets by using all available data for model calibration.
- It was also common (especially where manual optimisation was used) to fit different datasets separately and then to combine all available data for model calibration (e.g. by averaging parameter values obtained for different datasets).
- A significant number of modelling teams used only part of the available data for fitting. The remaining datasets were then simulated in a predictive application of the model.

The effect of using all or only part of the available dataset for model calibrations can be significant. To illustrate this, the various models used in TC4 are used as an example, although the conclusions would apply to any other case where multiple datasets corresponding to different conditions are available for model calibration.

Figure 5.1 summarises the modelling outcomes for the dataset provided in TC4, with errors shown for each of the six sub-datasets. The horizontal axis indicates the number of fitted parameters used in each model. The models fall into two distinct clusters. Cluster 1 includes models with overall errors between 0.3-0.5 ( $\leq 7$  model parameters), whereas cluster 2 includes models with overall errors between 0.1-0.2 ( $\geq 10$  model parameters). This analysis shows a critical difference in terms of error distributions between these two clusters:

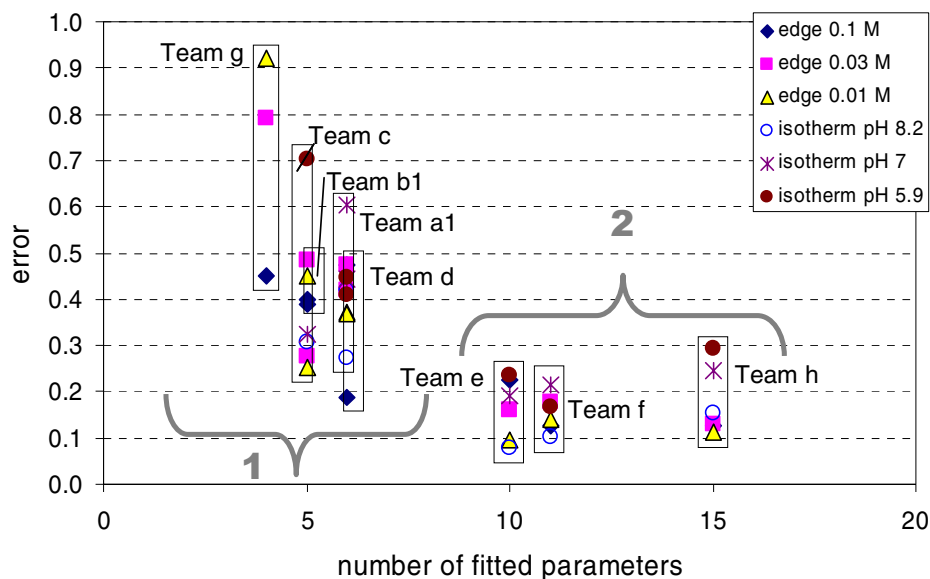
- The models in cluster 1 display a comparatively large spread of errors. These models produce relatively small errors for some of the sub-datasets but much larger errors for other sub-datasets.

- The models in cluster 2 not only have much smaller overall errors, but the error distribution is also significantly narrower.

The differences in model performance (Figure 5.1) for the two clusters can be attributed to the combined effect of model design, calibration procedure and optimisation method. The resulting mix of model approaches and fitting procedures makes the separation of the respective effects on model performance difficult. However, in this case, the reason behind the model outcomes can be attributed to the fitting procedures used by the various teams. The models in cluster 1 were fitted to one or a few datasets only, whereas the entire dataset was used for the parameterization of the models in cluster 2.

Cluster 1 contains simpler models (i.e. fewer fitting parameters), mainly because only limited datasets were fitted, while the rest of the data were either “blindly” predicted or ignored in model development. It is likely that consideration of the entire dataset would have revealed some shortcomings of the simpler models during the modelling process. This analysis shows that a comprehensive fitting strategy is as important for model performance as the overall model design.

Figure 5.1: Influence of fitting procedure and number of fitting parameters (surface complexation constants for nickel, surface acidity constants, ion exchange constants for nickel and major ions, as well as fitted site densities etc.) on model performance in TC4. Shown are errors (see eq. 2.1) for each sub-dataset vs. number of fitted parameters. The teams in cluster 2 used all available data (all 6 sub-sets indicated) for model calibration, The teams in cluster 1 used only some of the available sub-sets.



It can be concluded that if all available data (including sub-datasets for different conditions) are used for model development, the model will perform better than if only a part of the database is used. Models based on a single or limited range of input data are likely to be inadequate for simulating a broad range of experimental conditions. If only part of the database is considered, it is more likely that a significant governing process will be omitted from the model. This has two important implications regarding data needs:

- Identification of the governing processes that determine  $K_d$  requires adequate coverage of the relevant experimental parameters for the PA setting that is to be modelled. It should not be expected that a sorption model will adequately extrapolate to different

values of geochemical parameters (ionic strength,  $p\text{CO}_2$ , etc.), unless these parameters were tested in the experimental data used for model calibration. This holds for either GC or CA approaches. The results for systems where sorption of actinides took place in the presence of carbonate (Test Cases 1, 3, 5 and 6) illustrate that new surface species may be formed in the presence of new solutes. CA models should be built from single mineral models that were calibrated in the presence of the field-relevant solutes.

- This exercise demonstrated that shortcomings in the datasets available for calibration became evident only after a first round of fitting, implying that model development ideally requires a coordinated experimental and modelling effort, which would be preferable to a single experimental programme followed by a modelling exercise.

#### 5.1.4 Quality of fits

In most cases, the quality of the model fits to the experimental data was within one  $\log(K_d [\text{L/kg}])$  unit, both for model calibration as well as in extrapolations and predictive applications. Overall, the average absolute error varied between ca. 0.15-0.5 log units when data were fitted, and between ca. 0.2-1 log units in extrapolations. In a few cases, average absolute errors were higher for predictions. A summary is given in Table 5.1.

It must be emphasised that it is not realistic to expect better agreement between model fits and experimental data than the scatter in the data itself. Depending on experimental conditions, an analytical error of about 5-10% and uncertainties in phase separation can be expected to translate to an error of ca. 0.1-0.2  $\log K_d (\text{L/kg})$  units. Similar errors have been reported in the literature, for example by Bradbury and Baeyens (1997). As such, an error up to 0.2  $\log K_d$  units does not indicate any discrepancy between model and experiment.

Table 5.1: Overview of average absolute errors (log units)

Test case	Type of modelling	Average error (see eq. 3.1)	Range of $\log_{10}(K_d [\text{L/kg}])$ observed
1	fitting	0.30-0.50	1.40-5.31
2	fitting selenate	0.17-0.60	0.08-4.15
	fitting selenite	0.10-1.10	0.12-3.82
3	fitting	0.15-0.45	-0.56-2.80
	extrapolation quartz 1 $\rightarrow$ quartz 2	0.35-0.75	0.03-2.03
4	fitting	0.15-0.45	1.67-4.45
	extension Na- $\rightarrow$ Ca-mont.	0.10-0.55	0.79-4.42
	extrapolation Na-mont. 1 $\rightarrow$ Na-mont. 2	0.20-0.80	0.67-5.70
	extrapolation for bentonite (low I)	0.45-2.50	0.67-5.70
	extrapolation for bentonite (high I)	0.40-0.50	1.44-3.46
5	fitting	0.20-0.30	0.44-2.93
	extrapolation mont 1 $\rightarrow$ mont 2	0.20-1.00	0.81-3.53
6	various extensions/extrapolations	largely $< 1.0^*$	1.20-5.40
7	predictive CA	0.30-0.70	1.30-5.40
	GC fitting	0.30-0.45	1.30-5.40

“mont” denotes montmorillonite.

“I” denotes ionic strength.

\* Errors tend to be distributed in a highly systematic way; see Part 2 of this report.

## 5.2 Applications of TSMs for radionuclide sorption by complex materials

The relevance of substrates of varying complexity in relation to different PA tasks was discussed in Chapter 2. The key consideration with the more complex materials is the much greater array of potential surface sites. In the case of clay minerals, these include siloxane (layer, face) and edge surfaces; whereas in complex materials a wide range of amorphous oxides, clay minerals, humic materials, and other components may be present, each with a range of site types.

The SCM approach is generally attractive in that it offers chemical realism and predictive capability. This is demonstrated in Test Cases 3-7 by the application of SCMs for radionuclide sorption to a number of substrates across a range of conditions, in the presence and absence of competing ions and complexing ligands. The present inter-comparison demonstrated the shortcomings of the models in several specific situations. These are not attributed to fundamental problems with the SCM approach but rather to:

- lack of data for calibrating the models over a wide enough range of conditions;
- insufficient care in model calibration;
- disadvantageous initial modelling decisions; and
- errors in model development.

### 5.2.1 *Clay-dominated substrates as a special case*

As previously discussed, comparatively simple TSMs have significant predictive capability for clay-dominated materials relevant for radioactive waste disposal, such as bentonite and some natural clay formations (an organic-rich natural clay like the Boom clay would be more complex). The sorption properties of these materials tend to be dominated by clay minerals, and comprehensive and well-tested component models are available. The transferability of TSM parameters among clay minerals is relatively easy, since:

- clays are relatively well researched, with good literature information on their overall properties;
- clays are crystalline, meaning that there is relatively little variation in terms of certain parameter values (e.g. site density);
- as a result of the above, scaling can often be done on the basis of well-determined values such as the CEC.

The critical point for substrates like bentonite is often not the actual RN sorption model, but the fact that soluble impurities present in these materials may give rise to a rather complex overall geochemistry. The porewater concentrations of many important groundwater components are often controlled by the surface chemical reactions rather than the groundwater itself. This means that a good TSM is needed for major as well as some critical minor components in addition to the RN-specific TSM.

### 5.2.2 *Modelling sorption on complex materials: Complexity and model performance*

The test cases with complex materials (TC6 and TC7) indicated that the GC models provided better mathematical fits to the reference dataset with less complexity than CA models. For TC6, it may be argued that the modelling teams were different and self-selecting – in other words, some chose the CA approach and some the GC approach. However, in TC7, all teams attempted to perform both GC as well as predictive CA modelling. In this test case the errors were smaller for the same team using

the GC model. However, errors for the predictive CA models were still within acceptable limits ( $< 0.7 \log K_a$  units in all cases).

The complexity of the CA models may be greater because they may include several surface species carried across from component models, but which play an insignificant role in the model for complex materials. These extra species complicate the models, which raises the question of whether it would be warranted to delete them. While this would simplify the model, it is possible that such species will be needed under some conditions of interest to PA. Although the number of optimised parameters was generally greater in the GC approaches, these models tended to be simpler and usually incorporated only a minimum number of necessary species. The GC modellers were not limited in their choice of component reactions to those reported on component minerals, such as the bidentate uranyl surface complex on the ferrihydrite surface. In TC6, many assumed the simplest possible mono-dentate stoichiometry for the iron-oxide surface. There was at least one example where the GC models were possibly too simple, which led to model inadequacy for some experimental conditions.

The GC models tended to fit better than the CA models, but had a greater number of optimised parameters. Rather than simply fitting the sorption data with no pre-conceived model framework, the GC modellers preferred a guided approach, in which the model was based on concepts developed for component minerals.

### 5.2.3 *Site densities and types for complex materials*

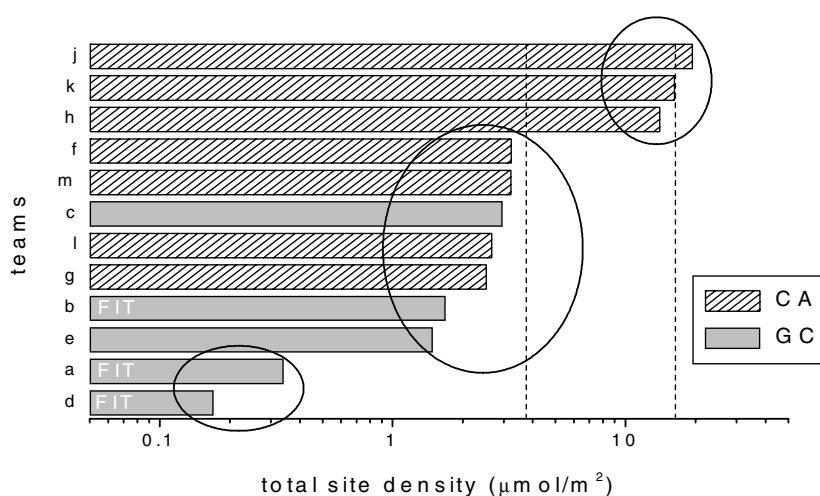
The site-density estimates are a very important part of the modelling, but are subject to considerable uncertainty. In TC6, the values that modellers selected covered a wide range of about two orders of magnitude (Figure 5.2). All the CA modellers estimated the site density, but most of the GC teams fitted this parameter to the sorption data. The better performance of the GC models may be linked to the greater tendency to fit site density (as well as  $\log K$  values). The large range of site-densities shown in Figure 5.2 is a major potential source of discrepancy, suggesting that further work may be required to gain a consensus and develop agreed methods of estimating site densities for natural substrates.

A problem in the CA approach in TC6 was the assumed dominance of ferrihydrite, to the extent that three of the seven CA teams did not utilise other site types (such as kaolinite sites). However, it was demonstrated that the properties of kaolinite were in some respects more similar to the complex substrate than those of ferrihydrite (see discussion in Part 2 of this report). Furthermore, the teams that optimised site density concluded that site-densities were much lower on the complex material than for ferrihydrite (Figure 5.2). The teams that included kaolinite sites could improve their models by increasing the assumed role of kaolinite above that expected on the basis of its weight fraction and assumed surface properties. The outcome of TC6 demonstrated that CA modelling of natural materials could benefit significantly from more availability of sorption data for a range of component minerals.

In test cases 4 and 5, most models treat the clay edge in terms of generic surface complexation (SOH) sites (rather than aluminol- and silanol-groups) and all of the corresponding site densities are based on acid-base and/or metal surface titration data. This holds for values fitted in this exercise and for values taken from the literature. These values for total site density lie within a comparatively narrow range ( $0.52\text{-}3.5 \mu\text{mol/m}^2$ ) for both test cases. In order to achieve a good fit to nickel sorption edges, strong sites had to be introduced, which represent only a small fraction of the total sites.

Notably, edge site densities for a model in TC4 (h) based on aluminol- and silanol sites were derived from crystallographic and EXAFS data (Dähn, 2001). A value of  $1.83 \mu\text{mol}/\text{m}^2$  was obtained for the RN-active aluminol sites, which agrees very well with the data cited above. Using outer- and inner-sphere complexes, this model was able to reproduce nickel sorption edges without the postulation of strong sorbing sites. While this does not invalidate the use of strong and weak sites, it shows that an appropriate combination of surface species can allow as good a fit to experimental data. In terms of their ability to predict sorption on different substrates, both approaches worked equally well.

Figure 5.2: **The total site densities used by the modelling teams in TC6 cluster into three groups, two of which approximate the densities employed by Dzombak and Morel (1990) and Waite *et al.* (1994) shown by vertical dotted lines at  $3.84 \mu\text{mol}/\text{m}^2$  and  $16.4 \mu\text{mol}/\text{m}^2$ , respectively. (TC6). Note that the fitted site densities (teams d,a,b) are lower than either of these values, and the GC densities tend to be lower than the CA densities**



It has to be pointed out that density and properties of strong sites can usually only be defined based on RN adsorption data that cover a wide enough range of pH and RN concentration. Because they make up only a small fraction of the total number of sites, surface acid-base titrations are not sensitive or precise enough to allow a determination of their population, or to extract protolysis constants. This has to be taken into account when CA models are constructed based on site densities of component models derived from acid-base titrations. CA models should be built from single mineral models which are based on a similar range of parameter variation that is foreseen in the CA model application.

#### 5.2.4 Issues relating to the CA approach

A potential criticism of the CA approach is whether it is inherently correct to build up a sorption model by an additive process. Some investigators have found that the sorption properties of mixed substrates differ from the component parts, even in a simple mixture such as a binary oxide suspension (Palmer *et al.*, 1981; Anderson and Benjamin, 1990). The possible non-additivity of sorption phenomena raises significant questions about the CA approach. For substrates where non-additivity is significant, the CA approach will not be applicable unless the interaction effects can be included in the component models or evaluated independently.



Possible sources of non-additivity may be, for example:

1. Alteration of EDL properties of e.g. an iron oxide surface when a different charged mineral surface (e.g. a clay) is located directly adjacent.
2. Alteration of EDL or surface properties caused by ions dissolving from one mineral phase and sorbing onto another.

It may be possible to handle non-additivity due to EDL interaction by doing experiments in model systems that are a better approximation of the complex substrate. For example, the EDL alteration by adjacent surfaces is probably an inherent feature of the SC and IE models for clays, due to possible spillover of permanent negative charge or positive edge charge at low pH (Chang and Sposito, 1996). However, since these two surfaces are always adjacent, EDL alteration effects are implicitly contained in TSMs for clays. The SCMs for the clay edge are often based on generic sites, sometimes in combination with an NEM approach. Similarly, it may be possible to develop models for binary components in cases where surface interaction may be important and CA models are desired for predictive applications. Non-additivity caused by effects of components dissolving from different minerals in a complex assemblage should largely be taken into account by component models that have been developed based on a realistic solution chemistry. The reason for this is that most of the components that may dissolve from a mineral substrate can be expected to be present in a natural groundwater in any case, often near their solubility limit. As pointed out previously, effects by major groundwater ions should be included in component models for single minerals.

Another potential difficulty with CA modelling is that the surface properties of individual minerals may be different in the complex materials compared to the assumed simple model substrates. This possibility led some CA modellers in TC6 to modify equilibrium constants to make their models fit adequately. This suggests that the selection of appropriate component models can be difficult and may limit the CA approach even when more data are available for RN sorption on component minerals.

### **5.2.5 Predictive capability and model flexibility**

Although the GC approach tended to produce models that were simpler and fitted the data better, they shared with the CA approach certain problems in extension to other substrates (in TC6). However, the GC approach appears to be superior for interpolation to other experimental conditions when a single substrate is involved. Because the GC approach is based on fitting sorption data with generic sites (and usually an NEM) as a function of aqueous speciation, the resulting model parameters have little value for extension to significantly dissimilar solid phase samples. GC models should be developed from sorption data collected for composite samples that are representative of a field site, or by simultaneously fitting all sorption data for several samples collected at a field site (Davis *et al.*, 2002).

The predictive CA simulations in TC6 showed that the CA approach was not able to provide satisfactory models without re-optimisation of parameter values. Even the optimised CA models did not fit the base-line datasets as well as the GC models, with a systematic pattern in the error distribution revealing some model inadequacy. This may be partly traced to the choice of a particular ferrihydrite component model, including the respective stoichiometry for uranium sorption and site densities, as main component mineral. As pointed out above, adequate and robust models for, as well as an educated choice of, component minerals are critical to successful CA modelling.

The predictive CA models performed reasonably well in TC7 to predict sorption in systems containing humic acids and for those without. Therefore, it can be concluded that CA-TSMs do offer

predictive capabilities for complex sorbents. GC models could be very useful to support  $K_d$  values and to perform sensitivity analyses within certain limits of conditions (e.g. within a PA reference scenario). At the same time, experience from such systems could be used to develop more realistic component models to include in CA approaches that may be used in connection with more extended variations of conditions (e.g. for alternative PA scenarios).

### 5.2.6 Summary

Sorption modelling for complex materials is far from standardised, and a wide range of fitting and modelling approaches was used in TC6 and TC7, but also in TC4 and 5. Even with fitted models, the transfer of models from one substrate to another is not yet readily accomplished in the CA approach, and is not recommended for dissimilar substrates in the GC approach (Davis *et al.*, 1998; 2002). Although there appear to be some inherent limitations with the CA approach in cases where non-additivity is significant, the available component models are not yet adequate for a full evaluation of CA modelling for complex materials. The most robust modelling will probably require sample-specific experimental data, or a close approximation by simplified systems.

### 5.3 Concluding remarks on the process of model design

The present inter-comparison provides a rare opportunity to test sorption modelling approaches for several datasets. Experimental data obtained under a wide range of conditions are important for this type of inter-comparison, because some types of model inadequacy were apparent only for particular test cases or datasets. Various TSM approaches were capable of simulating important features of RN sorption, such as the pH dependence and effect of carbonate and some major cations. The ability of the TSMs to model radionuclide sorption data obtained under various chemical conditions is a significant attribute of the approach.

As stressed in NEA, 2001, much of the usefulness and credibility of TSMs will depend on an internally consistent and transparent decision making process during model development. Many components of a final model can be justified on the basis that some possible options were evaluated at each point and a reasonable one was chosen. However, the selected examples show that modellers often follow their own personal preferences rather than an “objective” approach. Thus, there is no basis for asserting that any of the final preferred models were truly optimal.

Some major outcomes of the modelling inter-comparison are summarised below:

- The approaches selected by the different teams in each test case encompassed a diverse range of model designs.
- The decision-making process used by each modelling team is the key to model structure and ultimate capability. Modellers appear to follow, at least in a first step, their own personal preferences rather than an “objective” approach.
- The consideration of multiple datasets in the fitting procedure tends to increase model complexity, but clearly improves model performance.
- Data requirements for modelling should be considered during experimental programs, which should ideally involve modellers’ inputs.
- Ternary surface complexes appear to improve model performance in test cases involving actinides with variable  $p\text{CO}_2$ .
- The participating modelling teams seemed to prefer to incorporate surface acid/base reactions even in simple SC-NEM approaches.

- There is little consensus on methods for estimating total site density, particularly in complex materials.
- In GC models, the site density was often fitted to the sorption data. The fixed values adopted in CA models appeared to limit model performance.
- In TC6, the GC teams were apparently hesitant to employ entirely generic sorption sites, but many included a site described as an “Fe” surface site. This reveals a reluctance of the GC modellers in this project to use a generic site approach. The reason why is not clear, especially since some models for single minerals used in the CA approach (e.g. Waite *et al.*, 1994, model for ferrihydrite), also use a somewhat similar 2-site modelling approach.
- At the present time, GC approaches for complex materials appear to lead to simpler models that perform better than CA models in achieving a good description of sorption data as a function of chemical conditions. It should be noted, however, that the GC approach requires the collection of sorption data on the complex material, and thus, the respective substrate must be accessible for experimental investigations.

## 6. KEY ISSUES IN CONSISTENT APPLICATION OF THE TSM APPROACH TO RADIONUCLIDE TRANSPORT MODELLING

In the previous chapter, the model frameworks and underlying philosophies, as applied to the test cases in the NEA Sorption Project, were considered. Once these model frameworks are in place, there remain complex questions relating to the numerical values of key model parameters – such as site densities, equilibrium constants, etc. Ultimately the successful application of TSMs to real-world problems will rely on reasonable and consistent approaches to parameter estimation for sorption modelling (cf. Figures 6 and 7, NEA, 2001). A related issue for PA applications is the validity and justification of methods of extrapolating a TSM from a known, well-defined system to a geologic repository environment, which is a complex and sometimes poorly constrained system. These matters of application and extrapolation of TSM's are the subject of the present chapter.

### 6.1 Sources of parameter values

The SCMs developed in the current project incorporated a range of parameters for various model components. The numerical values of these parameters were obtained from a number of sources, which can be categorised as follows:

- Type 1.** Fixed values taken directly from the scientific literature or previous work.
- Type 2.** Estimated values derived with various assumptions and arrived at by a documented process (e.g. estimating a site population from a surface area).
- Type 3.** Values obtained by fitting separate experiments (i.e. not the RN sorption and surface titration datasets provided for this exercise); e.g. separate surface titration data, or independent component mineral phase data in CA models.
- Type 4.** Values obtained by fitting RN sorption and auxiliary (e.g. surface titration) data obtained for the substrate under consideration.

Parameter values obtained by all these methods must ultimately be derived from an estimation process (usually including some kind of fitting). However, only the last type of values (i.e. type 4, fitted to the provided sorption and surface titration data) was considered as fitted parameters for the purposes of the project. It should also be noted there is some overlap between type 1 and 2, since estimation is often justified by reference to the literature.

#### 6.1.1 Site density

Recommended values of surface site density for single mineral phases can be found in various compilations and reports in the literature (e.g. Davis and Kent, 1990). In the Group 1 (single minerals) test cases, a number of teams utilised these literature values. Other modelling teams derived the site densities from fitting acid-base titration data.

The selection of site density in Test Case 6 illustrated the different sources of parameter values utilised by modelling teams. Table 6.1 shows the sources of site-density, which included all of

the four types summarised above: Type 1 (literature), Type 2 (estimated), Type 3 (fitted to other data) and Type 4 (fitted to sorption dataset).

Table 6.1 shows distinctly different sets of data sources for the GC and CA teams in TC6, which can be directly traced to the philosophies behind these modelling approaches. As might be expected, many of the GC teams fitted the site density. However, some GC teams fitted other parameters (such as log K values), while using literature values or estimates of site density.

In contrast to the majority of the GC teams, the CA teams utilised literature values or estimates of the site density, rather than fitting (Table 6.1). Two of the CA teams used site densities which had been previously fitted to other uranium sorption data for component minerals (which is designated as a type 3 parameter source). This is consistent with the CA philosophy, where data for component phases are firstly simulated and the resulting models are incorporated into the final model for the complex substrate.

While the total site density was estimated by a variety of methods, many teams determined the strong site density by using ratios of strong to weak sites found in the literature. Two popular choices of the ratio of weak to strong sites for Fe-oxides in TC6 are indicated in Table 6.1. The ratio of ~40 in models “a”, “e” and “m” was recommended by Dzombak and Morel (1990) for hydrous ferric oxide (HFO). This reflects common assumptions derived from this model. Similarly, the weak/strong ratio of ~480 found in several models is the same value as the Waite *et al.* (1994) model for uranium sorption on ferrihydrite. These two models are among the major source models for HFO presently available in the literature.

There was a wide range of final estimates for site populations in TC6 (see Figure 5.2 and accompanying discussion). This demonstrates a lack of consensus on the numerical values for this parameter, which is partly due to the various methods of estimating it. Both the total site density as well as the weak/strong site ratio differ among the data sources considered here [i.e. values resulting from fits to the data provided in TC6, Dzombak and Morel (1990), Waite *et al.* (1994)]. This indicates that there may also be significant differences among the various hydrous iron oxides, which makes the choice of component models a critical and difficult step in the construction of a CA model.

In the Group 2 test cases (clays), all modelling teams used the measured cation exchange capacity (CEC) for the density of exchange sites. However, most of the edge site densities (fitted directly or taken from the literature) were based on fits to metal adsorption data. The edge site density is not easily assessed by independent experimental methods, as it does not contribute significantly to the total CEC. However, Team h in TC4 derived the total site densities from spectroscopic and crystallographic data and arrived at values that are consistent with the fitted values. It appears that site densities among different sources of smectite clays show relatively little variation in comparison to hydrous iron oxide.

### **6.1.2 EDL parameters**

The triple layer and diffuse layer electrical double layer models have parameters that are usually not fitted to sorption or acid-base titration data, but instead are fixed at values based on previous experience. For example, the outer-layer capacitance in triple layer models invariably has the value of 0.2 Farads/m<sup>2</sup>, and is rarely fitted to new data. Increasingly, there are compilations of models in the literature (e.g. Sverjensky and Sahai, 1997) that allow the selection of electrical double layer parameters for single mineral phases without the collection of new surface charge data. An alternative is to fit experimentally determined surface charge data to determine EDL parameter values.

A commonly used method is to re-fit previously published surface acid-base titration data with a new model in order to determine self-consistent EDL parameter values.

Table 6.1: **Sources of surface sites utilised in the base-line model for the W2 sample in Test Case 6 (referred to as Model A – see detailed discussion in Part II). Teams (a-e) are GC teams; teams (f-m) used the CA approach.**

Team	Site type*	Conc. ( $\mu\text{mol}/\text{m}^2$ )	Method	Origin (see text section 6.1.1)
<b>a</b>	Fe <sub>w</sub>	0.024	Fitted to RN sorption data.	Type 4 – fitted
	Fe <sub>s</sub>	0.0006	Weak/strong ratio (~40) from literature.	Type 1 – literature
	Ka	0.31	Estimated from composition.	Type 2 – estimated
	Mu	0.0022	Fitted to sorption data.	Type 4 – fitted
<b>b</b>	Fe	0.016	Fitted to sorption data.	Type 4 – fitted
	Ka	1.7	Fitted to sorption data.	Type 4 – fitted
<b>c</b>	Fe	3.0	Estimated from surface area.	Type 2 – estimated
<b>d</b>	Fe <sub>w</sub>	0.17	Fitted to sorption data.	Type 4 – fitted
	Fe <sub>s</sub>	0.0072	Fitted to sorption data.	Type 4 – fitted
<b>e</b>	Fe <sub>w</sub>	1.5	Estimated from composition	Type 2 – estimated
	Fe <sub>s</sub>	0.036	Weak/strong ratio (~40) from literature.	Type 1 – literature
<b>f</b>	Fe <sub>w</sub>	3.2	Estimated from surface area and composition	Type 2 – estimated
	Fe <sub>s</sub>	0.007	Weak/strong ratio (~480) from literature.	Type 1 – literature
	Ka <sub>w</sub>	0.047	Estimated from surface area and composition	Type 2 – estimated
	Ka <sub>s</sub>	0.01	Same weak / strong ratio as fitted kaolinite model	Type 3 – fitted to other data
<b>g</b>	Fe <sub>w</sub>	2.5	Estimated from extractable Fe	Type 2 – estimated
	Fe <sub>s</sub>	0.005	Weak/strong ratio (~480) from literature.	Type 1 – literature
<b>h</b>	Fe <sub>w</sub>	14.1	Estimated from surface area and composition	Type 2 – estimated
	Fe <sub>s</sub>	0.029	Weak/strong ratio (~480) from literature.	Type 1 – literature
	Ka <sub>w</sub>	0.03	Estimated from surface area and composition	Type 2 – estimated
	Ka <sub>s</sub>	0.006	Same weak/strong ratio as kaolinite component model	Type 1 – literature
<b>j</b>	Fe	18.8	Estimated from surface area using high site density	Type 2 – estimated
	Ka	0.74	Estimated from surface area	Type 2 – estimated
<b>k</b>	Fe <sub>w</sub>	16.3	Estimated from surface area using high site density	Type 2 – estimated
	Fe <sub>s</sub>	0.03	Weak/strong ratio (~480) from literature.	Type 1 – literature
<b>l</b>	Fe <sub>w</sub>	1.5	Estimated from surface area and composition	Type 2 – estimated
	Fe <sub>s</sub>	0.001	Same weak strong ratio as ferrihydrite component (~1000)	Type 3 – fitted to other data
	Ka <sub>w</sub>	1.2	Estimated from SA and composition	Type 2 – estimated
	Ka <sub>s</sub>	0.006	Same weak/strong ratio as fitted kaolinite model	Type 3 – fitted to other data
<b>m</b>	Fe <sub>w</sub>	3.2	Estimated from composition	Type 2 – estimated
	Fe <sub>s</sub>	0.08	Weak/strong ratio (~40) from literature.	Type 1 – literature

\* Fe – iron oxide, Ka – kaolinite, Mu – muscovite; the subscripts “w” and “s” denote weak and strong binding sites, respectively.

### **6.1.3 Surface areas**

Surface areas are required for charge compensation terms in SC-EDL models, and are often utilised for scaling site populations in all types of SCMs. For single, non-porous minerals, usually a BET surface area determined by adsorption of an inert gas is used. Various scaling factors can be utilised, with a popular choice being 3.84  $\mu\text{moles of sites/m}^2$  (Davis and Kent, 1990). For clay minerals, the edge surface area is often assumed to be equal to the outer surface area determined by the BET method (as was almost exclusively done in Test Case 4). Alternatively, the edge surface area can be assumed to comprise a fixed proportion (e.g. 10%) of the total surface area (i.e. the outer and inner surface area as determined by EGME adsorption or some other method). For example, Team h (TC4) estimated the edge area to make up 90% of the BET area, which would correspond to about 6.5% of the total surface area of montmorillonite based on crystallographic considerations.

### **6.1.4 Binding constants**

In this project, most surface binding constants for RNs were derived based on fitting RN sorption data. However, there is also an increasing number of compilations and reports (e.g. Dzombak and Morel, 1990) that provide binding constants for various ions, including major ions, such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Such parameters are conditional and model-dependent (i.e. depend on site density, type of EDL model or NEM, etc.; see Sverjensky, 2003) and must be used in a self-consistent fashion (see Section 6.2). Again, an alternative for obtaining such constants is to re-fit experimental data from the literature in order to derive stability constants for surface species that are consistent with the chosen modelling approach.

For the exchange of major cations in ion exchange models, which can become an issue in clay systems, most teams used the literature constants that were given in the test case instructions. Two formalisms (Gaines-Thomas or Vanselow) are available to account for the conditional nature of these constants; they allow conversion to other clays based on CEC or composition of exchangeable cations, respectively (cf. Sposito, 1981). Ion exchange constants that are not based on either of these formalisms are conditional and cannot be transferred directly.

## **6.2 Parameter transfer and internal consistency**

Thermodynamic constants for aqueous complex formation and precipitation/dissolution reactions can be applied in any system at the same temperature and pressure. Consequently, it is sometimes assumed by users of SCMs that model parameters can also be applied in a straightforward manner to other chemical systems. This is not the case, as many of the parameter values used in SCMs are conditional, model-dependent values rather than true thermodynamic properties (see Sverjensky, 2003).

While thermodynamic constants for aqueous complex formation usually have only a few qualifying conditions (T, p, zero ionic strength); surface complexation stability constants have many qualifying conditions (T, p, zero ionic strength, total site density, surface area, EDL model, etc.). For example, consider an acidity constant determined from titration data for the surface of hematite (as in Test Case 1). The calculated value of that acidity constant is dependent not only on the temperature and pressure of the system, but also on the total site density, the surface area of the sample, the electrical double layer model chosen, and perhaps even the major electrolyte cation in solution. Direct application of this calculated value to other hematite/water systems requires that these factors be taken into account, i.e. the new system must have the same temperature, pressure, total site density, etc., and must have the same EDL model applied.

In some cases corrections can be made, for example, for a different total site density or surface area, so that a model parameter in the literature can be utilised for a new system. A paradigm that has been accepted in the literature is the scaling of site densities with surface area. For example, if a model is published for a hematite sample with a surface area of 50 m<sup>2</sup>/g and a site density of 10 μmoles/m<sup>2</sup>, it is considered acceptable to apply the same model to a different hematite sample with a different surface area by using the site density of 10 μmoles/m<sup>2</sup> as a scaling factor. To apply a calibrated edge site density to another sample of a similar clay (e.g. to apply a montmorillonite model to bentonite), a constant ratio of SOH site density to total CEC is also often assumed, as an alternative to a constant SOH site density per unit area of edge surface. The CEC values of the two samples are then used as a scaling factor (with satisfactory results in the case of TC4) instead of the edge surface area, which is difficult to determine directly. Note that these two approaches lead to identical results only if the ratio of CEC/BET values remains constant from one sample to another. It is always important to show that a model adopted from the literature would still fit the original data in the literature if any changes are made to the model parameters or its conceptual basis.

Another important condition is the thermodynamic dataset for aqueous species that is used during the calibration of a surface complexation model. For example, the SCM equilibrium constants derived from fitting sorption data obtained in the presence of carbonate of a given RN (that forms carbonate complexes) are clearly dependent on the RN-carbonate stability constants contained in the TDB used at the time. Note that this is the case, even if no ternary RN-carbonate surface complexes are involved. If the stability constants in the TDB are subsequently changed (e.g. after a new review, such as Guillaumont *et al.*, 2003), this will affect the calculated equilibrium speciation of the RN in the presence of carbonate and lead to the calculation of a different  $K_d$ . To account for a change in the underlying TDB, it is necessary to recalibrate the SCM parameters using the original sorption data together with the new set of stability constants.

In summary, thermodynamic sorption modellers should use model parameter values from the literature with great care. The test cases in this project illustrated that some modelling teams believed that SC parameters could be used from the literature without conditions. Stability constants for SC parameters cannot be used from the literature, even for the same mineral surface, if a different total site density is utilised in the extrapolated model. In particular the GC modelling approach is semi-empirical, and surface stability constants for such models are valid only for the particular assemblage of solid phases being studied. The corresponding SCM parameters should not be extended directly to other materials. A partial solution to the problem of conditional SCM parameters would be the establishment of appropriate reference states (cf. Kulik, 2002; Sverjensky, 2003).

### **6.3 Requirement for multiple experimental sorption datasets**

The modelling demonstrated the value of multiple sorption datasets. The inadequacy of datasets used for model calibration tends to be glossed over in many published journal papers. For example, there are insufficient experiments where several experimental parameters (pH, RN concentration, ionic strength, mass loading,  $p\text{CO}_2$ ) are systematically varied. It is particularly important in the CA approach that the models for the component minerals are calibrated across a wide range of chemical conditions. There are few reported studies where radionuclide adsorption on single minerals has been studied in the presence of relevant groundwater cations and anions. If CA models are being constructed based on single minerals in simple, inert electrolytes, it is likely that important processes (e.g. related to competition or ternary surface complexation) are not included.

The complex materials Test Cases (6 and 7) required simulation of a wide range of experimental data – it is possible that the component models themselves were not sufficient to handle such a range. Whether a model is sufficient or not depends largely on whether the governing



mechanisms have been captured in the calibration process. The chance of missing a governing factor is significantly higher in limited datasets. For example, a component model for the sorption of neptunium(V) on montmorillonite based on the data for TC5 would not include any ternary neptunium-carbonate surface complexes if it were calibrated (i) using the two datasets without or with trace concentrations of carbonate, or (ii) using only data below pH 8.5. However, the modelling results in the presence of atmospheric  $p\text{CO}_2$  and at pH above 8.5 clearly demonstrate the necessity of such a surface species (see Part 2).

As a note of caution, the modelling in Test Case 6 indicated that provision of experimental data across a wide pH range can lead to a focus on pH extremes. These data are probably less relevant to performance assessment and tended to impact the models (particularly the CA models) negatively. Furthermore, it is possible that the processes occurring at these pH extremes may not be similar to those at moderate pH values, perhaps involving mineral dissolution. As a result, the data and models may be of limited value in these extreme pH regimes. Such experimental shortcomings must be balanced against the fact that calibration across a wide range of conditions provides a much better chance of capturing all relevant governing factors in the calibration process.

#### **6.4 Data requirements for TSM development**

The NEA Sorption Project, Phase II has indicated the potential value of TSMs in interpreting as well as predicting experimental sorption data for an assessment of the migration of radionuclides in the environment. An important conclusion from Chapter 5 was that modellers and experimentalists should not operate independently. Experimentalists should consider (and be provided with guidance regarding) the needs of the modellers. Similarly, modellers should be aware of limitations within the experimental dataset, such as imprecision of experimental  $K_d$  values under conditions of very high or low sorption. The chemically predictive nature of TSMs is particularly helpful for the definition of uncertainty limits, sensitivity analyses and the optimisation of experimental designs in an integrated  $K_d$  acquisition strategy for PA (see Figures 6 and 7 in NEA, 2001).

Part 2 of this report indicates how the availability or lack of specific information helped or hindered the model development process. Often, certain types of information were ignored for the actual model calibration process, usually with negative outcomes for model performance. Factors that limited the predictive capability of the developed models include the following:

- Adequacy of input RN sorption dataset. If the input data used to construct a TSM are obtained over a limited range of conditions only, or by varying only a small number of experimental parameters, the model is unlikely to simulate other geochemical conditions adequately. For example, a model derived from a sorption “isotherm” (where sorption is studied as a function of total radionuclide concentration) may not provide any predictive capability if information on the effect of another parameter, such as the pH, is required.
- Insufficient characterisation of the sorbing phase, in particular in terms of site density.
- Lack of consistency regarding computations of the chemical speciation in the aqueous phase. This was largely eliminated as a problem in the modelling exercise by the adoption of agreed thermodynamic data, although the occasional discrepancy was noted.
- Inadequate measurement of chemical species in experimental systems. In many examples, there was detailed information available of RN sorption but inadequate information on the distribution of other important components, such as ligands. Test Case 6 demonstrated the importance of information on dissolved carbonate concentration and carbonate complexation for an actinide containing system. However, much greater

information on the distribution of other ligands, such as phosphate would have been useful, particularly for some modelling approaches.

- Inadequate representation of overall chemical environment. For example, some sorption models failed because basic assumptions regarding the concentration of competing major cations or important ligands were erroneous.
- Lack of characterisation of poorly understood environmental components, such as humic materials and amorphous minerals.
- Lack of knowledge of the structure of surface complexes, particularly in the trace concentration ranges.

The data requirements for developing a TSM will be determined by the particular problem at hand. Consideration of the factors listed above leads to some recommendations:

- To constrain sorption models adequately, large “multi-dimensional” datasets, showing the dependence of sorption on numerous experimental parameters, are required. These parameters should include:
  1. aqueous conditions such as pH, ionic strength (and possibly temperature);
  2. solid/liquid ratio;
  3. radionuclide concentration; and
  4. preferably other variables such as the concentration of complexing ligands, including carbonate.
- Even with a simple substrate such as a clay, a wide range of information including CEC and surface area (possibly by more than one technique) is required. In the case of more complex substrates, bulk characterisations were insufficient and a detailed microanalysis and quantitative mineralogical composition would be beneficial. If a model with EDL-term is desired, surface charge data are also needed as a function of solution conditions (pH, ionic strength, carbonate, etc), determined for example by acid/base titrations (where permitted by the sorbent’s solubility). Even if a SC-NEM is going to be used, the titration data could be helpful in qualitatively interpreting sorbent behaviour.
- Further work on thermodynamic databases (including the related NEA TDB project) is essential for accurate input to generate robust sorption models.
- More chemical data (such as ligand concentrations) are required, both in experimental and real-world systems. This would reduce the need for estimating many of the boundary conditions that determine the geochemical environment, such as  $p\text{CO}_2$ , redox potential, and the amount of trace impurities in mineral phases.
- Further information regarding significant processes would be useful as model input, particularly as many processes could have interactive effects. For example, ion exchange at the layer surface of a natural clay may control major ion (Ca, etc.) concentrations in the porewater, as well as directly influencing radionuclide sorption. Dissolved calcium concentration will influence dissolved carbonate concentration via the solubility of calcite, which may again be critical for radionuclide sorption via the formation of dissolved or surface-bound (ternary) radionuclide-carbonate species at the clay edge SC sites.
- Structural and process information about poorly characterised environmental components, including humic materials, colloids, and amorphous phases is needed.

- Surface speciation at high concentrations has been obtained for some systems (e.g. by EXAFS measurements), but many systems have not been adequately studied. Appropriate methods for environmentally realistic concentration ranges remain elusive.

## 6.5 Advantages of TSMs relative to empirical approaches ( $K_d$ values and isotherms)

The TSM approach is obviously more complex than a constant  $K_d$  or isotherm approach for modelling sorption. However, experimental  $K_d$  values are applicable only to the chemical conditions under which they were measured. Any change in a chemical parameter, such as pH or ligand concentration, may have a large effect on the  $K_d$  value (as shown by numerous test case examples). Thus, a  $K_d$  model is difficult or impossible to apply meaningfully to an environment with temporally or spatially variable chemical conditions.

Sorption isotherms relate the amount of adsorbed contaminant to its dissolved concentration, and may take into account some of the properties of the solid phase, such as the population of sorbing sites. However, for most RNs, the adsorption isotherm is strongly dependent on chemical conditions. As observed by Bowden *et al.* (1977) the limitations of simple isotherm models become apparent when “fixed” model parameter values must be changed in order to accommodate changes in parameters such as the pH. Further modifications would be needed to describe the effects of complexing ligands. The isotherm approach is useful only if adsorption does not show a significant pH dependence or in circumstances where little variation in chemical conditions is expected.

Thus, TSMs have significant advantages, and the difficulties encountered in thermodynamic sorption modelling should be put into perspective by making comparisons with other PA-relevant fields. For example, hydrological models for modelling groundwater flow similarly rely on input parameters (conductivity, dispersivity, etc.) which can be subject to over-simplification and controversy.

While there are still many challenges associated with the TSM approach, the ability of TSMs to model a wide range of radionuclide sorption data obtained under various conditions is a unique and significant feature of the approach. This ability of TSMs can be used for careful predictive applications in situations that are difficult to assess experimentally. At the same time, TSMs can be used to increase confidence in PA studies by providing a scientifically defensible tool for:

- interpolating between different chemical conditions that are experimentally accessible;
- gaining a better understanding of governing and significant processes; and
- identifying the most sensitive chemical parameters that will determine  $K_d$  as well as quantitatively estimating their effects.

Thus, it is expected that TSMs will be increasingly adopted for modelling contaminant uptake by surfaces and ultimately guide in the selection of realistic  $K_d$  values for PA of radioactive waste disposal.

## 7. CONCLUSIONS AND RECOMMENDATIONS

The preceding two chapters presented an overview of modelling undertaken in the NEA Sorption Project, Phase II, within the broad context of model framework (Chapter 5) and specific issues relating to model calibration, parameter values and extrapolation (Chapter 6). This chapter summarises the conclusions and implications that have been identified during the model assessment process of Phase II of the NEA Sorption Project, including specific recommendations regarding the use of TSMs for PA. To provide a general framework and to illustrate the potential utility of TSMs, key aspects of deriving  $K_d$  values for PA purposes are reviewed first (Section 2.2.1); some aspects of this overview can also be found in NEA (2001).

### 7.1 Selection of $K_d$ values for PA: Sources and management of data uncertainty

In any PA exercise, the retention of radionuclides is quantitatively assessed for every environmental compartment that may be encountered along the migration path between waste form and biosphere. These compartments include the EBS, the repository-perturbed near field, and all relevant geological formations constituting the far field. As pointed out in NEA (2001), these compartments can be expected to differ significantly in their physical-chemical properties. Because of the conditional nature of  $K_d$ , different estimates of  $K_d$  values for each RN to be used in PA are required for each compartment. In addition, two additional sources of variability or uncertainty of geochemical conditions, and thus of  $K_d$ , usually have to be addressed within each compartment.

- Both groundwater and solid phase composition for a given compartment can often be determined only within a certain range. In particular for some of the relevant RN migration pathways, such as bentonite pores or rock fractures, the *in situ* water or solid phase composition can often be estimated or predicted only through geochemical models.
- Where very long timeframes need to be considered, such as in the disposal of high-level and many intermediate-level wastes, it is necessary to estimate possible future conditions, for example by coupled geochemical/mass-transfer models. Usually this has to be done for a reference scenario as well as for alternative scenarios (features, events and processes, FEPs) to address “what-if” questions (irrespective whether a deterministic or probabilistic approach to PA is followed).

It is obvious that it will not be possible to determine  $K_d$  for every system and condition experimentally. Moreover, some of the above systems are difficult to reproduce in the laboratory, and the determination of *in situ*  $K_d$  values is questionable or impossible (e.g. in case of future conditions). Therefore, selected  $K_d$  values for PA are typically based on experimental sorption data from:

- a limited set of solid substrate samples obtained directly from a given site; and/or
- simplified or generic systems, supplemented with a system-specific geochemical database.

A schematic overview of  $K_d$  derivation for PA and the associated principal uncertainties is provided in Figure 7.1. While it is appreciated that in certain situations it could be possible to measure  $K_d$  directly under *in situ*<sup>1</sup> conditions, it is assumed for this generalised illustration that such an approach is not feasible, based on the brief discussion above. In such a case,  $K_d$  values for PA have to be derived based on experimental data in simplified and/or approximated experimental systems. The resulting overall uncertainty of the selected  $K_d$  is composed of the experimental errors and any uncertainties introduced in making the transfer from approximated, experimental to the actual *in situ* geochemical conditions. Taking into account the variability of  $K_d$  as a function of key geochemical parameters (illustrated in many of the test cases modelled in this project), the following critical issues with regard to uncertainty of selected  $K_d$  values can be identified:

- In all cases where a direct measurement of  $K_d$  under PA-relevant conditions is not possible, a transfer of sorption data from one set of conditions to another will be required. This must take into account any differences in mineralogy as well as surface and solution speciation. This transfer can be made:
  - i) fully quantitatively through the use of TSMs, using their unique capability to directly couple sorption and geochemistry in a single thermodynamic model;
  - ii) in a semi-quantitative way, by taking into account differences in e.g. CEC, RN speciation, etc.; or
  - iii) by qualitative “expert judgement”.
- The larger the difference between the experimentally investigated systems and the PA conditions, the more the overall uncertainty will be determined by uncertainties in transferring sorption data from one set of conditions to another. Note that this will apply regardless of the method used for data transfer.
- Uncertainties in the selected  $K_d$  will be compounded by any uncertainties in the expected geochemical conditions. For example, Figure 4.2 in Part 2 illustrates that an uncertainty of one pH-unit may translate into an uncertainty for the  $K_d$  of uranium(VI) of more than one order of magnitude. Further uncertainties in other parameters, such as total site density (CEC) or solution composition can increase uncertainty in  $K_d$  by many factors again.

Based on these points, the following general recommendations can be made:

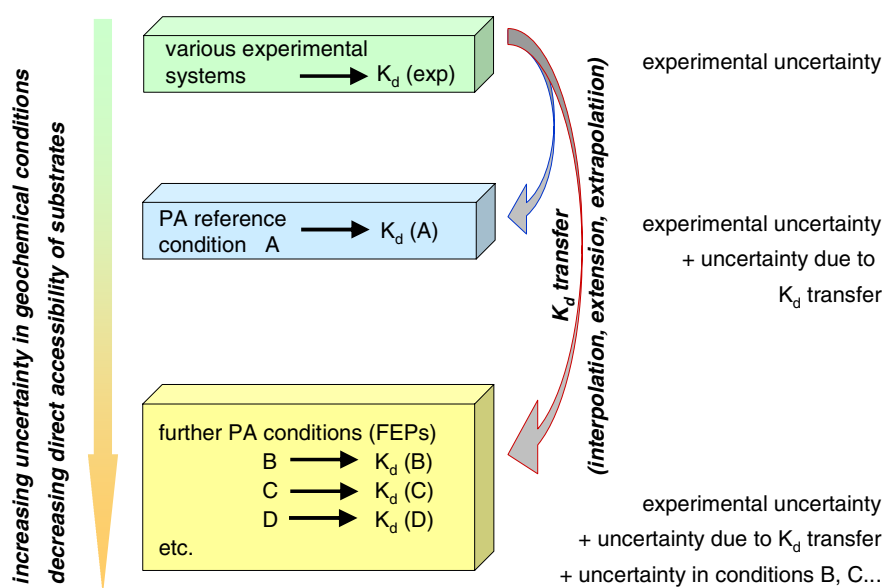
- It is obvious that uncertainties will be smaller in cases where data transfer to PA conditions can be done through interpolation, rather than through extension or extrapolation.
- Even if extrapolation becomes necessary, it is a significant advantage if several source datasets are available, as this will allow one to test internal consistency.
- It follows from the above that in order to reduce uncertainty in  $K_d$ , the expected PA-relevant conditions should be approximated as much as possible in experiments. While it can be very helpful (or necessary, in case of CA models) to start TSM development from simplified systems, effects of key geochemical parameters need to be included in the final model parameterisation.

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1. “*In situ*” in this context refers to the actual geochemical conditions along the relevant RN migration pathways (as used in all PA calculations). It is not meant to include any engineering factors for up-scaling to intact whole rock, for example.

- The likely requirement of having to transfer  $K_d$  from one set of conditions to another underscores the importance of understanding the influence of geochemical key parameters. Independent of the method used for data transfer, this requires the systematic variation of such parameters in experimental investigations.

Figure 7.1: A schematic and simplified example of the derivation of  $K_d$  values for performance assessment and of the associated uncertainties (modified from Ochs and Talerico, 2004).  $K_d$  data transfer includes any procedures (TSM approaches, expert judgment, etc.) to take into account differences in mineralogy and solution composition.



It follows from this discussion that the utility of TSMs is by no means restricted to predictive applications. Much of the value of TSMs can be seen in providing a thermodynamic framework to integrate quantitatively the influence of all relevant geochemical parameters on  $K_d$ . This unique capability renders TSMs also an ideal tool for guiding  $K_d$  acquisition programmes. A detailed discussion of a TSM-based strategy for deriving  $K_d$  values for PA is given in Chapter 4 of NEA (2001).

## 7.2 Status of TSMs for radionuclide sorption modelling

The present inter-comparison provided a rare opportunity to test and compare different sorption modelling approaches for several datasets. The analysis of the very large number of modelling results presented in Part 2 constitute a strong body of evidence to underpin the conclusions and recommendations given in this chapter. Major outcomes of this project include the following:

### *Utility of TSMs for PA*

- The thermodynamic sorption models tested in this project were able to reproduce trends, and in most cases magnitude, of  $K_d$  values in experimental data, over a very wide range of simple to complex mineral substrates and aqueous chemical conditions (pH,  $p\text{CO}_2$ , etc). The ability of the TSMs to simulate radionuclide sorption data under various chemical conditions is a significant attribute of the approach, and represents a major advantage in comparison to constant  $K_d$  or isotherm models.

- The value of TSMs in quantifying the geochemical factors that determine  $K_d$  was demonstrated in a variety of systems.
- Average absolute errors of model predictions in comparison to experimental data were in the range of 0.5 log  $K_d$  units or less for a number of cases and a range of conditions. This capability of TSMs can be used to demonstrate mechanistic system understanding and as support for the selection of  $K_d$  values for PA.
- It also has to be pointed out, however, that modelling personnel and their decisions and preferences have a major influence on model design and performance. In several cases, this influence became clear only after a detailed analysis by the TDT. Such examination is beyond what can normally be done when reviewing a report or manuscript. This is important to keep in mind, and an important issue brought up in NEA (2001) needs to be restated: In order to increase the traceability and credibility of TSM approaches, it would be helpful if modellers always clearly documented the chain of decisions that led to the final choice of TSM.

#### *Implications for acquisition of experimental sorption data*

- Some types of model inadequacy, and thus, lack of system understanding, were apparent only for more extensive test cases or datasets. This implies that experimental data obtained under a wide range of conditions is important for understanding a system and being able to derive a reliable  $K_d$ .
- Even though many test case datasets had been modelled before, the concerted effort involved in this exercise allowed new insights to identify critical supplementary experiments to extend the dataset.
- At present, the experimental database is a major limiting factor for the further development of TSMs for complex natural materials.

#### *Possible future developments from the NEA Sorption Project*

- It was not possible to find a suitable dataset for the modelling exercise that was not previously widely available to the scientific community. Indeed, there were few datasets of adequate quality for this exercise which had not been previously modelled. A possibility for a future development from the NEA Sorption Project would be a blind modelling exercise, in which an entirely new sorption dataset was acquired specifically for the purposes of a modelling inter-comparison. In a second step, the modelling outcomes could be used to identify shortcomings in the experimental data and develop improved experimental designs to arrive at a final dataset. This could be done in the form of a demonstration exercise, with a focus on  $K_d$  acquisition for a real PA problem following the layout given in Figures 6 and 7 of NEA (2001).
- This project showed that model parameters available in the literature are often not used to full benefit or in a correct fashion. This can be traced to the following reasons:
  - i) It appeared that not all modellers are fully aware of the requirements that need to be met in order to arrive at internally consistent sets of model parameters. These requirements are discussed in Section 6.2.
  - ii) In the case of solution chemistry and solubility calculations, the development of standard thermodynamic databases by the NEA significantly decreased the potential for contradictory approaches by different organisations. In comparison, very few recommended, standard data are available for use in TSMs.

For the long term, a need for such data can be identified, and future international collaborations could aim at filling this gap. One of the problems will be the establishment of appropriate standard states for such reference data; partial solutions to this problem are discussed in Kulik (2002) and Sverjensky (2003).

### 7.3 Recommendations for modelling sorption in complex systems

The selection of either a GC model or CA model as the most appropriate is still a matter of uncertainty. The choice involves consideration of two issues: the complexity of the substrate and its accessibility for experimental investigation. A schematic summary of these issues and an approximate guidance regarding the use of GC and CA approaches is presented in Figure 7.2.

The choices of TSMs comprise a range of mathematical simplicity and chemical plausibility on one hand, and of the feasibility of parameterising a model on the other:

- i) The chemically most plausible models are invariably those where the nature of surface species and/or sites is confirmed by spectroscopy (see model h in TC4, for example), or models that use the most detailed description of the EDL (see Hiemstra and van Riemsdijk, 1996, for example). While chemically most correct, these models are often not very useful for PA applications, for two reasons: First, they are complex and there are significant difficulties in parameterisation for relevant substrates. Second, these models are still evolving with time and must be regarded as research tools.
- ii) As the other extreme one can cite the SC-NEMs, particularly when used in a GC approach. These approaches emphasise a good mathematical fit to experimental data, possibly at the cost of having to formulate less plausible surface species. However, these models still provide a thermodynamic framework for predicting  $K_d$  in an interpolative fashion as a function of conditions. For very complex substrates, these models may be the only choice that allows parameterisation. Because of their conditional nature, GC models have little or no predictive power beyond the range of conditions investigated experimentally.
- iii) The traditional EDL models (DLM, BSM, TLM) that may also use generic sites make up the large middle ground between the above extremes. They can be more chemically correct than the SC-NEMs, but are often more difficult to parameterise.

To determine the best TSM modelling method for a complex material, the purpose and desired applicability of the model must be clear. For example, is the goal to model  $K_d$  for an accessible system, such as a near-surface environment (e.g. a contaminated site)? Or is it necessary to apply the model to an inaccessible or future system, such as a clay in contact with a hypothetical groundwater (e.g. for an alternative scenario in a PA exercise). In particular, the range of chemical variability that should be covered by the model needs to be taken into account.

One issue is the complexity of the substrates. Based on the present project, it appears that CA models are difficult to apply to a truly complex natural substrate. At present, it cannot be assessed with certainty whether this is an inherent problem or due to inappropriate component models, for example. For such materials, a GC approach, using a SCM without EDL term, is more pragmatic, and probably at least as justified.

The second issue is experimental accessibility. GC models can be expected to perform better than CA models (and with less effort and data needs) when the task at hand is achieving a good fit to experimental data obtained with a complex substrate. They are less constrained by known or assumed



properties of the chosen component minerals. On the other hand, they are restricted to material that can be experimentally studied in a laboratory.

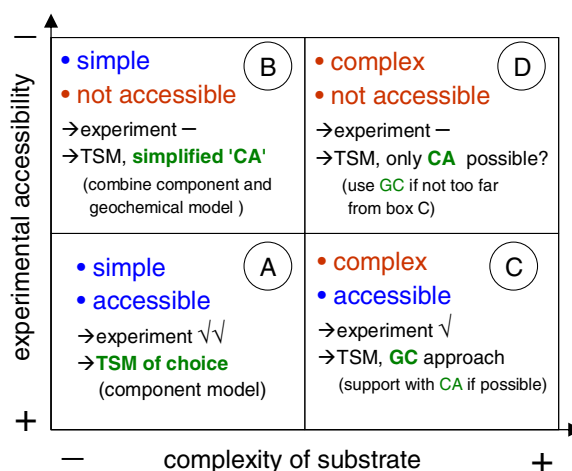
PA often encounters situations where a  $K_d$  is required for a non-accessible material, such as a compacted bentonite, or a host rock after being altered, etc. The real advantage of CA models is their predictive applicability for such systems, which are otherwise very difficult to assess. It has been demonstrated by the modelling results obtained in TC7 that CA-TSMs offer predictive capabilities even for complex sorbents.

On the other hand, if the substrate in question is accessible for experimental approaches, a GC approach is possible. GC models could be fitted to sorption data to back up  $K_d$  values and perform sensitivity analysis within certain limits of conditions (e.g. within a PA reference scenario). At the same time, knowledge gained from such an approach could be used to develop more realistic component models. These can be incorporated in CA approaches, which may then be used in connection with more extended variations of conditions (e.g. for alternative PA scenarios).

Almost invariably,  $K_d$  values for PA need to be derived for conditions that had not been covered as such in experiments. TSMs are the only tools that allow a direct coupling of variable solution chemistry or mineralogy with  $K_d$  in a thermodynamic framework. Therefore, TSMs represent the most traceable and defensible method to derive  $K_d$  as a function of conditions. Ideally, this derivation is done by interpolation between different experimental systems that bracket the PA-relevant conditions. If extension to another substrate or extrapolation to different conditions becomes necessary, the introduction of additional uncertainties cannot be completely avoided. The key to reducing these uncertainties is to reduce the chemical differences in key parameters that need to be covered in the prediction. TSMs can also be a very valuable tool in identifying and narrowing down the number of geochemical key parameters that need to be covered.

RN sorption is a very important and technically challenging issue for repository safety, and all available means of working out reliable values should be used. Modelling and experiments are complementary in this respect.

Figure 7.2: **Schematic overview of the complexity of substrates and their accessibility to experimental investigations vs. the resulting TSM options. The order of difficulty would be  $A < (B, C) < D$ . Note that the terms “simple” and “complex” refer exclusively to the sorbent, not to the entire system. In this sense, the prediction of  $K_d$  in bentonite backfill based on a model calibrated on pure montmorillonite (similar to TC4) would fall in box B since it involves only one component model. The system used in TC6 would fall in box C.**



## 7.4 General recommendations for modelling RN sorption with TSMs

Following on the major conclusions summarised in Section 7.2, together with the considerations regarding the selection and uncertainty of data values for PA (Section 7.1), it is possible to make some general recommendations regarding the development of TSMs and their applications to RN sorption modelling. Specific conclusions on particular model features can be found in the appropriate sections of Chapters 5 and 6; and are not repeated here:

- The influence of the chosen procedure for model parameterisation in comparison to model design must not be neglected. If all available data (including sub-datasets for different conditions) are used for model development, the model is likely to perform better, and will be more representative than if only a part of the database is used. Models based on limited range of input data are likely to be inadequate for simulating a broad range of experimental conditions. If only part of the database is considered, it is more likely that a significant governing process will be omitted from the model.
- Shortcomings in the datasets available for calibration became evident only after a first round of fitting. This implies that model development ideally requires a coordinated experimental and modelling effort. This would be preferable to a single experimental program followed by a modelling exercise.
- Experimentalists should consider (and be provided with guidance regarding) the needs of the modellers. Similarly, modellers should be aware of limitations within the experimental dataset, such as imprecision of experimental  $K_d$  values under conditions of very high or low sorption.
- In general, model development may proceed from simplest possible to more complex. It needs to be clear, however, that a simple model is not necessarily one with only one site, or with a simple EDL model, but is a model with a small number of adjustable or total parameters. As well as the number of parameters, the source and justification of the parameter values are also important issues.
- Care must be taken to ensure internal consistency. In particular, this includes the following considerations:
  1. If parameters are taken from previous work, they must be shown to be appropriate for and consistent with the characteristics and composition of the systems being modelled.
  2. Inappropriate transfer of surface chemical parameters (in particular site densities and SC or IE constants) has to be avoided.
  3. The surface chemical model must be internally consistent with any larger framework used for geochemical calculations (such as the underlying TDB).
- In order to increase the traceability and credibility of TSM approaches, modellers should clearly document the chain of decisions that led to the final model design (see Section 4 as well as Figures 6 and 7, NEA, 2001).
- To constrain sorption models adequately, datasets are required that show the dependence of  $K_d$  on key geochemical parameters. The substrate for sorption as well as the overall system chemistry needs to be known sufficiently as well. A more detailed discussion on data requirements can be found in Section 6.4.

- The underlying thermochemical database needs to be adequate. Obviously, it will be difficult to develop a TSM (or even meaningful  $K_d$  values, for that matter) for a carbonate-type groundwater if the thermodynamic data for RN-carbonate interaction are missing or erroneous.
- Within an overall framework of  $K_d$  acquisition, TSMs are particularly suitable to carry out a sensitivity analysis to elucidate the effects that uncertainties in different chemical parameters have on uncertainties in  $K_d$ . This will allow one to focus experimental data acquisition on the relevant parameters.

## 8. REFERENCES FOR PART 1

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## **Part 2**



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## **1. ORGANISATION OF PART 2**

This is Part 2 of the report on the NEA Sorption Project, Phase II. The entire project report is organised into three parts. Part 1 contains the actual status report of the project; Part 3, contains all data tables and plots that form the basis for parts 1 and 2.

Part 2 contains a detailed description, assessment and interpretation of the modelling approaches and results of all test cases (summaries of each test case setup are given in Appendix 1). The discussion is organised in a logical sequence from simple to the most complex systems. Key issues are discussed where most appropriate:

- Modelling of radionuclide sorption on simple oxide minerals with surface complexation models (Test Cases 1-3) is discussed in Chapter 2, together with some key issues for single mineral phases.
- The application of combined surface complexation-ion exchange models to radionuclide sorption on clays is discussed in Chapter 3. This chapter also contains discussions on key issues in extrapolating and data requirements.
- Chapters 4 and 5 deal with modelling radionuclide sorption on different complex substrates using thermodynamic sorption models in top-down and bottom-up approaches (TC6, 7).
- Key issues in sorption modelling of complex substrates are discussed in more detail in Chapter 6.

### **Further acknowledgements for Part 2**

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## 2. MODELLING RADIONUCLIDE SORPTION ON OXIDE MINERAL PHASES BY SURFACE COMPLEXATION MODELS

The first three test cases (TC1-TC3) were chosen to demonstrate the usefulness of surface complexation (SC) modelling in describing changes in  $K_d$  values for radionuclide sorption as a function of chemical conditions. The specific datasets for these test cases were selected in order to cover a variety of radionuclides, oxide phases, and solution conditions. Three different adsorbing elements (Np(V), Se(VI and IV), and U(VI)) and oxides (hematite, goethite, and quartz) were chosen, and the significant solution variables were pH, ionic strength, and the concentration of complexing ligands.

Although these test cases involving single oxide phases as adsorbents were considered relatively simple compared to the more complex solid phases that were examined in TC4-TC7, these test cases were included in the project to answer some fundamental questions about SC models that arose as an outcome of discussions during the Phase I Sorption Project (NEA, 2001). For example, the following questions were addressed in TC1-TC3:

1. How important are the electrical double layer (EDL) terms in modelling radionuclide sorption data? The question relates to the tension between building more chemically sophisticated models versus mathematically simple ones. There are no doubts about the existence of the EDL on oxide minerals, however, from a mathematical point of view, one can ask whether it is simpler to fit radionuclide data with non-electrostatic models (SC-NEM)? If one uses EDL terms, are more fitting parameters required for SC-EDL models than for SC-NEM models? Are there additional data requirements to develop SC-EDL models?
2. If SC-EDL models are used, does the triple layer model (TLM) perform any better than the diffuse layer model (DLM), and if so, how much better is the fit to sorption data? Do variable ionic strength conditions influence the answer to the previous question? How many additional fitting parameters are required for TLM models and what are the additional data requirements to develop them?
3. How should total site densities be chosen for SC models? Are model fits improved significantly by using two-site versus one-site models?
4. How are surface species chosen for use in SC models? Are the surface reactions chosen by modelling groups based on chemical plausibility or mathematical fitting?
5. What are the data requirements for various SC modelling approaches? Do more complex models require more data collection? Do SC models with more fitting parameters achieve better fits to radionuclide sorption data? If so, at what cost?
6. Are SC models for radionuclide anions as successful as those for radionuclide cations?
7. Are SC models able to account for changes in radionuclide sorption caused by strong aqueous complex formation with ligands, especially those that occur naturally and at highly variable concentrations, such as carbonate?

8. Can SC models developed for one sample of a mineral phase be easily extended to model radionuclide sorption data on another sample of the same mineral phase without changing the values of fitting parameters of the SC model?

## **2.1 Neptunium(V) sorption on hematite (Test Case 1)**

### **2.1.1 Overview of test case**

A laboratory study (Kohler *et al.*, 1999) of neptunium(V) adsorption onto a synthetic preparation of pure hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) in sodium perchlorate (NaClO<sub>4</sub>) solution was used for this test case. The laboratory batch systems were at a temperature between 20-22°C during equilibration, and sorption was studied as a function of pH (6.5-9.0), NaClO<sub>4</sub> concentration (0.005-0.1M), the partial pressure of carbon dioxide gas (<5 ppm-1.95% CO<sub>2</sub> gas), and the hematite/water ratio (10-1000 mg/L). The hematite precipitate had a specific surface area of 14.4 m<sup>2</sup>/g, as measured by BET nitrogen gas adsorption. Acid-base titrations of the hematite suspension were conducted at 25°C as a function of NaClO<sub>4</sub> concentration (0.01-0.27M) to characterise the hematite precipitate in terms of surface charge and the point-of-zero charge (pH = 9.4). Carbonate adsorption on the hematite suspension was also measured as a function of pH for one set of chemical conditions in a closed system containing a known amount of total carbonate.

Np(V) K<sub>d</sub> values measured in the study were significantly dependent on pH and the partial pressure of carbon dioxide (*p*CO<sub>2</sub>). The goal of the modelling in this test case was to determine whether the dependence of the K<sub>d</sub> values on pH and *p*CO<sub>2</sub> could be described with surface complexation (SC) models. In particular, the importance of fitting the experimental data with and without an electrostatic correction term in the mass laws for SC reactions was examined. The test case was completed by nine modelling teams from seven countries using SC models with (SC-EDL) and without (SC-NEM) electrical double layer terms.

### **2.1.2 Methodology**

The test case was implemented by providing the modelling teams with a selected set of the Np(V) sorption data from the study by Kohler *et al.* (1999) (Table 2.1) and standard aqueous Np thermodynamic data based on a critical review (Guillaumont *et al.*, 2003). There were 8 sets of chemical conditions for the test case, and the pH was varied for each set of conditions. In all there were 52 data points (K<sub>d</sub> values) and the pH ranged from 5.5 to 10.25. In addition, tables of data on carbonate adsorption and surface charge data from acid-base titrations of the hematite were supplied to the modelling teams for optional use. The modelling teams were instructed to assume that the Np(V) sorption data were collected after the experimental systems achieved chemical equilibrium. The instructions stated that each team should develop SC models to describe the data using chemically plausible surface species and as few fitting parameters as deemed feasible.

Table 2.1: **Summary of experimental data for Np(V) sorption data provided to the modelling teams in Test Case 1<sup>a</sup>**

Dataset number	Hematite (g/L)	Total Np(V) concentration	NaClO <sub>4</sub> concentration	Gas phase	Number of data points
1	1.0	1.2·10 <sup>-7</sup> M	0.005M	Air with <5 ppm CO <sub>2</sub>	5
2	1.0	1.2·10 <sup>-7</sup> M	0.01M	Air with <5 ppm CO <sub>2</sub>	6
3	1.0	1.2·10 <sup>-7</sup> M	0.05M	Air with <5 ppm CO <sub>2</sub>	7
4	1.0	1.22·10 <sup>-7</sup> M	0.1M	Air with <5 ppm CO <sub>2</sub>	5
5	1.0	1.13·10 <sup>-6</sup> M	0.1M	Air with <5 ppm CO <sub>2</sub>	9
6	0.1	1.24·10 <sup>-6</sup> M	0.1M	Air with <5 ppm CO <sub>2</sub>	9
7	1.0	1.2·10 <sup>-7</sup> M	0.1M	Air (3.16·10 <sup>-4</sup> atm CO <sub>2</sub> )	4
8	1.0	1.1·10 <sup>-7</sup> M	0.1M	1.95% CO <sub>2</sub>	7

<sup>a</sup> pH was an additional variable for each set of chemical conditions.

### 2.1.3 Model descriptions

#### 2.1.3.1 Overall modelling strategies

A diverse range of modelling approaches were used, including: a) one- and two-site models (Table 2.2), b) different electrical double layer models, c) a variation of total site densities and methods for determining the parameter, d) multiple Np(V) surface species, and e) a consideration of carbonate surface species (Table 2.3). Each modelling team was consistent in the choice of one- and two-site models for SC-EDL and SC-NEM models. That is, when a team used a one-site model for the SC-EDL model development, they also used it for the SC-NEM model.

Table 2.2: **Summary of computer codes and surface site types for Test Case 1**

Modelling team	Computer code	Hematite sorption sites
a	FITEQL 4	≡FeOH <sup>1</sup>
b	PHREEQC 2	≡FeOH
c	FITEQL 2 and MINTEQA2	≡FeOH <sub>w</sub> and ≡FeOH <sub>s</sub> <sup>2</sup>
d	STAMB-2002 and PHREEQC	≡FeOH
e	FITEQL 2 and 4 and UCODE	≡FeOH
f	FITEQL 3.2	≡FeOH
g	HARPHRQ 2 and HARFIT 2	≡FeOH <sub>w</sub> and ≡FeOH <sub>s</sub>
h	FITEQL 4	≡FeOH <sub>w</sub> and ≡FeOH <sub>s</sub>
i	FITEQL 4	≡FeOH

<sup>1</sup> Denotes a single type of surface hydroxyl group on the hematite surface.

<sup>2</sup> Denotes two types of surface hydroxyl groups on the hematite surface, one with stronger Np(V) binding, ≡FeOH<sub>s</sub>, than the other, ≡FeOH<sub>w</sub>.



There was little consensus among the modelling teams for the method to use to set the total surface site density. Three Teams (a, e, and h) used values from the literature, but these values differed in each of the three cases by as much as an order of magnitude (Table 2.3). The other six teams used the acid-base titration data provided to estimate the total surface site density. Three of these Teams (c, f, and i) determined the value by a numerical optimisation method, while the other three used the value in the original data reference of Kohler *et al.*, (1999). These values were all smaller than those obtained from the literature (Table 2.3).

Teams a, c, and f (Table 2.3) did not use the carbonate adsorption data provided in model development. The other six modelling teams considered the adsorption of carbonate in model development in both SC-EDL and SC-NEM models. These teams typically had a larger number of fit parameters because of the consideration of the carbonate surface reactions (Table 2.3 and Table 2.4).

In the SC-NEM models, seven of the nine teams modelling teams still considered the acid-base titration data and derived acidity constants without EDL correction terms to describe these data. However, Teams e and h did not use the acid-base titration data for the SC-NEM model development, and this decreased the number of fitting parameters for these two teams (Table 2.4).

Twelve different Np(V) surface reactions were used by the modelling teams to fit the Np(V) sorption data (Table 2.5). Generally the teams used reaction number 1-2 in both SC-EDL and SC-NEM models, probably because it is the most chemically plausible surface reaction and because the simple cation-proton exchange reaction is commonly used in the literature. However, Team h did not use reaction 1-2 in its SC-EDL model and Team e had a modified version of the reaction because of the use of the one  $pK_a$  model for surface charge. For SC-EDL models, seven of the nine modelling teams had two Np(V) surface species (Table 2.3). Team a had one Np(V) surface species (as in reaction 1-2) and Team g had three Np(V) surface species. As is apparent in Table 2.5, although almost every team used reaction 1-2 for one Np(V) surface species, there was a huge range of reactions chosen for a second Np(V) surface species. Little discussion was provided by the modelling teams as to why or how the surface species were chosen. It appears that in many cases, the choice was based on best-fit to the data after a number of other modelling decisions had been made (e.g. one-site versus two-site models, type of EDL model, carbonate surface reactions, total site density, etc.). It seems possible that these earlier modelling decisions affected the selection of Np(V) surface species that provided the best fit to the sorption data.

In the SC-NEM models, there was generally a greater number of Np(V) surface species used to model the sorption data (Table 2.4). In this case, four teams used three Np(V) surface species to model the data, but two teams used only one Np(V) surface species.

Table 2.3: Summary of modelling approaches for SC models with EDL in test case 1

Modelling team	EDL model type <sup>a</sup>	Total surface site density ( $\mu\text{moles/m}^2$ )	Source of total surface site density	Number of Np(V) surface species <sup>b</sup>	Number of carbonate surface species <sup>b</sup>	Total number of fit parameters
a	DLM	3.84	Literature <sup>c</sup>	1	0	3
b	DLM	1.86	Titration <sup>d</sup>	2	2	7
c	DLM	2.69	Titration <sup>e</sup>	2	0	6
d	CCM	1.86	Titration <sup>d</sup>	2	2	8
e	BSM	8.0	Literature <sup>c</sup>	2 <sup>f</sup>	2 <sup>f</sup>	7 <sup>g</sup>
f	CCM	2.32	Titration <sup>e</sup>	2	0	6
g	DLM	1.86	Titration <sup>d</sup>	3	2	8
h	TLM	36.7	Literature <sup>c</sup>	2 <sup>f</sup>	2 <sup>f</sup>	6 <sup>h</sup>
i	TLM	2.58	Titration <sup>e</sup>	2	1	9

<sup>a</sup> DLM = Diffuse layer model; CCM = Constant capacitance model; BSM = Basic Stern model; TLM = triple layer model.

<sup>b</sup> The number of surface species is affected by the choice of using a one- or two-site model (Table 2.2); if the same chemical species is proposed to form on both  $\equiv\text{FeOH}_w$  and  $\equiv\text{FeOH}_s$  site types, it was counted as two species.

<sup>c</sup> Total site density value taken from the literature, not counted as a fit parameter.

<sup>d</sup> Fit to acid-base titration data by Kohler *et al.* (1999); counted as a fit parameter.

<sup>e</sup> Fit to acid-base titration data by modelling team; counted as a fit parameter.

<sup>f</sup> Used charge-distribution as part of the modelling approach for surface species.

<sup>g</sup> Four model parameters not considered as fit, one for the site density and three for charge distribution values of surface species. Used a one- $pK_a$  model to fit acid-base titration data.

<sup>h</sup> Six model parameters not considered as fit, one for the site density and five for EDL parameters taken from the literature. Charge distribution (CD) values for the Np(V) and carbonate surface species were fit; same CD values were used for both  $\equiv\text{FeOH}_w$  and  $\equiv\text{FeOH}_s$  type species.

Table 2.4 Summary of modelling approaches for SC models without EDL (SC-NEM) in Test Case 1

Modelling team	Total surface site density ( $\mu\text{moles}/\text{m}^2$ )	Source of total surface site density	Number of Np(V) surface species <sup>a</sup>	Number of carbonate surface species <sup>a</sup>	Total number of fit parameters
a	3.84	Literature <sup>b</sup>	1	0	3
b	1.86	Titration <sup>c</sup>	2	2	7
c	2.21	Titration <sup>d</sup>	3	0	7
d	1.86	Titration <sup>c</sup>	2	2	7
e	8.0	Literature <sup>b</sup>	3 <sup>f</sup>	1 <sup>f</sup>	8 <sup>f,g</sup>
f	2.21	Titration <sup>d</sup>	1	1	5
g	1.86	Titration <sup>c</sup>	3	2	8
h	0.576	Sorption <sup>e</sup>	3	0	5 <sup>g</sup>
i	2.58	Titration <sup>d</sup>	2	1	6

<sup>a</sup> The number of surface species is affected by the choice of using a one- or two-site model (Table 2.2); if the same chemical species is proposed to form on both  $\equiv\text{FeOH}_w$  and  $\equiv\text{FeOH}_s$  site types, it was counted as two species.

<sup>b</sup> Total site density value taken from the literature, not counted as a fit parameter.

<sup>c</sup> Fit to acid-base titration data by Kohler *et al.* (1999); counted as a fit parameter.

<sup>d</sup> Fit to acid-base titration data by modelling team; counted as a fit parameter.

<sup>e</sup> Fit to Np(V) sorption data by modelling team; counted as a fit parameter.

<sup>f</sup> Non-integer stoichiometry used for the proton in the mass laws to form surface species; non-integer stoichiometric coefficients counted as fit parameters.

<sup>g</sup> Did not use acidity reactions in the NEM modelling approach.

Table 2.5: Summary of Np(V) surface reactions in SC models in Test Case 1<sup>a</sup>

Np(V) surface reaction	Number	Modelling team								
		a	b	c	d	e	f	g	h	i
$\equiv\text{FeOH} + \text{NpO}_2^+ \leftrightarrow \equiv\text{FeOHNpO}_2^+$	1-1			NEM						NEM
$\equiv\text{FeOH} + \text{NpO}_2^+ \leftrightarrow \equiv\text{FeONpO}_2 + \text{H}^+$	1-2	EDL, NEM	EDL, NEM	EDL, NEM	EDL, NEM		EDL, NEM	EDL, NEM	NEM	EDL
$\equiv\text{FeOH}^{0.5-} + \text{NpO}_2^+ \leftrightarrow \equiv\text{FeONpO}_2^{0.5-} + \text{H}^+$	1-3					EDL <sup>b</sup>				
$\equiv\text{FeOH} + \text{NpO}_2^+ \leftrightarrow \equiv\text{FeOH}_x\text{NpO}_2 + (1-x)\text{H}^+$	1-4					NEM <sup>c</sup>				
$\equiv\text{FeOH} + \text{NpO}_2^+ + \text{H}_2\text{CO}_3 \leftrightarrow \equiv\text{FeONpO}_2\text{H}_2\text{CO}_3 + \text{H}^+$	1-5				EDL, NEM					
$\equiv\text{FeOH} + \text{NpO}_2^+ + \text{H}_2\text{CO}_3 \leftrightarrow \equiv\text{FeOH}_2\text{NpO}_2\text{CO}_3 + \text{H}^+$	1-6							EDL, NEM		EDL
$\equiv\text{FeOH} + \text{NpO}_2^+ + \text{H}_2\text{CO}_3 \leftrightarrow \equiv\text{FeOHNpO}_2\text{CO}_3^- + 2\text{H}^+$	1-7								NEM	
$\equiv\text{FeOH} + \text{NpO}_2^+ + \text{H}_2\text{CO}_3 \leftrightarrow \equiv\text{FeONpO}_2\text{CO}_3^{2-} + 3\text{H}^+$	1-8				EDL, NEM				EDL	
$\equiv\text{FeOH} + \text{NpO}_2^+ + \text{H}_2\text{CO}_3 \leftrightarrow \equiv\text{FeOH}_x\text{NpO}_2\text{CO}_3^{2-} + (3-x)\text{H}^+$	1-9					NEM <sup>c</sup>				
$\equiv\text{FeOH} + \text{NpO}_2^+ + 2\text{H}_2\text{CO}_3 \leftrightarrow \equiv\text{FeONpO}_2(\text{HCO}_3)_2^{2-} + 3\text{H}^+$	1-10		EDL, NEM				EDL			
$\equiv\text{FeOH} + \text{NpO}_2^+ + 2\text{H}_2\text{CO}_3 \leftrightarrow \equiv\text{FeONpO}_2(\text{CO}_3)_2^{4-} + 5\text{H}^+$	1-11				EDL, NEM					
$\equiv\text{FeOH}^{0.5-} + \text{NpO}_2^+ + 2\text{H}_2\text{CO}_3 \leftrightarrow \equiv\text{FeONpO}_2(\text{CO}_3)_2^{4.5-} + 5\text{H}^+$	1-12					EDL <sup>b</sup>				

<sup>a</sup> EDL indicates species used in SC-EDL model; NEM indicates species used in SC-NEM model.

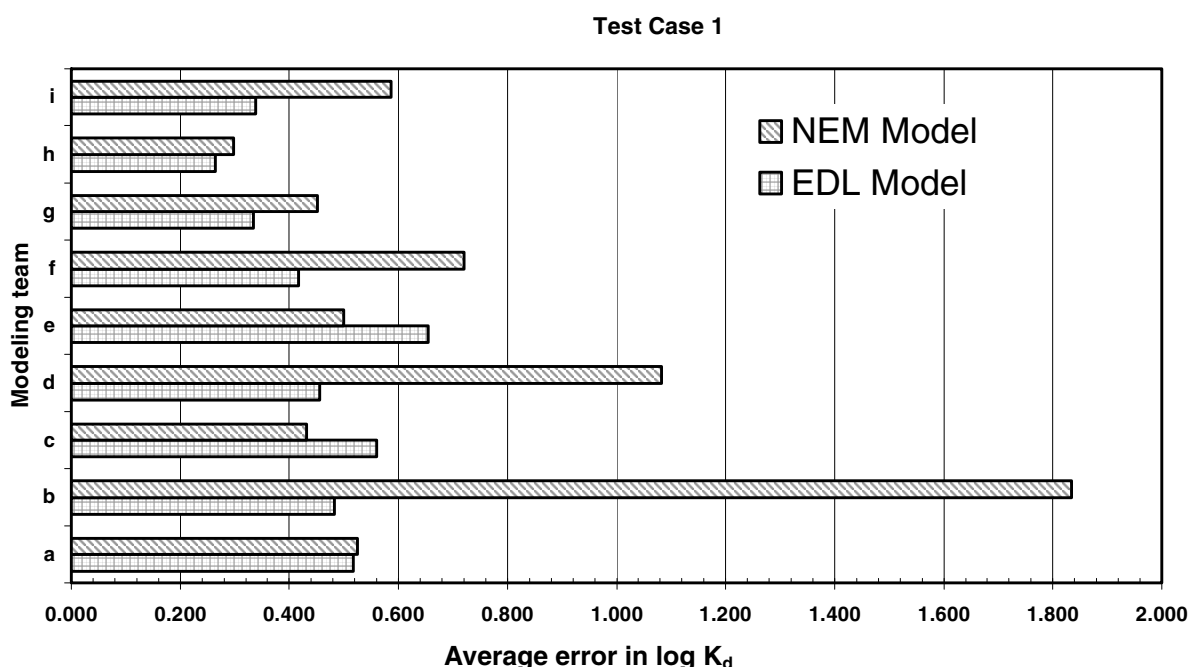
<sup>b</sup> EDL model had one acidity constant for the reaction:  $\equiv\text{FeOH}_2^{0.5+} \leftrightarrow \equiv\text{FeOH}^{0.5-} + \text{H}^+$ .

<sup>c</sup> Model used non-integer stoichiometry for the proton,  $\text{H}^+$ .

### 2.1.4 Modelling results and discussion

Figure 2.1 compares the average error (absolute values) in calculated and experimental  $\log K_d$  values for all data points for the SC-EDL and SC-NEM models. In most cases, the average error varied between 0.3 and 0.5 log units. Most modelling teams achieved a better fit to the  $N_p(V)$  sorption data with the SC-EDL models, although two teams had a better fit with SC-NEM models. However, an important observation is that the SC-EDL model fits were not dramatically better than SC-NEM model fits (Figure 2.1). In fact, the variation in fits achieved by the different modelling teams was perhaps greater than the difference between the SC-EDL and SC-NEM fits for many of the modelling teams. Team h had an SC-NEM model with lower average error than the SC-EDL models of the other eight modelling teams, illustrating that choosing an NEM modelling approach does not mean that model will not fit the data well.

Figure 2.1 **Model performance for Test Case 1 showing the sum of the errors (absolute value of difference between calculated and experimental  $\log K_d$  values) divided by the number of data points. Team b did not recalibrate model parameters in the case of the NEM modelling approach. This resulted in the very large error shown**



Another observation worth noting is that the number of fitting parameters in the SC-NEM models was not less than for SC-EDL models (Tables 2.3 and 2.4), as might have been expected. This may have been partly because seven of the nine modelling teams still retained acid-base reactions in the SC-NEM models, which seems unnecessary. Once the decision is made to adopt an SC-NEM modelling approach, model agreement with acid-base titration data is not needed. In addition, it is very difficult to model surface charge data without EDL correction terms to the mass laws.

As mentioned above, Figure 2.1 shows the average error between the calculated and experimental  $\log K_d$  values for all datasets. Figure 2.2 and Figure 2.3 show the average error for each modelling team for each individual dataset (or set of chemical conditions) for the SC-EDL and SC-NEM models, respectively.

Figure 2.2: Model performance for Test Case 1 showing the errors (absolute value of difference between calculated and experimental  $\log K_d$  values) for individual datasets with SC-EDL models (chemical conditions given in Table 2.1)

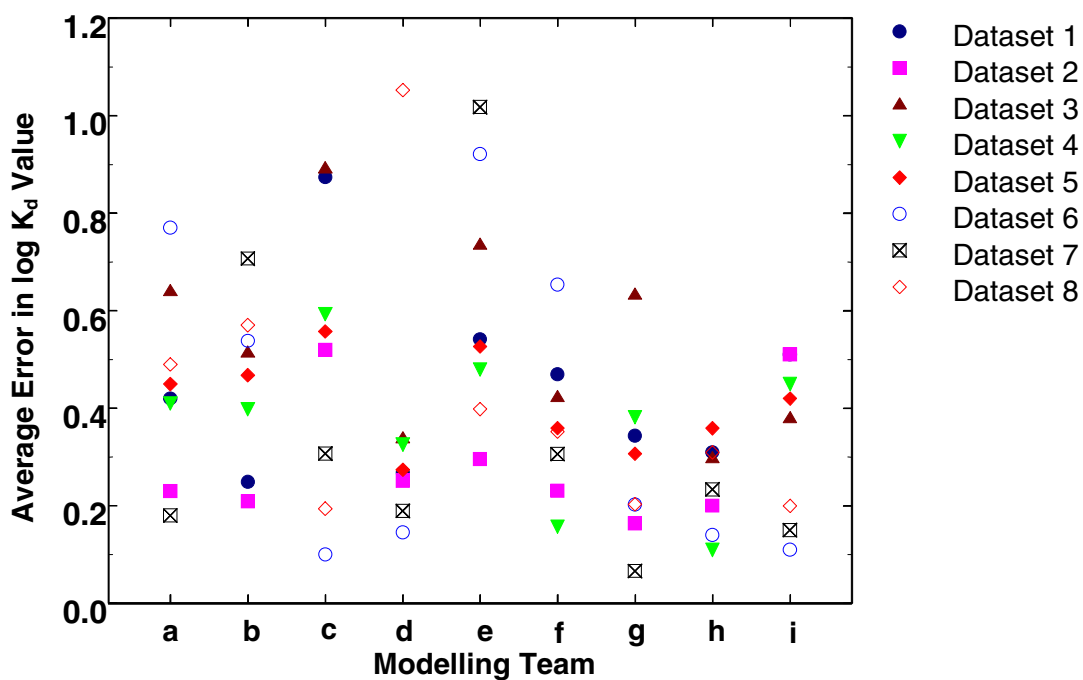
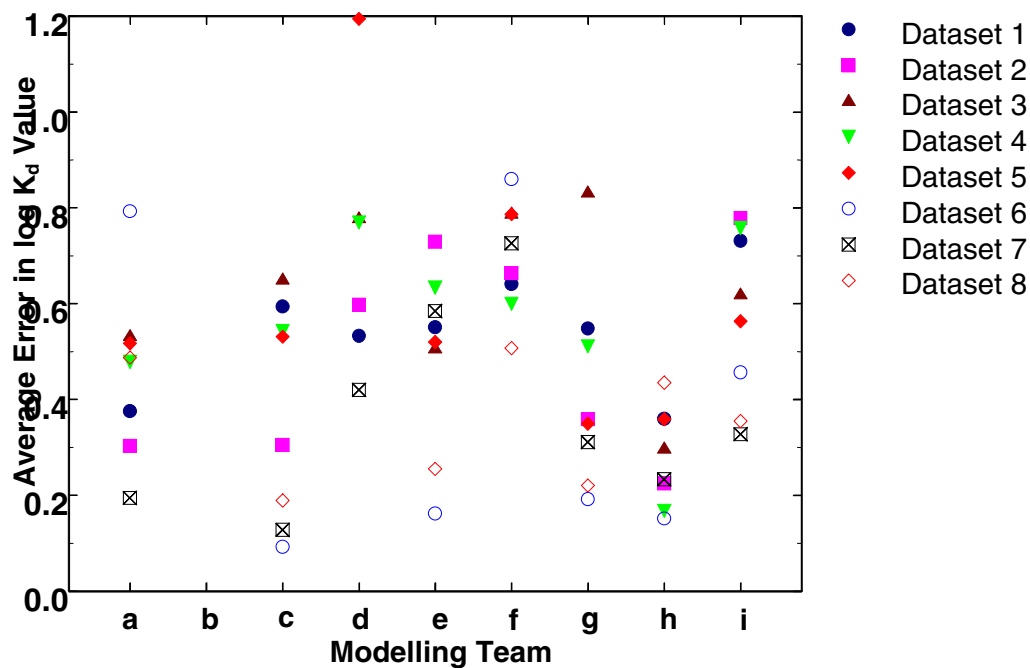


Figure 2.3 Model performance for Test Case 1 showing the errors (absolute value of difference between calculated and experimental  $\log K_d$  values) for individual datasets with SC-NEM models (conditions given in Table 2.1). Team b not shown due to lack of refitting parameters for SC-NEM. Some errors off scale for Team d



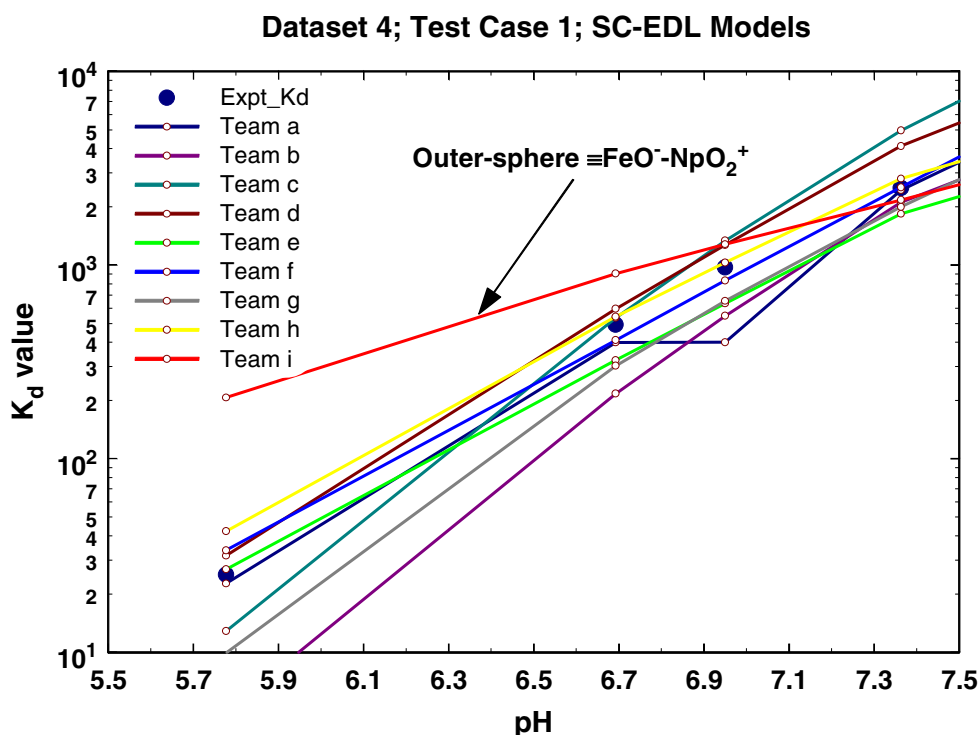
Teams c, g, and h used two-site models (Tables 2.3 and 2.4), and it can be seen in Figure 2.1 that these teams achieved a better fit to the data with their models than in most other cases. The two-site modelling approach was important in fitting the sorption data as a function of Np(V) concentration. One of the extremes in Np(V) adsorption density was for dataset 6 (Table 2.1), where the Np(V) concentration was high relative to the hematite in suspension. Figures 2.2 and 2.3 show that Teams c, g, and h achieved a better fit than most other modelling teams for dataset 6, which lowered their average error for all data.

The modelling teams that used two-site models used the strong binding site density as an additional fitting parameter. Generally the population of strong binding sites determined by fitting sorption data is small (1% or less of the total site density), and it is not possible to select this parameter value from literature studies. At the NEA Sorption workshop in El Escorial, Spain in October 2002, there was discussion of the “chemical plausibility” or evidence that such strong binding sites exist. This remains an open question for research, because non-linear adsorption isotherms suggest that stronger binding sites probably exist, yet there are no experimental techniques available to quantify the population(s) on mineral surfaces. Still, a modelling approach that assumes a two-site model for a single mineral phase is similar in some ways to the top-down (GC) modelling approach that is applied to heterogeneous soils and sediments. Thus, so-called bottom-up (CA) modelling approaches that are applied to sediments as a summation of calculated adsorption for single mineral phases may also contain some elements of the top-down approach within the model parameters for the single mineral phases.

Most modelling teams included a ternary surface-Np-carbonato complex of some form in their SC-EDL and SC-NEM models (Table 2.5). Notable exceptions were Teams a and c, which did not include either the sorption of carbonate species or the formation of ternary surface complexes (Tables 2.3, 2.4 and 2.5). Datasets 1 through 6 were experiments with minimal carbonate present, but datasets 7 and 8 were for systems equilibrated with air or 1.95% CO<sub>2</sub>(g). Team a had relatively poor agreement with dataset 8, and this contributed significantly to their overall error for the entire dataset. Despite the lack of a surface-Np-carbonato ternary complex in their SC-EDL and SC-NEM models, Team c had good agreement between calculated and experimental log K<sub>d</sub> values for datasets 7 and 8 (Figures 2.2 and 2.3). However, this agreement was achieved at the expense of relatively poor agreement with the experiments with minimal carbonate present. The best performing models (using average error, see Figure 2.1) by Teams g, h, and i all had a surface-Np-carbonato ternary complex in their models, and it appeared necessary to have such a species in the model in order to achieve an excellent fit to all of the Np(V) sorption data.

Among the EDL models chosen, the triple layer model (TLM) chosen by Teams h and i appeared to give better results than the diffuse layer or constant capacitance models (Figure 2.1 and Table 2.3). Datasets 1-4 had ionic strength as the main variable in chemical conditions, and it can be seen in Figure 2.2 that Team h had a better fit to the data for datasets 1-4 than most modelling teams, perhaps validating the choice of the triple layer model. Team i, however, did not have a superior fit for datasets 1-4, and the reason appeared to be that the team assumed that an outer-sphere complex was formed in reaction 1-2 (Table 2.5). This assumption yielded a significantly different pH dependence to the calculated Np(V) sorption at all ionic strengths and contributed substantial error to some of the calculated log K<sub>d</sub> values by this modelling team at high ionic strength, as can be seen in Figure 2.4.

Figure 2.4: SC-EDL model performance for Dataset 4 of Test Case 1 showing calculated and experimental  $K_d$  values as a function of pH



### 2.1.5 Conclusions for Test Case 1

Test Case 1 demonstrated that SC modelling could describe the variation in Np(V)  $K_d$  values that were observed as a function of pH, ionic strength, and the partial pressure of carbon dioxide gas in equilibrium with the aqueous phase. The latter variable is considered to very important in subsurface modelling and to PA.

SC-EDL models achieved better fits to the experimental data than SC-NEM models, although the fits were not dramatically better as might have been expected. In fact, the variation in modelling approaches taken by the modelling teams was a far more important aspect in fitting data than was the choice of an EDL or NEM approach (see Figure 2.1). A somewhat surprising conclusion was that the number of fitting parameters for SC-NEM was not significantly less than SC-EDL models. This occurred because SC-NEM models usually have more surface species in order to fit the experimental data, and this compensates for the exclusion of EDL parameters. Among the SC-EDL models, the TLM achieved better fits to the data than DLM, and this occurred because of a better fit to the data as a function of ionic strength.

Two-site models fit the experimental data as a function of Np(V) concentration better than one-site models, and as a result had lower average error for the entire dataset. The strong site density was used as a fitting parameter, and thus, the strong site density was not determined via an experimental characterisation technique or based on an estimate with chemical significance.

The models that included a neptunyl-carbonate ternary surface complex had better fits to the data than those that did not. The reason for this was that only these models were able to fit the  $K_d$  data well at both low and high partial pressures of carbon dioxide gas. The existence of such a species has



not yet been confirmed in spectroscopic studies, but the structure is chemically plausible because of analogous complexes observed for uranium(VI) (Bargar *et al.*, 2000, 1999).

## **2.2 Selenium sorption on goethite (Test Case 2)**

### **2.2.1 Introduction**

A laboratory study (Hayes *et al.*, 1987; Hayes, 1987) of selenium (VI and IV) adsorption onto a synthetic preparation of goethite in sodium nitrate (NaNO<sub>3</sub>) solution was used for this test case. The selenium sorption study was selected because it provided a rare example of a dataset suitable for modelling and describing sorption of an anion. The solid was well-characterised and data were available for a range of pH values and solid loadings. Further, the study involved both Se(VI) and Se(IV), so the different oxidation states could be compared. An additional feature was that EXAFS data were available for both oxidation states, and this test case provided an opportunity to study the added value of EXAFS data to support modelling choices.

Test Case 2 was perhaps the simplest of the test cases. Modellers were asked to fit the data provided using the most appropriate model, balancing the conflicting tensions between model simplicity and accuracy. There was no formal requirement for extrapolation of a model to different chemical conditions.

### **2.2.2 Summary of experimental data for Test Case 2**

The following experimental data were modelled:

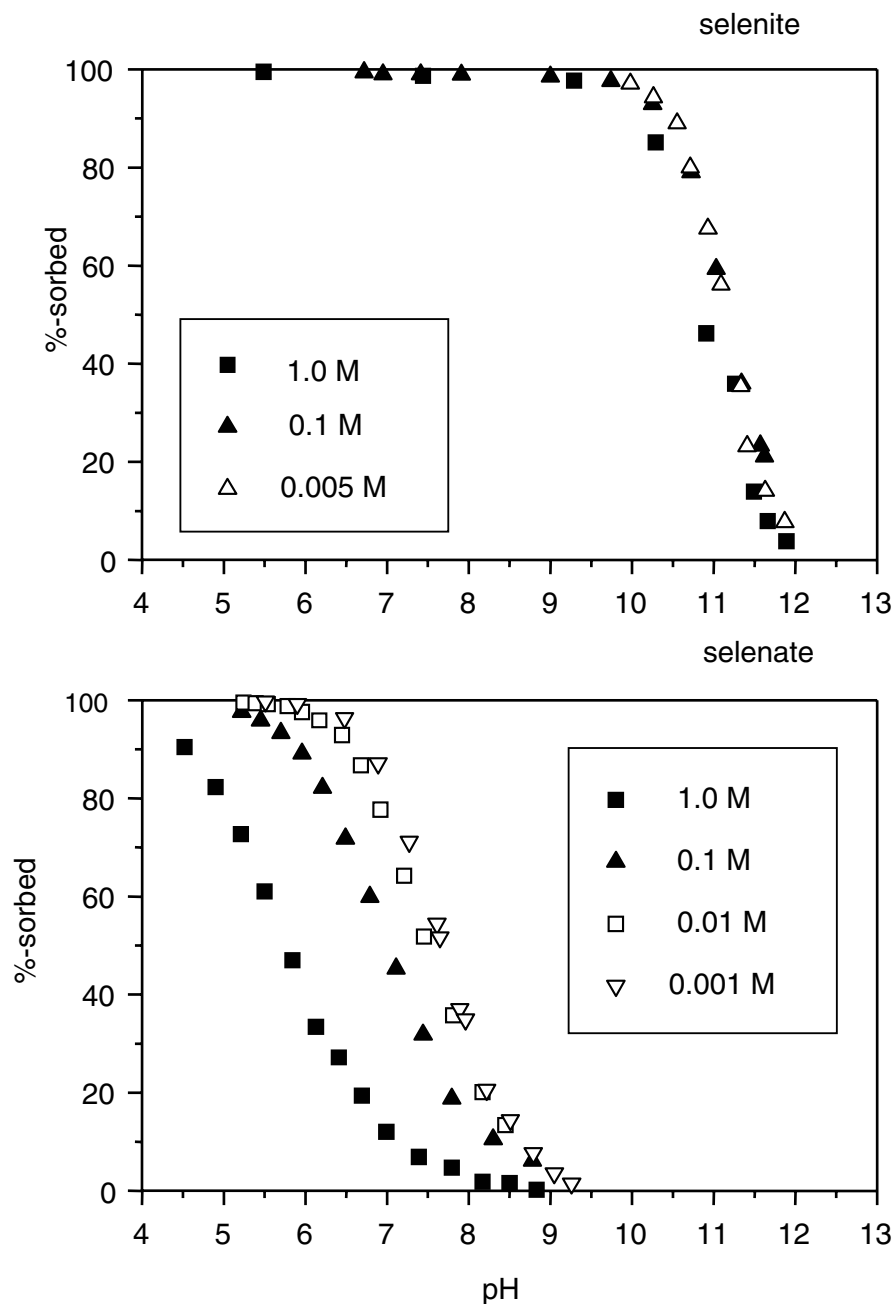
- Experiments with Se(VI) at two mass loadings of goethite (3 g/L and 30 g/L). The background electrolyte was NaNO<sub>3</sub> at various ionic strengths: 0.01, 0.1 and 1.0 M NaNO<sub>3</sub> (In addition, 0.001 M NaNO<sub>3</sub> was also used for the 30 g/L goethite loading). In all the studies the total Se(VI) concentration was fixed at 100 µmoles/L.
- Experiments with the total Se(IV) concentration of 100 µmoles/L with a goethite loading of 30 g/L, and ionic strengths of 0.005, 0.1 and 1.0 M.

EXAFS data were available for both oxidation states. The study by Hayes (1987) concluded that “Se(IV) forms an inner-sphere coordinative complex at the goethite surface, whereas Se(VI) retains its hydration sphere upon adsorption.” Some information about the structure of the Se(IV) surface complex was obtained, with a binuclear structure (i.e. Se(IV) bonding to two surface Fe atoms) appearing most likely.

A subsequent EXAFS study in the goethite/Se(VI) system concluded that “the Se(VI) oxyanion forms an inner sphere surface complex on goethite” (Manceau and Charlet, 1994). Modellers were asked to make their own value judgments of these apparently conflicting interpretations of spectroscopic data.

The goethite precipitate had a specific surface area of 52 m<sup>2</sup>/g, as measured by BET nitrogen gas adsorption. Acid-base titrations of the goethite suspension were conducted at 25°C as a function of NaNO<sub>3</sub> concentration (0.001-0.03M) to characterise the goethite precipitate in terms of surface charge. The experimental Se sorption data are reproduced in Figure 2.5.

Figure 2.5: **Experimental data for percentage of selenium (IV, VI) as a function of pH, Test Case 2**



## 2.2.3 Results

### 2.2.3.1 Modelling approaches

Five modelling teams participated in Test Case 2. One of these teams provided a number of different models and these datasets provided an opportunity to compare directly the effect of modelling decisions on the fit to the data. A total of 8 models were therefore available for comparison. These are described as Teams a-h in the discussion that follows. The main modelling choices are summarised below.

### 2.2.3.2 *Code and data choices*

A range of modelling codes was employed. Two teams used FITEQL. Two other teams used codes based on PHREEQE. The remaining four models were obtained using a modified version of FITEQL coupled to UCODE.

One team had chosen to use the truncated Davies method of ionic strength correction, and another team used the tabulated values for activity coefficients given in Dzombak and Morel (1990). The experimental data covered the range up to 1.0 M, and so further comment on this aspect might have been expected from the other modelling teams. It was assumed that the remaining teams used the Davies equation without further modification.

Standard thermodynamic data were supplied with the test case and most teams chose to use these without modification. One team chose to include additional protonation reactions based on data from Lemire and Fuger (2001).

### 2.2.3.3 *Type of model*

Six of the eight teams included electrostatic correction terms in the mass laws for surface reactions. Two Teams (f and h) used an NEM.

The choice of electrostatic model varied between teams. Two groups selected a version of the TLM (Teams c and d). One team made this choice because the experimental data showed an ionic strength effect. The other team started with a DLM, but was unable to fit the data, and then switched to the TLM. Two teams selected a DLM (Teams a and b). The reason for this was described as being “for simplicity”. Teams e and g used a basic Stern model (BSM). One-site models were used by all teams.

### 2.2.3.4 *Fitting method*

The teams that had selected FITEQL/UCODE used an automated fit based on the experimental data presented as % sorbed (Teams e-h). Teams e and f optimised the fit to  $K_d$  values, while Teams g and h optimised the fit to % sorbed data. Teams a-d used fitting by eye. Team d used a Monte Carlo method to investigate the sensitivity of the model response to the choice of log K values.

In some cases teams chose to fit a subset of the data, most choosing the data at the highest ionic strength. One team chose to use the lowest ionic strength for data fitting.

### 2.2.3.5 *Acid-base titration data*

All teams fitted the acid-base titration data as part of their model. Sodium nitrate is often considered to be an inert electrolyte. However, for this system, all teams found it necessary to account for interaction of this electrolyte. Most teams chose to include sorption of sodium or both sodium and nitrate into their reaction. (Team b commented that, although they had included the nitrate reaction, their model was not sensitive to the log K value ascribed to it, under the particular conditions of these experiments).

### 2.2.3.6 *EXAFS data*

Although EXAFS data were provided, most teams made little reference to this information when electing their surface species to model the sorption data. Most teams selected their surface species based on the observed macroscopic sorption behaviour as a function of ionic strength. Where

an ionic strength dependence of sorption was observed [i.e. for Se(VI)], an outer sphere complex was assumed. Inner sphere complexes were chosen where the observed sorption behaviour was independent of ionic strength, i.e. for Se(IV).

One team did base its choice of surface species on the EXAFS data. In this case, inner-sphere bidentate bonding was used for Se(IV) surface species, in agreement with EXAFS results. For modelling Se(VI) adsorption, this team used a combination of inner- and outer-sphere monodentate surface species, again in agreement with surface spectroscopic results. The net surface charge was not assumed to occur in only one plane for these species; instead a charge distribution for each surface species was fitted.

### 2.2.3.7 Fitted parameters

The modelling choices, selected reactions and associated log K values are shown in Tables 2.6 to 2.11 below.

Table 2.6: **Stability constants and reactions for Team a, TC2**

Surface reaction	Log K
<b>Se(VI)</b>	
$\text{YOH} + \text{H}^+ + \text{SeO}_4^{2-} \rightarrow \text{YSeO}_4^- + \text{H}_2\text{O}$	10.75
$\text{YOH} + \text{NO}_3^- \rightarrow \text{YOHNO}_3^-$	1.82
<b>Se(IV)</b>	
$\text{YOH} + \text{H}^+ + \text{SeO}_3^{2-} \rightarrow \text{YSeO}_3^- + \text{H}_2\text{O}$	15.4
$\text{YOH} + \text{NO}_3^- \rightarrow \text{YOHNO}_3^-$	1.82
<b>Acidity constants</b>	
$\text{YOH} + \text{H}^+ = \text{YOH}_2^+$	5.1
$\text{YOH} = \text{YO}^- + \text{H}^+$	-10.61

Table 2.7: **Stability constants and reactions for Team b, TC2**

Surface reaction	Log K
<b>Se(VI)</b>	
$\text{Fe\_sOH} + \text{H}^+ = \text{Fe\_sOH}_2^+$	6.0
$\text{Fe\_sOH} = \text{Fe\_sO}^- + \text{H}^+$	-9.3
$\text{Fe\_sOH} + \text{SeO}_4^{2-} = \text{Fe\_sOHSeO}_4^{2-}$	2.7
$\text{Fe\_sOH} + \text{NO}_3^- = \text{Fe\_sOHNO}_3^-$	-0.2
<b>Se(IV)</b>	
$\text{Fe\_sOH} + \text{H}^+ = \text{Fe\_sOH}_2^+$	6.0
$\text{Fe\_sOH} = \text{Fe\_sO}^- + \text{H}^+$	-9.3
$\text{Fe\_sOH} + \text{H}^+ + \text{SeO}_3^{2-} = \text{Fe\_sSeO}_3^- + \text{H}_2\text{O}$	15.8
$\text{Fe\_sOH} + \text{NO}_3^- = \text{Fe\_sOHNO}_3^-$	-0.2

Table 2.8: **Stability constants and reactions for Team c, TC2**

Surface reaction	Log K
$XOH + H^+ = XOH_2^+$	5.9
$XOH = XO^- + H^+$	-10.286
$XOH + H^+ + NO_3^- = XOH_2^+ - NO_3^-$	6.2
$XOH + Na^+ = XO^- - Na^+ + H^+$	-9.5
<b>Se(VI)</b>	
$XOH + SeO_4^{2-} = XOHSeO_4^{2-}$	1.49
$XOH + SeO_4^{2-} + H^+ = XOH_2SeO_4^{2-}$	7.96
$XOH + SeO_4^{2-} + 2 H^+ = XOH_2HSeO_4^{2-}$	16.254
<b>Se(IV)</b>	
$XOH + SeO_3^{2-} + H^+ = XSeO_3^- + H_2O$	16

Table 2.9: **Stability constants and reactions for Team d, TC2**

<b>Se(VI)</b>	
Surface reaction	Log K
$SOH - H^+ = SO^-$	-10.34
$SOH + H^+ = SOH_2^+$	5.42
$SOH - H^+ + Na^+ = SO-Na^+$	-13.5
$SOH + H^+ + NO_3^- = SOH_2^+NO_3^-$	4.7
$SOH + NO_3^- = SOH NO_3^-$	-1.02
$SOH + H^+ + SeO_4^{2-} = SOH_2^+SeO_4^{2-}$	9.23
$SOH + SeO_4^{2-} = SOH SeO_4^{2-}$	2.3
<b>Se(IV)</b>	
Surface reaction	Log K
$SOH - H^+ = SO^-$	-10.34
$SOH + H^+ = SOH_2^+$	5.42
$SOH - H^+ + Na^+ = SO-Na^+$	-13.5
$SOH + H^+ + NO_3^- = SOH_2^+NO_3^-$	4.7
$SOH + NO_3^- = SOH NO_3^-$	-1.02
$SOH + H^+ + SeO_3^{2-} = SOH_2^+SeO_3^{2-}$	15.91
$SOH + H^+ + SeO_4^{2-} = SOH_2^+SeO_4^{2-}$	9.23
$SOH + SeO_4^{2-} = SOH SeO_4^{2-}$	2.3

Table 2.10: Stability constants and reactions for Teams e and g, TC2. Team e optimised on log  $K_d$  values, Team g on % adsorbed data; both teams used otherwise identical SC-BSMs

Team e		Team g	
<b>Goethite Acid/base</b>		<b>Goethite Acid/base</b>	
Surface reaction, Log K		Surface reaction	
$\text{SOH}^{-0.5} + \text{H}^+ = \text{SOH}^{+0.5}$	8.49	$\text{SOH}^{-0.5} + \text{H}^+ = \text{SOH}^{+0.5}$	8.49
$\text{SOH}^{-0.5} + \text{Na}^+ = \text{SOH}^{-0.5} \text{Na}^+$	0.43	$\text{SOH}^{-0.5} + \text{Na}^+ = \text{SOH}^{-0.5} \text{Na}^+$	0.43
$\text{SOH}^{-0.5} + \text{H}^+ + \text{NO}_3^- = \text{SOH}^{+0.5} \text{NO}_3^-$	8.83	$\text{SOH}^{-0.5} + \text{H}^+ + \text{NO}_3^- = \text{SOH}^{+0.5} \text{NO}_3^-$	8.83
Stern layer capacitance	0.6 F/m <sup>2</sup>		0.6 F/m <sup>2</sup>
<b>Selenate</b>		<b>Selenate</b>	
Surface reaction, Log K		Surface reaction, Log K	
$\text{SOH}^{-0.5} + \text{H}^+ + \text{SeO}_4^{2-} = \text{SOH}_2^{-0.19} \text{SeO}_4^{-1.31}$	9.77	$\text{SOH}^{-0.5} + \text{H}^+ + \text{SeO}_4^{2-} = \text{SOH}_2^{-0.15} \text{SeO}_4^{-1.35}$	9.81
$\text{SOH}^{-0.5} + \text{H}^+ + \text{SeO}_4^{2-} = \text{SOH}_2^{0.3} \text{SeO}_4^{-1.80}$	9.4	$\text{SOH}^{-0.5} + \text{H}^+ + \text{SeO}_4^{2-} = \text{SOH}_2^{0.3} \text{SeO}_4^{-1.80}$	7.77
<b>Selenite</b>		<b>Selenite</b>	
Surface reaction, Log K		Surface reaction, Log K	
$2\text{SOH}^{-0.5} + 2\text{H}^+ + \text{SeO}_3^{2-} = (\text{SOH}_2)_2^{-0.33} \text{SeO}_3^{-0.67}$	25.41	$2\text{SOH}^{-0.5} + 2\text{H}^+ + \text{SeO}_3^{2-} = (\text{SOH}_2)_2^{-0.33} \text{SeO}_3^{-0.67}$	25.55

Table 2.11: Stability constants and reactions for Teams f and h, TC2. Team F optimised on log  $K_d$  values, Team h on % adsorbed data; both teams used otherwise identical SC-NEMs. Note that the net charges of the surface species are indicated for reasons of formal consistency (the SC-NEM is only based on mass-balances)

Team f		Team h	
<b>Se(VI)</b>		<b>Se(VI)</b>	
$\text{SOH} + 0.09 \text{H}^+ + \text{SeO}_4^{2-} = \text{SOH}_{1.09} \text{SeO}_4^{1.91-}$	0.45	$\text{SOH} + 0.11 \text{H}^+ + \text{SeO}_4^{2-} = \text{SOH}_{1.11} \text{SeO}_4^{1.89-}$	1.87
$\text{SOH} + 0.66 \text{H}^+ + \text{SeO}_4^{2-} = \text{SOH}_{1.66} \text{SeO}_4^{1.34-}$	6.72	$\text{SOH} + 0.58 \text{H}^+ + \text{SeO}_4^{2-} = \text{SOH}_{1.58} \text{SeO}_4^{1.42-}$	5.88
<b>Se(IV)</b>		<b>Se(IV)</b>	
$2\text{SOH} + 0.99 \text{H}^+ + \text{SeO}_3^{2-} = (\text{SOH})_2 \text{H}_{0.99} \text{SeO}_3^{1.01-}$	14.66	$2\text{SOH} + 1.66 \text{H}^+ + \text{SeO}_3^{2-} = (\text{SOH})_2 \text{H}_{1.66} \text{SeO}_3^{0.34-}$	22.22

## 2.2.4 Model intercomparison and lessons learned

### 2.2.4.1 Modelling of Se(VI) data

The comparison between prediction and experiment is shown in Figure 2.6 below. For the Se(VI) data, the quality of the fits was good, with almost all model values within an order of magnitude of the data. However, this type of error distribution would look like a Gaussian-type bell curve if errors were unbiased (symmetrical) and predictions were basically accurate with random outliers.

Thus, the data were modelled reasonably well with a range of models, including both electrostatic and non-electrostatic SCMs. Although all fits were good, the closest representations of the experimental data were obtained by Teams d, e and g. A summary of the fits is given in Table 2.12.

Figure 2.6: Error distribution between calculated and experimental  $\log K_d$  values for Se(VI) adsorption in TC 2

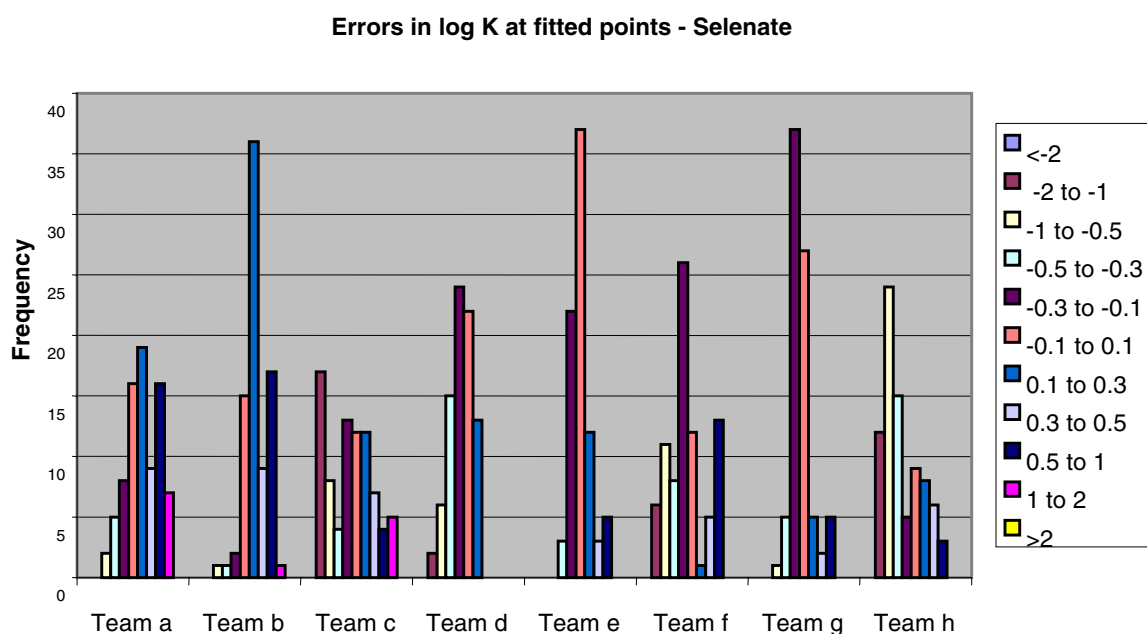


Table 2.12 Errors in  $\log K_d$  values for Se(VI) sorption in TC 2

Error	Team a	Team b	Team c	Team d	Team e	Team f	Team g	Team h
Average deviation in $\log K_d$	0.361	0.209	0.601	0.214	0.165	0.358	0.173	0.435
Points within one order of magnitude (out of 82 points)	75	81	60	80	82	76	82	70

### 2.2.4.2 Modelling of Se(IV) data

Fits to the Se(IV) data were generally less satisfactory (Figure 2.7). The models were able to reproduce the pH edges, but deviated significantly from the experimental data in the lower pH region, where sorption was very strong. This point is illustrated in Figure 3.8, which shows the 0.1M NaNO<sub>3</sub> data. A summary of the fits is given in Table 2.13.

Team c only provided modelled parameters for a subset of the data. Team d obtained a good numerical fit to the experimental data by assuming that the Se(IV) contained a small proportion (1.5%) of residual Se(VI). There is no evidence in the experimental data to support this assumption. Therefore, although the numerical fit was good, these results are not directly comparable with those for the other teams.

Figure 2.7: Error distribution between calculated and experimental log K<sub>d</sub> values for Se(IV) adsorption in TC 2

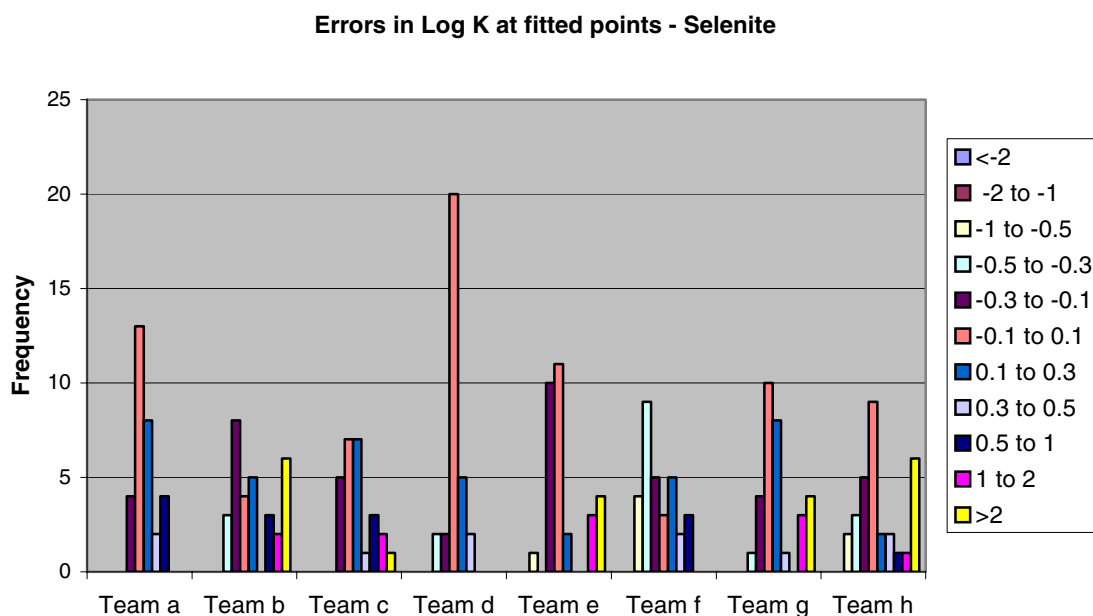


Table 2.13: Errors in log K<sub>d</sub> values for Se(IV) sorption in TC 2

Error	Team a	Team b	Team c	Team d	Team e	Team f	Team g	Team h
Average deviation in log K <sub>d</sub>	0.214	0.991	0.424	0.102	0.727	0.318	0.728	1.099
Points within one order of magnitude	31	23	23	31	24	31	24	24
Total number of points	31	31	(26)	31	31	31	31	31



Figure 2.8a: Comparison of experimental data with model  $K_d$  values for Se(IV) sorption in TC 2

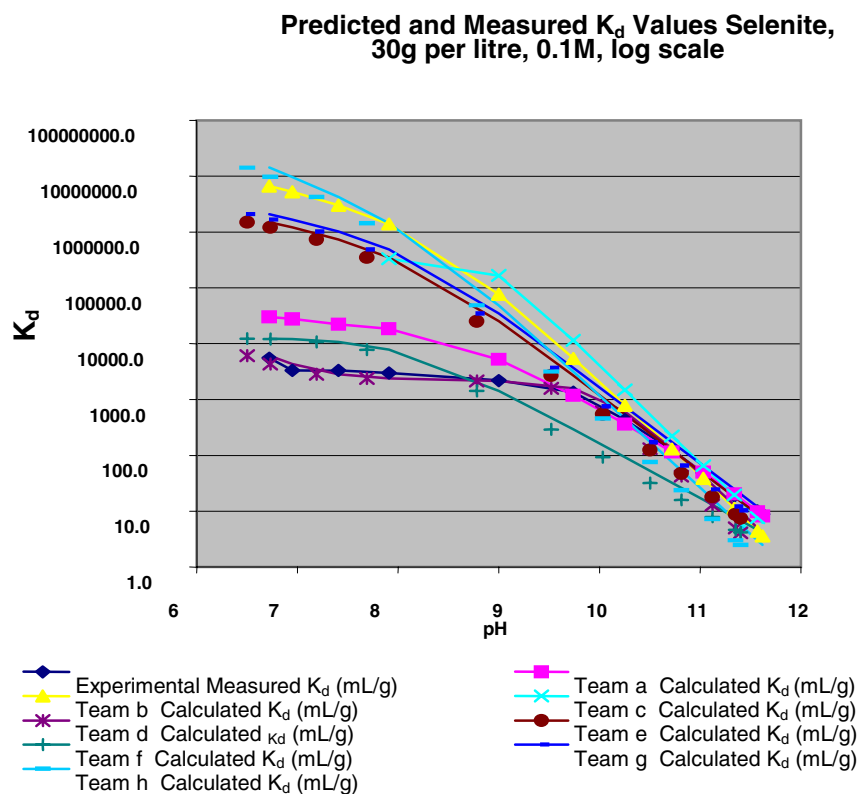
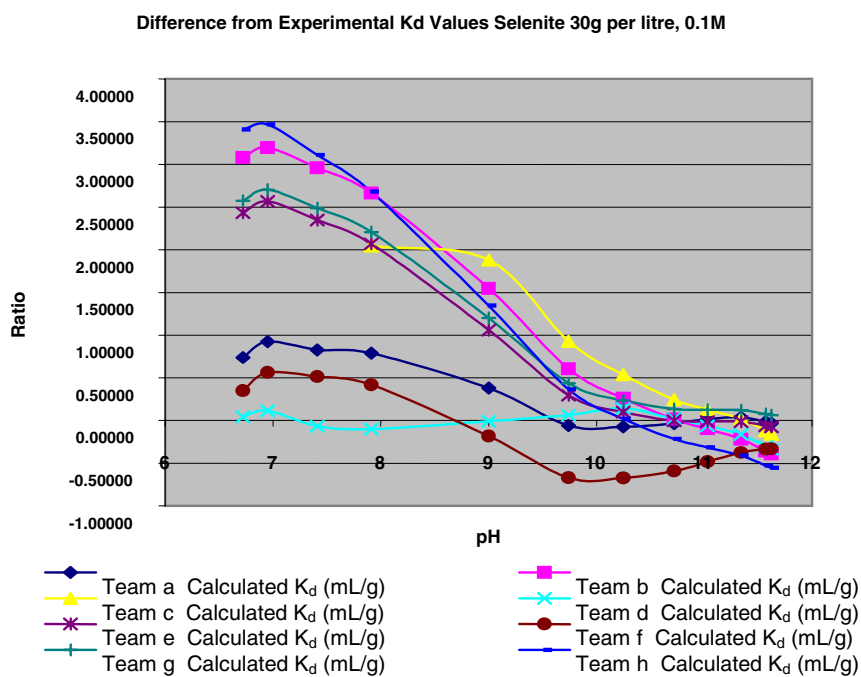


Figure 2.8b: Ratio of experimental to model log  $K_d$  values for Se(IV) sorption in TC 2



The experimental data in this test case illustrate an important point relevant to experimental design. Where very strong sorption is observed, there are often significant errors in the experiment as the residual amount of sorbing ion in solution is so small. Small errors in solid/liquid phase separation can cause large uncertainties (error bars) in the experimental data.

## **2.2.5 Comparison of the effect of using EDL correction terms**

### *2.2.5.1 Comparison of models with and without EDL correction term*

The effect of introducing electrostatic correction terms into the sorption model can be observed by comparing the results of Teams e and f. The models compared were the Basic Stern model with an NEM. In both cases, an automatic data fitting method was used, involving FITEQL/UCODE coupled to a general regression code, and the models were optimised for fit on  $K_d$  values using all the experimental data. Thus, the data used in model parameterisation covered a range of ionic strengths from 0.001M to 1M and also two mass loadings of the solid, 3 and 30 g/L. In the electrostatic model, the effect of the background electrolyte was represented by bidentate sorption of  $\text{Na}^+$  and  $\text{NO}_3^-$ . As the range of ionic strength was broad, the team noted that the experimental data were not ideally suited to an NEM approach, and the fit was improved significantly by the inclusion of the ion pair for the background electrolyte (sodium nitrate) as an additional aqueous species. Log K for this species was fitted by assuming an analogy with sodium sulphate and using the value without further adjustment. All other parameters were unchanged.

For the Se(VI) data, the average error in log  $K_d$  for the electrostatic model was 0.165, whereas for the NEM the average error was 0.358. The improvement in fit in introducing electrostatics into this model is clearly demonstrated. The case of the Se(IV) data appears less clear. The best fit was for Team f, an NEM optimised on  $K_d$  values. The NEM was less sensitive in the region of very high Se(IV) sorption.

### *2.2.5.2 Comparison between DLM and TLM*

A comparison between DLMs and TLMs was obtained by comparing the results of Teams a and b with those of Teams c, d, and g. Based on these results, no significant difference between the predictions based on different EDL models was observed.

## **2.2.6 Optimising on % sorbed or log $K_d$ values**

It was noted that a measure of fit based on  $K_d$  values was inconsistent with the optimisation used in the frequently used computer program, FITEQL. FITEQL calculates the amounts adsorbed and then balances on a parameter such as total concentration to reach a solution. In order to study the effect of this inconsistency, one modelling organisation created an amended version of FITEQL that optimised on  $K_d$  values and compared these results to those using the standard FITEQL code. The effect can be illustrated by comparing the results of Teams e and g (EDL models) or Teams f and h (NEM). Teams e and f optimised on  $K_d$  values; Teams g and h used the original version of FITEQL and optimised on % sorbed data.

The effect of the optimisation method on the results appeared to be very minor. The fits optimised on  $K_d$  values were only slightly better than those optimised on % sorbed data.

### 2.2.7 Conclusions

Test Case 2 clearly demonstrated that sorption onto a single mineral oxide surface can be accurately represented using SCM models. However, even for such a simple system, there were many differing choices for model parameterisation. For this simple system, both SC-EDL and SC-NEM models gave adequate representations of the experimental data, although the SC-EDL models did yield a slight improvement in the fit to experimental data.

## 2.3 Uranium(VI) sorption on quartz (Test Case 3)

### 2.3.1 Overview of Test Case

An unpublished laboratory study of uranium(VI) adsorption onto a cleaned and sized, crushed quartz powder in sodium nitrate ( $\text{NaNO}_3$ ) solution was used for the model calibration part of this test case. The laboratory batch systems were at a temperature between 20-22°C during equilibration, and sorption was studied as a function of pH (3.5-9.1), the partial pressure of carbon dioxide gas (air and 7.5%  $\text{CO}_2$  gas), the concentration of fluoride (0 or  $5 \cdot 10^{-4}\text{M}$ ), and the total U(VI) concentration ( $10^{-8}$  to  $10^{-5}\text{M}$ ). The quartz had a specific surface area of  $0.33 \text{ m}^2/\text{g}$ , as measured by BET krypton gas adsorption. The quartz grains had a size range from 8 to 30 microns as determined by settling. Acid-base titrations of quartz suspensions were conducted at 25°C as a function of  $\text{NaNO}_3$  concentration (0.004-0.1M) to characterise the quartz powder in terms of surface charge.

U(VI)  $K_d$  values measured in the study were significantly dependent on pH, the partial pressure of carbon dioxide ( $p\text{CO}_2$ ), and the concentrations of fluoride and total U(VI). The goal of the modelling in this test case was to determine whether the dependence of the  $K_d$  values on these chemical variables could be described with surface complexation (SC) models. In particular, the importance of fitting the experimental data with and without an electrostatic correction term in the mass laws for SC reactions was examined. In addition, the calibrated model was tested to see how well it could predict U(VI)  $K_d$  values for quartz measured in a study with a different quartz sample (Pabalan *et al.*, 1998). The test case was completed by five modelling teams from four countries using SC models with and without electrical double layer terms.

### 2.3.2 Methodology

The test case was implemented by providing the modelling teams with a selected set of the U(VI) sorption data from a study by Kohler *et al.* (unpublished) (Table 2.14) and standard aqueous U thermodynamic data based on a critical review (Grenthe *et al.*, 1992; Silva *et al.*, 1995). There were 9 sets of chemical conditions for the test case, and the pH was varied for each set of conditions. In all there were 113 datapoints ( $K_d$  values) and the pH ranged from 3.5 to 9.1. In addition, a table of surface charge data from acid-base titration of the quartz was supplied to the modelling teams for optional use. The modelling teams were instructed to assume that the U(VI) sorption data were collected after the experimental systems achieved chemical equilibrium. The instructions stated that each team should develop SC models to describe the data using chemically plausible surface species and as few fitting parameters as deemed feasible.

The second part of Test Case 3 was an exercise to test how well the models developed for each team could be extrapolated to U(VI) sorption data in a separate study with a different quartz sample (Pabalan *et al.*, 1998). One of the main differences was that the quartz in the second study had a specific surface area of  $0.03 \text{ m}^2/\text{g}$ , about 10 times less than in the first study. The laboratory batch systems were at a temperature between 18-22°C during equilibration, and sorption was studied as a function of pH (3.95-8.1) and the total U(VI) concentration ( $10^{-8}$  to  $2 \cdot 10^{-6}\text{M}$ ).

Table 2.14 **Summary of experimental data for U(VI) sorption data provided to the modelling teams in Test Case 3 for the model calibration step<sup>a</sup>**

<b>Dataset number</b>	<b>Total U(VI) concentration</b>	<b>NaF concentration</b>	<b>Gas phase</b>	<b>Number of data points</b>
1	$1 \cdot 10^{-8}$ M	0	Air	18
2	$1 \cdot 10^{-7}$ M	0	Air	17
3	$1 \cdot 10^{-6}$ M	0	Air	18
4	$1 \cdot 10^{-5}$ M	0	Air	5
5	$1 \cdot 10^{-6}$ M	$5 \cdot 10^{-4}$ M	Air	18
6	$1 \cdot 10^{-8}$ M	0	7.5% CO <sub>2</sub>	8
7	$1 \cdot 10^{-7}$ M	0	7.5% CO <sub>2</sub>	5
8	$1 \cdot 10^{-6}$ M	0	7.5% CO <sub>2</sub>	12
9	$1 \cdot 10^{-5}$ M	0	7.5% CO <sub>2</sub>	6

<sup>a</sup> pH was an additional variable for each set of chemical conditions. All systems had a quartz/liquid ratio of 100 g/L and an ionic strength of 0.1 M.

### 2.3.3 *Model descriptions*

#### 2.3.3.1 *Overall modelling strategies*

As in TC 1, a diverse range of modelling approaches were used, including: a) one- and two-site models (Table 2.15), b) different electrical double layer models, c) a variation of total site densities and methods for determining the parameter, and d) several U(VI) surface species (Table 2.16). Each modelling team was consistent in the choice of one- and two-site models for SC-EDL and SC-NEM models. That is, when a team used a one-site model for the SC-EDL model development, they also used it for the SC-NEM model.

Three Teams (a, c, and e) used total site density values from the literature, but the values chosen differed by a factor of two (Table 2.16). Team b used the acid-base titration data provided to estimate the total surface site density and Team d did not provide information on how its total site density was obtained (Table 2.17). As in TC 1, when the total site density was determined by fitting surface charge data, its value was lower than the values chosen from the literature (Table 2.16).

In the SC-NEM models, at least two of the four teams modelling teams (Teams c and d) still considered the acid-base titration data and derived acidity constants without EDL correction terms to describe these data. Team e did not use the acid-base titration data for the SC-NEM model development, and this decreased the number of fitting parameters for these two teams (Table 2.17). Team A did not state whether they determined an acidity constant for their SC-NEM model.

Table 2.15: Summary of computer codes and surface site types for Test Case 3

Modelling team	Computer code	Quartz sorption sites
a	FITEQL 3.2 and manual fitting with PHREEQC	$\equiv\text{SiOH}^1$
b	FITEQL 3.2	$\equiv\text{SiOH}$
c	FITEQL 4	$\equiv\text{SiOH}$
d	JCHESS 2.0	$\equiv\text{SiOH}$
e	FITEQL 4	$\equiv\text{SiOH}_w$ and $\equiv\text{SiOH}_s^2$

<sup>1</sup> Denotes a single type of surface hydroxyl group on the quartz surface

<sup>2</sup> Denotes two types of surface hydroxyl groups on the quartz surface, one with stronger U(VI) binding,  $\equiv\text{SiOH}_s$ , than the other,  $\equiv\text{SiOH}_w$ .

Table 2.16: Summary of modelling approaches for SC models with EDL in Test Case 3

Modelling team <sup>a</sup>	EDL model type <sup>b</sup>	Total surface site density ( $\mu\text{moles}/\text{m}^2$ )	Source of total surface site density	Number of U(VI) surface species <sup>c</sup>	Total number of fit parameters
a	DLM	3.84	Literature <sup>d</sup>	2	3
b	DLM	1.35	Titration <sup>e</sup>	2	4
c	DLM	3.84	Literature <sup>d</sup>	2	3
e	TLM	7.66	Literature <sup>d</sup>	5 <sup>f</sup>	10 <sup>g</sup>

<sup>a</sup> Modelling Team d did not complete the SC-EDL model according in a manner consistent with the test case instructions.

<sup>b</sup> DLM = Diffuse layer model; TLM = triple layer model.

<sup>c</sup> The number of surface species is affected by the choice of using a one- or two-site model (Table 2.15); if the same chemical species is proposed to form on both  $\equiv\text{SiOH}_w$  and  $\equiv\text{SiOH}_s$  site types, it was counted as two species.

<sup>d</sup> Total site density value taken from the literature, not counted as a fit parameter.

<sup>e</sup> Fit to acid-base titration data by modelling team; counted as a fit parameter.

<sup>f</sup> Used charge-distribution as part of the modelling approach for surface species.

<sup>g</sup> Two model parameters not considered as fit, one for the total site density and one for an EDL parameter taken from the literature. Charge distribution (CD) values for the U(VI) surface species were fit; same CD values were used for both  $\equiv\text{SiOH}_w$  and  $\equiv\text{SiOH}_s$  type species.

Table 2.17: Summary of modelling approaches for SC models without EDL (SC-NEM) in Test Case 3

Modelling team <sup>a</sup>	Total surface site density ( $\mu\text{moles/m}^2$ )	Source of total surface site density	Number of U(VI) surface species <sup>b</sup>	Total number of fit parameters
a	3.84	Literature <sup>c</sup>	2	2
c	3.84	Literature <sup>c</sup>	2	3
d	1.00	Not given	4	6
e	3.84	Literature <sup>c</sup>	4	5

<sup>a</sup> Modelling Team b did not complete an SC-NEM model.

<sup>b</sup> The number of surface species is affected by the choice of using a one- or two-site model (Table 2.15); if the same chemical species is proposed to form on both  $\equiv\text{SiOH}_w$  and  $\equiv\text{SiOH}_s$  site types, it was counted as two species.

<sup>c</sup> Total site density value taken from the literature, not counted as a fit parameter.

Eight different U(VI) surface reactions were used by the modelling teams to fit the sorption data (Table 2.18). Unlike TC 1, there was not a single reaction that was particularly predominant among the modelling teams, although reactions 3-6 and 3-7 were used by 3 of the 5 modelling teams. However, the only difference between reactions 3-2 and 3-6 was that reaction 3-2 was written as a monodentate U(VI) complex with the quartz surface and 3-6 as a bidentate complex. From a mathematical point of view, there is little difference whether reaction 3-2 or 3-6 is used to describe the data, except at adsorption densities that approach the total site density.

Generally the teams used the same reactions in both SC-EDL and SC-NEM models (with the exception of modelling Team e). Every modelling team found it necessary to use at least two U(VI) surface reactions to describe the sorption data (Tables 3.18). Team d used four surface reactions.

Teams b, c, and e used similar reactions (3-6 and 3-7) for their SC-EDL models, with the only difference being that Team e also included a third reaction (3-5). As in TC 1, it appears that in many cases, the choice of species was based on best fit to the U(VI) data after a number of other modelling decisions had been made (e.g. one-site versus two-site models, type of EDL model, total site density, etc.). Again, as in TC 1, it seems likely that these earlier modelling decisions affected the selection of U(VI) surface species that provided the best fit to the sorption data.

### 2.3.4 Modelling results and discussion

Figure 2.9 compares the average error (absolute values) in calculated and experimental  $\log K_d$  values for all data points for the SC-EDL and SC-NEM models. The average error varied between 0.14 and 0.43 log units. The three modelling teams that completed both SC-EDL and SC-NEM models achieved a better fit to the U(VI) sorption data with the SC-EDL models. However, as in TC 1, the SC-EDL model fits were not dramatically better than SC-NEM model fits (Figure 2.9). Again, as in TC 1, the variation in fits achieved by the different modelling teams was greater than the difference between the SC-EDL and SC-NEM fits of individual modelling teams. Team e had an SC-NEM model with lower average error than the SC-EDL models of all other modelling teams, although the number of fitting parameters for the SC-NEM model by Team e was slightly higher due to its choice of a two-site model. (Tables 2.15, 2.16, and 2.17). The number of fitting parameters in the SC-NEM models was generally not less than for SC-EDL models (Tables 2.16 and 2.17), although the range was greater than in TC 1.

Table 2.18 Summary of U(VI) surface reactions in SC models in Test Case 3<sup>a</sup>

U(VI) surface reaction <sup>b</sup>	Number	Modelling team				
		a	b	c	d	e
$\equiv\text{SiOH} + \text{UO}_2^{2+} \Leftrightarrow \equiv\text{SiOUO}_2^+ + \text{H}^+$	3-1				EDL, NEM	
$\equiv\text{SiOH} + \text{UO}_2^{2+} + \text{H}_2\text{O} \Leftrightarrow \equiv\text{SiOUO}_2\text{OH} + 2\text{H}^+$	3-2	EDL, NEM			EDL, NEM	
$\equiv\text{SiOH} + 3\text{UO}_2^{2+} + 3\text{H}_2\text{O} \Leftrightarrow \equiv\text{SiO}(\text{UO}_2)_3(\text{OH})_5 + 6\text{H}^+$	3-3				EDL, NEM	
$\equiv\text{SiOH} + \text{UO}_2^{2+} + \text{H}_2\text{CO}_3 \Leftrightarrow \equiv\text{SiOUO}_2\text{CO}_3^- + 3\text{H}^+$	3-4	EDL, NEM			EDL, NEM	
$\equiv\text{Si}(\text{OH})_2 + \text{UO}_2^{2+} \Leftrightarrow \equiv\text{SiO}_2\text{HUO}^{2+} + \text{H}^+$	3-5					EDL
$\equiv\text{Si}(\text{OH})_2 + \text{UO}_2^{2+} \Leftrightarrow \equiv\text{SiO}_2\text{UO}_2 + 2\text{H}^+$	3-6		EDL	EDL, NEM		EDL, NEM
$\equiv\text{Si}(\text{OH})_2 + \text{UO}_2^{2+} + \text{H}_2\text{CO}_3 \Leftrightarrow \equiv\text{SiO}_2\text{UO}_2\text{CO}_3^{2-} + 4\text{H}^+$	3-7		EDL	EDL, NEM		EDL
$\equiv\text{Si}(\text{OH})_2 + \text{UO}_2^{2+} + 2\text{H}_2\text{CO}_3 \Leftrightarrow \equiv\text{SiO}_2\text{UO}_2(\text{HCO}_3)_2^{2-} + 4\text{H}^+$	3-8					NEM

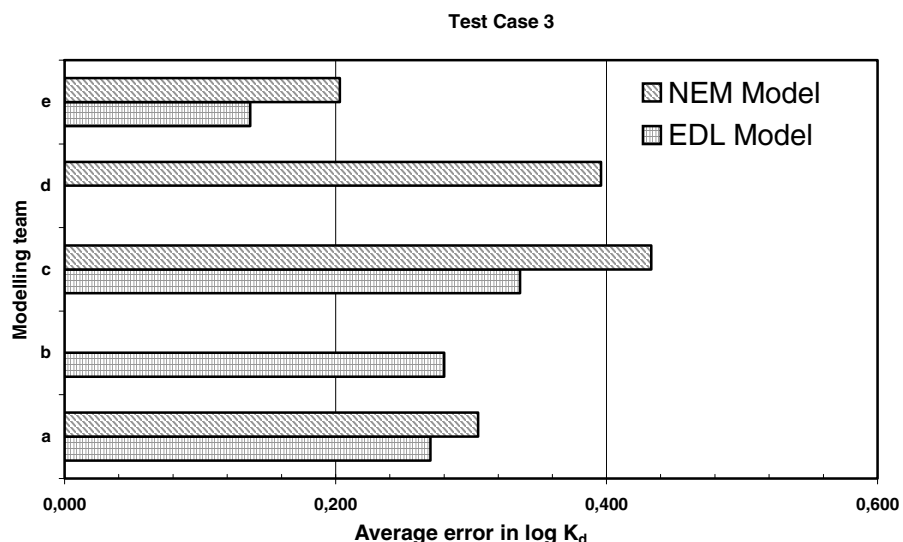
<sup>a</sup> EDL indicates species used in SC-EDL model; NEM indicates species used in SC-NEM model.

<sup>b</sup>  $\equiv\text{SiOH}$  denotes a surface hydroxyl that forms a monodentate uranyl surface complex;  $\equiv\text{Si}(\text{OH})_2$  denotes a surface hydroxyl moiety that forms a bidentate uranyl surface complex.

As mentioned above, Figure 2.9 shows the average error between the calculated and experimental log  $K_d$  values for all datasets. Figures 2.10 and 2.11 shows the average error for each modelling team for each individual dataset (or set of chemical conditions) for the SC-EDL and SC-NEM models, respectively.

Team e was the only team that used two-site models (Tables 2.16 and 2.17), and it can be seen in Figure 2.9 that this team achieved a better overall fit to the data with their models than the other teams. The two-site modelling approach was important in fitting the sorption data as a function of U(VI) concentration. The U(VI) adsorption density varied significantly in datasets 1 through 4 (Table 2.14). Figure 2.10 shows that Team e achieved a better fit than most other modelling teams at low U(VI) adsorption density (dataset 1), which can be attributed to their choice of a two-site modelling approach. However, Team e used the strong binding site density as an additional fitting parameter, and this adds to the model complexity.

Figure 2.9: **Model performance for Test Case 3 showing the sum of the errors (absolute value of difference between calculated and experimental  $\log K_d$  values) divided by the number of data points. Team d did not complete the SC-EDL model in a manner consistent with the test case instructions**



As was discussed above for TC 1, the parameter value chosen for strong binding site density is an open question for research. The U(VI) adsorption data on quartz exhibit non-linear adsorption isotherms, suggesting that stronger binding sites exist. The two-site modelling approach adopted by Team e for quartz is similar in some ways to the top-down modelling approach that is applied to heterogeneous soils and sediments.

Figure 2.10: **Model performance for Test Case 3 showing the errors (absolute value of difference between calculated and experimental  $\log K_d$  values) for individual datasets with SC-EDL models (conditions given in Table 2.14). Team d did not complete the EDL model in a manner consistent with the test case instructions**

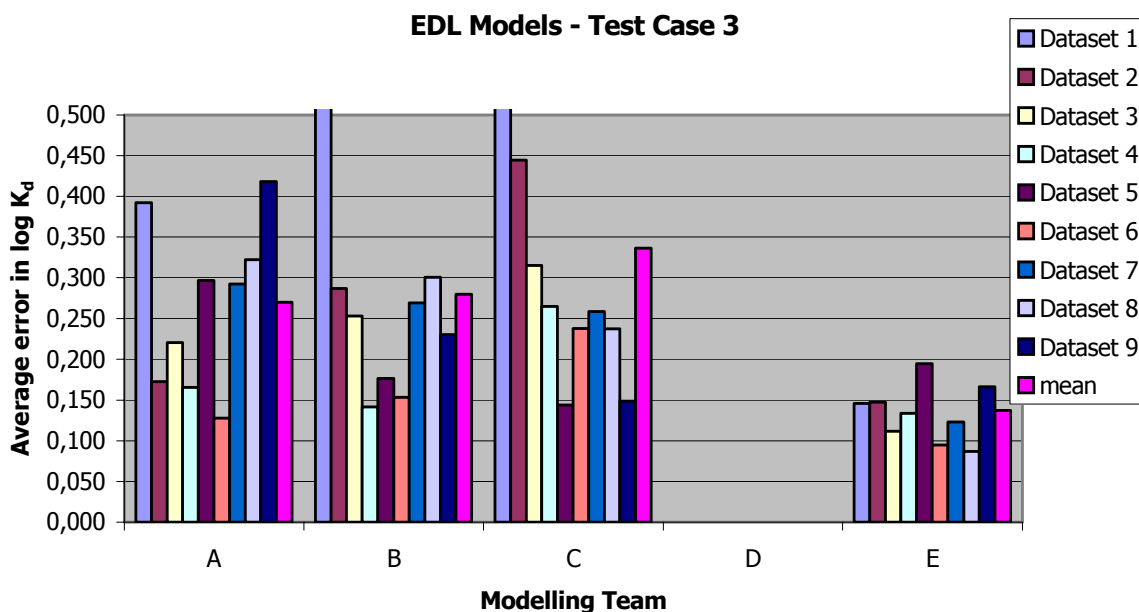
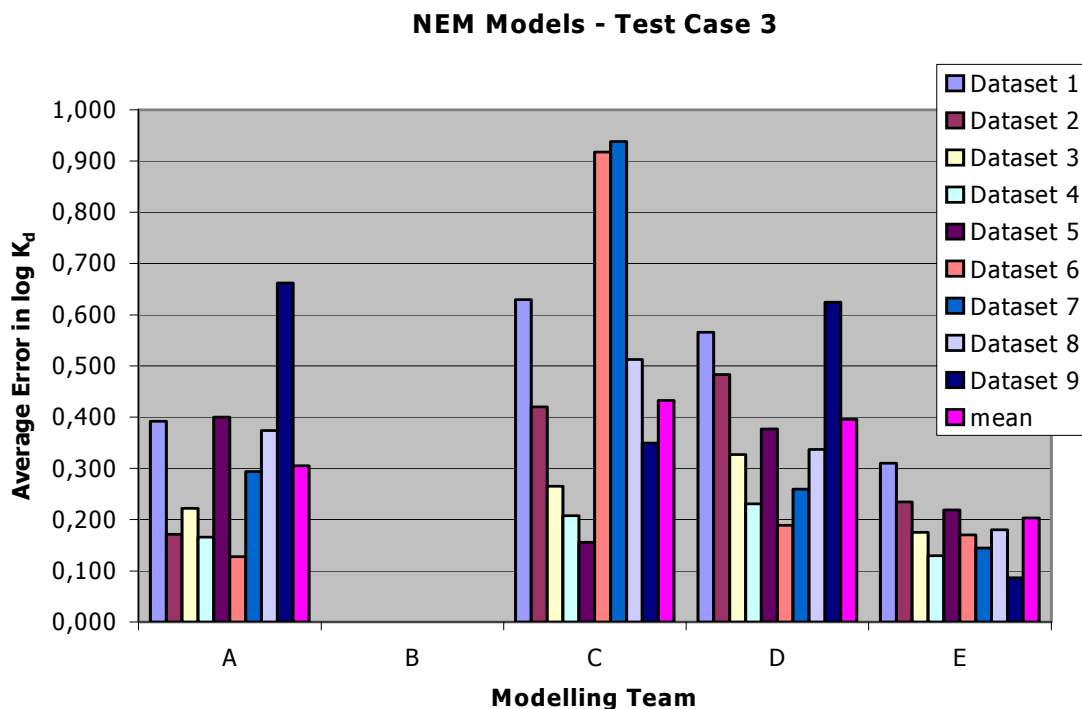




Figure 2.11 Model performance for Test Case 3 showing the errors (absolute value of difference between calculated and experimental  $\log K_d$  values) for individual datasets with SC-NEM models (chemical conditions given in Table 2.14). Team b did not complete an SC-NEM model



All of the modelling teams included a ternary surface-U-carbonato complex of some form in their SC-EDL and SC-NEM models (Table 2.18). Datasets 1 through 5 were for experiments equilibrated with air, and datasets 6 through 9 were for systems equilibrated with 7.5%  $\text{CO}_2(\text{g})$ . Team a had greater average error for the systems equilibrated at 7.5%  $\text{CO}_2(\text{g})$  than those equilibrated with air (Figures 2.10 and 2.11), and perhaps this was due to their choice of reaction 3-4 (Table 2.18). Note that the ternary surface reactions chosen by Teams b, c, and e (reaction 3-7) had four protons on the right side of the mass law whereas reaction 3-4 only had three protons on the right side. Teams b, c, and e generally chose the same reactions, except Team e included reaction 3-5 for the SC-EDL model and reaction 3-8 for the SC-NEM model. The choice of reaction 3-5 added an additional fitting parameter but apparently improved the fit to the experimental data in comparison to Teams b and c.

Among the EDL models chosen, the triple layer model chosen by Team e gave better results than the diffuse layer model (Figures 2.9 and Table 2.16). However, since the ionic strength was not varied in this test case, it is not believed that the choice of EDL model had a very significant influence in this particular case. Instead, it is believed that the other modelling decisions made by Team e [two-site model, choice of U(VI) surface reactions] caused the superior model performance, although at the expense of additional fitting parameters.

A second part of TC 3 was the extrapolation of the models calibrated above to predict U(VI) sorption data on another sample of quartz with much lower surface area. The data to be predicted consisted of 69 individual  $K_d$  values where the main variables were pH, total U(VI) concentration, and the quartz/liquid ratio (Table 2.19). All experiments were equilibrated with air and had an ionic strength of 0.1.

Errors were greater for the predicted U(VI)  $K_d$  values in the extrapolation (Figures. 2.12 and 2.13) than was observed during the calibration with the other quartz sample, as might be expected. Whereas mean errors ranged from 0.14 to 0.43 log units in the calibration models, mean errors ranged from 0.35 to 0.73 log units in the model predictions for the second quartz sample. The predictions made by the Team e models were better than those made by the other modelling teams, again suggesting that the two-site modelling approach might be important.

Interestingly, the mean errors in the predictions were slightly lower for the SC-NEM models than SC-EDL models (Figures. 2.12 and 2.13). The greatest errors were generally for datasets 1 and 2 (Table 2.19), which had the more extreme U(VI) adsorption densities, high in dataset 1 and low in dataset 2.

Table 2.19 Summary of experimental data for U(VI) sorption data provided to the modelling teams in Test Case 3 for the model extrapolation step<sup>a</sup>

Dataset number	Quartz/liquid ratio (grams/L)	Total U(VI) concentration	Number of data points
1	2.1	$2.1 \cdot 10^{-7}$ M	16
2	21	$1.9 \cdot 10^{-8}$ M	17
3	21	$2.1 \cdot 10^{-7}$ M	17
4	51	$2 \cdot 10^{-6}$ M	13
5	54	$2 \cdot 10^{-7}$ M	16

<sup>a</sup> pH was an additional variable for each set of chemical conditions. All experiments equilibrated with air and in 0.1M NaNO<sub>3</sub> solution.

Figure 2.12 Model performance for the Test Case 3 extrapolation to a different quartz sample, showing the errors (absolute value of difference between calculated and experimental log  $K_d$  values) for individual datasets with SC-EDL models (chemical conditions given in Table 2.19)

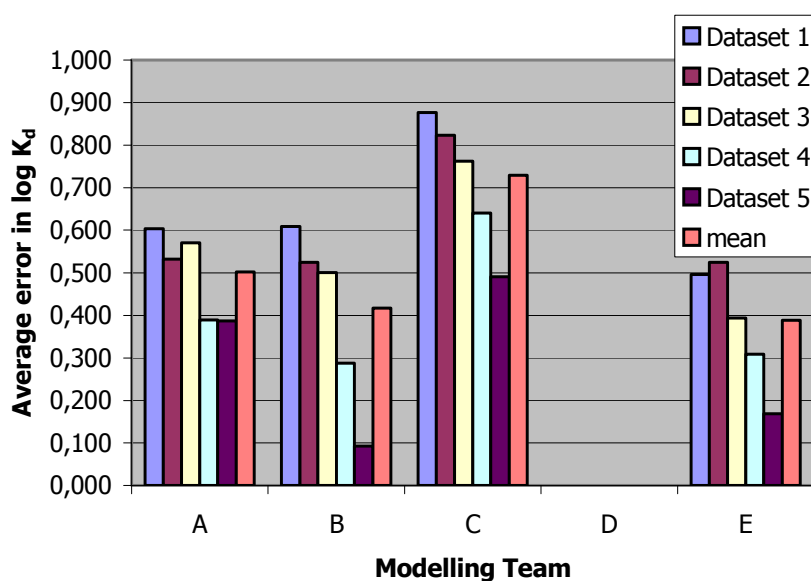
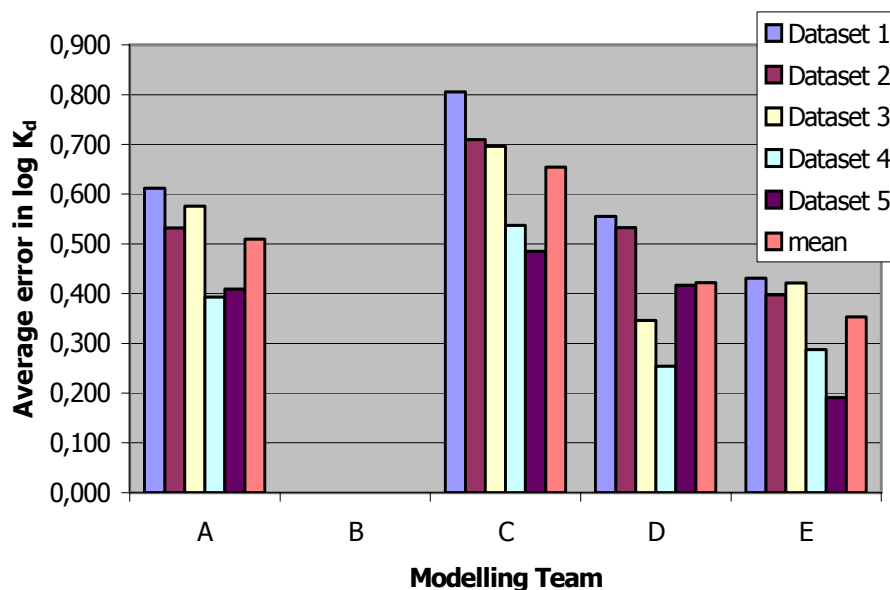


Figure 2.13: **Model performance for Test Case 3 extrapolation to a different quartz sample, showing the errors (absolute value of difference between calculated and experimental log  $K_d$  values) for individual datasets with SC-NEM models (chemical conditions given in Table 2.19)**



### 2.3.5 Conclusions for Test Case 3

Test Case 3 demonstrated that SC modelling could describe the variation in U(VI)  $K_d$  values that were observed as a function of pH, U(VI) concentration, and the concentrations of the complexing ligands, fluoride and carbonate.

As in TC1, SC-EDL models achieved better fits to the experimental data than SC-NEM models, and again the fits were not dramatically better. Also, as in TC 1, the variation in modelling approaches taken by the modelling teams was a far more important aspect in fitting data than was the choice of an EDL or NEM approach (see Figure 2.9). The number of fitting parameters in the SC-NEM models was generally not less than for SC-EDL models, although the range was greater than in observed in TC 1.

Only one team used a two-site model to fit the experimental data as a function of U(VI) concentration, and this team achieved a better fit than those using any of the one-site models. As in TC1, the strong site density was used as a fitting parameter, and thus, the strong site density was not determined via an experimental characterisation technique or based on an estimate with chemical significance.

All models in this test case (both SC-EDL and SC-NEM) included at least one uranyl-carbonate ternary surface complex in order to fit the experimental data.

Errors were greater for the predicted U(VI)  $K_d$  values in the extrapolation to a second quartz sample than was observed in model calibration with the first quartz sample, as might be expected. The extrapolations (predicted  $K_d$  values) made by the team using a two-site model were better than the one-site models. Interestingly, the mean errors in the extrapolated  $K_d$  values were slightly lower for the SC-NEM models than SC-EDL models.

## 2.4 Discussion of modelling results for single mineral phase systems

The results of TC1-3 show that the EDL improved the fit to experimental data in each test case. The performance of the SC-NEM was also good, perhaps surprisingly so, but the overall result is that the SC-EDL both provide a better fit to sorption data for single minerals in simple electrolyte solutions and provide models that are viewed as chemically superior to SC-NEM. The results also showed that SC-NEM typically have the same number of fitting parameters as SC-EDL, and thus, elimination of the EDL did not actually decrease the number of fitting parameters. SC-EDL models, however, do require additional data collection, i.e. the determination of surface charge as a function of chemical conditions.

The results showed that the triple layer model (TLM) was more versatile than the diffuse layer model (DLM) as a choice of EDL model. The versatility of the TLM was key to the improvement in fits obtained by certain modelling teams, as surface species with electrical charge distributed between surface planes could be used as a modelling approach (TC1 and 3), and the effects of ionic strength were better simulated (TC1). The TLM has a few additional fitting parameters (these are related to fitting surface charge, not RN sorption), but actually does not require more data collection than does the development of a DLM.

It was clear from the modelling submissions that there is not a consensus in the modelling community on the selection of site densities, and the project results highlight this as a topic needing further focus if a future NEA sorption project is developed. Methods for selecting total site density varied and included: a) based on crystallographic considerations, b) taken from the literature, including the somewhat arbitrary value of  $3.84 \mu\text{moles/m}^2$  of Dzombak and Morel (1990) and Davis and Kent (1990), c) based on tritium exchange data between surface hydroxyls and water, d) based on fitting RN sorption data, and e) based on fitting acid-base titration data in simple electrolyte solutions (it has been argued in the recent literature that this is not an appropriate method, see Lützenkirchen *et al.*, 2002).

In addition to the lack of consensus on the total site density, there is another problem relating to the performance of models as a function of RN concentration. It is widely realised that RN and metal ion sorption are non-linear with respect to RN aqueous concentration, viz. plots of the log of RN sorption versus the log of RN aqueous concentration generally have a slope less than one. The typical approach in SC modelling to this problem is to develop a two-site model (as was done by Dzombak and Morel, 1990), where the site density of the stronger sites (which are less numerous) is determined by fitting RN sorption data. However, during the Project workshop in Spain in October 2002, it was clear that some modelling teams believed that the existence of such a second site should be based on experimental evidence or crystallographic considerations and that it was “inappropriate” to use such a parameter to fit experimental data. Other teams viewed this question more pragmatically, acknowledging that it is experimentally difficult to know the non-idealities of the surface structure caused by steps, kinks, etc. These teams implicitly adopt a GC-type modelling philosophy for single mineral phases by accepting that the experimental data as a function of RN concentration will be “fit” using a variable that is not experimentally accessible, i.e. the strong site density.

Surface species for the models in TC1-3 were generally chosen based on chemical simplicity and plausibility. Most modelling groups tended to start with the simplest species and then add more species as needed to fit the sorption data; however, the additional species that are added are also chemically plausible. Spectroscopic data for species is consulted and used when it is available, but for many systems such data are not available to constrain the species selection. When it is available, it is clear that more flexible EDL models (e.g. the TLM) are needed in order to achieve good fits to

experimental data along with consistency with the spectroscopy. This is achieved via the charge distribution concept, in which the net charge on the surface species is fractionally distributed to the planes of the TLM.

In general, it can be stated that models with more fitting parameters did not necessarily achieve better fits to experimental data. Instead, it appeared that model performance was based more on the initial assumptions of the modelling teams (e.g. one-site versus two-site, TLM versus DLM) rather than the number of fitting parameters. It is also clear that the models are more robust if the experimental data are collected for a wide range of chemical conditions rather than a small range of conditions. SC models for RN anions appear to be just as successful as those for RN cations.

One of the most encouraging aspects of the results for Test Cases 1 and 3 was the ability of the SCM to simulate the important effect of carbonate ligand concentration on RN sorption. The effect of carbonate concentration on  $K_d$  values for Np(V) and U(VI) sorption in experiments is quite large, and in general, the SC models were quite successful in simulating the magnitude of this effect. This result is extremely important and demonstrates clearly the advantage that SCM can provide to reduce the uncertainty in  $K_d$  values for PA.

The extension of the U(VI)-quartz models to a second sample of quartz (without changing the values of model parameters) was a success, but the errors in model simulations of  $K_d$  values increased by about a factor of two on average. The extension of the models was done by most modelling teams by scaling to the different surface area of the second quartz sample, which differed by about an order of magnitude. The results suggest that this method of extension was valid, but there was likely another factor besides the surface area that differed between the two samples. To improve on the extension methodology would likely require additional surface characterisation of the two samples. Thus, scaling by surface area is supported by the results as the factor of greatest importance in substrate extension to similar solid phase samples, but other more subtle features may increase the error in predicted  $K_d$  values.

### **3. MODELLING RADIONUCLIDE SORPTION ON CLAYS BY COMBINED SURFACE COMPLEXATION – ION EXCHANGE MODELS**

#### **3.1 Introduction**

Two Test Cases (TC4, TC5) were concerned with the application of thermodynamic sorption models to clay-dominated mineral substrates ranging from purified montmorillonite to crude natural bentonite with a clay mineral content < 50%. Several reasons for including these materials and test cases were identified:

- In many radioactive waste management programs, clays play a very important role as buffer materials (bentonite) or as potential host rocks (e.g. Boom Clay, Opalinus Clay).
- These two test cases provide the needed transition from “simple” sorbents (Test Cases 1-3) to multi-sorbent, complex mineral assemblages (Test Cases 6-7): While some of the clays considered are complex in the sense that they contain a number of accessory minerals that may lead to a complex water chemistry, the actual sorption processes were expected to be dominated by the clay minerals.
- It was expected that these test cases would require the combination of surface complexation and ion exchange models.
- These test cases allowed participants to calibrate models and to subsequently test them in a predictive mode for different or more complex conditions.
- Several of the data subsets to be modelled require taking into account the interaction of carbonate with radionuclides, and its influence on pH and the concentration of competing major cations.

A total of 10 modelling teams undertook the modelling tasks of Test Cases 4 and 5. Two teams undertook both test cases, six teams undertook only TC4, and two teams only TC5. The teams will be referred to as follows:

- Teams a and b: both Test Cases (a1, b1 – TC4; a2, b2 – TC5).
- Teams c - h: TC4 only.
- Teams i and j: TC5 only.

#### **3.2 Overview of modelling approaches employed**

The ten modelling teams participating in Test Cases 4 and 5 employed a variety of modelling approaches, fitting procedures, and computer codes. An overview is provided below in Table 3.1.

Table 3.1: Overview of modelling approaches used for Test Cases 4 and 5

Team test case	surface sites <sup>1</sup> (# / type)	surface species <sup>2</sup> (# / species)	Model <sup>4</sup>	SOH density ( $\mu\text{moles/m}^2$ ) <sup>10</sup> CEC (meq/100g)	surface area edge ( $\text{m}^2$ )
a1 4	1 / SC 1 / IE	1 / SONi+ 1 / X2Ni	SC-DLM IE-GT	1.45 87 <sup>11</sup>	35 <sup>14</sup>
b1 4	1 / SC 1 / IE	1 / SOHNi+2 1 / X2Ni	SC-DLM <sup>5</sup> IE-GT	2.34 <sup>11</sup> 87 <sup>11</sup>	35 <sup>14</sup>
c 4	1 / SC 1 / IE	1 / SONi+ 1 / X2Ni	SC-NEM IE-GT	2.34 <sup>11</sup> 87 <sup>11</sup>	35 <sup>14</sup>
d 4	2 / SC (w/s) 1 / IE	1 / SONi+ 1 / X2Ni	SC-NEM IE-GT	SwOH: 2.06; SsOH: 0.004 87 <sup>11</sup>	35 <sup>14</sup>
e 4	2 / SC (w/s) 1 / IE	3 / SsONi+, SwONi+, SsONiOH 1 / X2Ni	SC-NEM <sup>6</sup> IE-GT	SwOH: 1.9, SsOH: 0.02/0.06 <sup>12</sup> 87 <sup>11</sup>	35 <sup>14</sup>
f 4	2 / SC (w/s) 1 / IE	3 / SsONi+, SwONi+, SsONi(OH)2- 1 / X2Ni	SC-NEM <sup>7</sup> IE-GT	SwOH: 0.16, SsOH: 0.004 87 <sup>11</sup>	500 <sup>15</sup>
g 4	2 / SC (Al/Si) 1 / IE	2 / SAIONi+, SSiONi(OH)3-2 2 / X2Ni, XNiOH	SC-DLM IE-GT	SSiOH: 0.9, SAiOH: 126 87 <sup>11</sup>	35 <sup>14</sup>
h 4	2 / SC (Al/Si) 1 / SC	2 / SAIONiOH, SAIO-Ni+2 <sup>3</sup> 2 / X2Ni, XNiOH	SC-BSM <sup>8</sup> SC-TLM <sup>9</sup>	SAiOH: 1.83, SSiOH: 8.1 <sup>3</sup> IE: 1.66 $\mu\text{mol/m}^2$ <sup>13</sup>	31.5 <sup>16</sup>
a2 5	1 / SC 1 / IE	1 / SONpO2 1 / XNpO2	SC-DLM IE-GT	0.52 87	97 <sup>14</sup>
b2 5	2 / SC (Al/Si) no IE	2 / AlONpO2(OH)-, SiOHNpO2+	SC-DLM	3.8 <sup>11</sup>	97 <sup>14</sup>
i 5	2 / SC (w/s) 1 / IE	6 / SsONpO2, SwONpO2, SsONpO2(OH)-, SwONpO2(OH)- SsONpO2CO3-2, SsONpO2CO3-2 1 / XNpO2	SC-NEM IE-GT	SwOH: 2.3; SsOH: 0.057 87 <sup>11</sup>	35 <sup>14</sup>
j 5	1 / SC 1 / IE	2 / SOHNpO2+, SONpO2(OH)- 1 / XNpO2	SC-DLM IE-GT	3.3 120	97 <sup>14</sup>

- <sup>1</sup> SC = surface complexation, IE = ion exchange, w/s = weak and strong sites, Al/Si = aluminol and silanol sites.
- <sup>2</sup> surface functional groups: surface complexation - SOH (weak: SwOH, strong: SsOH, aluminol: SAiOH, silanol: SSiOH) ion exchange - Xna.
- <sup>3</sup> SAIO-Ni+2 is an outer-sphere complex (an approach with two inner-sphere complexes was abandoned as unsuccessful) The silanol site SSiOH was only used for adsorption of H+.
- <sup>4</sup> see glossary for model abbreviations.
- <sup>5</sup> an approach with a SC-BSM had been abandoned.
- <sup>6</sup> an approach with a SC-DLM had been abandoned.
- <sup>7</sup> SC-DLM using a very high specific surface area.
- <sup>8</sup> a SC-TLM was also investigated, but gave no improvement in fitting the data.
- <sup>9</sup> ion exchange was modeled using outer-sphere SC in an extended SC-TLM, rather than exchange reactions (see Part 2); a corresponding SC-BSM had been abandoned.
- <sup>10</sup> SOH density = site density SC sites on clay edge surface, CEC = site density IE sites on clay layer (siloxane) surface.
- <sup>11</sup> taken directly from the study of Bradbury and Baeyens (1997), only CEC had been supplied with the test case.
- <sup>12</sup> 0.02 and 0.06  $\mu\text{mol/m}^2$  were obtained by neglecting or taking into account the clay's Zn- and Mn-inventory, respectively (models 1A and 2A, see Appendix on TC4).
- <sup>13</sup> This value is based on crystallographic and EXAFS data; it corresponds to the CEC if a surface area of 525  $\text{m}^2/\text{g}$  (i.e., BET<sup>15</sup>) is used for the siloxane surface).
- <sup>14</sup> BET surface area determined by Bradbury and Baeyens (1997) and Turner et al. (1998), had been supplied.
- <sup>15</sup> taken from Morel and Kraepiel (1997).
- <sup>16</sup> from the BET value, geometric considerations, and consistency with a expected edge site density of 6 sites per  $\text{nm}^2$  (based on White and Zellazny, 1988).

With regard to the approaches taken to model radionuclide sorption on clay minerals and clay-rich substrates, several general issues can be identified:

- In terms of treating permanent and variable charge surfaces, most approaches (10 out of 12) used a combination of ion exchange and surface complexation formulations.
- All teams used SCMs; there was no attempt to represent RN sorption on clays by ion exchange only.
- All ion exchange models were based on the equivalent fraction (GT) convention.
- One team (Team h, TC4) used a SCM on both types of surfaces: They used a BSM for the clay edge and a TLM for the siloxane surface.
- One team (b2) used only a SCM applied to the edge surface (i.e. used no ion exchange at all).
- Most (nine out of twelve) SCM had (implicitly) a top-down view of clay edge (generic sites, two-site models distinguish between weak/strong). Three approaches distinguished explicitly between Si- and Al-sites on the clay edge.

Further, it clearly has to be stated that in many cases, a pre-conceived approach was followed (for a variety of reasons, see below), rather than choosing a modelling approach that would achieve the best mathematical fit to the data. In the end, initial decisions by modelling teams on (i) how to approach the modelling task at hand or (ii) on the type of model to aim for appear to be the most important factor for determining the final model setup and the outcome of the model calibration, as well as of the model application (prediction). Initial decisions largely determined the framework for choices on:

- type of EDL/NEM model;
- site densities and type;
- type of RN surface species.

Modelling teams made choices on these three points not separately, but in a strongly interconnected fashion. Accordingly, contributions by the various modelling teams can be organised into groups of similar modelling strategies for further analysis (Table 3.2). It is interesting to note that the approach of group C differs significantly from approaches by other groups not only with regard to surface complexation modelling, but also with regard to ion exchange modelling.

Table 3.2: **Overview of groups of modelling approaches**

Groups	Surface complexation		Ion exchange	
	#/type of sites	EDL model	model	# of RN exchange species
A: (Teams: a1, a2, b1, c, j)	1/generic SOH	mostly DLM	GT	1
B: (Teams: d, e, f, i)	2/generic SOH	mostly NEM	GT	1
C: (Teams: b2, g, h)	2/SiOH, AlOH	DLM/BSM	TLM, GT, none	2, 2, 0



### 3.3 Characterisation and analysis of main modelling approaches

The following sections focus on the models developed for Ni(II) in TC4, Np(V) in TC5. In TC4, modellers had been asked to develop models with and without considering the inventory of Zn and Mn in the clay. However, the influence of Zn and Mn inventories on the development and characteristics of models was very small. Moreover, the models set up for Zn and Mn differed only in one case from that for Ni. Therefore, the Zn and Mn models are not addressed in detail in the present report.

#### 3.3.1 Group A: one-site SCMs

##### 3.3.1.1 Overview

Group A comprises five models that all used only one edge surface complexation site, mostly in combination with a DLM. All teams used the GT formalism and one RN exchange species to model RN sorption on the layer surface. All of these one-site SCMs do not allow a very good fit to the experimental data (see below). Thus, it appears that once a one-site SCM is chosen, the choice of EDL/NEM is not very relevant.

##### 3.3.1.2 Motivation behind choice of approach

The motivation in all cases was to obtain simple (or simplified) models:

- Team a (1, 2): Approach: use the simple setup that is typically being used by Team a for porewater modelling in clays: one-site DLM for TC4 and TC5.
- Team b1: Approach: start from Bradbury and Baeyens (1997) model, which could not be reproduced using FITEQL; therefore, the simplest approach (one-site DLM) was pursued.
- Team c: Goal: simplify Bradbury and Baeyens (1997) model as much as possible: Restricted to NEM (TC4).
- Team j: based on the simple one-site/diffuse layer model for montmorillonite developed by Wanner *et al.*, (1994) (TC 5).

##### 3.3.1.3 EDL/NEM, site density and types, surface species

Edge surface:

- One-site SCM (one generic SOH site). This choice appears to have been made largely for reasons of simplicity. It proved to be not very successful when being applied to the large dataset given in TC4, Ref. 1: In particular, it appears that a one-site SCM does not allow both the slope and peak of Ni sorption edges or more than one of the isotherms in TC4 to be matched. It is noteworthy that the more limited dataset given in TC5 proved to be more forgiving in this respect; i.e. would make it less likely to detect model shortcomings during calibration.
- Four out of these five models used a DLM; only one model used a NEM.
- Site densities for both TC4 and TC5 (in micromoles/m<sup>2</sup>) cover a narrow range. For TC4, values range from 1.45 (one team, fitted from titration) to 2.34 [two teams, taken from Bradbury and Baeyens (1997)]. The two values for TC5 are 0.52 (taken from TC4 and applied to the BET surface area of 97 m<sup>2</sup>/g given for Turner *et al.*, (1998) and 3.3 (taken

from Wanner *et al.*, 1984, scaled to the CEC and 1/10 of the BET area given for Turner *et al.*, 1998).

- Surface species:
  - a) Ni (TC4) Two teams chose (a priori)  $\text{SONi}^+$  as the simplest species, one team selected  $\text{SOHNi}^{+2}$  as giving the best fit. No attempts of adding a second surface species are reported for TC4.
  - b) Np (TC5) Team a chose  $\text{SONpO}_2$ , Team j chose two surface species  $\text{SOHNpO}_2^+$  and  $\text{SONpO}_2\text{OH}^-$ ; providing one of the few examples of a one-site model with two RN surface species.

Layer surface:

All teams used the CEC reported by Bradbury and Baeyens (1997) in case of TC4 and by independent literature sources in case of TC5. Ion exchange constants for Ni were fitted, with  $\text{X}_2\text{Ni}$  and  $\text{XNpO}_2$  as the sole RN surface species.

### 3.3.2 **Group B: two-site SCMs**

#### 3.3.2.1 *Overview*

Group 2 comprises four models that all use two edge surface complexation sites, mostly in combination with a NEM. All teams used the GT formalism and one RN exchange species to model RN sorption on the layer surface.

All SCM in group B distinguish between generic weak/strong SOH sites. In comparison to group A, these models gave a better fit to the experimental data (this potential is not realised by some teams because of restrictive fitting procedures). All of these two-site models are NEM or, in one case a “pseudo” NEM (a DLM with a very high edge surface area to minimise the effect of the EDL correction term, following the approach of Morel and Kraepiel, 1997).

#### 3.3.2.2 *Motivation behind choice of approach*

Three out of four teams used pre-conceived approaches in terms of model setup. Only one team was flexible in this respect.

- Team d stated as goal to simplify the model of Bradbury and Baeyens (1997): two-site NEM with less reactions (no acid/base).
- The approach of Team f was to start from the model developed by Morel and Kraepiel (1990) and to investigate possible improvements or simplifications.
- Team i used the model setup that they had developed (for Ni) in earlier work.
- Team e had no pre-conceived model set-up. A one-site DLM was abandoned due to fitting problems, the EDL term dropped, and a second site was introduced to fit Ni edges

#### 3.3.2.3 *EDL/NEM, site density and types, surface species*

Edge surface:

- All of the two-site SCMs in group B use one weak plus one strong generic SOH site. The introduction of the second site appears to be necessary in these models in order to fit the gradual slope of the Ni sorption edge (or both edge and isotherms in case where both types of data were used for calibration). Team i was the only team that used a two-

site NEM in TC5, and their approach was based on the model of Bradbury and Baeyens (1997) for Ni sorption.

- Weak site densities for the three NEMs were in the narrow range of 1.9-2.06 micromoles/m<sup>2</sup> (all fitted from titration data by the modelling teams or taken from Bradbury and Baeyens (1997), irrespective of the source of the clay. Strong site densities were 0.004 and 0.06 micromoles/m<sup>2</sup> (all fitted from Ni sorption data). In case of the DLM with a surface area of 500 m<sup>2</sup>, a weak site density of 0.16 micromoles/m<sup>2</sup> (fitted from titration data) and a strong site density of 0.004 micromoles/m<sup>2</sup> (taken from Morel and Kraepiel, 1990) were used.
- Surface species:
  - Team d SwONi<sup>+</sup>, SsONi<sup>+</sup>.
  - Team e SwONi<sup>+</sup>, SsONi<sup>+</sup>, SsONiOH (initially assumed).
  - Team f SwONi<sup>+</sup>, SsONi<sup>+</sup> (assuming complexation of the simple Ni<sup>2+</sup> ion), SsONi(OH)<sup>2-</sup> [“sorption of hydrolysis product” was needed to fit Ni data at high pH, the species NiOH<sup>+</sup> was not expected to be important enough in comparison with Ni(OH)<sub>2</sub>(aq)].
  - Team i SONpO<sub>2</sub>, SONpO<sub>2</sub>OH<sup>-</sup>, as well as a ternary surface complex (SONpO<sub>2</sub>CO<sub>3</sub><sup>2-</sup>) to explain Np sorption in the presence of carbonate.

Layer surface:

- All teams in TC4 used the CEC reported by Bradbury and Baeyens (1997). In TC5, Team i used an independent value (120 meq/kg) by Van Olphen and Fripiat (1979) for calibration; and the value of 79.2 meq/kg reported by Gorgeon (1994).
- Ion exchange constants were fitted, with X<sub>2</sub>Ni and XNpO<sub>2</sub> as the sole RN surface species.

### 3.3.3 *Group C: two-site SCMs distinguishing between silanol and aluminol sites*

#### 3.3.3.1 *Overview*

Group C comprises three models that all used two edge surface complexation sites, distinguishing between silanol and aluminol sites, rather than using generic SOH sites. In one case (Team h) this was done based on crystallographic and EXAFS data for montmorillonite, whereas the other two teams invoked analogy with Si- and Al-oxide surfaces. Two teams used a DLM, one team used a BSM. It is interesting to note that these were also the only models that used an approach to ion exchange different than the GT-one RN species setup (see below).

#### 3.3.3.2 *Motivation behind choice of approach*

In all three models, an explicit distinction of silanol vs. aluminol sites was made based on the tetrahedral-octahedral-tetrahedral layer structure of smectite minerals.

- Team h: started from crystallographic and EXAFS constraints in trying to build a chemically accurate model.
- Team g: used analogy with single oxides, as had been done before for kaolinite by the same group.

- Team b2: accepted the model given in Turner *et al.* (1998), which is based on analogy with Si- and Al-oxide surfaces, as starting point and attempted to achieve a better fit by adding or removing reactions.

### 3.3.3.3 EDL/NEM, site density and types, surface species

Edge surface:

- All three models are two-site SCMs using silanol and aluminol sites, based on the structure of smectite. In one case (Team h), one site was used for acid-base reactions only (i.e. a one-site model with regard to Ni sorption was used). Team g and Team b used a DLM (Team g because it is already implemented in the speciation code used – PHREEQC, Team b2 presumably because Turner *et al.*, 1998, had already used a DLM). Team h used a BSM (tested as an alternative to TLM, and in the end selected as simpler and equally good for describing both H<sup>+</sup> and metal sorption)

- Site density (in units of micromoles/m<sup>2</sup>):

Team g fitted site density based on acid-base reactions taken from single oxides, >SiOH = 2.6E-5, >AlOH = 0.0036; which ultimately renders only ion exchange important (standard approach of this team, decided a priori). Team h based site density on independent data for clay: total site density was derived from crystallographic and EXAFS data. The respective fraction of >AlOH sites was fitted from titration data, the density of >SiOH was taken as the difference between >AlOH and total sites. Team b2 used the total site density (3.8 micromoles/m<sup>2</sup>) reported by Turner *et al.*, 1998.

- Surface species:

Team g used >AlONi<sup>+</sup>, >SiONi(OH)<sub>3</sub><sup>-2</sup> surface species (from single oxide data, Marmier, 1998). Team b2 assumed >AlONpO<sub>2</sub>(OH)<sup>-</sup>, >SiOHNpO<sub>2</sub><sup>+</sup> as Np-species bound to aluminol- and silanol groups. Team h considered inner- and outer-sphere binding of Ni to aluminol groups, based on EXAFS interpretations by Dähn (2001): >AlONiOH was assumed as inner-sphere surface complex on octahedral sites, >AlO-Ni<sup>+2</sup> was assumed as outer-sphere complex on vacancy-sites. Team h notes that fitting Ni sorption data was not possible with two inner-sphere species on aluminol sites.

Layer surface:

All teams use a setup that contrasts with other approaches. Team b completely neglected ion exchange. Two Teams (g, h) used two ion exchange species of Ni for TC4: X<sub>2</sub>Ni, XNiOH. Team g used the reported CEC and a conventional ion exchange formalism (GT). On the other hand, Team h used an extended TLM to describe Ni sorption via outer-sphere complexes instead of ion exchange. A surface site density of 1.66 μmoles/m<sup>2</sup> was used for this model (this value corresponds to the measured CEC if a surface area of 525 m<sup>2</sup>/g; i.e. BET × 15, is assumed).

## 3.4 Model intercomparison and lessons learned

It is in many cases not possible to make direct comparisons of quantitative model performance (errors) between different approaches (modelling teams), because not all teams chose to utilise the entire dataset provided for model calibration, but used only parts of this dataset (e.g. some teams restricted calibration to one ionic strength). In case of datasets that cover a range of conditions, such as the data by Bradbury and Baeyens (1997) in TC4, use of the full vs. limited datasets for calibration can make a significant difference for model performance (see also section on calibration and extrapolation).

### 3.4.1 Simple vs. more complex models

A comparison of the different simple models of group A with the more complex models of groups B and C can be used to illustrate several issues that are critical for test case group B, and also of more general relevance:

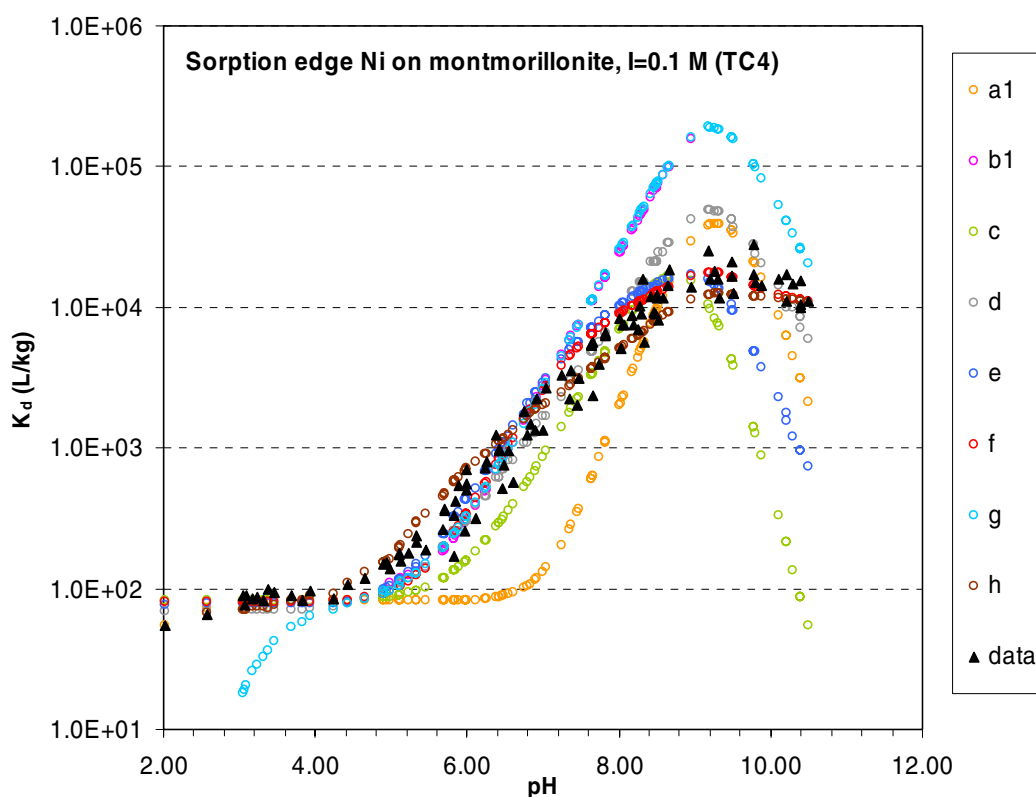
- the appropriateness of modelling approaches to describe RN sorption data;
- model calibration and extrapolation; and
- data requirements.

“Simple” here means a one-site SCM in combination with a NEM or simple EDL model (e.g. DLM).

#### 3.4.1.1 Ability to fit provided data and model robustness

The results from group A above show that very simple models may be sufficient for limited datasets but do not permit to fit or explain experimental data for RN sorption to clays over a wide range of conditions. While good fits to part of the experimental data can be achieved, such a model setup does not allow the entire dataset to be described satisfactorily. In particular, these models allow fitting either the slope or the peak of pH-edges for Ni, but do not allow achieving good fits to both portions of these datasets. This is illustrated in Figure 3.1 using an example from TC4 for a Ni sorption edge on SWy-1 montmorillonite (model calibration, data from Bradbury and Baeyens, 1997).

Figure 3.1 Experimental data (Bradbury and Baeyens, 1997) and model results from TC4 for the sorption of Ni on SWy-1 montmorillonite (selected dataset: sorption edge,  $I = 0.1 \text{ M NaClO}_4$ ). The different teams are indicated



### 3.4.1.2 Chemical plausibility and model complexity

Among the models that cover all relevant conditions and that may be regarded as chemically plausible (e.g. the TC4 models that fit the entire dataset well, see cluster 2 in Figure 3.3), there still is a range in terms of complexity. The models by Teams e and f suggests that the total number of model parameters required to achieve a good model fit to this particular dataset is not larger than ca. 10-12 (including site densities, any EDL parameters, protolysis constants, etc.).

Only Team h made a priority of making their model consistent with crystallographic and spectroscopic data. In comparison to the models by Teams e and f, the model of Team h employs a significantly larger number of total parameters. About half of those are not fitted but are based on independent evidence. Thus, the Team h model is consistent with recent spectroscopic evidence (Dähn, 2001) that indicates the existence of silanol and two types of aluminol sites on the edge surface of montmorillonite. The model by Team h attempts to take that into account by using an SC-EDL model that allows to distinguish between outer and inner-sphere surface complexes at the clay edge. The large number of parameters is also significantly related to the decision of Team h to use a SC-TLM for modelling ion exchange instead of using a conventional exchange formalism. As shown in panel B of Figure 3.3, the number of fitting parameters in the SC model is about the same among models e, f and h. At this point, the following conclusions can be drawn:

- The chemically most correct and plausible representation of the chemistry of the clay edge-water interface (as it is known presently) by model h requires the inclusion of a large number of additional parameters. Many of these additional parameters can be defined independently, and while the handling of SC by Team 8 appears to be more complex than in case of models e and f, the number of adjustable parameters for SC is actually lower.
- At first glance, the larger model complexity and data requirements of model h do not appear to lead to a corresponding increase in model performance. However, the nominal errors of models e, f and h are in an area where overall uncertainty may be determined by experimental rather than model uncertainty: As pointed out in section 5.1.4 in Part 1, it cannot be expected that the agreement between models and experiments is better than about  $0.1-0.2 \log K_d$ .
- This example shows that it is difficult to say how chemical plausibility should be evaluated. The model of Team h reflects more of the details of the clay edge-water interface, such as chemical identity of sites, and is more consistent with independent crystallographic and EXAFS data than models e and f. On the other hand, it may not be significantly more plausible than the other models in terms of more “macroscopic” model features, such as surface reactions and species.
- It is questionable whether a model using generic surface sites is necessarily less plausible than an otherwise similar model that addresses the chemical identity of sites (as revealed only by spectroscopy, not by macroscopic sorption or titration data).
- One potential issue of chemical implausibility can be identified in case of the models that use generic weak/strong sites: While it is assumed that the two types of sites have very different affinities towards radionuclides, identical protolysis constants are often used for both site types. The reason for this is that strong sites typically make up only a small fraction of the total number of sites, and surface acid-base titrations are not sensitive or precise enough to allow the extraction of protolysis constants for these sites.

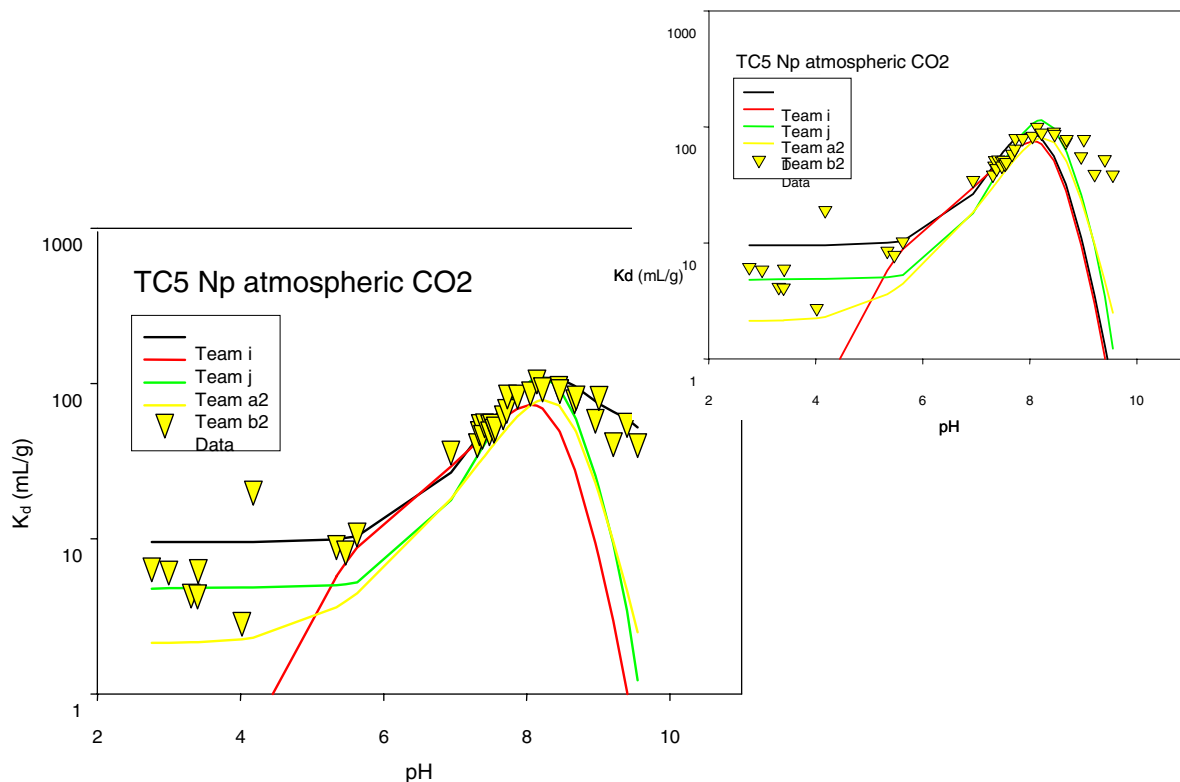
### 3.4.2 *Approaches to surface complexation modelling of clay edges*

#### 3.4.2.1 *Introducing a second surface species vs. a second surface site*

In order to achieve a better fit to the RN sorption data over a substantial range of conditions, most modelling teams chose to use a second edge site, rather than using a second RN surface species. In analogy with RN speciation in solution, the use of a second surface species would seem to be an obvious (chemically plausible) possibility. In this light, it is interesting that few attempts of introducing a second Ni surface species are reported. Only Team j used a one-site model with two sorbed Np species to describe Np sorption to the clay edges. Their fit to the experimental data is not very good, but they attribute this to a problem with their fitting procedure/code, rather than to the model set-up. A comparison with the models for Ni (TC4, Team h) indicates that a one-site SCM with two Ni surface species could describe the experimental data very well, but only if an inner- and outer-sphere Ni surface complex are selected instead of two inner-sphere complexes. Team h as well as Bradbury and Baeyens (1997) claim that fitting the experimental data proved to be impossible using a one-site SCM with two inner-sphere Ni surface complexes. It appears, therefore, that a more complex EDL model, allowing the formulation of outer-sphere surface complexes, may be required in combination with a one-site SCM. The requirement of using outer-sphere Ni surface species (in combination with a one-site model) may be related to the need for accounting for competition by major cations.

One team (i) introduced a ternary Np-carbonato surface complex to explain Np sorption in the presence of carbonate at  $\text{pH} > 8$ . The modelling outcomes of both TC 1 (Chapter 1) and TC6 (Chapter 4) showed that the inclusion of a ternary Np(V)- or U(VI)-carbonato surface complex allows a much improved description of the sorption of these actinides on iron oxides. Figure 3.2 shows that a ternary Np-carbonato surface complex is necessary to explain the sorption of Np(V) on montmorillonite in the presence of carbonate and at  $\text{pH} > 8$ . Omission of this complex leads to a clear underprediction of the experimental data under these conditions. There are no indications that a ternary Ni-carbonato surface complex is needed to explain Ni sorption under similar conditions. This is chemically plausible based on an analogy with the solution chemistry of Ni and Np(V): In contrast to Ni, Np(V) forms mixed hydroxo-carbonato complexes in solution (see Appendix 1 for sources of thermodynamic data).

Figure 3.2: **Model results for the adsorption of Np(V) on montmorillonite in the presence of carbonate (TC5). The insert shows the effect of omitting a ternary Np-carbonato surface complex from the model of Team i; all other data are the same as in the main panel**



### 3.4.2.2 Generic weak/strong surface sites vs. silanol and aluminol groups

It is well known that both Si and Al atoms are exposed at the edge surfaces of clay minerals, offering at least two types of surface functional groups, silanol and aluminol groups. Further, there is ample work in the literature that demonstrates that surface chemistry, and in particular protolysis behaviour, differs significantly between silica and alumina surfaces (see e.g. Stumm, 1992, and references therein). In contrast, most published models that deal with metal or  $H^+$  sorption on the edge surface of clays do not distinguish between silanol and aluminol sites, but use generic SOH surface groups with presumably averaged properties (e.g. Wanner *et al.*, 1994; Bradbury and Baeyens, 1997). Exceptions to this exist in the literature; e.g. Zachara and McKinley, 1993; Turner *et al.*, 1998. This is reflected in the present exercise, where also most approaches (nine out of twelve, groups A, B) used generic SOH-type surface sites to describe the chemistry of the clay edge surface.

On the other hand, three teams (group C) distinguished between aluminol and silanol sites on the clay edge surface. Among these, two completely different approaches were pursued, however. Team h based their approach on spectroscopic data of Ni sorption on montmorillonite (Dähn, 2001) and attempted to represent the chemistry of Si- and Al-sites located on clay edges. In contrast, Teams b2 and g based their approach on an analogy with single Si- and Al-oxides.



It is difficult to draw general conclusions based on the modelling approaches used in this test case group, because the models differ in several aspects. However, several interesting points can be noted:

- The spectroscopic and other data which had been used by Team h as a basis for their model strongly indicate that silanol sites are actually not involved in the binding of Ni. Accordingly, the model by Team h uses only one site for Ni binding (aluminol site), but two Ni-surface species, one inner- and one outer-sphere.
- Rather than trying to mimic the actual relations at the clay edge, Team g used data (protolysis constants, site densities) obtained independently on silica and alumina surfaces. When adjustments became necessary to fit the Ni data of TC4, they decided to keep the protolysis constants unchanged and to vary the site density values. This resulted in extremely low site densities (see Section 3.3.3). As a result, the contribution of the edge surface to overall Ni sorption is very small in this case, rendering ion exchange the only relevant sorption process.

### 3.4.3 EDL models

#### 3.4.3.1 EDL-philosophy of teams that aimed at a simple model

All except one of the one-site SCM use a DLM to correct for coulombic effects. One team (Team c) used a one-site SCM without an EDL term. However, this choice was clearly related to an a priori decision by this team to develop a simpler model than the one published by Bradbury and Baeyens (1997), and not to technical modelling considerations. At the same time, it is very interesting that only one of the teams that had the stated goal of building a simple model opted for a two-site NEM (Team d). Overall, it appears that teams aiming at a simple model have been more willing to restrict the number of surface sites to one and to add an EDL model than to use two surface sites and dispense with the EDL term. The modelling teams expressed the view that the inclusion of an EDL term is chemically correct and more plausible than the addition of a second edge site. In contrast, the total number of required fitting parameters was rarely cited as an argument for a “simple” model.

It is worth noting that none of the teams that chose a one-site SCM considered using a more complex EDL model, such as TLM or BSM. The approach of Team h shows that these EDL models could lead to a significantly better SCM, because they allow to use outer-sphere surface complexes (see Section 3.4.2.1).

#### 3.4.3.2 Reasons for using NEM (or for minimising the effect of the EDL term)

The two main reasons for choosing a NEM (or for minimising the effect of the EDL term) are:

- difficulties encountered in fitting experimental data with an EDL model;
- the explicit goal to develop a simple model.

Team e encountered difficulties in fitting the titration data provided for TC4 using a one-site DLM and therefore dropped the EDL term. Team i had also abandoned the EDL term due to fitting problems using a one-site DLM in earlier model development work (for a dataset different than TC5) and retained this approach for the present exercise. In both cases, a second site, having the same protolysis behaviour, was introduced subsequently to fit the RN sorption data, but it was not tested whether the two-site model would benefit from re-introducing an EDL-term. Team f used a DLM, but assumed a very high edge surface area (500 m<sup>2</sup>/g) to minimise the effect of the coulombic correction term, following the approach of Morel and Kraepiel (1997).

Two teams (c, d) chose a NEM explicitly in order to keep their model simple, but utilised this setup in different ways: Team d developed a two-site SCM without acid-base reactions, thereby significantly reducing the number of adjustable parameters. On the other hand, Team c kept a more conventional setup, including SOH site protolysis. It is very interesting that of all the teams that used a NEM, only one team (Team d) made use of the possible simplifications and developed a model that does not include surface acid-base reactions. Apparently, in most cases modelling teams felt that surface acid-base reactions should be kept, even if the chosen EDL model (NEM) would allow otherwise. This point is further illustrated by the fact that Team e dropped the EDL term due to problems in fitting the titration data, but kept acid-base reactions in their NEM. Team i had already followed this sequence in their earlier work and kept the resulting setup (NEM including acid-base reactions).

#### 3.4.3.3 Comparison of SCM approaches: Summary

- Generally, it can be stated that EDL models were used in combination with (i) one-site models, or (ii) in combination with models that distinguished edge SiOH and AlOH groups. In contrast, NEM were favoured by teams that used generic two-site SCM for the clay edges.
- Among the generic two-site models, the model by Team d (NEM without surface acid-base reactions) has by far the fewest fitting parameters. It does not perform very well, but the main reason for this may be that only a subset (sorption edge at  $I=0.1$  M) of the available data had been used for calibration.
- It appears at first sight that the DLM approaches are not very suitable for fitting the experimental data. However, it cannot be excluded that this is related to the fact that DLMs are used mainly in combination with one-site SCM.

#### 3.4.4 Approaches to ion exchange modelling

Nearly all approaches (11 out of 12) used surface complexation at clay edges and ion exchange at the siloxane surface to describe Ni/Np sorption (as well as the general water chemistry in predictive applications). Only one team (Team b) neglected ion exchange in their model for TC5; but used ion exchange in TC4, however. The reason for this is not clear.

Most teams modelled ion exchange in a conventional fashion, using the Gaines-Thomas (equivalent fraction) formalism, which is easy to implement. No other ion exchange formalisms have been reported (i.e. Vanselow or mole-fraction, or a simpler approach without activity correction). Most teams considered only exchange of the un-hydrolyzed RN (and major element) cations. As the only exception, Team g (TC4) considered both  $Ni^{2+}$  and  $NiOH^+$  to take part in ion exchange.

One team (Team h) used a SCM on both types of surfaces: They used a BSM for the clay edge and a TLM for the siloxane surface to describe ion exchange via outer-sphere surface complexes. Sorption on the siloxane surface was modelled through the competitive, outer-sphere sorption of a number of species ( $Ni^{2+}$ ,  $NiOH^+$ , as well as all electrolyte and groundwater cations and positively charged complex species).

### 3.4.5 *Conclusions on overall model choices*

- Most of the generic two-site models (group B) used a NEM (one exception: Team f).
- When aiming at the development of a simple model, it appears that several modelling teams think of simple in the sense of using only 1 site, or using a simple EDL model (DLM), rather than in purely quantitative terms (number of fitting parameters).
- It appears that there are typical combinations of surface complexation and EDL models (groups A-C, see Table 3.2). In addition, group C used different ion exchange models than the other groups. This grouping of approaches makes it difficult to compare e.g. different EDL models directly.
- Similarly, the actual fitting procedure (e.g. fitting one sorption edge vs. fitting all available data) differed among the various teams. The resulting mix of model approaches and fitting procedures makes the separation of the respective effects on model performance difficult.

### 3.5 **Influence of trace element (Zn, Mn) inventories (TC4 only)**

As already pointed out in the section on model implementation, modellers had been asked in TC4 to develop models with (model 2) and without (model 1) considering the inventory of Zn and Mn in the clay. The original motivation behind this request was based on the findings presented in the original publication by Bradbury and Baeyens (1997). They observed (i) that the purified clay used in their study contains significant amounts of Zn, (ii) that Zn sorbs more strongly than Ni, and (iii) that model fits for the strong site density is critically dependent on whether Zn is taken into account or not.

In the present modelling exercise it turned out that the influence of Zn and Mn inventories on the development and characteristics of models for Ni was very small. Also, the model set-up for Zn and Mn differed only in one case from that for Ni. However, it has to be pointed out that due to a variety of reasons (including time or budget limits), not all teams were willing or able to develop independent models considering or neglecting the mentioned trace element inventories. Therefore, the following interpretations are based on a selection of contributions.

Despite the somewhat limited database, the following observation can be made. As long as the internal consistency of model parameters and sorbent characteristics is maintained, it is of relatively little importance (at least in case of TC4) whether the trace element inventories are accounted for or not: The overall errors (mean absolute log  $K_d$  values) of models including or excluding Zn/Mn are practically indistinguishable. The reason for this can be explained as follows:

- There is only enough Zn present to occupy a significant portion of the strong sites in a two-site model; and even less Mn. The corresponding available weak or total site density is not noticeably affected, on the other hand.
- In most cases, the density of the strong site is derived from Ni sorption data, and this number already includes the fraction that is occupied and not available to Ni. All that the presence of Zn does is lower the site density that can be measured by Ni adsorption.
- In extending the calibrated model to other datasets, modellers used either the model with or without Zn/Mn in a consistent fashion. While no direct comparisons between models with and without Zn/Mn are available, there are no indications that this modelling choice had a significant effect. This indicates that the inventory of such trace elements is not very important, or that different clays have very similar inventories, which would then be lumped implicitly into fitted (available) site densities.

### 3.6 Model performance and relation to model complexity

At least in the case of Test Case 4, it has to be clearly stated that the following analysis of number of fit parameters vs. model performance has to be interpreted with great care: Differences in the general approach to model calibration and in the actual fitting procedure (full vs. partial datasets) can make as much difference for model performance as the actual surface chemical model setup:

- Not all teams participating in TC4 used the full dataset available (three pH-edges at different ionic strengths, three isotherms at different pH) for fitting. Models calibrated using only a subset of the available data generally performed less well.
- Models calibrated on a log  $K_d$  basis perform better than models calibrated on a % sorbed basis.

#### 3.6.1 Test case 4: Model calibration (Bradbury and Baeyens, 1997)

In the following two figures, the number of model parameters is compared to model performance in fitting the data provided for calibration in Test Case 4. Figure 3.3 shows the mean overall errors of the model fits for the entire dataset. Only those contributions that cover the entire dataset are included; therefore, two contributions that covered only the sorption edges are missing from this figure. The errors for the entire dataset are compared with both the number of actual fitting parameters for each model, and with the number of all model parameters, including those taken or derived from independent sources. It shows that the models with more parameters tend to get a better fit to the data. Note, however, that the models can be organised into two clusters:

- One cluster includes models with  $\leq$  seven parameters and overall errors between 0.3-0.5.
- The second cluster includes model with  $\geq$  11 parameters and overall errors between 0.1-0.2. As pointed out in section 5.1.4, Part 1, a disagreement of that magnitude can be the result of experimental scatter alone. Therefore, a better agreement between model and data cannot be expected.

In Figure 3.4, the overall errors shown in Figure 3.3 are separated into the mean errors for fitting each of the six sub-datasets provided, and plotted vs. the number of fitting parameters used in each model. This analysis shows again the clusters that were already observed in Figure 3.3. It also shows a critical difference in terms of error distributions between these two clusters:

- The models in cluster 1 display a comparatively large spread of errors. These models produce actually relatively small errors for some of the sub-datasets in Bradbury and Baeyens, (1997), but much larger errors for other sub-datasets.
- The models in cluster 2 not only have much smaller overall errors, but the error distribution is also significantly narrower.

The reason for this observation has to be explained with the actual fitting procedures used by the various teams, rather than with model characteristics. The models in cluster 1 were fitted to one or a few datasets only, whereas the entire dataset was used for the parameterisation of the models in cluster 2. Based on this analysis, we have to conclude that a comprehensive fitting strategy may be as important as the actual model setup for obtaining good models. It only can be speculated that cluster 1 contains simple models mainly because only limited datasets were fitted, while the rest of the data was either “blindly” predicted or simply ignored. It is likely that a consideration of the entire dataset would have shown (at least some) of the shortcomings of the simpler models in an early stage of the modelling process, and the teams may have made the necessary model modifications (this process of successive model building can e.g. be followed in the case of Team e).

Figure 3.3: Number of fitted (closed symbols) and total (open symbols) model parameters plotted vs. the overall errors (mean of absolute error in terms of  $\log K_d$ , see eq. 2.1 in Part 1) for the entire dataset of Bradbury and Baeyens (1997), TC4. Panel A refers to all TSM parameters (SC plus IE), panel B refers to the SCM only

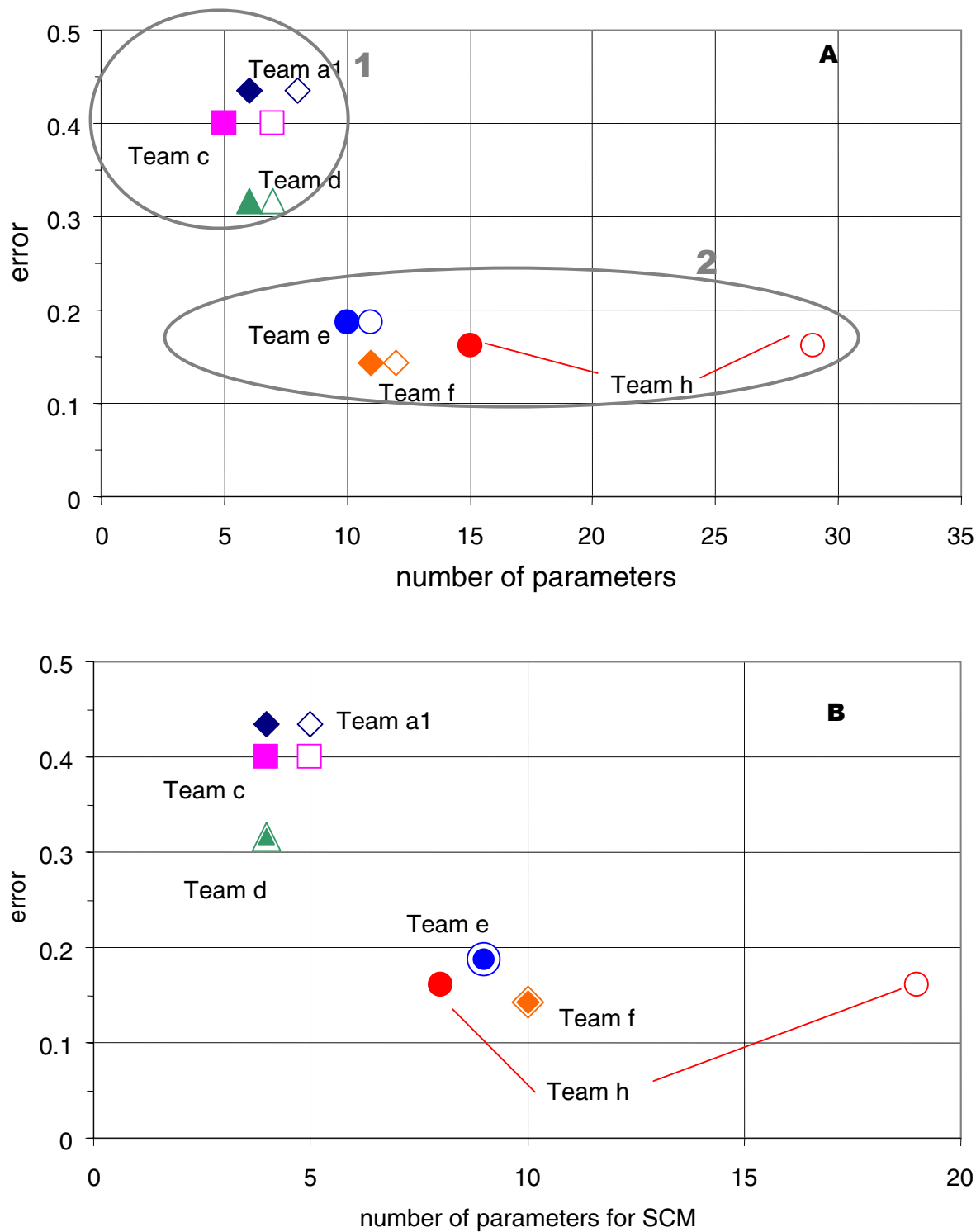
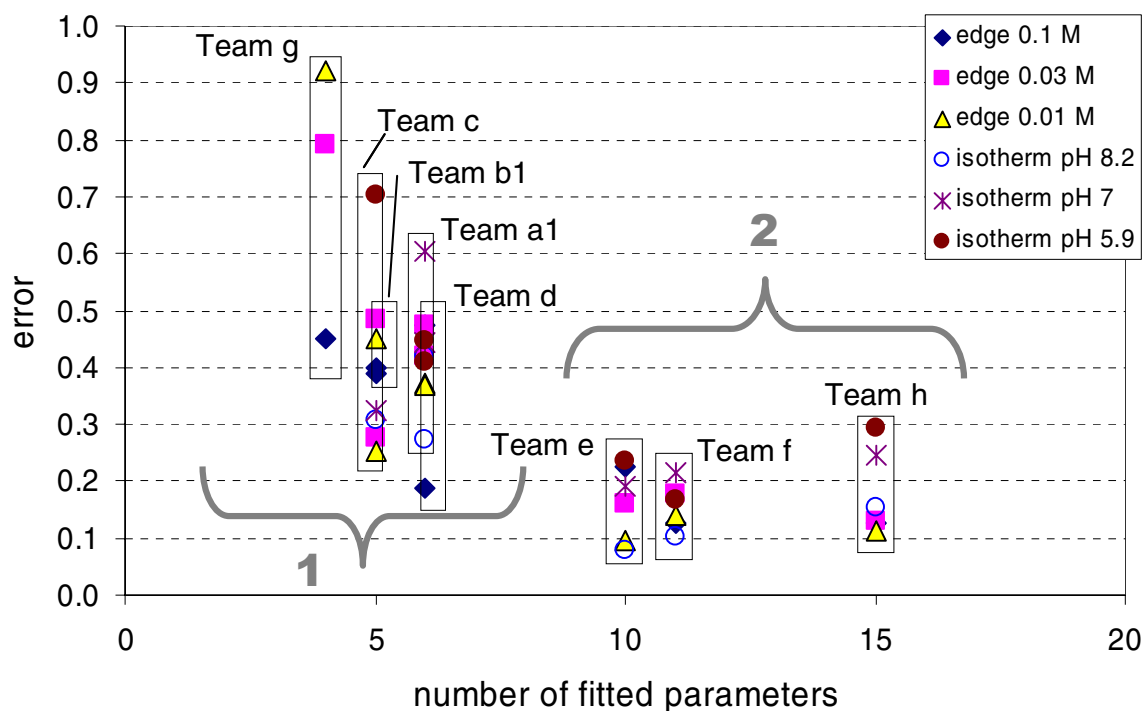


Figure 3.4: Number of fitted model parameters plotted vs. the errors (mean of absolute error in terms of  $\log K_d$ , see eq. 2.1 in Part 1) for every sub-dataset of Bradbury and Baeyens (1997), TC4



### 3.7 Performance of models in applications to other datasets and conditions

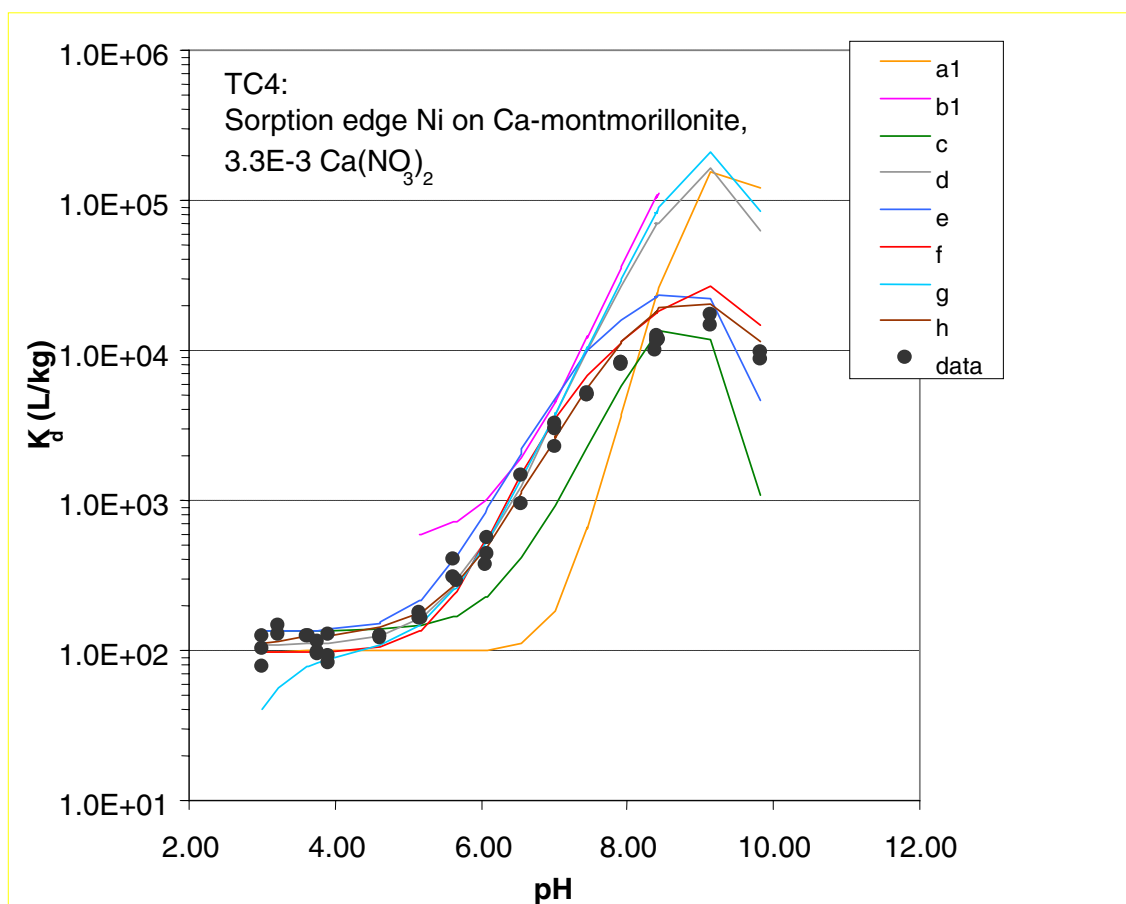
Because the performance of thermodynamic sorption models applied in a predictive mode is strongly influenced by the type of extrapolations required, the following discussion is organised in a case-by-case fashion. Modelling teams had been asked to perform three predictive extrapolations in TC4 and one in TC5.

#### 3.7.1 Model application to the data of Bradbury and Baeyens (1999), TC4

This required the application of models developed for a pure Na-montmorillonite to the corresponding pure Ca-form of the same montmorillonite (see Appendix 1). The experimental conditions were also identical or very similar to those of Bradbury and Baeyens (1997). As the Na-Ca ion exchange constant is relatively well known, this extrapolation does not, therefore, require any additional calibration (the Ca-Ni exchange constant follows directly from combining the Ca-Na and Na-Ni constants).

A representative example of model results is shown in Figure 3.5. The number of fitted parameters for this case is plotted against overall errors in Figure 3.6. A comparison of the number of fitted parameters with the respective value for Bradbury and Baeyens (1997) shows that all teams used at least one additional fitting parameter (Figure 3.3). An exception to this was Team d, who did not add or re-fit any parameters. However, they performed calculations only for one of the data-subsets and are, therefore, not included in this evaluation. The number and type of additional fitting parameters used for the extrapolation to Bradbury and Baeyens (1999), TC4, is summarised in Table 3.3.

Figure 3.5: **An example of model performance in the application to the data by Bradbury and Baeyens (1999); modelling teams are indicated. See Part 3 for a more detailed documentation of model results**



It can be seen that the general trend of performance vs. number of fitted parameters is very similar to that already observed in model calibration (Bradbury and Baeyens, 1997, TC4), which may be expected considering the similarity of the systems. While the presence of Ca (and the switch from  $\text{ClO}_4^-$  to  $\text{NO}_3^-$  as electrolyte anion) could have been included in most models in a purely predictive fashion by taking the ion exchange constant for Ca-Na from independent literature (a suggested value was given in TC4), most teams preferred to fit or directly take this value from Bradbury and Baeyens (1997).

The constants for the outer-sphere surface species used by Team h had been given initial values based on analogy considerations (i.e. had been independently derived, rather than fitted). Since they were slightly adjusted in the course of the modelling, they are counted as fitted parameters. Note also that the use of outer-sphere species for the siloxane surface is only necessary due to that team's choice of using a SC-TLM instead of conventional ion exchange.

In the end, a claim can be made that nearly the same model performance could have been achieved with no (Teams a-g) or only two (Team h) additional fitting parameters.

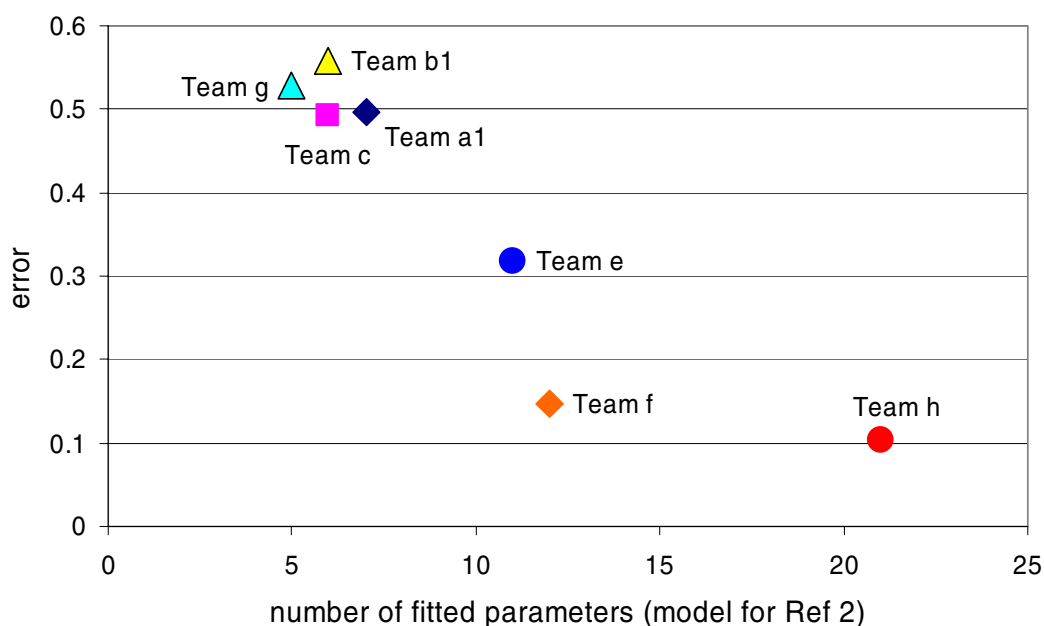
Table 3.3: **Number and type of additional fitting parameters used for the extrapolation to the data of Bradbury and Baeyens (1999), TC4**

Team	Number	/	Type of additional fitting parameters
a1	1	/	ion ex. constant for Ca from Bradbury and Baeyens (1999)*
b1	1	/	ion ex. constant for Ca from Bradbury and Baeyens (1999)*
c	1	/	ion ex. constant for Ca from Bradbury and Baeyens (1999)*
d	0	/	–**
e	1	/	ion ex. constant for Ca from Bradbury and Baeyens (1999)*
f	1	/	ion ex. constant for Ca from Bradbury and Baeyens (1999)*
g	1	/	ion ex. constant for Ca from Bradbury and Baeyens (1999)*
h	16	/	capacitance, charge density for aluminol sites, four constants for sorption of outer-sphere complexes (three for Ca and NO <sub>3</sub> on edge, one for NiNO <sub>3</sub> on layer surface)

\* Alternatively, these constants could have been counted as fitting parameters for the model calibrated with the data of Reference 1. However, they were not put to use for the modelling of the dataset from Bradbury and Baeyens (1997)\* but only in extrapolation. See also Appendix 3.

\*\* Because Team d had used ion exchange of Ca already in modelling the data of Bradbury and Baeyens (1997), this parameter is not counted again as fitted.

Figure 3.6: **Number of total fitted model parameters plotted vs. the overall errors (mean of absolute error in terms of log K<sub>d</sub>, see eq. 2.1 in Part 1) for all sorption edges of Bradbury and Baeyens (1999), TC4. Team d is not included, because they modelled only one sorption edge**





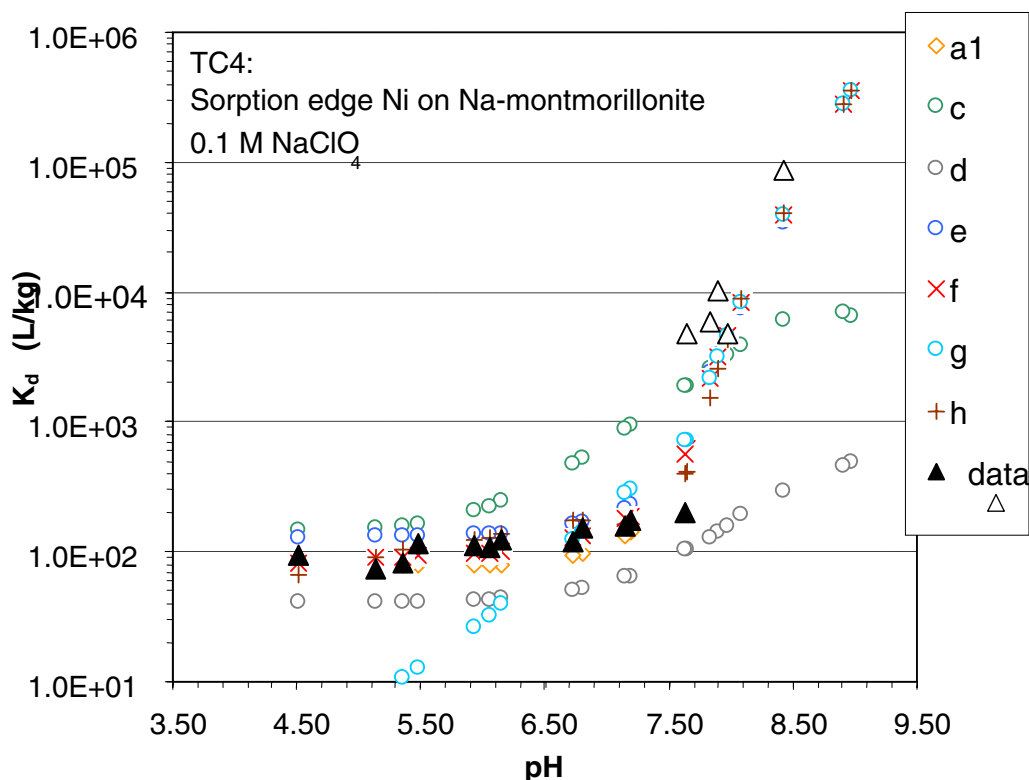
### 3.7.2 Model application to the data of Lothenbach *et al.* (1997), TC4

This required the application of the models developed for a highly purified Na-montmorillonite (SWY-1, Bradbury and Baeyens, 1997) to a different Na-montmorillonite (same clay source, but less extensively purified, Lothenbach *et al.*, 1997). In addition, traces of carbonate were introduced into the experimental system. At high pH values, (surface) precipitation of Ni occurred (see Figure 3.7).

Model results for the sorption of Ni in 0.1 M NaClO<sub>4</sub> are shown in Figure 3.7. The approaches taken by various teams are very similar to those for the model application to Bradbury and Baeyens (1999). Consequently, no additional fitted sorption parameters were introduced by the modelling teams for this case. Team h slightly adjusted the solubility product of Ni(OH)<sub>2</sub>(s) to model the data at high pH. The relation between number of parameters used by the various models and overall agreement between experimental and predicted data is similar as in the model application to Bradbury and Baeyens (1999).

The desorption of Ni in the presence of Ba was modelled only by four teams (Teams c, e, f, and g). In comparison to the modelling of sorption, the error increased by about 0.1, irrespective of whether the ion exchange between Ni and Ba was fitted or assumed to be equal to Ni-Ca or Ni-Na.

Figure 3.7: **Model results in the application to the sorption edge data by Lothenbach *et al.*, 1997); modelling teams are indicated. See Part 3 for a documentation of model results in the presence of Ba(ClO<sub>4</sub>)<sub>2</sub>. The data points represented by open triangles correspond to conditions where Ni solubility in solution may have been exceeded**



### 3.7.3 Model application to Tachi and Shibutani (1999), TC4

This required the application of models developed for a pure Na-montmorillonite to sorption experiments involving a crude bentonite in contact with 0.001 M and 0.1 M NaCl. In this extrapolation, several new features were introduced:

- The bentonite consisted of about 50% smectite clays, the rest consisted of chalcedony and other accessory minerals, as well as soluble impurities (salts).
- These accessory minerals and impurities exerted an important influence on solution chemistry, especially in case of the 0.001 M NaCl input solution.
- Exchangeable ions on the clay layer surface included Na, Ca, Mg, and K.
- The experiments had been carried out under ambient conditions, introducing substantial carbonate concentrations.

A comparison of the errors associated with the various models in the systems with 0.001 M and 0.1 M NaCl (Figure 3.8) shows that most models did significantly better at the higher electrolyte concentration than in the more dilute system. Several teams (a, c, g) did about as well in predicting  $K_d$  values for Ni in this system as in fitting the data of Bradbury and Baeyens (1997). It is also interesting that in the 0.1 M NaCl system, all errors are within a very narrow range. A significant part of this error may stem from the experimental uncertainties themselves, rather than from model uncertainties.

(Figure 3.8) shows that with the exception of Teams c, e and h, all teams introduced additional parameters into their overall model and/or re-fitted previously determined parameters:

Team a1: They adjusted the total concentration of dissolved carbonate to correspond to an *equilibrium* with a  $p\text{CO}_2$  of  $10^{-3.5}$  atm at pH 6.35. While this is probably reasonable, there is no direct experimental evidence, and this adjustment was *nominally* counted as fitting parameter.

Team f: Adjustments involved geochemical parameters:  $p\text{CO}_2$  was adjusted and fixed within reasonable constraints (as in the case of Team a1, this was then counted *nominally* as fitting parameter), and the dissolved concentrations of the major cations was set equal to the (provided) measured concentrations for each datapoint (again, this was *nominally* counted as fitting parameter, purely for the purpose of distinguishing Team f from other teams who predicted cation concentrations based on bentonite composition).

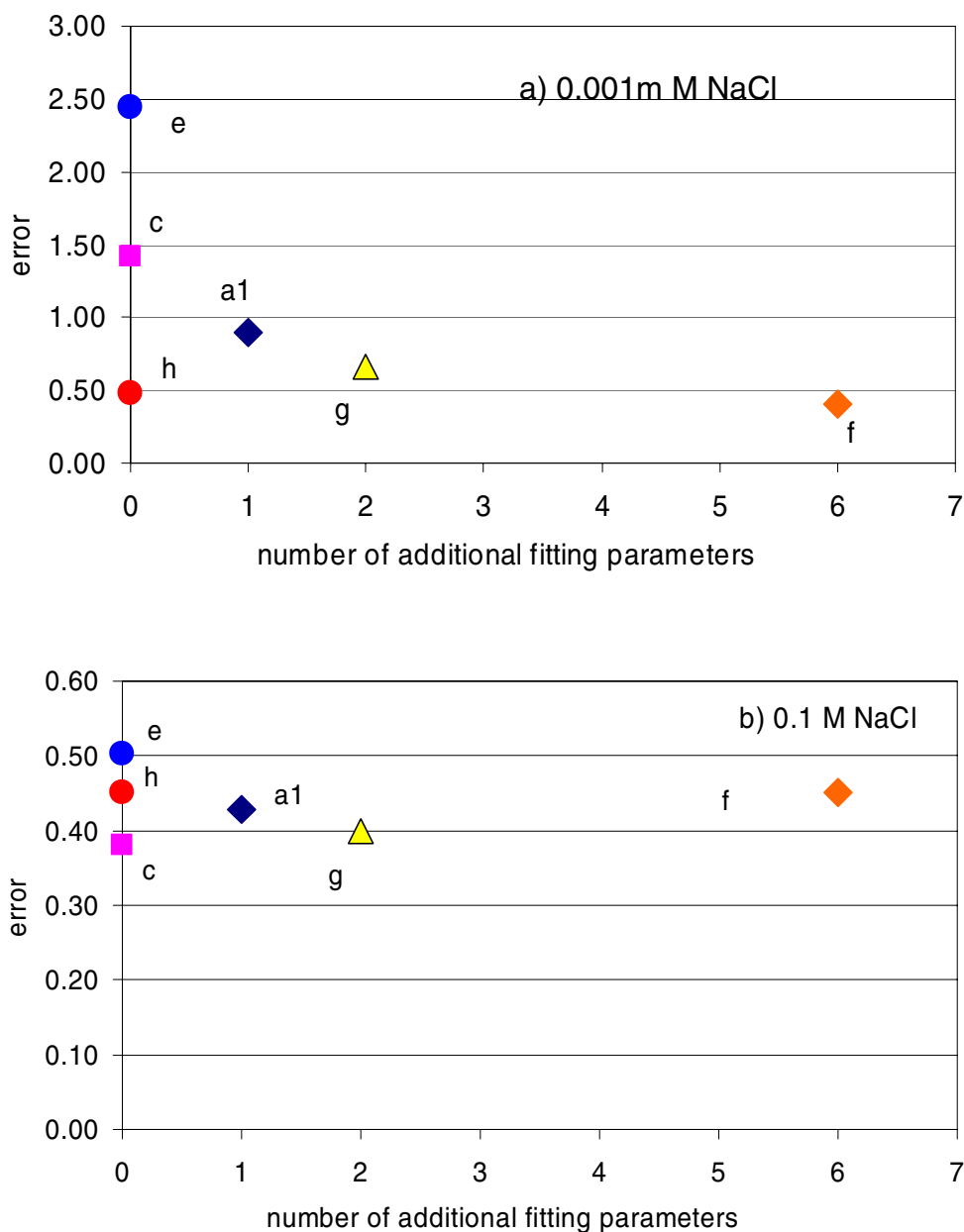
Team g: They re-fitted the silanol and aluminol site density in their model to optimise the fit to the experimental data.

Team h: Due to the chosen modelling approach for the siloxane surface (SCM/TLM instead of ion exchange), this team had to introduce several additional outer-sphere surface complexes for the X- site plus an outer-sphere complex for the AlOH site to describe clay-solution interaction. The respective (provisional) constants were derived independently (based on electrostatic principles), and are, therefore, counted as non-adjustable parameters.

As can be seen from the above compilation, several teams carried out significant modifications of the original model. In that sense, some of the models are not predictive extrapolations.

This illustrates a major difference between extrapolations to different simple systems and extrapolations to more complex “geochemical” situations. In the latter case, it is not sufficient to have a good RN-specific sorption model. Instead, this model needs to be embedded in an appropriate overall geochemical model that is able to address all relevant solution/mineral equilibria as well as all surface chemical *equilibria* involving major dissolved ions (see Section on calibration and extrapolation).

Figure 3.8: **Number of additional fitted and additional overall model parameters (see text for explanation in cases of Teams a1 and f) plotted vs. the overall errors (mean of absolute error in terms of log  $K_d$ ) for the data corresponding to 0.001 M (a, b) and 0.1 M NaCl (c, d); Tachi and Shibutani (1999), TC4**



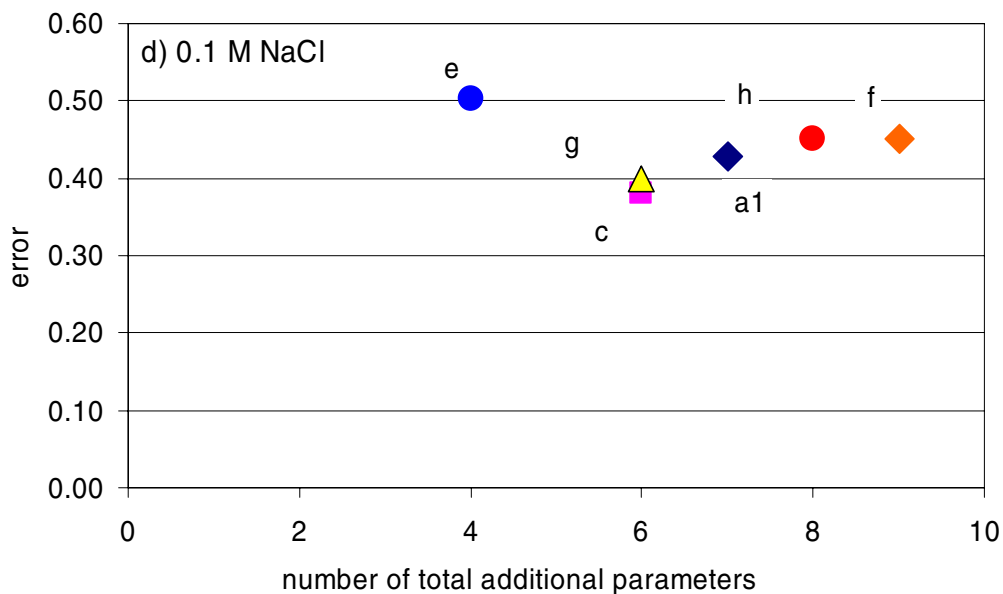
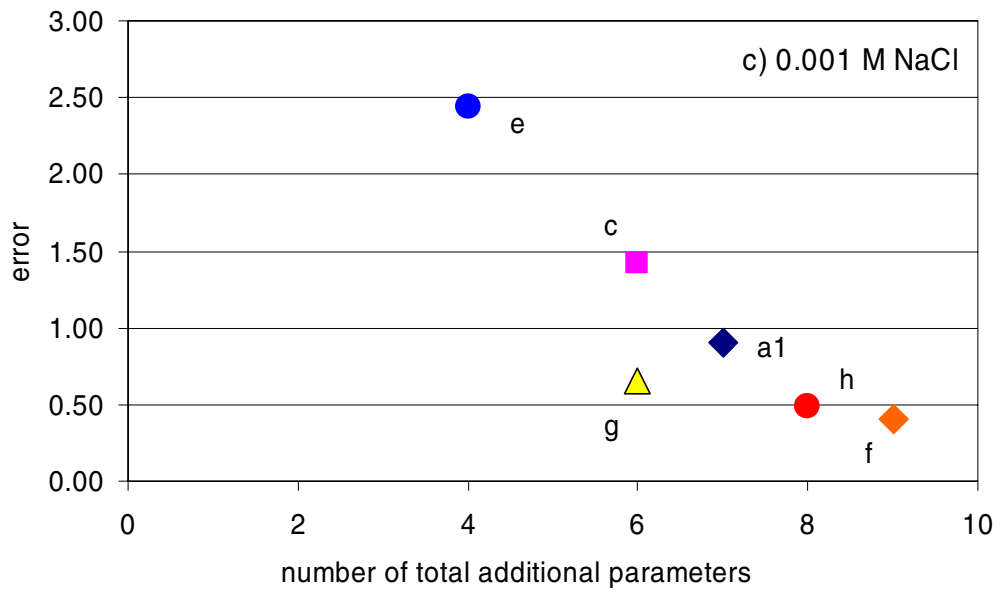


Figure 3.8 shows that several of the models that allowed a good fit of the data by Ref. 1 also predicted the experimental data for the crude bentonite very well. However, one of the models (Team e) that achieved a very good fit in calibration overpredicted  $K_d$  values for Ni on crude bentonite by several orders of magnitude. On the other hand, models that were deliberately kept simple and clearly had limitations in fitting the data by Reference 1, were comparatively successful when applied to the crude bentonite. As will be explained below on the basis of selected models, this apparent discrepancy has nothing to do with the actual sorption models, but can be completely explained by the ways in which the calcite/carbonate system was handled:

- Figure 3.9 below shows that the overprediction of Ni sorption by the model of Team e is entirely due to the high Ni concentration on the ion exchange sites.

- As shown in Figure 3.10, this is caused by the weak competition by Ca ions, whose surface concentration is several orders of magnitude smaller than in the other models.
- A close inspection of the model shows that the low Ca surface concentrations in the calculation of Team e are not related to the ion exchange model, but are directly caused by the low Ca concentration in solution (Figure 3.11). This is the result of the fact that Team e neglected the calcite impurity contained in the crude bentonite (possibly due to a mistake in extracting the large amount of information given in the test case file).
- Because the solution composition in the 0.001 M NaCl case is strongly influenced by the solid itself, which is often the case in case of mineral assemblages that contain easily or moderately soluble components, a correct treatment of the general solid-water interaction is as (or more) important than the actual sorption model.
- In case of the 0.1 M NaCl system, the solution is largely dominated by the added electrolyte. The model errors are much smaller (Figure 3.8), because the actual sorption models can be applied to a relatively well-defined system.
- Because of the low porosity (very high solid/water ratio) of natural systems or engineered barriers, it can be expected that a significant influence of the solid on the solution composition is the rule.

In the present case, the neglect of calcite by Team e was probably due to overlooking a piece of information in the test case file. In reality, however, it is often not trivial to characterise natural systems and sorbents to a degree that would reduce the difficulty in sorption modelling to the actual surface chemical problem.

Figure 3.9: **Surface concentrations of Ni on layer and edge sites of crude bentonite. Data by Tachi and Shibutani (1999), TC4**

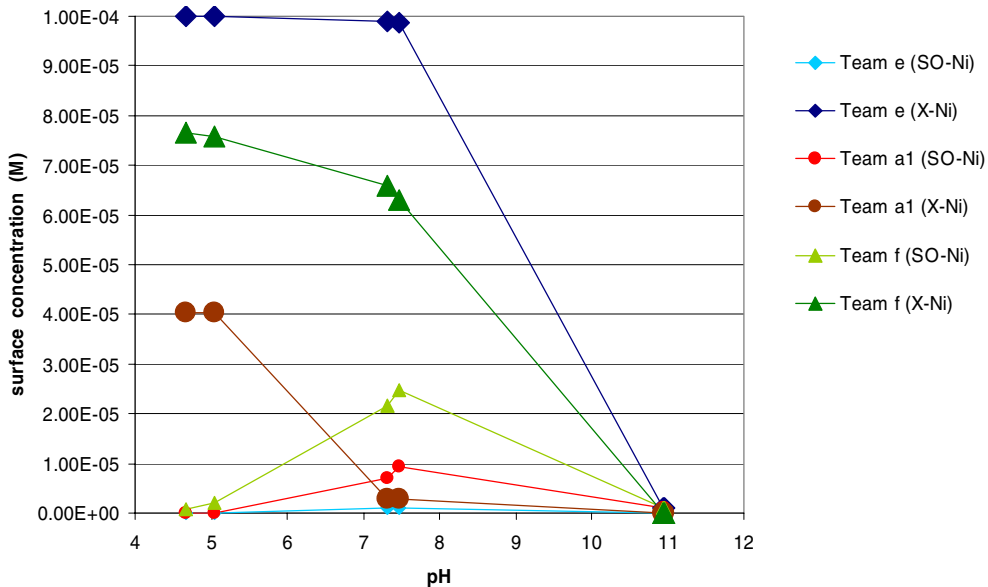


Figure 3.10: **Surface concentrations of Ni and Ca on layer sites of crude bentonite. Data by Tachi and Shibutani (1999), TC4**

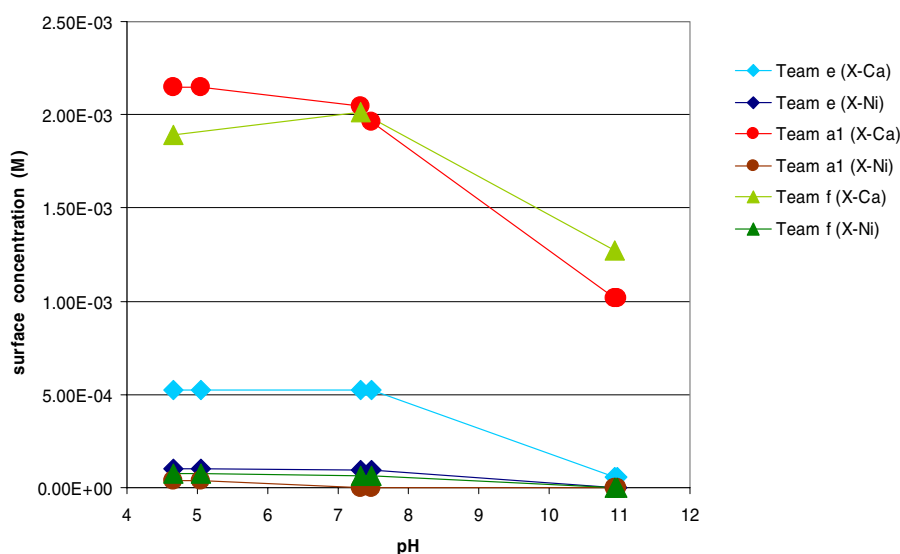
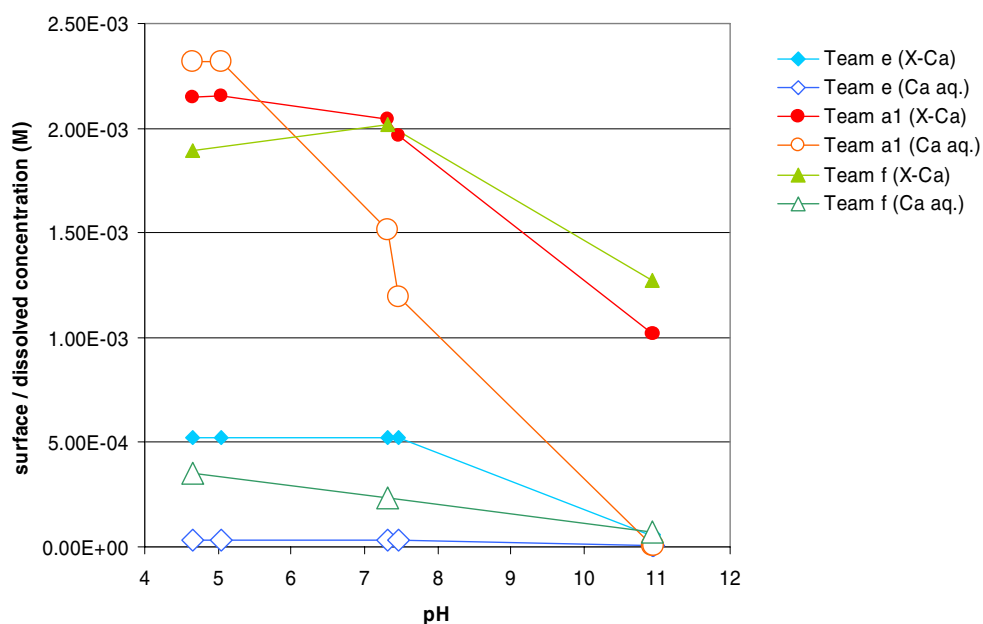


Figure 3.11: **Surface (bound to ion exchange sites) and dissolved concentrations of Ca as a function of pH. Data by Tachi and Shibutani (1999), TC4**



### 3.7.4 Transfer/acquisition of model parameters

In addition to the discussion given in the section on transferability of model parameters, some additional points deserve special attention in the case of clays.

It appears that the assignment of surface area to the edge and layer surface of clays is not straightforward. Various teams assigned either the BET area, or a certain fraction thereof (e.g. 10%) to the edge surface, based on a variety of arguments. There was no consensus among the teams. This becomes an important issue when model parameters are being transferred from one clay to another (in

an otherwise consistent fashion). If the BET area is accepted as a measure for the edge surface area, one may face the following choices for the transfer of site densities from one clay to another:

- The site density per unit area is kept, adjusting the site density per unit mass.
- The site density per unit mass is kept, adjusting the site density per unit area.

Because of the ill-defined nature of the edge surface area, it may also be possible to scale edge site density with regard to total CEC, as long as the parameter transfer is made among the same clay minerals.

If a conventional ion exchange formalism is used to model reactions at the siloxane surface, surface area and site density per area is not an issue. In case of a SCM/TLM, as developed by Team h, surface area becomes important for the layer surface also.

### **3.7.5 Key issues in extrapolating**

Clays as a complex substrate seem to differ from soils and sediments in terms of the predictive capability of thermodynamic sorption models. While blind predictions of sorption onto a complex soil or sediment appears to be difficult with models calibrated with simple minerals, it seems to be possible to extend a model calibrated on pure montmorillonite to a natural bentonite that contains < 50% clay minerals, which include montmorillonite, beidellite, and nontronite. Based on the results for the limited number of clay samples studied in this project, it appears that the critical surface chemical properties of clays are much more transferable from one substrate to another than the parameters of Fe-(hydr)oxides, for example. In case of clay-dominated mineral assemblages, the additional difficulty presented by complex systems appears to be largely restricted to the model representation of solution chemistry as controlled by the various mineral equilibria, the dissolution of easily soluble impurities and the exchange of major cations. The influence of important ligands, such as carbonate, would be the same in case of clays as for any other mineral. Through the link of carbonate *equilibria* – calcite solubility –  $\text{Ca}^{2+}$  competition for ion exchange sites,  $p\text{CO}_2$  and dissolved carbonate concentration are of critical importance even if direct RN-carbonate interaction are not very relevant.

## **3.8 Data requirements**

It appears that one-site models are not compatible with the shape of RN sorption edges on clays. There are also some indications that it is difficult with a DLM to model surface titration data, but the evidence on this is not conclusive. Bradbury and Baeyens (1997) observed that a DLM is not incompatible with titration data, only with Zn sorption.

In fact, it appears that model set-ups that are based on titration data may not be the best approach to fitting RN sorption data. One reason for this may be that the clay edge possesses different sites that are not distinguishable by titration, but by RN sorption experiments (i.e. most metals are more sensitive probes than the proton). The usefulness of fitting titration data (first) can therefore be questioned.

The most successful models include two-site NEMs and a two-site BSM. On this basis, both NEMs and models with an EDL term appear to be suitable choices.

## 4. URANIUM SORPTION ON KOONGARRA SCHIST (TEST CASE 6)

### 4.1 Overview

This was one of the two test cases in the NEA sorption modelling inter-comparison involving complex geological substrates. A large dataset for a radionuclide on a complex soil material was required to carry out the modelling exercise. The selected dataset comprised experimental results for uranyl adsorption on weathered schist materials from the Koongarra uranium deposit in northern Australia. The adsorption experiments were carried out with samples denoted W1, W2, W7 and W2c. A summary description of these samples is given in Table 4.1. A description of the field site and the experimental procedures is provided in Payne *et al.* (2001). Table 4.2 summarises the experimental U sorption datasets provided as part of this test case.

Table 4.1: Koongarra samples used for U sorption experiments

Sample	Depth (m)	Total U ( $\mu\text{g/g}$ )	Labile U content <sup>a</sup> ( $\mu\text{g/g}$ )	BET surface area ( $\text{m}^2/\text{g}$ )
W1	13.0-13.2	356	42.6	24.6
W2	14.0-14.2	426	225	52.3
W7	13.0-13.2	10.4	1.0	51.9
W2c	12.0-12.2	213.5	97.3	20.3

<sup>a</sup> Determined by extraction with Tamm's acid oxalate (see Yanase *et al.*, 1991).

The overall objective of the modelling exercise was to evaluate the present capabilities and limitations of SC models in describing uranium sorption by these complex materials. Specific aims were to:

- test the ability to transfer sorption models from pure mineral substrates to complex materials;
- assess which models were most successful in terms of ability to predict adsorption data with a small number of adjustable parameters;
- compare the uranyl surface speciation computed in various modelling approaches;
- determine which solid-characterisation parameters were most useful for model development;
- ascertain the amount of parameter variation required to simulate sorption data obtained with different substrates; and
- compare the generalised composite (GC) and component additivity (CA) approaches (Davis *et al.*, 1998) for the development of sorption models for complex substrates.



This test case was undertaken by twelve modelling teams from eight countries. Five of the teams attempted the “limited” version of the test case, which was based on the GC approach. The remaining teams undertook the “extended” version of the test case, in which they were directed to firstly develop surface complexation models for U sorption on component minerals. Uranyl sorption data for two of the component phases (ferrihydrite and kaolinite) were supplied. As such, the extended version had more of the character of the component additivity (CA) approach. However, it should be emphasised that considerable freedom was afforded the modellers in developing their models, and consequently the final models tended to combine features from both the GC and CA approaches.

Table 4.2: **Summary of experimental data provided to modelling teams. Typically experimental data comprise  $K_d$  as a function of pH for each set of experimental conditions**

Substrate	Gas phase	U added	NaNO <sub>3</sub>
W2	air	Trace	0.1M
W2	1% CO <sub>2</sub>	Trace	0.1M
W2	air	Trace	0.02, 0.2M
W2	air	100 µmol/L	0.1M
W1	air	Trace	0.1M
W7	air	trace, 1 µM, 100 µM	0.1M
W2c	air	Trace	0.02, 0.1, 0.5M

## 4.2 Methodology

In the CA approach (as implemented in this test case), the modellers were asked to predict adsorption on one of the complex Koongarra materials (the W2 sample), utilising models derived for individual minerals, which were assumed to make a major contribution to the overall sorption behaviour. The modellers were free to incorporate models for any component minerals including (but not limited to) the U sorption models for kaolinite or ferrihydrite. This predictive model was denoted Model 0 (Table 4.3). An improved Model “A” was then developed from the predictive CA model using parameter optimisation or other modifications.

The modelling teams that selected the GC approach were requested to fit the W2 sorption data by utilising generic surface sites and choosing sorption reactions that best fitted the sorption data. Following these initial models for the W2 substrate both the CA and GC teams then modified their models to simulate other sets of U sorption data.

The modelling teams were provided with complete sets of sorption data (Table 4.2), standard thermodynamic data [based on the reviewed NEA compilation (Grenthe *et al.*, 1992)], and tables of supplementary data. The supplementary data for both CA and GC modelling teams included the data summarised in Table 4.2, plus characterisation data including mineralogy and chemical composition of the solid phases. The CA modelling teams were additionally provided with an extensive set of U sorption data for kaolinite and ferrihydrite [previously presented in Waite *et al.* (1994) and Payne (1999)]. The CA modelling teams were also encouraged to utilise any other sorption data for uranyl on substrates that they considered were relevant. The modelling teams were also provided with data on the chemistry of Koongarra groundwaters, and access to various other data collected during the natural analogue project. The modelling instructions and nomenclature for models are summarised in Table 4.3.

In both CA and GC approaches, the modellers were requested to extend their sorption models to describe other solid phases and (in particular) a range of chemical conditions, including higher  $p\text{CO}_2$ , various ionic strengths and total U concentrations. These “extrapolation” exercises were expected to test the transferability of the models and the validity of their underlying assumptions.

It is important to emphasise that the exercise was not a competition to identify the modelling team that produced the “best” model. The twelve modelling teams varied in terms of their experience, modelling philosophy, computer codes, resources and time dedicated for the task. It was recognised that there could be valuable lessons from mistakes or unprofitable modelling decisions. For this reason modelling teams were encouraged to submit all outcomes, with the aim being to learn from the shortcomings that could become apparent from individual modelling efforts. Thus, the exercise aimed to compare the modelling approaches and learn from both successes and failures of models.

Table 4.3: **Summary of modelling as implemented in the CA and GC approaches. Note that Model A is the baseline model for inter-comparison purposes in discussing both GC and CA modelling**

Component additivity (CA)	Generalised composite (GC)
<b>Model 0.</b> Predictive model for Koongarra W2 materials based on sorption behaviour of component minerals	
<b>Model A.</b> Improved model for W2 sample with parameter adjustment or optimisation.	<b>Model A.</b> Model for U sorption on Koongarra W2 material, optimised to fit the sorption data.
<b>Model B.</b> Model for W1 sorption data. Based on model A, scaled if desired according to properties of W1 sample. Preferably, without re-optimisation of model parameters.	<b>Model B.</b> Model for W1 sorption data. Based on model A, scaled if desired according to properties of W1 sample. Preferably, without re-optimisation of model parameters.
<b>Model C.</b> Model for W7 data. Similar to Model B.	<b>Model C.</b> Model for W7 data. Similar to Model B.
<b>Model D.</b> Model for W2c data. Similar to Model B.	<b>Model D.</b> Model for W2c data. Similar to Model B.

### 4.3 Model descriptions

#### 4.3.1 Modelling strategies

A diverse range of modelling approaches was used in this test case (see Table 4.4). Note that the model teams are referred to by the letters “a-m”. Teams “a” to “e” were the GC teams and the remaining teams used the CA approach. The selected computer codes were mostly versions of either Fiteql or Phreeqc. The choice of electrical double layer model was almost entirely the diffuse layer model (DLM). This underlines the attractiveness of this simple model as popularised by Dzombak and Morel (1990) and others. The similar computer codes and double layer models mean that these factors can generally be excluded as factors determining the differences in modelling outcomes.

Table 4.4a: **Summary of modelling approaches – GC teams**

Team	a	b	c	d	e
Code	PhreeqcC	Fiteql2	PhreeqcC	PhreeqcC	PhreeqcC
EDL	DLM	DLM	DLM	DLM	DLM
Extra Ligands <sup>1</sup>	PO <sub>4</sub>			SiO <sub>4</sub> , SO <sub>4</sub>	PO <sub>4</sub> , F
Sorbing sites <sup>2</sup>	Fe <sub>w</sub> , Fe <sub>s</sub> Ka, Mu	Fe Ka	Fe	Fe <sub>w</sub> , Fe <sub>s</sub>	Fe <sub>w</sub> , Fe <sub>s</sub>

Table 4.4b: **Summary of modelling approaches – CA teams**

Team	f	g	h	j	k	l	m
Code	Fiteql Minteqa2	PhreeqcC	PhreeqcC	In-house	Fiteql4	Harphrq	Geochem · workbenc h
EDL	DLM + NEM	DLM	DLM + NEM	DLM	DLM	DLM	DLM + NEM
Extra Ligands1					PO4		
Sorbing sites2	Few, Fes Kaw, Kas	Few, Fes	Few, Fes Kaw, Kas	Fe Ka	Few, Fes	Few, Fes Kaw, Kas	Few, Fes

<sup>1</sup> Ligands in addition to hydroxyl, carbonate and nitrate (considered by all teams).

<sup>2</sup> Fe-oxide(Fe), Kaolinite(Ka), Muscovite(Mu). Subscripts denote weak (w) and strong (s) sites.

Some modelling teams chose to include ligands such as phosphate in their models. Although phosphate was not added to the experiments or measured, it is reasonable to expect it to be present. Phosphate is a component of the solid phase samples, and is present in measurable concentrations in Koongarra groundwaters. Indeed, the importance of phosphate in the Koongarra systems has been pointed out by Yanase *et al.* (1994). This points out a deficiency in the supplied datasets – a potentially important ligand was not adequately characterised in the experimental data. One modelling team (Team “d”) included silicate. Silicate may be present in the experiments by dissolution of silica containing minerals.

#### 4.3.2 *Aqueous and surface species*

The uranyl speciation in pure NaNO<sub>3</sub> systems exposed to the atmosphere comprises a series of uranyl hydroxo complexes and uranyl carbonate complexes (see Grenthe *et al.*, 1992). As noted above, a standard set of aqueous uranyl thermodynamic data was utilised by all modelling teams. Therefore, there were few significant differences between the aqueous speciation computed by the various modelling teams.

However, some modelling teams assumed that significant aqueous concentrations of ligands such as phosphate were present. Consequently, the computed aqueous speciation differed slightly for these modelling teams. However, the aqueous phosphate complexes only comprised a small fraction of the total uranyl species. The main effects of ligands were on the suite of surface complexes chosen

for modelling, the presence of competitive sorption reactions involving these ligands, and the effects of the sorbing ligands on surface charge.

The major areas of differences between the CA and GC modelling approaches were in the selection of the surface species (Table 4.5). Although GC models are typically characterised by generic sites, three of the GC approaches used a monodentate Fe sorption site (Fe-O-UO<sub>2</sub>). In contrast, all of the CA teams included bidentate Fe sorption sites (Fe-O<sub>2</sub>-UO<sub>2</sub>) on the Fe-oxide surface. This can be traced to the fact that the CA teams utilised (and modelled) the supplied set of ferrihydrite sorption data. These teams appeared to incorporate a previous model for U sorption on ferrihydrite that utilised bidentate surface complexes (Waite *et al.*, 1994), which was developed on the basis of spectroscopic evidence (EXAFS).

The approach of modelling Team a resembled a CA model in many ways. Although the modelling team was assigned to the GC group, they used a component model for muscovite which they assumed to play a significant role in the complex sample (see Table 4.4), as well as incorporating kaolinite type sites and a bidentate Fe-site. Although it could be argued that this approach should be considered to be a CA model, the “active proportions” of both goethite and muscovite were optimised to fit the sorption data. Therefore, the site populations were chosen to fit the data. With this degree of fitting, this approach is more appropriately categorised as a GC approach.

There is generally a greater number of surface complexes in the CA models compared to the GC models (Table 4.5). Five of the seven CA teams had more than five surface species. In contrast, only one of the five GC teams had more than five surface species (this was Team a, which used a combined CA/GC approach (mentioned above) with 9 surface complexes). The higher number of species in the CA models appears to be related to the number of surface complexes in the component models in the CA approach. These extra species are carried across into the final model for the complex materials, although in some cases they may not play a significant role in the computed surface speciation.

The GC teams were apparently hesitant to employ entirely generic sorption sites (e.g. with general identifiers such as types “x” or “y”). All these teams visualised that the sorbing sites included a site described as an “Fe” surface site, which implies some type of Fe-oxide surface. This reveals a reluctance of GC modellers to use a totally “black-box” approach to site designations (i.e. with no pre-determined concepts of surface sites), or a lack of familiarity with developing a model with generic sites. However, it should be noted that in the modeller’s minds the “Fe” terminology may have functioned largely as a “label” rather than being associated with a particular sorption site. This is indicated by the fact that most of the GC teams modelled the Fe-site as monodentate whereas the CA teams (which assumed ferrihydrite as a significant role) used only bidentate species. The monodentate site is possibly the simplest initial assumption to develop a GC model, unless prior knowledge of U surface co-ordination is utilised.

Table 4.5: **Surface species in U sorption models**

	Modelling team											
	a	b	c	d	e	f	g	h	j	k	l	m
	Top-down (GC)					Bottom-up (CA)						
<b>Fe – bidentate</b>												
FeO <sub>2</sub> UO <sub>2</sub>	y (w,s)				y (w,s)	y (w,s)	y (w,s)	y (w,s)	y	y (w,s)	y (w,s)	y (w,s)
FeO <sub>2</sub> UO <sub>2</sub> CO <sub>3</sub> <sup>2-</sup>	y (w,s)				y (w,s)	y (w,s)	y (w,s)	y (w,s)	y	y (w,s)	y (w,s)	
FeO <sub>2</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>4-</sup>									y		y (w,s)	
Fe(OH <sub>2</sub> ) <sub>2</sub> UO <sub>2</sub> (HPO <sub>4</sub> ) <sub>2</sub>					y (w)							
FeO <sub>2</sub> UO <sub>2</sub> PO <sub>4</sub> <sup>3-</sup>	y (w,s)											
<b>Fe – monodentate</b>												
FeOHUO <sub>2</sub> <sup>2+</sup>		y	y									
FeOUO <sub>2</sub> <sup>+</sup>			y	y (w,s)								
FeOUO <sub>2</sub> OH			y									
FeOUO <sub>2</sub> CO <sub>3</sub> <sup>-</sup>		y										
FeOH <sub>2</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup>			y									
FeOH <sub>2</sub> UO <sub>2</sub> PO <sub>4</sub>										y (w,s)		
<b>Kaolinite</b>												
KaOUO <sub>2</sub> <sup>+</sup>						y (s)	y (w,s)	y		y (w,s)		
KaOUO <sub>2</sub> OH	y	y				y (w)						
KaOUO <sub>2</sub> CO <sub>3</sub> <sup>-</sup>						y (s)	y (w,s)	y		y (w,s)		
KaOUO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>3-</sup>								y				
<b>Muscovite</b>												
MuO <sub>2</sub> UO <sub>2</sub>	y											
MuOUO <sub>2</sub> <sup>+</sup>	y											
<b>Total</b>	<b>9</b>	<b>3</b>	<b>4</b>	<b>2</b>	<b>5</b>	<b>7</b>	<b>4</b>	<b>8</b>	<b>6</b>	<b>6</b>	<b>10</b>	<b>2</b>

### 4.3.3 Site densities and populations

The site density of each type of surface site is an important component of the modelling. It determines the total number of each site type available for sorption, and thus determines the saturation behaviour (i.e. the amount of sorbed species required to fully populate each site). As the equilibrium constants for sorption reactions are directly related to site density, the transfer of log K values from one model to another with a differing site density is a common modelling error. For these reasons,

both the numerical values and the sources of the site density used in the models are worth close examination. The values of these parameters are summarised in Table 4.6.

Many of the models have a few micromoles of high affinity sites, although modelling teams “c” and “j” did not utilise high affinity sites. As discussed in later sections, these models differentiated themselves from other models for some types of experimental data and this is related to their in-built choice of site-densities.

Some models had very low populations ( $<0.5 \mu\text{mol/L}$ ) of particular site types (e.g. models “a” and “l”). In some cases the number of a few specific sites is significantly lower than the U content in these experiments ( $3.9 \mu\text{mol/L}$ ). These sites are present because they were carried across from U sorption models for component minerals. Possibly these may not play a significant role except at low U concentrations. This raises the possibility of model simplifications. Although modelling Team a was considered GC, the carrying across of site densities from a component mineral shows that the model character was also partly CA.

Table 4.6 shows that many of the total site densities or ratios of weak to strong sites can be traced to component models. For example, the w/s ratio of  $\sim 40$  in models “a”, “e” and “m” is the same as recommended by Dzombak and Morel (1990) for hydrous ferric oxide (HFO). This reflects common assumptions derived from this popular model. Similarly, the w/s ratio of  $\sim 480$  found in several models is the same value as the Waite *et al.* (1994) model for U sorption on ferrihydrite. These two models are among the major source models presently available in the literature. The adoption of these values infers a preference of modellers to assume similar values, even when models are implemented partly by the GC approach. A complete GC approach would not be constrained by these types of assumptions.

The total site densities used in the sorption models can be determined by adding all surface site types (expressed as  $\mu\text{mol/m}^2$  in Table 4.6). As summarised in Figure 4.1, these total densities cluster into three groups. In the first (and lowest) group, two GC modelling teams used data-fitting to obtain a site density of 0.2 to  $0.3 \mu\text{mol/m}^2$ . This density is lower than either the average site density recommended by Dzombak and Morel ( $3.84 \mu\text{mol/m}^2$ ) or the density utilised by Waite *et al.* (about  $16.4 \mu\text{mol/m}^2$ ). A large group of seven teams utilised total site densities similar to (but slightly lower than) Dzombak and Morel’s value. Finally three CA teams (basing their models on ferrihydrite) used much higher site densities, similar to the Waite *et al.* (1994) value. It appears significant that the teams that used site density as a fitting parameter obtained optimised values significantly below the densities recommended for ferrihydrite by previous authors. This may suggest that surface site densities on these natural materials may be much lower than for ferrihydrite.

Table 4.6: **Surface sites utilised in the baseline model A (numerical values refer to W2 sample, 4g/L loading). For these experiments, the total uranium concentration was 3.9  $\mu\text{mol/L}$**

Team	Site	Conc. ( $\mu\text{mol/L}$ )	Source #	Total sites ( $\mu\text{mol/L}$ )	Total site density ( $\mu\text{mol/m}^2$ )
<b>h</b>	Fe <sub>w</sub>	5.10	Fitted	71	0.34
	Fe <sub>s</sub>	0.13	Assumed w/s ratio (~40)		
	Ka	65.30	Estimated from composition		
	Mu	0.46	Fitted		
<b>b</b>	Fe	3.3	Fitted	353	1.69
	Ka	350.0	Fitted		
<b>c</b>	Fe	622.0	Estimated from SA	622	2.97
<b>d</b>	Fe <sub>w</sub>	35.0	Fitted	37	0.17
	Fe <sub>s</sub>	1.5	Fitted (resulting w/s is ~23)		
<b>e</b>	Fe <sub>w</sub>	305.0	Estimated from composition	313	1.49
	Fe <sub>s</sub>	7.6	Assumed w/s ratio (~40)		
<b>f</b>	Fe <sub>w</sub>	667.0	Est from SA and composition	680	3.25
	Fe <sub>s</sub>	1.4	Assumed w/s ratio (~480)		
	Ka <sub>w</sub>	9.9	Est from SA and composition		
	Ka <sub>s</sub>	2.0	Same w/s as kaolinite model		
<b>g</b>	Fe <sub>w</sub>	529.0	From extractable Fe	530	2.53
	Fe <sub>s</sub>	1.1	Assumed w/s ratio (~480)		
<b>h</b>	Fe <sub>w</sub>	2 940.0	Est from SA and composition	2 950	14.10
	Fe <sub>s</sub>	6.1	Assumed w/s (~480)		
	Ka <sub>w</sub>	6.2	Est from SA and composition		
	Ka <sub>s</sub>	1.2	Same w/s as kaolinite model		
<b>j</b>	Fe	3 920.0	Est from SA using high site density	4 070	19.47
	Ka	154.0	Est from SA		
<b>k</b>	Fe <sub>w</sub>	3 400.0	Est from SA using high site density	3 410	16.28
	Fe <sub>s</sub>	7.1	Assumed w/s ratio (~480)		
<b>l</b>	Fe <sub>w</sub>	309.0	Est from SA and composition	558	2.67
	Fe <sub>s</sub>	0.3	Same w/s as HFO model (~1 000) <sup>#</sup>		
	Ka <sub>w</sub>	247.0	Est from SA and composition		
	Ka <sub>s</sub>	1.2	Same w/s as kaolinite model <sup>#</sup>		
<b>m</b>	Fe <sub>w</sub>	660.0	Est from composition	677	3.23
	Fe <sub>s</sub>	16.5	Assumed w/s ratio (~40)		

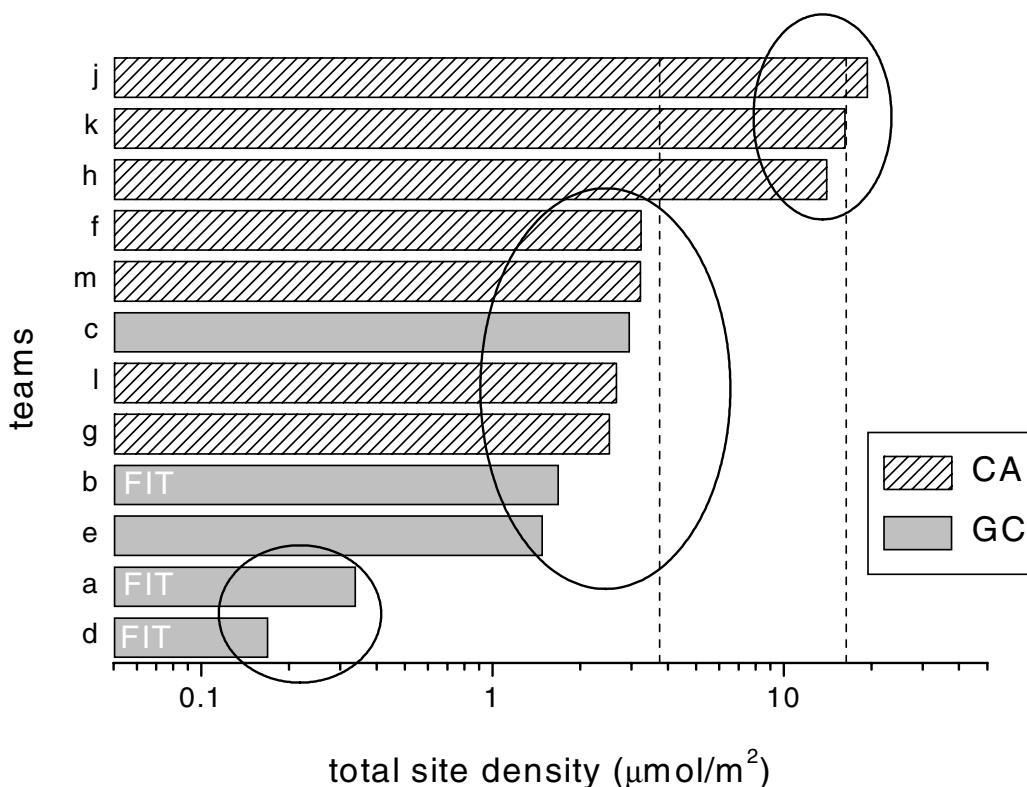
\* w/s – ratio of weak to strong sites, SA = surface area (BET)

<sup>#</sup> Team “l” derived their own models for ferrihydrite (HFO) and kaolinite.

In a similar result Payne (1999) reported that kaolinite behaves as if its active surface site density is about  $0.4 \mu\text{mol}/\text{m}^2$ , in sorption of both U and phosphate. This conclusion was supported by analytical electron microscopy measurements of the distribution of U on the surface of the kaolinite. This suggested that there may be considerably fewer U-sorbing sites on the KGa-1 surface than would be expected on the basis of the BET surface area (if normalised according to the values recommended by the authors cited above).

The site-density estimates are an important part of the modelling. The large range of site-densities used in the sorption models for the W2 materials (nearly two orders of magnitude – Table 4.6) is a major potential source of discrepancy among the modelling teams. This suggests that further work may be required to gain a consensus on the most appropriate values for modelling natural substrates.

Figure 4.1: **The total site densities used by the modelling teams cluster into three groups, two of which approximate the densities employed by Dzombak and Morel (1990) and Waite *et al.* (1994) shown by vertical dotted lines at  $3.84 \mu\text{mol}/\text{m}^2$  and  $16.4 \mu\text{mol}/\text{m}^2$ , respectively. Note that the fitted site densities are lower than either of these values, and the GC densities tend to be lower than the CA densities**



#### 4.3.4 Number of adjustable parameters in baseline model (model A)

In order to undertake a discussion of the numbers of adjusted and optimised parameters in the modelling, it is important to distinguish between parameters that were fitted to the W2 sorption data and those that were estimated from other data such as characterisation data.



For the purpose of this discussion, the number of adjusted parameters in the models is taken to be the number of parameters that were optimised to create the base-line model A for the sorption data on the W2 substrate (refer to the top line in Table 4.7). For the GC teams, this is simply a fit to the W2 sorption datasets.

In the CA case, the teams considered their blind prediction (model 0) and attempted to improve it by parameter adjustment to produce model A. It is important to note that in the CA case, parameters are not considered as optimised *unless* these were re-optimised in order to fit the W2 sorption data to generate model “A”. Some CA modelling teams did this – as shown in Table 4.7. The rationale for this parameter fitting offered by these teams was that the properties of the model substrates in the complex materials differed from the properties of the simple substrates. This strategy indicates the blurring of the distinction between the true CA and GC approaches as implemented by the modelling teams in this project.

As would be expected, all the GC modelling Teams (“a” to “e”) optimised some parameters to fit the U sorption data for the W2 substrate. The number of optimised parameters was either 3 or 5 (Table 4.7).

In contrast to the GC teams, many of the CA modelling teams optimised only 2 parameters to develop a sorption model for the W2 sample. Modelling Teams “f” and “i” did not adjust any parameters to develop model A. Instead, they used the same parameter values as for the simple substrates (kaolinite, ferrihydrite, etc). However, these teams did modify their assumptions about the relative roles of various surface sites to generate model A from model 0. As noted above, all CA models include parameters that were optimised during the development of sorption models for the simple substrates.

The parameters that were optimised in the modelling are listed in Table 4.8. Mostly log K values for the postulated surface reactions were used as a fitting parameter. In some case the site densities were optimised and the amount of P in the systems was also used as a fitting parameter by some modelling teams.

#### **4.3.5 Method used for extension to other substrates**

This section considers how model A for the W2 substrate was modified in order to develop models B-D for the other substrates. This is important in terms of the performance of the models (accuracy of fit against number of adjustable parameters) as well as the ease of transferability from one substrate to another.

In general, most modelling teams attempted to alter their model for sample W2 (Model A) according to the measured parameters of the solid substrates (Table 4.9). Many of the teams used the BET surface area as the basis for this parameterisation – this approach has been advocated by several authors, for example Bertetti *et al.* (1998).

Some modelling teams utilised the total Fe content or the TAO- or DCB-extractable Fe as a basis for parameterising the models. As shown in Table 4.9, only 2 teams (c and g) used the Fe content data independently of the BET surface area. An important difference between the two approaches was that Team c visualised the entire Fe content as behaving similarly to goethite whereas Team g used the extraction data to estimate the amount of ferrihydrite in the sample. This latter approach was based on the assumption that the TAO extractable Fe-content would be the best indicator of the amorphous Fe content (ferrihydrite) with its assumed dominant role in U sorption. As will be later shown, these assumptions had implications for the transferability of the models. The

approach of Team c again demonstrates a merging of CA and GC approaches, because of the scaling related to Fe content and its assumption of being like goethite.

Table 4.7: **Number of optimised parameters in the models**

	GC teams					CA teams						
	a	b	c	d	e	f	g	h	j	k	l	m
<b>Number of optimised parameters (model A)</b>	3	5	3	5	3	0	2	2	2	2	0	2
<b>Re-optimised parameters (models B-D)</b>	3	0	0	2	1*	0	0	0	2	2	0	0

\*an additional parameter was optimised to fit the U sorption data at high ionic strength

Table 4.8: **Parameters optimised in model A (W2 sample) and models B-D (W1, W7, W2c substrates)**

<b>Parameters optimised during modelling of W2 sample (model A).</b>		
<b>Team</b>	*	<b>indicates parameter(s) were re-optimised to fit each individual substrate (models B-D).</b>
<b>a</b>	*	Proportions of 2 minerals (goethite and muscovite)
	*	Aqueous phosphate was fitted to sorption data.
<b>b</b>		Site densities for 2 sites (ferrinol and aluminol) Log K for 3 sorption reactions.
<b>c</b>		Log K for 3 sorption reactions.
<b>d</b>		Log K for 3 sorption reactions.
	*	Site densities for 2 sites (strong and weak).
<b>e</b>		Log K for 2 sorption reactions
	*	Aqueous phosphate was fitted to sorption data.
<b>f</b>		None
<b>g</b>		Log K for 2 sorption reactions.
<b>h</b>		Log K for 2 sorption reactions.
<b>j</b>	*	Log K for 2 sorption reactions.
<b>k</b>	*	Log K for 1 sorption reaction
	*	Aqueous phosphate was fitted to sorption data.
<b>l</b>		None
<b>m</b>		Log K for 2 sorption reactions.

Table 4.9: **Methods used to generate simulations for W1, W7 and W2c substrates (models B, C, D) by modifying the baseline model “A”. Note that ‘re-fitted’ means optimisation to fit the U sorption data for each substrate whereas “scaling” implies a calculation based on sample characterisation data**

<b>Team</b>	<b>Method of development of generate models B-D</b>
<b>a</b>	Re-fitted 2 site populations (goethite and muscovite surface sites) and refitted estimate of phosphate.
<b>b</b>	Scaled site concentrations using BET surface area.
<b>c</b>	Scaled site concentrations using Fe content (assumed to represent goethite).
<b>d</b>	Re-fitted 2 site densities (strong and weak).
<b>e</b>	Scaled site populations with BET area and optimised phosphate.
<b>f</b>	Scaled site populations using BET surface area.
<b>g</b>	Scaled site populations using TAO- and DCB-extractable Fe-content.
<b>h</b>	Scaled site populations using BET surface area.
<b>j</b>	Scaled site populations using BET surface area and re-fitted log K’s for 2 sorption reactions.
<b>k</b>	Scaled site populations using BET surface area and re-fitted one log K and amount of phosphate.
<b>l</b>	Scaled site populations using BET surface area and Fe contents.
<b>m</b>	Scaled site populations using the BET surface area.

#### **4.4 Modelling results and discussion**

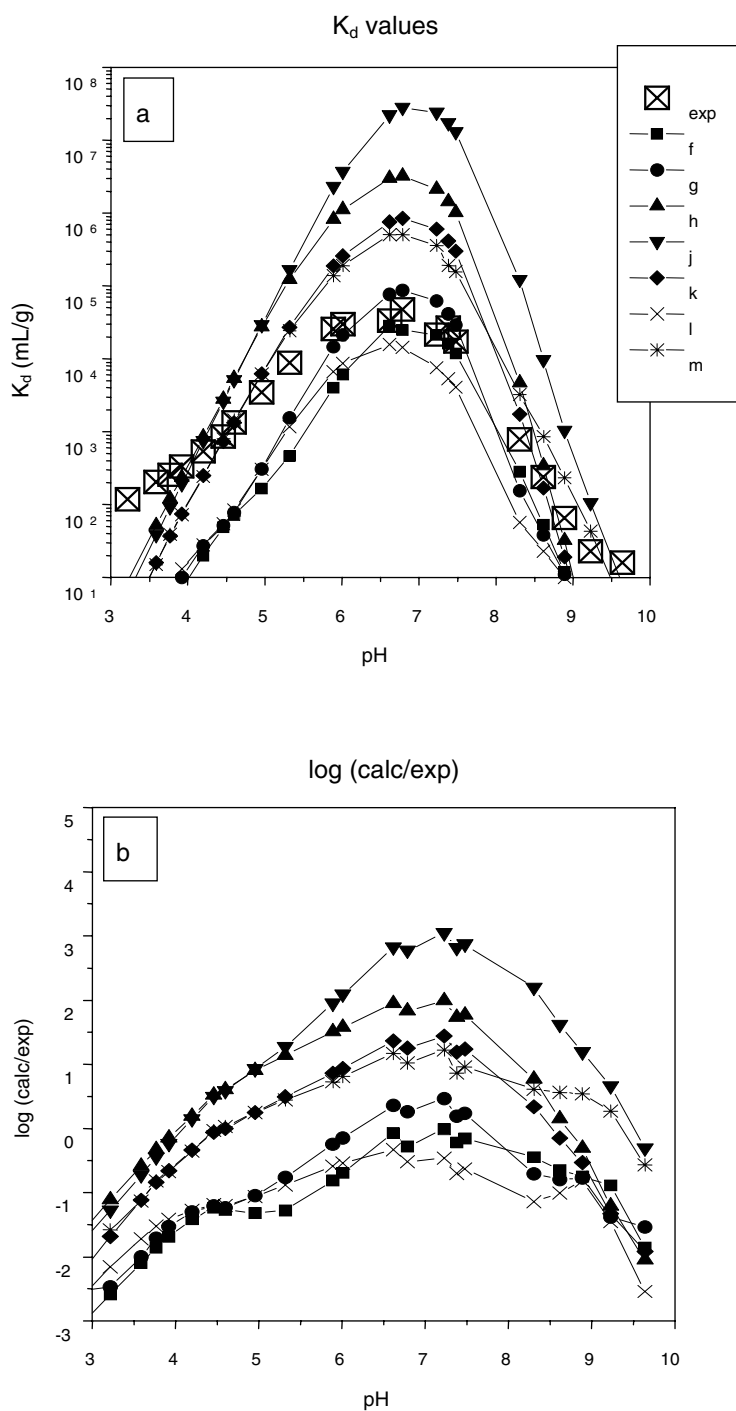
In this section, the modelling results for the various aspects of the modelling exercise are described. Unless otherwise noted, the modelling described below was undertaken by both the CA and GC modelling teams.

##### **4.4.1 Initial predictions without parameter adjustment (CA approach – Model 0)**

The modellers using the component additivity approach were requested to develop a model for U sorption on the Koongarra materials. This was denoted model 0 (see Table 4.3). These initial models were based on prior models developed for sorption data for uranyl on ferrihydrite, kaolinite, or other mineral phases, which were assumed to play an important role in the Koongarra materials. (This part of the modelling was not undertaken in the GC approach, which is by definition a fitting exercise).

The “Model 0” was predictive in that the modellers were requested to develop a model without reference to the reported sorption data on the Koongarra material. However, the modellers were aware of the experimental results and therefore the outcomes cannot be considered to be “blind” predictions. (A “blind-prediction” exercise was not possible because most of the sorption data used in this test case was previously published in the open literature).

Figure 4.2: **Experimental data and model predictions for uranyl sorption on sample W2 expressed as a)  $K_d$  vs pH and b) ratio of calculated to experimental  $K_d$  vs pH. Modelling predictions are for the component additivity approach without optimisation (Model 0)**



A detailed analysis of the models for the component minerals is beyond the scope of this chapter. However, the modelling teams were generally able to adequately model the U sorption data for ferrihydrite. This model invariably formed a major component of the models for the Koongarra W2 samples. As indicated in Tables 4.5 and 4.6, many of modelling Teams (i.e. f, g, h and k) used the Waite *et al.* (1994) model for U sorption on ferrihydrite, in some cases with minor changes to the basic model. This can be verified by the existence of key aspects of this model in the final models, for example in terms of the ratio of weak to strong sites (Table 4.6). The model of Team l was very similar, except parameterised slightly differently, in that the estimated values of some key parameters were re-derived.

The ferrihydrite model developed by Team m was based on the approach of Dzombak and Morel (1990). The key distinctive features of this model for ferrihydrite included the lower site density (see discussion above), and the assumed importance of both strong and weak sites. Unlike all other CA teams, no ternary uranyl carbonate surface complex was present in this model.

Model Team j produced a totally different model to the other CA models. This team developed a simple one-site model for ferrihydrite with an in-house code. They assumed sorption of two ternary uranyl-carbonate surface complexes. The model for the Koongarra W2 sample included a second site on a kaolinite surface. Their model 0 was therefore a two-site model, with the highest site density of all models (Table 4.6).

The modelling outcomes for this prediction exercise are summarised in Figure 4.2a. There was a tendency for the predictive models to over-estimate the sorption maximum for the central pH range, in some cases (e.g. model “j”) by as much as three orders of magnitude. Some models exhibited a lower discrepancy near the pH of maximum sorption, but these models substantially under-estimated sorption in the lower pH range (models f, g, l). The models which most greatly over predicted sorption had the highest site densities (i.e. models h, j, k – compare Table 4.6 with Figure 4.2a).

The trend shown in the error graph (Figure 4.2b) clearly exhibits a distinct curved shape with a peak around pH 7 for all models. This reveals a systematic error distribution, which enables some of the possible sources of discrepancy between model and experimental data to be assessed. It shows that the problem is not only one of parameterisation (i.e. the values selected for adjustable parameters). It suggests that either 1) the component minerals proposed as playing a substantial role in the Koongarra system may not be sufficient as a basis for a sorption model on the combined substrate, or 2) the component minerals have different properties in the Koongarra system than they had when studied in pure form in simple electrolyte solutions. As an example of 2), consider that the ferrihydrite in the Koongarra system likely had sorbed silicate, phosphate, and organic acids, each of which could change the EDL properties and reactivity of the phase with respect to U(VI) sorption.

A comparison between the experimental U sorption data on the W2 material and the simple ferrihydrite and kaolinite mineral phases is shown in Figure 4.3 (the experimental conditions for the experiments in this comparison are given in Table 4.10). Examination of Figure 4.3 shows that both the magnitude and the slope of the U sorption edge on the Koongarra W2 material is more similar to kaolinite than to ferrihydrite. This comparison indicates that minerals other than ferrihydrite probably contribute substantially to their sorption behaviour of the W2 sample. It is remarkable that at least one of the models predicts that U sorption on the Koongarra W2 material is much stronger than pure ferrihydrite (model j in Figure 4.2a), with a maximum  $K_d$  exceeding  $10^7$  mL/g. This model prediction is difficult to explain, even after allowing for the very high site density which was employed.

Some of the shortcomings in model 0 may be ascribed to the fitting of the sorption edges using FITEQL and similar codes. These models tend to fit based on percentage sorption, which tends to reduce the accuracy of  $K_d$  predictions at high sorption. This is illustrated by Figure 4.2, where the maximum is substantially over-predicted.

Figure 4.3: Comparison of U sorption data for the Koongarra W2 sample with comparable data for simple mineral materials provided to the CA modelling teams. Background electrolyte was 0.1 M  $\text{NaNO}_3$ . A summary of some other experimental conditions is given in Table 4.10

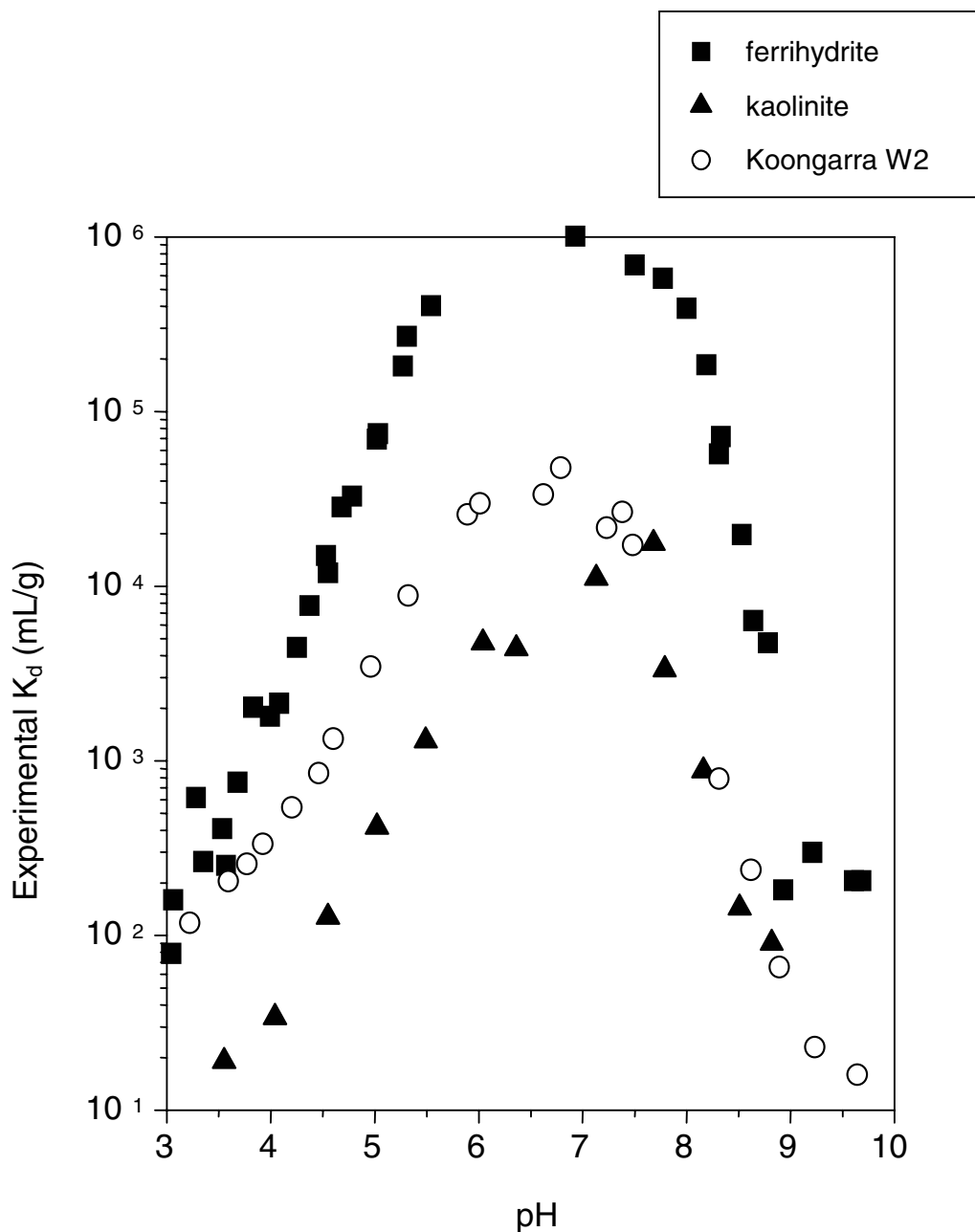


Table 4.10: Summary of experimental conditions for data shown in Figure 3

	<b>Kaolinite (KGa-1)</b>	<b>Ferrihydrite</b>	<b>Koongarra W2</b>
Mass loading	4 g/L	0.089 g/L	4 g/L
Total U	1 $\mu\text{mol/L}$	1 $\mu\text{mol/L}$	3.9 $\mu\text{mol/L}$
Surface area	46.8 $\text{m}^2/\text{L}$	53.4 $\text{m}^2/\text{L}$	209.2 $\text{m}^2/\text{L}$

#### 4.4.2 Model optimisation for W2 sorption data (model A)

In developing the baseline model A, both the CA and GC teams were directed to produce a model which fitted the data adequately, where necessary optimising parameters. It should be noted that the modellers were requested to simultaneously fit several datasets (discussed below) which are presented in separate figures.

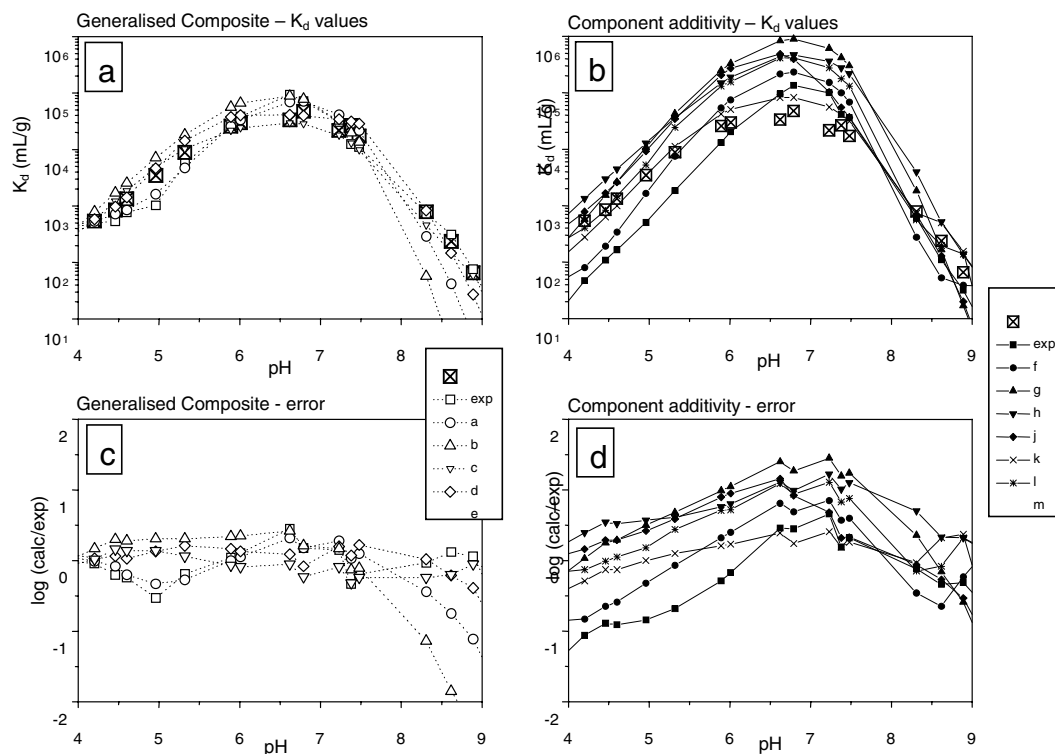
The GC model provided a good simulation of the W2 dataset (shown in Figures 4.4a and 4.4c). There are only minor discrepancies between the model and experimental data, with significant deviation only apparent at relatively high pH values. The error distribution curve (Figure 4c) shows little systematic error.

Comparison of Figure 4.4b with Figure 4.2a shows that the model A produced by the CA teams considerably improved the simulation of the W2 data (relative to the predictive model “0”). Teams f and l modified only the assumptions about the proportions of the active minerals (i.e. kaolinite and ferrihydrite), whereas all the other teams improved their models by fitting log K values and in one case (Team k) fitting the assumed aqueous phosphate concentration (Table 4.8). These modifications made the CA models much improved relative to the predictive model 0. Nonetheless, the error curve (Figure 4.4d) shows some residual systematic discrepancies, with an upward hump being generally discernible. This reveals the problems associated with scaling the models to fit the data are not totally eliminated by adjustment of parameter values.

In general, the comparison between the GC and CA approaches (Figure 4.4a and 4.4b) indicates that the GC modellers were able to fit the data better, with the average error usually well within a factor of 10 over the pH range 4 to 8.5 and no apparent systematic errors. In comparison, there is a distinctly curved shape with a peak around pH 7 in the error distribution of the CA models (Figure 4.4d) and all of the CA models over-predict sorption in the neutral pH range. It might be considered that the discrepancy in this part of the pH range could be improved by adjusting the log K values for the sorption reactions. However, the CA modellers may have been hesitant to do this because the fit criteria (discussed in section 3.2.2, Part 1) required less than an order of magnitude discrepancy across the full pH range. Many of the CA modellers chose to settle for a relatively poor fit in the central pH range in order to satisfy this criteria across a wider pH range (despite the fact that the neutral pH range it is arguably more important than the pH extremes in the “real world”).

This raises an important aspect of this modelling exercise, that the provision of data across a wide pH can lead to a focus on pH extremes, which are probably less relevant to performance assessment. Furthermore, the processes occurring at these pH extremes may be dissimilar to those in the mid pH range, perhaps involving mineral dissolution. As a result, the data and models may be of limited value in these pH regimes. These shortcomings must be balanced against the fact that performance across a wide range of conditions could provide a rigorous test of the models (in the absence of processes, such as dissolution, that may confound interpretation).

Figure 4.4: **Models for the W2 (equilibrated with air) data with model optimisation by parameter refinement. Data are for both CA and GC approaches, presented in both predicted vs experimental  $K_d$  and ratio format (denoted model A)**



#### 4.4.3 Experiments with elevated $p\text{CO}_2$

The dataset provided in the experiments with elevated  $p\text{CO}_2$  (1%  $\text{CO}_2$  rather than air) was simulated by both GC and CA modelling teams, using model A without alteration from the model used for the W2-air data (discussed in the previous section).

In the GC case, the models showed a slightly greater spread relative to the experiments equilibrated with air (compare Figures 4.5 and 4.4). Overall, there is a good simulation of the data with acceptable error values and a similar error distribution to that observed with the air dataset.

The simulation of the elevated  $\text{CO}_2$  data by the CA models was again less satisfactory than the GC modelling. Figure 4.5d shows a curved error distribution, revealing some systematic errors within each model. One model (model “j”) seems to consistently over-predict sorption. This is one of the simpler models and incorporated only two surface sites with high site densities.

It is important to appreciate the influence of increased  $\text{CO}_2$  on the experimental data. As shown in Figure 4.6, there is no discernible effect of  $\text{CO}_2$  on the low pH edge (experimental  $K_d$  results are similar to data obtained in air up to about pH of 6). However, at higher pH values, the presence of elevated  $\text{CO}_2$  significantly decreases U sorption. The maximum  $K_d$  values occur at a lower pH relative to air and the high pH “desorption” edge is displaced to the left (lower pH) by about one pH unit.

In terms of their ability to simulate the experimental data both with and without elevated  $\text{CO}_2$ , it is apparent that the GC models are quite successful (Figure 4.6). The decrease of U sorption in



the presence of CO<sub>2</sub> at high pH values is fairly well predicted by all GC models. At the same time, there is no change in the position of the low pH sorption edge.

The CA models correctly predict the movement of the high pH edge to the left in the presence of elevated CO<sub>2</sub> (Figure 4.6b). However, the scatter in the models is much greater than the CA models and, to some extent, this obscures the effect of the CO<sub>2</sub>. Overall, both the positions of the sorption maximum and the closeness of the models to the experimental data are much less satisfactory than in the GC case. As noted above, model “j” provides a relatively poor simulation of the data. It also incorrectly predicts a significant increase of U sorption on the W2 material in the vicinity of the low pH edge. In general, the other models simulate the data on the high pH edge slightly better than the lower pH edge, which is subject to considerable scatter.

Figure 4.5: **CA and GC models for the W2 data (equilibrated with 1% CO<sub>2</sub>) with optimisation by parameter refinement (denoted model A). Data are presented in both predicted vs experimental K<sub>d</sub> and error ratio format**

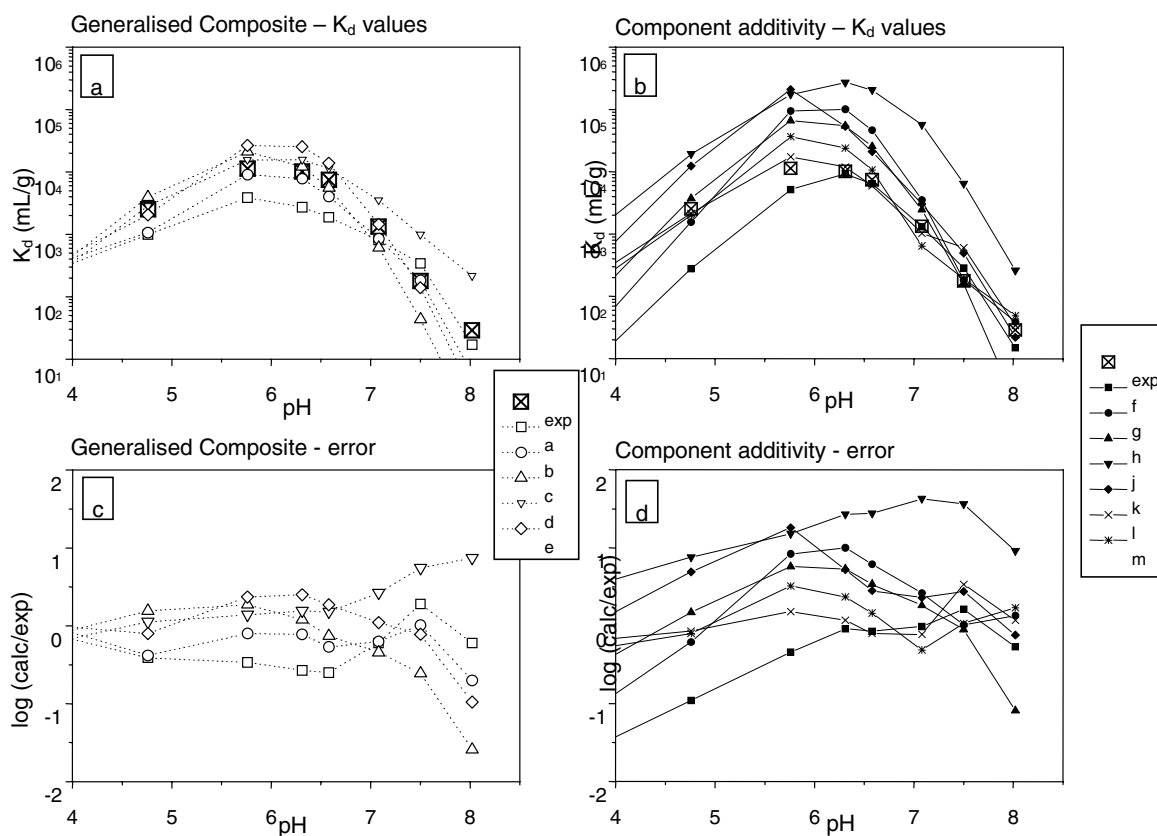


Figure 4.6:

Comparison of CA and GC model outcomes in air (closed symbols) and CO<sub>2</sub> (open symbols) with experimental data. Note the general trend in both types of models is to correctly predict the decreased sorption at high pH in the elevated CO<sub>2</sub> conditions. However, the CA models are more scattered. There is a predicted increase in U sorption for lower pH values in model “j” – which has several ternary uranyl carbonate complexes

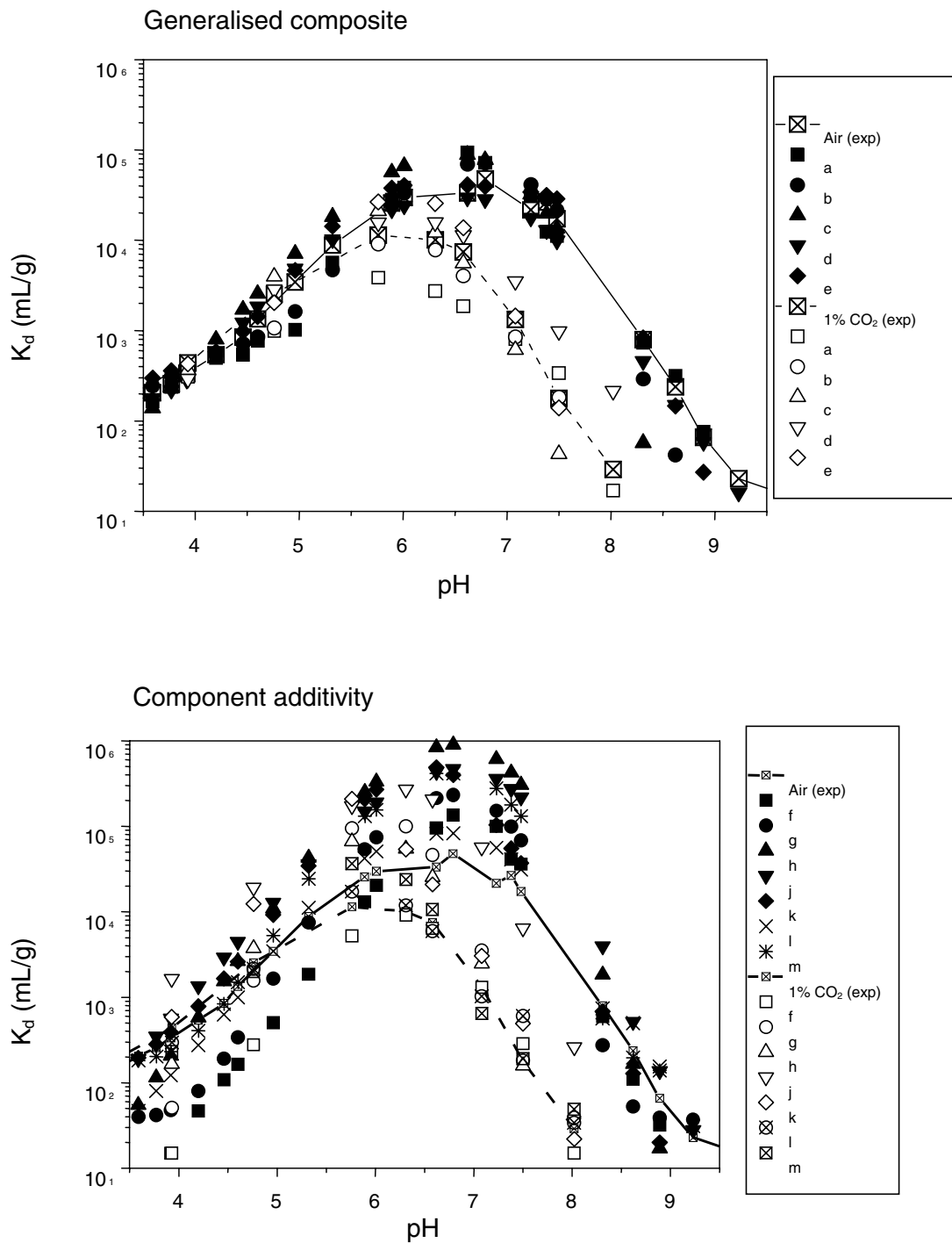
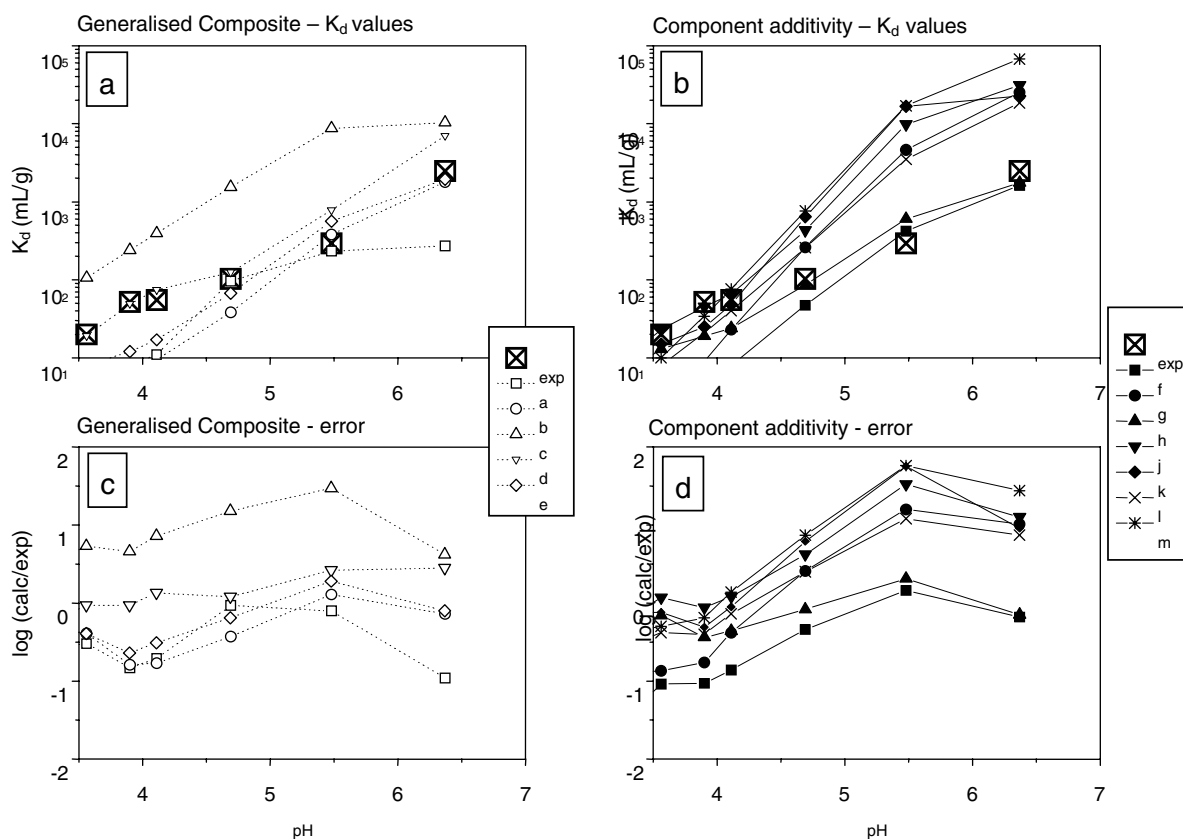


Figure 4.6 demonstrates that both types of SC models are able to predict the approximate scale of decreased sorption with higher  $p\text{CO}_2$ . This ability derives from the models being based on representations of chemical equilibrium. This predictive power is clearly an important positive aspect of the mechanistic SC modelling approach. However, this comparison does indicate that the GC approach performed better at simulating the experimental data.

#### 4.4.4 Experiments with increased total U ( $\Sigma\text{U}$ of 100 $\mu\text{mol/L}$ )

The effect of elevated U on the experimental U sorption data was to decrease the experimental  $K_d$  values. The maximum experimental  $K_d$  in Figure 4.7 is about  $10^3$  mL/g compared to above  $10^4$  mL/g in the data given in Figure 4.4. In a qualitative sense, this can be attributed to increasing site saturation. As the amount of U in the system increases, the high-affinity sorption sites become fully occupied, and the low affinity sites play a greater role. This decreases  $K_d$  values in the experiments with a high total U concentration. The objective of this part of the modelling exercise was to ascertain the degree to which this behaviour is adequately simulated by the sorption models.

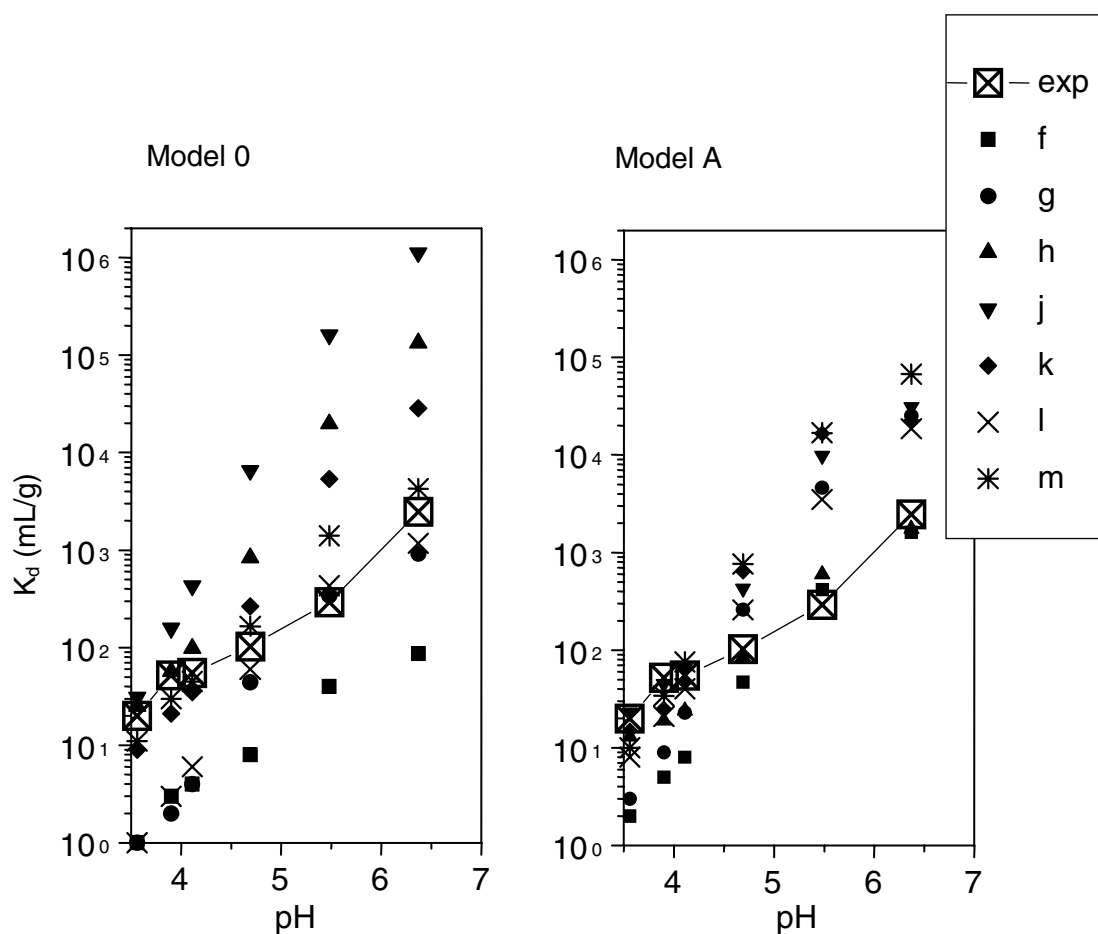
Figure 4.7: **Models for the W2 data (high  $\Sigma\text{U}$  experiments) with model optimisation by parameter refinement (model A). Data for both CA and GC approaches, presented in both predicted vs. experimental  $K_d$  and ratio format**



The experimental data and model predictions for the GC models (Figure 4.7a) show that most of the GC models are able to adequately simulate the U-sorption data. The exception is Team c, which utilised a single site model. This type of model is typically unable to simulate non-linear sorption data and significantly over-estimates the sorption in the 100  $\mu\text{mol/L}$  experiments.

The CA models perform less well, with 4 of the 6 over-predicting U sorption across the pH range from 4 to 6.

Figure 4.8: **Effect of model “optimisation” on fit of CA models to high  $\Sigma\text{U}$  sorption data. In general the models fits are improved, however for this dataset the predictive model 0 developed by Team m was actually superior to Model A**



A comparison of the (optimised) model A with the (predictive) model 0 for the CA simulations is shown in Figure 4.8. There is a noticeable improvement for many of the CA teams going from model 0 to model A (compare Figure 4.8b with 4.8a). However the model A of Team m performed worse than model 0 on this dataset. Although the reasons for this are not clear, it may be that the optimisation process which was undertaken across several datasets actually decreased the ability to fit some individual sets of sorption data.

#### 4.4.5 Limited pH range

The GC modelling teams were requested to produce a second model to simulate the U sorption data on sample W2 across a limited pH range of environmental interest. The selected pH range 5 to 8.5, which is the pH range of Koongarra groundwaters. The sorption dataset was a sub-set of the W2 data previously modelled, only including data-points in the required pH range.

The modifications to the models are summarised in Table 4.11. Two of the modelling teams did not consider it necessary to improve the models at all, and the remainder made minor changes including re-derivation of log K for sorption reactions.

In general, the improvements to the model fits were quite minor (Figure 9), and this revealed that the GC models were fairly robust across both a limited and wider pH range.

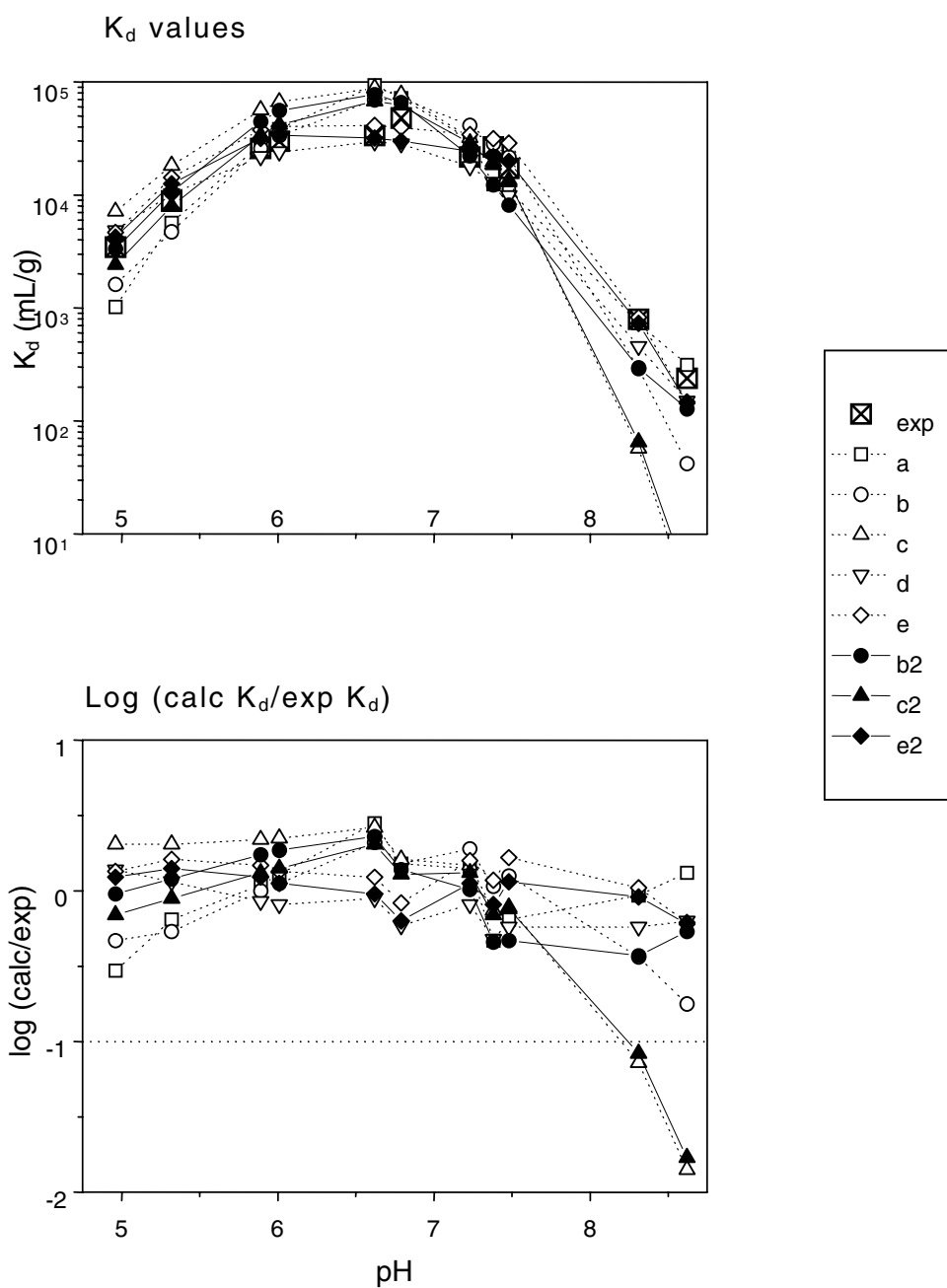
Table 4.11 shows that Team b simply re-optimised their model parameters to obtain an improved fit in the limited pH range. Teams a and d did not consider it necessary to alter their models for the limited pH range, as the model simulation was already adequate. The other two GC teams actually simplified their models in order to simulate the limited pH range. Team c deleted one adsorption reaction whereas Team e found that the numerical value of one constant did not affect the fit of the model, so did not require it to be optimised. This reflects the philosophy of the GC approach – where reactions were not needed, the GC modellers dispensed with them.

The outcome of this part of the modelling would have been entirely different if the limited pH simulation had been undertaken by the CA modelling teams. The CA models had much greater problems in accurately simulating the pH dependence of sorption. As shown by Figure 4.4b, the CA models tended to over-predict sorption in the near neutral pH range. One of the CA teams (Team f) focussed more on the natural pH range and largely disregarded the data for low pH values. The model produced by this team would have required less modification for the limited pH data. [However, it should be noted that the model of Team f was a poor representation of the data at very low pH values (<4.5)]. The other CA modelling teams would have required substantial changes to the sorption models to improve the simulation of the data in the environmental pH range.

Table 4.11: **Summary of changes for simulating the limited pH range experimental data in GC modelling (Teams a-e)**

Team a – No change
Team b – Re-optimised 3 log K, 2 site densities
Team c – Dispensed with one adsorption reaction (SOH-UO <sub>2</sub> <sup>+</sup> )
Team d – No change
Team e – One log K not optimised

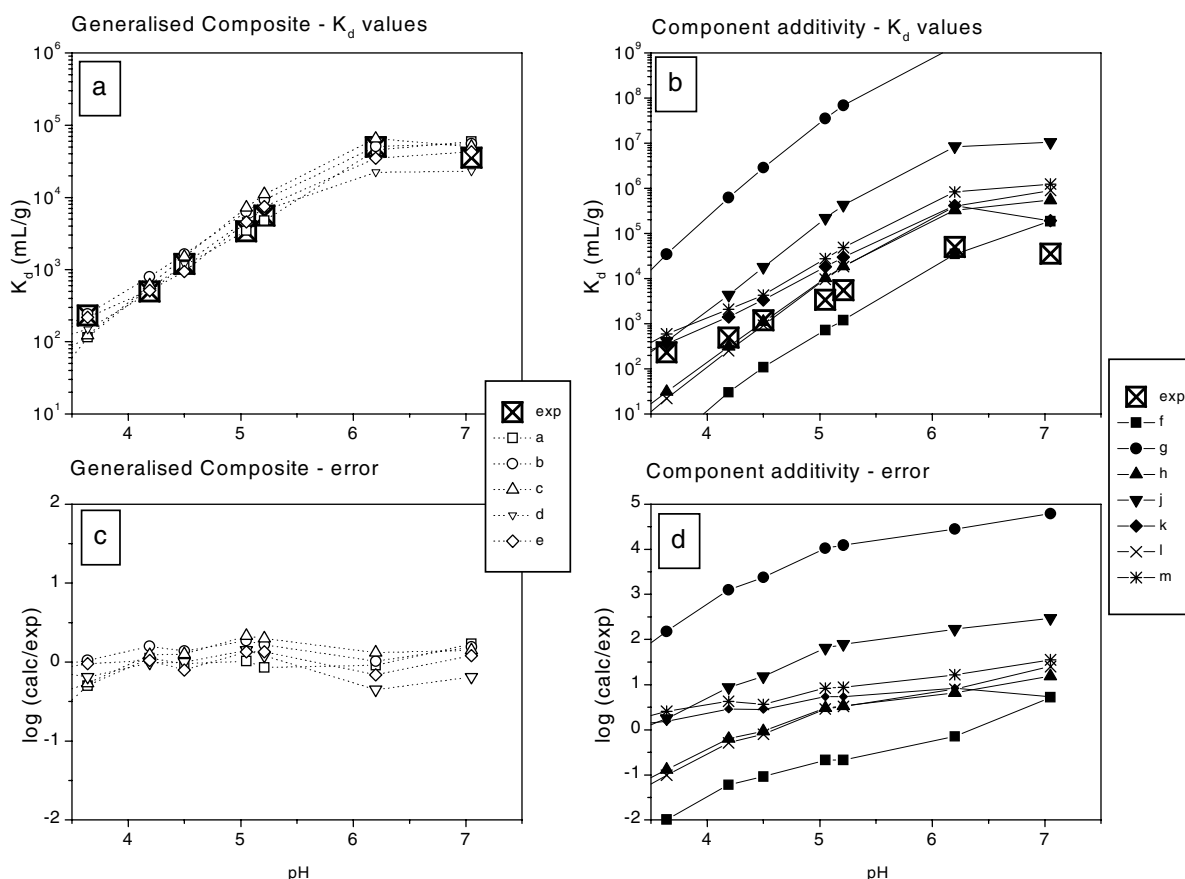
Figure 4.9: **Modelling outcomes for limited pH range exercise in the GC approach. Note that models denoted “b2”, “c2” and “e2” are the revised models for the limited pH range. Teams “a” and “d” did not modify their models**



#### 4.4.6 Extension to other substrates

The extension to other substrates was a test of the transferability of the models. The first case was the substrate referred to as the W1 sample.

Figure 4.10: Model simulations and experimental data for the W1 sample



The results of the GC modelling showed that all of the five GC teams produced an acceptable model for this dataset. (Figure 4.10). As indicated in Table 4.8, all GC teams except b and c re-optimised parameters to achieve this fit.

Of the CA modellers, Team k achieved an excellent fit, but like many of the GC teams they optimised some parameters. The outcome for Team j appears poor, considering that they also re-optimised equilibrium constants for two sorption reactions.

The remaining CA models can be considered to be predictive in the sense that the model was scaled according to the properties of the solid phase, without parameter optimisation. The model of Team f generally under-predicted sorption, particularly at low pH values. This model was noted as being suitable only for the environmental pH range. With the exception of Team g, the other CA teams models fitted the data fairly well. This suggests that scaling the models with the BET surface area provided a reasonable method of developing the CA models for the different substrate.

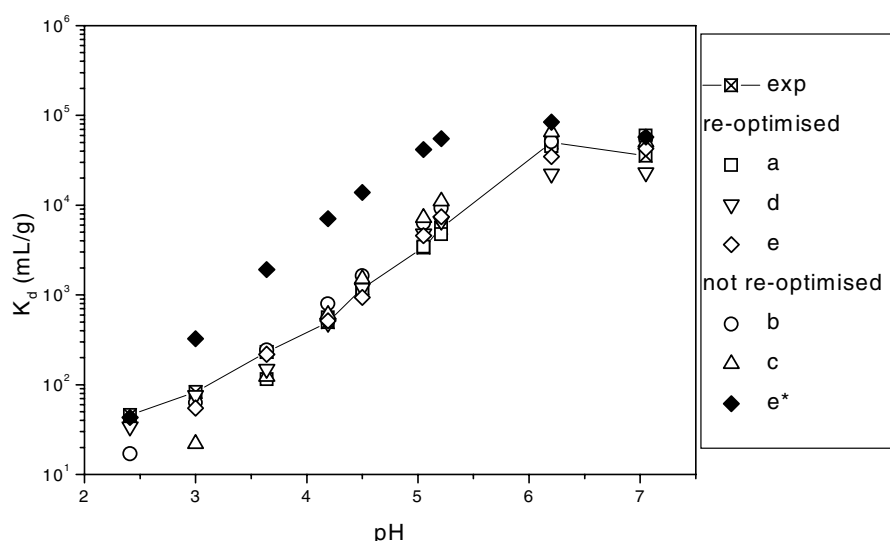
The extremely poor model fit of Team g is instructive. This team assumed that all the TAO and CDB extractable Fe in the W1 sample comprised material with the same surface properties as

ferrihydrate. This led to a complete breakdown of the model with sorption  $K_d$  values being over-estimated by several orders of magnitude. A likely reason for this model failure is that the Fe extracted by the CDB reagent is crystalline and therefore should be representative of minerals such as goethite, which are much weaker adsorbers than ferrihydrate. In keeping with the spirit of this exercise to comment on both successes and failures, we report this outcome, which is useful input for model development exercises. It indicates that chemical extraction results should be approached with extreme caution in developing and extrapolating sorption models. Note that Team c (in the GC group) used the total Fe content to represent goethite surfaces and seemed to obtain a reasonable model.

Team m also reported that the BET area was preferable in extrapolation, although observing that there is a logical inconsistency in using the BET surface area rather than the Fe content to estimate the amount of sorbing surface sites when assuming that ferrihydrate is the sorbing surface. However, the experience of Team g shows that the extractable Fe content is not a good indicator of the sorption behaviour of the sample. There are a number of possible reasons for this conclusion – many of which were raised by the modelling teams. For example:

- BET is a surface technique whereas extraction involves removal of a phase, not all of which may be “seen” by U at the surface.
- The extraction techniques may not actually reflect the amounts of different types of sorbing phases with differing surface properties.
- Other phases apart from Fe minerals likely play a role, for example clay minerals.
- The precise role of Fe minerals is not clearly established. Since Fe may play a blocking role, increased amounts of Fe extracted may not mean greater surface reactivity.
- Although the ferrihydrate may have a very great surface reactivity, it still may not be sufficiently dominant that Fe extraction is an accurate predictor of reactivity.

Figure 4.11: Predictions of GC models divided into models with re-optimisation and those which were scaled according to mineralogical properties



Although the modelling teams were encouraged not to re-optimize parameters to fit the W1 dataset, many of them did. Modelling Team e also provided results showing their fit to the W1 data when the parameter optimisation was not carried out (see Figure 4.11). This shows that for this model, the adequacy of the fit to the W1 sorption data was greatly decreased when the model was used in a

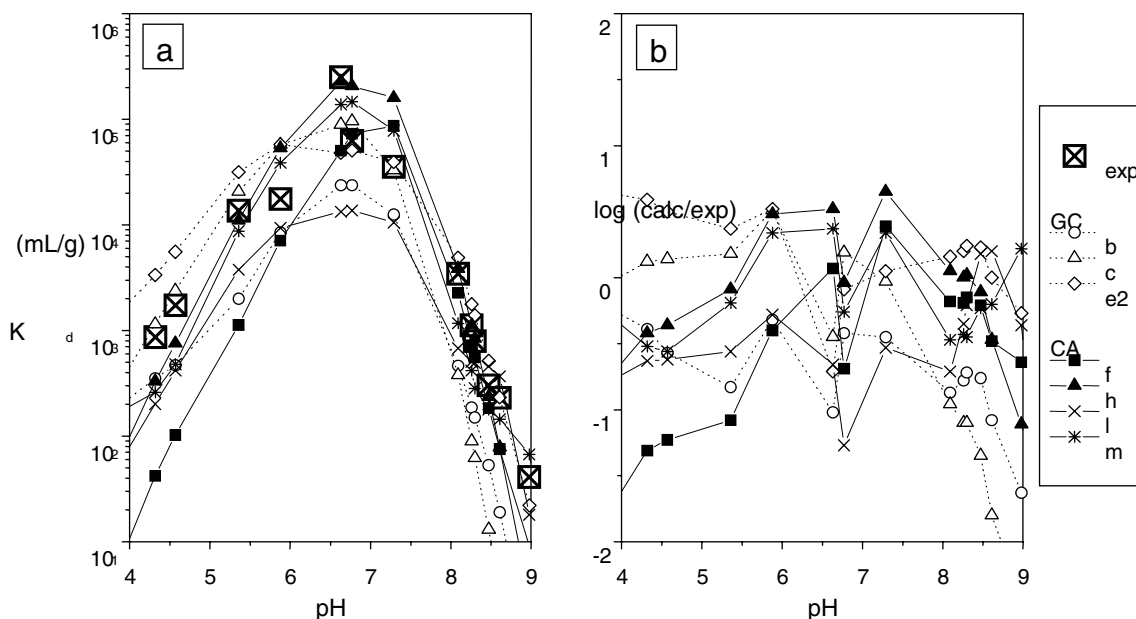


predictive sense. However in this example, models “b” and “c”, which were not re-optimised, performed well.

As another example, we consider all predictive models for the W2c dataset (Figure 4.12). The figure includes all models in the GC and CA teams which did not involve parameter optimisation (these Teams are b, c, f, h, l and m – see Table 4.7). In addition, the non-optimised model from Team e is also included. Note that the response of Team g was excluded from this comparison as the extrapolation method was considered introduce a major source of error, as discussed above.

Figure 4.12 shows that the models simulate the data reasonably well, although with appreciable spread around the experimental data. The comparison appears to indicate that the predictive power of the GC models and the CA models, when transferred from one substrate to another is very similar. This contrasts to the results when the models were used on the substrates for which they were calibrated – in which case the GC models perform much better than the CA models (see Figure 4.2). In other words, once the re-optimisation component is removed from the GC models, their advantage relative to the CA models is decreased. However, the reader is reminded this comparison is being made to the A models; the CA models were already re-optimised from the true CA predictive models (the 0 models).

Figure 4.12: **Models for W2c data (models without parameter re-optimisation). (a)  $K_d$  (b) errors. Note that in this extrapolation example, the performance of GC and CA models is similar (compare Figure 4.2). Note that this Figure incorporates some additional data for a non-optimised model provided by Team e**



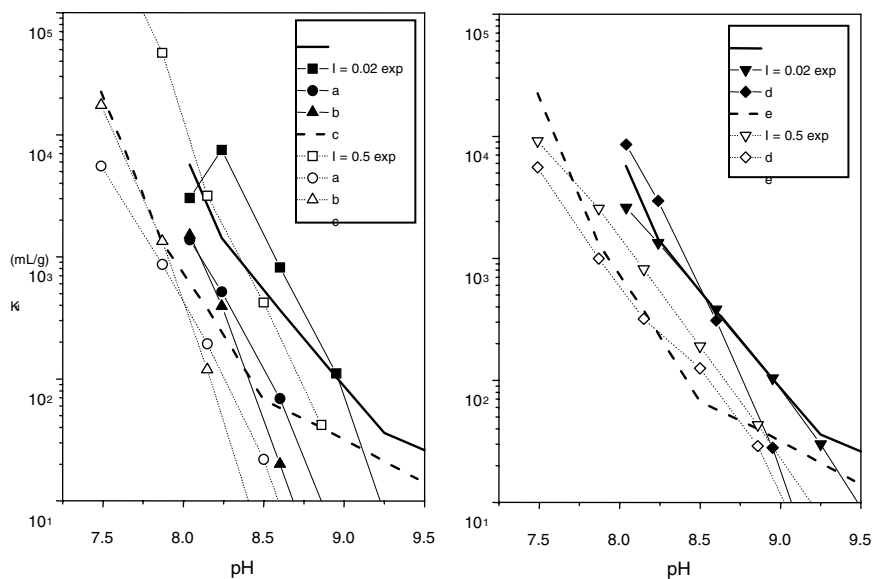
#### 4.4.7 High pH data for W2c sample at variable ionic strength

This exercise was the most complex modelling example, requiring a considerable degree of extrapolation. Whereas the original models were calibrated across a wide pH range at fixed ionic strength with the W2 sample, the data here refer to the W2c sample with variable ionic strength and in the high pH range. A key feature of the experimental data is that the position of the high pH edge is dependent on the ionic strength. The results for each modelling teams are quite complex and both the

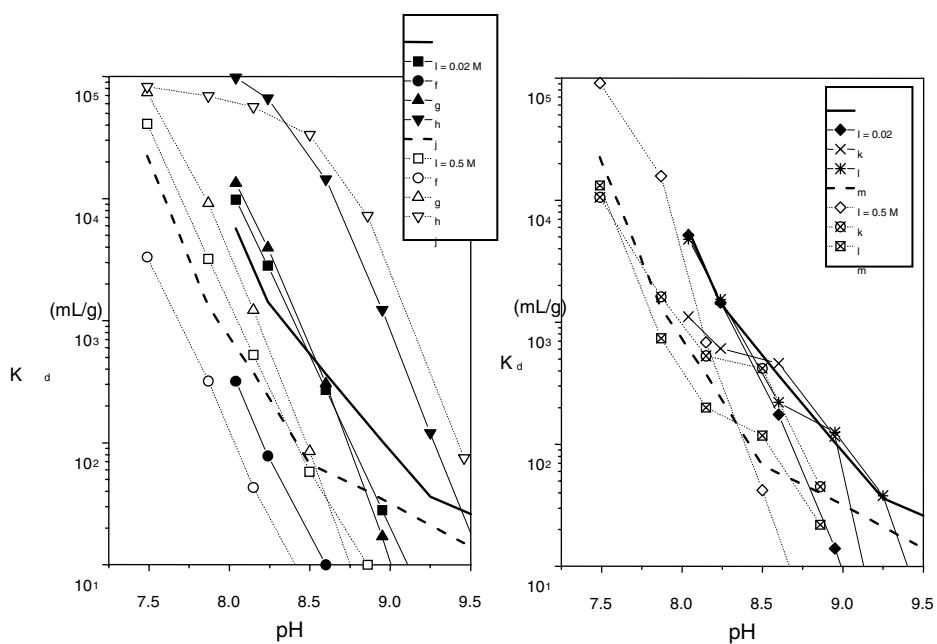
GC and CA groups have been broken into two frames in Figure 4.13. Note that the groups were divided simply for simplicity in presenting the results.

**Figure 4.13: Modelling the high pH U data on the W2c sample at various ionic strengths. The experimental data are indicated by heavy solid or dashed lines. The responses of both GC and CA modelling teams are broken into two frames to simplify the interpretation of the figure. Note that model Team e introduced an extra adjustable parameter for the I = 0.5 M case**

### Generalised composite



### Component additivity



The key feature of the results is that almost all the models qualitatively predict lower U sorption at the higher of the two ionic strengths (Figure 4.13). The exception was that produced by Team j, which predicted the opposite effect. In terms of quantitative prediction, the model curves are quite scattered. However, it should be noted that the expanded horizontal scale in Figure 4.13 exaggerates the horizontal displacement of the models from the experimental data. Almost all models predict the position of the high pH fairly accurately in both sets of model conditions – i.e. less than 0.5 of a pH unit.

This exercise required the models be extended beyond their calibrated range to simulate pH edges which are very steep and closely spaced. The models perform well in a semi-quantitative sense. However, accurate modelling in these circumstances would require collection of experimental data and development of models specifically for this pH range. Even the best predictive models need some experimental validation and calibration when sorption data is very sensitive to an experimental variable – in this case both pH and ionic strength.

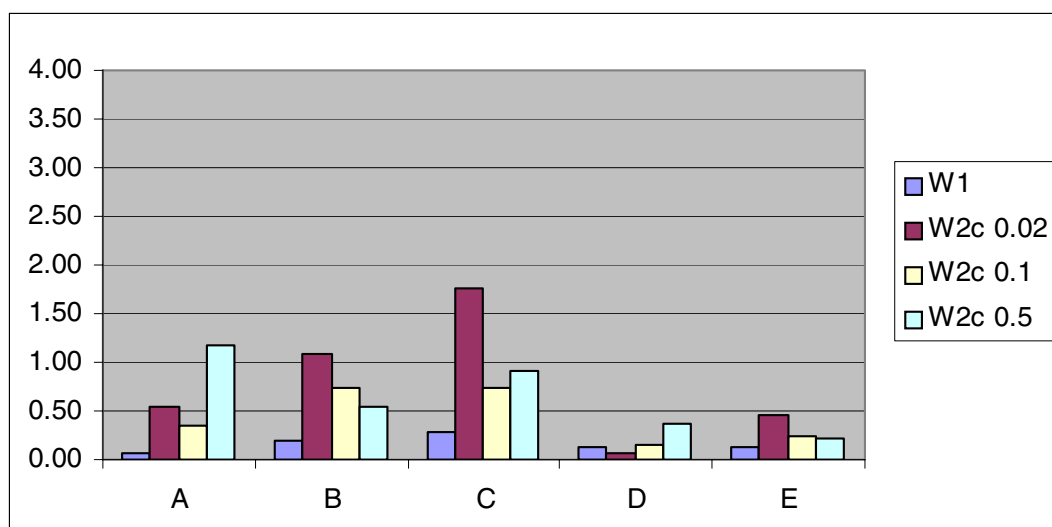
## 4.5 Model assessment

### 4.5.1 Overall model performance and range of applicability

When comparing the models produced in this test case, it must be appreciated that the errors and model failures are most apparent in particular datasets or for specific conditions. This has been noted at several points in the above discussion. For example, the model of Team c generally performed satisfactorily but did not reproduce the dataset obtained with elevated  $\Sigma U$  (Figure 4.7). Or the model of Team f performed well in the neutral and high pH range in most examples, but poorly at low pH values. Thus, the global performance of a given model is difficult to evaluate, as the importance of simulating particular datasets is subjective. Thus, it is more useful to compare the model performance on the basis of individual simulations.

The distribution of errors in the different models is very instructive, as shown by the average errors in extrapolation to the W1 and W2c substrates (Figure 4.14).

Figure 4.14: **Average errors of models applied to the W1 and W2c datasets. The error is expressed as the mean of the absolute value of the ratio of calculated to experimental  $K_d$  values (in log units). The three experimental conditions of the W2c sample refer to ionic strengths of 0.02M, 0.1M and 0.5 M  $\text{NaNO}_3$**



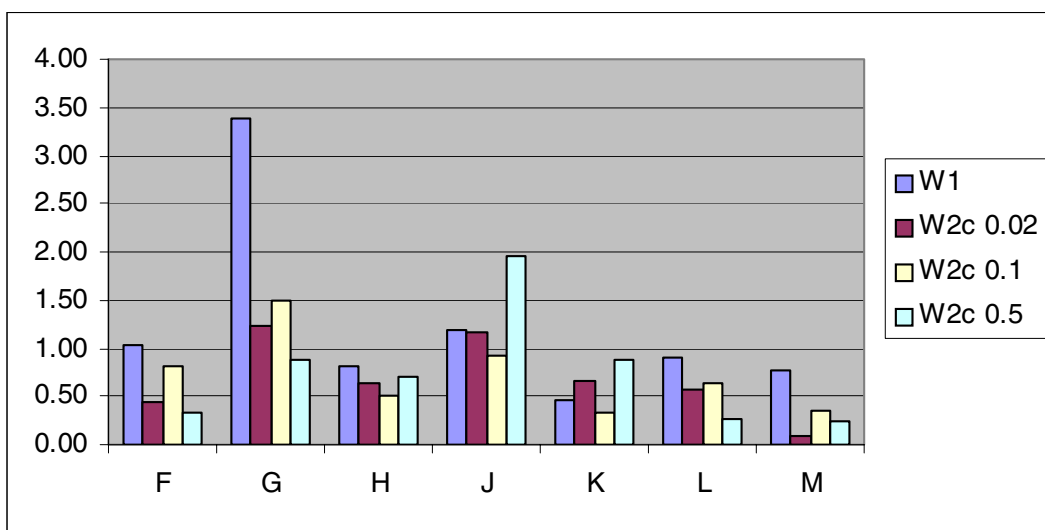


Figure 4.14 highlights the fact that the GC models with parameter optimisation (a, d, e) tended to perform the best across a range of datasets. This is not surprising. Of the GC models, model “c” shows the poorest performance. As noted above, this is a single site model and tended to have problems at high pH values. Thus, it performs quite well for the W1 dataset and poorly for the data for the ionic strength effect at the high pH edge (shown in Figure 4.13).

In contrast, model “f” shows the opposite behaviour, with a poor simulation of the low pH edge on the W1 sample and better simulations for the W2c data. The failure of model “g” to simulate the W1 dataset has been discussed above and attributed to the method of extrapolation. Model “j” tends to poorly simulate the data.

Limitations on the applicability of models can be divided into two types:

- a) in-built limitations of the model knowingly incorporated by the modelling team during model development. For example, a decision to use a simpler model applicable for a limited range of conditions or samples, rather than a more complex, widely applicable model. Model “f” is an example of a very simple model which is only suited to a limited range of pH.
- b) an unexpected inability of the model to accurately simulate other conditions or extension to other samples. The failure of model “g” to extend properly to another substrate is an example.

In addition, it should be noted that limitations of transferability for several of the models may have been hidden by a high degree of parameter optimisation. The supplementary data provided by Team e showed that their model performed much more poorly when not re-optimised for each dataset. Although not a part of this exercise, one approach to minimising error in simulating the data of several similar substrate samples (collected in a single geologic formation at a single site) is to use all the data simultaneously in calibrating or optimising the parameters of a model. An example of this for the Koongarra samples is given in Davis *et al.* (2002).

It is clear that many of the models fail to adequately simulate all the experimental data and many of these failings are only apparent for particular sorption datasets. This underlines the importance of obtaining a large sorption dataset for a wide range of conditions. Many accounts published in the literature provide models that are not adequately tested. Examples would include

U sorption data obtained at only one ionic strength, a single U concentration or only in air or under nitrogen. It is uncommon in the literature for sorption results to be obtained for more than one sample of a complex substrate from one field site, although a few reports exist (Fuller *et al.*, 1996; Robin *et al.*, 1991). Therefore, the model “failures” observed in the present study are partly attributed to the variety of datasets which are modelled. This shows the importance of a large amount of experimental data for developing robust models.

The results show that for this test case, an average error parameter is not very useful because the errors tend to be distributed in a highly systematic way. Some models performed poorly with particular experimental datasets, in given pH ranges, or with particular substrates.

#### 4.5.2 Comparison of CA and GC modelling approaches

The overall comparison of the GC and CA modelling approaches was complicated by the fact that some model failures could be directly traced to model characteristics that were unrelated to the general approach used. Examples of this include:

- the optimisation problems experienced by Team j;
- single site model density leading to model failure at high sorption densities;
- problems in the transfer to other substrates experienced by Team g.

Examples of all these types of model failures are discussed above.

Despite the above limitations some general conclusions about the two modelling approaches appear justified:

- a) The CA approach at this stage is not well enough established to enable blind prediction without refinement of parameter values (see Figure 4.2).
- b) The modellers using the GC approach were reluctant to use a modelling approach with generic surface sites and generalised surface reactions. Rather they tended to employ the building blocks of the basic CA approach. It could be interpreted that the modellers preferred a guided GC approach where the model was still based on concepts developed for component minerals.
- c) Both CA and GC modellers preferred the DLM model for the electrical double layer. This is contrast to other GC models in the literature, which generally use an NEM (e.g. Davis *et al.*, 2002; Davis *et al.*, 1998).
- d) Both types of modelling approaches were capable of simulating important features of U sorption, such as the general pH dependence. Perhaps most impressively, the models simulated the effect of elevated  $p\text{CO}_2$  (Figure 4.6). The GC modelling produced the better simulations.
- e) Even when optimisation is permitted in the CA approach, for a single dataset, the GC approach appears to be superior. For example, consider Figure 4.4. Here we compare a GC and CA model, both having used some parameter optimisation. The GC models fit better. It would appear that the component minerals do not simulate the experimental data adequately. In particular, there is a systematic pattern in the error distribution in the CA models, which reveals some model inadequacy.
- f) Despite its inferior ability on the single substrate, the CA approach appears to be comparable in terms of its transferability from one substrate to another (Figure 4.12). This is despite the smaller number of fitted parameters in the initial models. Models developed by the GC approach appear to be very sensitive to changes in parameter

values. The conclusion can thus be made that CA models may often be better when modelling requires extension to other complex samples with significantly different properties. If the complex samples are relatively similar, it is better to optimise GC model parameters using all the available experimental data simultaneously.

- g) A major problem with the CA model is a lack of sufficient component mineral data. More experimental work is required.
- h) Some CA modellers chose to modify equilibrium constants for their models. This was justified on the basis that the surface properties in the complex materials differed from the simple substrates. However, this means such models are not truly predictive, and the models produced are actually a hybrid of CA and GC models.



## 5. COBALT SORPTION ON MINERAL SURFACES (TEST CASE 7)

### 5.1 Overview

The dataset used in this modelling exercise was obtained to determine the effects of humic substances on Co(II) adsorption by a sub-surface material consisting of layer silicates with Fe and Al oxides (Zachara *et al.*, 1994). The objective of the test case was to test whether the effect of introducing humic substances to the sub-surface material was additive for Co(II) sorption or whether more complex interactions were influential in determining Co(II) sorption by the composite material. To test these questions, top-down (GC) versus bottom-up (CA) models were composed for the Co<sup>2+</sup> adsorption data in the presence and absence of humic substances.

### 5.2 Field site and experimental data

The experimental work was carried out on a clay-sized isolate separated from ultisol saprolitic material from South Carolina, USA (Zachara *et al.* 1994). Mineralogical composition by weight of the material was goethite and hematite (5.9%), gibbsite (10%), kaolinite (70%), and 2:1 layer silicates (14.1%). The experimental sorption data consisted of various pH edges (fractional sorption of Co as a function of pH over the range 4.4 to 8.1) equilibrated under a nitrogen gas atmosphere. The aqueous solution was 1 µM Co(II) solution with NaClO<sub>4</sub> background electrolyte (0.01 and 0.1 M). Added humic concentrations were 0 or about 10-11 ppm. Thus, the aqueous chemical variables in the dataset were pH, ionic strength, and the presence or absence of humic substances (Table 5.1). Log Co(II) K<sub>d</sub> values in the study ranged from 1.3 to 5.4.

Table 5.1: **Summary of experimental data for Co(II) sorption data provided to the modelling teams in Test Case 7<sup>a</sup>**

Dataset number	NaClO <sub>4</sub> concentration	Humic substances added (mg/L as organic C)	Number of data points
1	0.01M	0	18
2	0.1M	0	18
3	0.01M	10.0	18
4	0.1M	10.8	18

<sup>a</sup> pH was an additional variable for each set of chemical conditions. Total Co(II) was about 1 µM and ultisol concentration was 1.29 g/L for all experiments.

Other ancillary data provided in the test case included: (their use by the modelling teams was optional):

- Co(II) sorption on kaolinite, gibbsite and Al-goethite.
- Co(II) complexation by the humic acid.
- Humic acid sorption by the ultisol sample.
- Humic acid desorption from the ultisol sample.



- Electrophoretic mobilities of soil particles.
- Co(II) sorption on the ultisol after DCB extraction.

### 5.3 Model descriptions

Four modelling teams completed GC and CA models for the sub-surface material without humic substances; two teams completed models with the humic substances present (Table 5.2).

#### 5.3.1 Overall modelling strategies

A diverse range of modelling approaches were used, including: a) GC one- and two-site models (Table 5.3) with and without ion exchange, b) different electrical double layer models (Table 5.2), c) a variation of total site densities and methods for determining the parameter (Table 5.3), d) multiple Co(II) surface reactions, and e) a consideration of various species, including protonated ion exchange sites, humic colloidal particles, adsorbed humate molecules, and ternary surface-humic-cobalt complexes (Table 5.4). Each modelling team was consistent in the choice of EDL models for GC and CA modelling approaches. That is, if a team used a DLM model for a CA model, it was also used for the GC model. Teams a and c had additional parameters in their models due for the acidity constants in the DLM models.

##### 5.3.1.1 GC-1 Models (without humic acid)

Methods for setting the types and populations of surface sites varied considerably. Three of the four modelling teams included ion exchange as part of their modelling approach (Table 5.3). Team a did not include ion exchange because it interpreted the modelling instructions requesting a simple model to mean that ion exchange should not be included. Teams a and b used two-site models for SC reactions; Teams c and d used a one-site model. Team a assumed a total site density, while Teams b, c, and d used the surface-area to estimate total site density with the conversion factor of  $3.84 \mu\text{moles}/\text{m}^2$ . Team b used the Co(II) sorption data to optimise a value for the cation exchange capacity (CEC). Teams c and d used the values given in the original test case paper (Zachara *et al.*, 1994), although Team c used the pH-dependent CEC and Team d fixed the CEC at the value measured at pH 6 (Table 5.3).

Table 5.2: Summary of computer codes and electrical double layer models used for Test Case 7

Modelling team	Computer code	Model Types Completed <sup>a</sup>	EDL Models <sup>b</sup>
a	CHESS-1	GC-1 and 3, CA-2 and 4	DLM
b	FITEQL 2	GC-1 and CA-2	NEM
c	STAMB-2002	GC-1 and CA-2	DLM, CCM, NEM
d	FITEQL 4	GC-1 and 3, CA-2 and 4	NEM

<sup>a</sup> Model codes are Generalised Composite models without (GC-1) and with (GC-3) humic substances present, and the predictive Component Additivity models without (CA-2) and with (CA-4) humic substances present.

<sup>b</sup> Teams used the same EDL model type for all modelling approaches.

### 5.3.1.2 CA-2 Models (without humic acid)

Methods for determining the site densities in the CA predictions also varied from one modelling team to another. All four modelling teams predicted Co(II) sorption based on the addition of calculated adsorption for the kaolinite, gibbsite, and Al-goethite component mineral phases. For the most part, all the modelling teams made a similar assumption in carrying out the CA predictions: each team assumed that the surface areas of the reference mineral phases were the same as the surface areas of those minerals in the ultisol in order to calculate the site density of that mineral component in the ultisol. For example, the kaolinite sample (KGA-1) that was used for the study of Co(II) sorption had a surface area of 11.4 m<sup>2</sup>/g; each team assumed that the kaolinite particles in the ultisol also had a surface area of 11.4 m<sup>2</sup>/g. The assumption was a reasonable one to make given that no other information was provided in the test case, but perhaps it would be better to use an average surface area for kaolinite found in soils throughout the world or a surface area inversely scaled by average grain size. It is important to recognise that this is an assumption commonly being used in CA model predictions, and its validity or significance had not been well tested. Similar assumptions were made for the gibbsite and Al-goethite predicted contributions to Co(II) sorption.

Table 5.3: Summary of surface site types used for Test Case 7

Modelling team	Model type	Site types <sup>A</sup>	Site density <sup>B</sup> (μmoles/m <sup>2</sup> )	Source
a	GC-1	≡SOH <sub>w</sub>	1.0	Assumed
		≡SOH <sub>s</sub>	0.003	C
≡SOH <sub>w</sub>		3.84	D	
≡SOH <sub>s</sub>		8.69·10 <sup>-4</sup>	C	
X <sub>na</sub>		0.87	C	
≡SOH		3.84	D	
X <sub>na</sub>		f(pH)	E	
≡SOH		3.84	D	
X <sub>na</sub>		0.88	F	
a		CA-2	≡KaOH <sub>w</sub>	1.41
	≡KaOH <sub>s</sub>		8.69·10 <sup>-4</sup>	G
	≡GiOH		0.071	H
	≡AlGoOH		Unknown	I
b	≡GiOH		0.023	J
	≡AlGoOH		0.62	K
	KaX <sub>Na</sub>		0.31	C
c	≡KaOH		0.45	L
	≡GiOH		0.023	J
	≡AlGoOH		0.62	K
	KaX <sub>Na</sub>		f(pH)	E
	GiX <sub>Na</sub>		f(pH)	E
d	≡KaOH <sub>w</sub>		0.44	L
	≡KaOH <sub>s</sub>		0.0045	Assumed
	≡GiOH		0.023	J
	≡AlGoOH		1.08	M
	KaX <sub>Na</sub>	0.88	F	

Table 5.3: **Summary of surface site types used for Test Case 7** (continued)

Modelling team	Model type	Site types <sup>A</sup>	Site density <sup>B</sup> ( $\mu\text{moles}/\text{m}^2$ )	Source
<b>a</b>	GC-3	$\equiv\text{SOH}_w$	As in GC-1	
		$\equiv\text{SOH}_s$	As in GC-1	
HumCOOH		0.12	N	
<b>d</b>		$\equiv\text{SOH}$	As in GC-1	
		XNa	As in GC-1	
<b>a</b>	CA-4	$\equiv\text{KaOH}_w$ and $\equiv\text{KaOH}_s^2$ , $\equiv\text{GiOH}$ , $\equiv\text{AlGoOH}$ ,	As in CA-2	
		HumCOOH	As in GC-3	
<b>d</b>		$\equiv\text{KaOH}_w$ and $\equiv\text{KaOH}_s^2$ , $\equiv\text{GiOH}$ , $\equiv\text{AlGoOH}$ , KaXNa	As in CA-2	

<sup>A</sup> Site type designations are:  $\equiv\text{SOH}$  – generic site;  $\equiv\text{SOH}_w$  and  $\equiv\text{SOH}_s$  – generic weak- and strong-binding sites; XNa – generic Na-saturated ion exchange site;  $\equiv\text{KaOH}$  – kaolinite site;  $\equiv\text{KaOH}_w$  and  $\equiv\text{KaOH}_s$  – kaolinite weak- and strong-binding sites; KaXNa – kaolinite Na-saturated ion exchange site;  $\equiv\text{GiOH}$  – gibbsite site; GiXNa – gibbsite Na-saturated ion exchange site;  $\equiv\text{AlGoOH}$  – aluminous goethite site; HumCOOH – carboxyl binding site on humic substance colloid particles.

<sup>B</sup> Site density given relative to the surface area of the ultisol used in the experiments ( $88 \text{ m}^2/\text{L}$ ).

<sup>C</sup> Fit to Co(II) sorption data on ultisol without humic substances.

<sup>D</sup> Total site density taken from literature source.

<sup>E</sup> Cation exchange capacity determined experimentally as a function of pH.

<sup>F</sup> Cation exchange capacity determined experimentally at pH 6.

<sup>G</sup> Site density optimised from fit to Co(II) sorption data on kaolinite; kaolinite surface area in ultisol assumed to be the same as the kaolinite reference mineral; data for kaolinite weight (70%) in ultisol used.

<sup>H</sup> Site density optimised from fit to Co(II) sorption data on gibbsite; gibbsite surface area in ultisol assumed to be the same as the gibbsite reference mineral; data for gibbsite weight (10%) in ultisol used.

<sup>I</sup> Site density optimised from fit to Co(II) sorption data on Al-goethite; Al-goethite surface area in ultisol assumed to be the same as the Al-goethite reference mineral; not known what weight % of Al-goethite in ultisol used.

<sup>J</sup> Site density for gibbsite from literature; gibbsite surface area in ultisol assumed to be the same as the gibbsite reference mineral; data for gibbsite weight (10%) in ultisol used.

<sup>K</sup> Site density for Al-goethite from literature; Al-goethite surface area in ultisol assumed to be the same as the Al-goethite reference mineral; data for crystalline Fe oxides weight (5.9%) in ultisol used.

<sup>L</sup> Site density for kaolinite from literature; kaolinite surface area in ultisol assumed to be the same as the kaolinite reference mineral; data for kaolinite weight (70%) in ultisol used.

<sup>M</sup> Site density for Al-goethite from literature; Al-goethite surface area in ultisol assumed to be the same as the Al-goethite reference mineral; Al-goethite weight (10.3%) in ultisol estimated from DCB-extractable Fe and other data.

<sup>N</sup> Literature data for Boom Clay in CHESS-1 programme used.

**Kaolinite models.** Teams a, c, and d included Co(II) sorption on kaolinite edge sites as part of their kaolinite model (Teams a and d had a two-edge-site kaolinite model; Team c had a one-edge-site kaolinite model). Team a optimised the total site density as a fitting parameter for their kaolinite model; Teams c and d used the kaolinite BET surface-area to estimate the total site density, with the conversion factor of 3.84  $\mu\text{moles/m}^2$ . Co(II) sorption by ion exchange on kaolinite was part of the models of Teams b, c, and d, but the Team b model, however, considered Co(II) sorption to occur only by ion exchange and not by SC reactions at edge sites (Table 5.3). Team b fit the CEC of the kaolinite using the Co(II) sorption data for kaolinite. Team d assumed that the CEC of the ultisol was caused entirely by its kaolinite component, and since the kaolinite composed 70% by weight of the ultisol, the kaolinite CEC was equal to the soil CEC divided by 0.7. As in model GC-1, Team c used the pH-dependent CEC equation given in Zachara *et al.* (1994), but also assumed that the gibbsite mineral contributed to ion exchange (Table 5.3).

Table 5.4: Summary of surface reactions in SC models in Test Case 7<sup>a</sup>

Surface reaction	#	Modelling team			
		a	b	c	d
$\equiv\text{SOH} + \text{Co}^{2+} \leftrightarrow \equiv\text{SOCo}^+ + \text{H}^+$	7-1	GC-1, GC-3	GC-1	GC-1	GC-1, GC-3
$2\text{XNa} + \text{Co}^{2+} \leftrightarrow (\text{XNa})_2\text{Co} + 2\text{Na}^+$	7-2		GC-1	GC-1	GC-1, GC-3
$\equiv\text{SOH} + \text{Co}^{2+} + \text{H}_2\text{O} \leftrightarrow \equiv\text{SOCoOH} + 2\text{H}^+$	7-3				GC-1
$2\equiv\text{S}(\text{OH}) + \text{Co}^{2+} \leftrightarrow (\equiv\text{SO})_2\text{Co} + 2\text{H}^+$	7-4			GC-1	
$\equiv\text{KaOH} + \text{Co}^{2+} \leftrightarrow \equiv\text{KaOCo}^+ + \text{H}^+$	7-5	CA-2, CA-4		CA-2	CA-2, CA-4
$2\text{KaXNa} + \text{Co}^{2+} \leftrightarrow (\text{KaXNa})_2\text{Co} + 2\text{Na}^+$	7-6		CA-2	CA-2	CA-2, CA-4
$2\equiv\text{Ka}(\text{OH}) + \text{Co}^{2+} \leftrightarrow (\equiv\text{KaO})_2\text{Co} + 2\text{H}^+$	7-7			CA-2	
$\equiv\text{KaOH} + \text{HumCOOH}(\text{aq}) \leftrightarrow \equiv\text{KaHumCOO}$	7-8				CA-4
$\equiv\text{KaHumCOO} + \text{Co}^{2+} \leftrightarrow \equiv\text{KaHumCOOC}^{2+}$	7-9				CA-4
$\equiv\text{GiOH} + \text{Co}^{2+} \leftrightarrow \equiv\text{GiOC}^{2+} + \text{H}^+$	7-10	CA-2, CA-4	CA-2	CA-2	CA-2, CA-4
$2\text{GiXNa} + \text{Co}^{2+} \leftrightarrow (\text{GiXNa})_2\text{Co} + 2\text{Na}^+$	7-11			CA-2	
$2\equiv\text{Gi}(\text{OH}) + \text{Co}^{2+} \leftrightarrow (\equiv\text{GiO})_2\text{Co} + 2\text{H}^+$	7-12			CA-2	
$\equiv\text{GiOH} + \text{HumCOOH}(\text{aq}) \leftrightarrow \equiv\text{GiHumCOO}$	7-13				CA-4

$\equiv\text{GiHumCOO} + \text{Co}^{2+} \leftrightarrow \equiv\text{GiHumCOOCO}^{2+}$	7-14				CA-4
$\equiv\text{AlGoOH} + \text{Co}^{2+} \leftrightarrow \equiv\text{AlGoOCO}^+ + \text{H}^+$	7-15	CA-2, CA-4	CA-2	CA-2	CA-2, CA-4
$2\equiv\text{AlGo(OH)} + \text{Co}^{2+} \leftrightarrow (\equiv\text{AlGoO})_2\text{Co} + 2\text{H}^+$	7-16			CA-2	
$\equiv\text{AlGoOH} + \text{Co}^{2+} + \text{H}_2\text{O} \leftrightarrow \equiv\text{AlGoOCO}^+\text{OH} + 2\text{H}^+$	7-17				CA-2, CA-4
$\equiv\text{AlGoOH} + \text{HumCOOH(aq)} \leftrightarrow \equiv\text{AlGoHumCOO}$	7-18				CA-4
$\equiv\text{AlGoHumCOO} + \text{Co}^{2+} \leftrightarrow \equiv\text{AlGoHumCOOCO}^{2+}$	7-19				CA-4
$\text{HumCOOH(s)} + \text{Co}^{2+} \leftrightarrow \text{HumCOOCO}^+ + \text{H}^+$	7-20	GC-3, CA-4			
$\equiv\text{SOH} \leftrightarrow \equiv\text{SO}^- + \text{H}^+$	7-21	GC-1, GC-3		GC-1	
$\equiv\text{SOH} + \text{H}^+ \leftrightarrow \equiv\text{SOH}_2^+$	7-22	GC-1, GC-3		GC-1	
$\text{XNa} + \text{H}^+ \leftrightarrow \text{XH} + \text{Na}^+$	7-23		GC-1		GC-1, GC-3
$\equiv\text{KaOH} \leftrightarrow \equiv\text{KaO}^- + \text{H}^+$	7-24	CA-2, CA-4		CA-2	
$\equiv\text{KaOH} + \text{H}^+ \leftrightarrow \equiv\text{KaOH}_2^+$	7-25	CA-2, CA-4		CA-2	
$\text{KaXNa} + \text{H}^+ \leftrightarrow \text{KaXH} + \text{Na}^+$	7-26		CA-2		CA-2, CA-4
$\equiv\text{GiOH} \leftrightarrow \equiv\text{GiO}^- + \text{H}^+$	7-27	CA-2, CA-4		CA-2	
$\equiv\text{GiOH} + \text{H}^+ \leftrightarrow \equiv\text{GiOH}_2^+$	7-28	CA-2, CA-4		CA-2	
$\equiv\text{AlGoOH} \leftrightarrow \equiv\text{AlGoO}^- + \text{H}^+$	7-29	CA-2, CA-4		CA-2	
$\equiv\text{AlGoOH} + \text{H}^+ \leftrightarrow \equiv\text{AlGoOH}_2^+$	7-30	CA-2, CA-4		CA-2	
$\text{HumCOOH(s)} \leftrightarrow \text{HumCOO}^- + \text{H}^+$	7-31	GC-3, CA-4			
$\text{HumCOOH(aq)} + \text{Co}^{2+} \leftrightarrow \text{HumCOOCO}^+(\text{aq}) + \text{H}^+$	7-32				CA-4
$\text{HumCOOH(aq)} + \text{Na}^+ \leftrightarrow \text{HumCOONa(aq)} + \text{H}^+$	7-33				CA-4

<sup>a</sup>. **Site** type designations are:  $\equiv\text{SOH}$  – generic site;  $\equiv\text{SOH}_w$  and  $\equiv\text{SOH}_s$  – generic weak- and strong-binding sites;  $\text{XNa}$  – generic Na-saturated ion exchange site;  $\equiv\text{KaOH}$  – kaolinite site;  $\equiv\text{KaOH}_w$  and  $\equiv\text{KaOH}_s$  – kaolinite weak- and strong-binding sites;  $\text{KaXNa}$  – kaolinite Na-saturated ion exchange site;  $\equiv\text{GiOH}$  – gibbsite site;  $\text{GiXNa}$  – gibbsite Na-saturated ion exchange site;  $\equiv\text{AlGoOH}$  – aluminous goethite site;  $\text{HumCOOH}$  – carboxyl binding site on humic substance colloid particles;  $\text{HumCOOH(aq)}$  – dissolved humic molecule.

**Gibbsite models.** There was more consistency among the models for gibbsite site density; all the modelling teams used a one-site model. Teams b, c, and d used the gibbsite BET surface-area

to estimate the total site density, with the conversion factor of  $3.84 \mu\text{moles/m}^2$  (Table 5.3). Team a used the total site density as a fitting parameter in calibrating its model to the Co(II) sorption data on gibbsite. Team c included ion exchange as part of the Co(II) sorption on gibbsite.

**Al-goethite models.** All the modelling teams used a one-site model. As in the case of the gibbsite models, Teams b, c, and d used the BET surface-area to estimate the total site density, while Team a used the total site density as a fitting parameter in calibrating its model to the Co(II) sorption data on Al-goethite.

#### *1.1.1.1 GC-3 and CA-4 models (with humic acids)*

The two modelling teams (a and d) that completed GC and CA models for the Co(II) sorption in the presence of humic acids used the same site densities as they had in their GC-1 and CA-2 models. The addition of humic acids to the model, however, was treated very differently by each modelling team. Team a considered the humic substances as an additional colloidal sorbent in the GC-3 and CA-4 models. Solid-phase carboxyl binding groups were used as the complexation site (reactions 7-20 and 7-31, Table 5.4), and their site density was estimated from published information about humic characteristics in the Boom clay (Table 5.3). Team d, however, considered the humic substances as additional dissolved ligands (reactions 7-32 and 7-33), utilising all the data given in the test case for aqueous humic-Co complexation (reactions 7-32 and 7-33) and for humate sorption and desorption on the ultisol (reactions 7-8, 7-13, and 7-18; Table 5.4).

#### *1.1.1.2 Co(II) surface reactions*

Four different Co(II) surface reactions were used by the modelling teams to fit the Co(II) sorption data for the GC-1 models (reactions 7-1 to 7-4; Table 5.4). Each team used reaction 7-1, because it is the most chemically plausible surface reaction and because the simple cation-proton exchange reaction is commonly used in the literature. Teams c and d had an additional reaction with two protons released (reactions 7-3 and 7-4); Teams b, c, and d used the same simple ion exchange reaction. In addition to the Co(II) surface reactions, Teams a and c had acidity reactions for the ultisol (reactions 7-21 and 7-22). Teams b and d had a proton-sodium ion exchange reaction (7-23) as part of their model. Team c didn't need this reaction because they used a pH-dependent CEC.

As in Test Case 6, the number of reactions considered in the CA model predictions are larger because of the summation of calculated adsorption using models for each mineral component. The reactions for the individual minerals are remarkably similar for each mineral component, with the exception that kaolinite was considered as an ion exchanger.

For the models with humic acids, as mentioned above, Team a treated the humic substances as an additional sorbent and added the humic component to both its GC-3 and CA-4 models. Team d, however, did not consider the humic acid component explicitly in its GC-3 model. In its CA-4 model, Team d added reactions for surface complexation of Co(II) by adsorbed humic molecules (reactions 7-9, 7-14, and 7-19).

## **5.4 Modelling results and discussion**

Figure 5.1 compares the average error (absolute values) in calculated and experimental  $\log K_d$  values for all data points for the GC-1 and CA-2 models (without humic acids). The average error varied between 0.3 and 0.7 log units, with the largest errors observed for the CA models. Most modelling teams achieved a better fit to the Co(II) sorption data with the GC models (error range from 0.3 to 0.45), although Team d actually had a better fit with its CA prediction. The greater errors for Team a in both the GC and CA models generally resulted in their use of the simpler model without

ion exchange, which had problems in predicting Co(II) sorption as a function of ionic strength (Figure 5.2). The lower error of Team d for the predictive CA model (Figure 5.3) seemed to be due to the different method used to estimate the site density of Al-goethite in the ultisol (Team d used the DCB-extractable Fe data rather than the weight % data, Table 5.3), resulting in lower errors at high pH.

Figure 5.1: Model performance for Test Case 7 (datasets 1 and 2, without humic acids) showing the sum of the errors (absolute value of difference between calculated and experimental  $\log K_d$  values) divided by the number of data points. Team c results are shown for the three different EDL models used

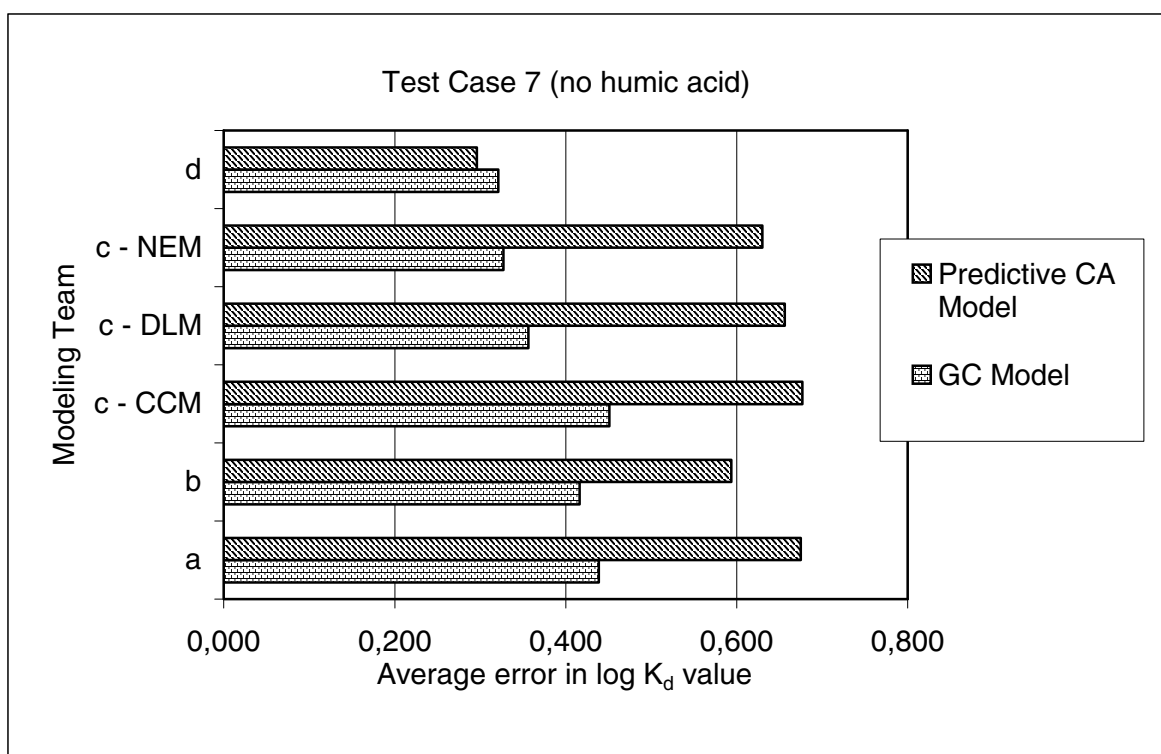


Figure 5.4 compares the average error (absolute values) in calculated and experimental  $\log K_d$  values for all data points for the GC-3 and CA-4 models (with humic acids). The errors are not greater than for the data without humic acids, showing that environmental sorbents with significant humic acids can be modeled well with either GC or CA modelling approaches. The performance of the Team a models were negatively affected by the lack of consideration of ion exchange. The data requirements for the CA modelling approach, however, are much greater when humic acids are present in significant quantities. Zachara *et al.* (1994) collected very detailed data for Co(II) complexation with humic acids and for humic acid sorption and desorption on the ultisol. These data were required in order to employ the CA modelling approach.

Figure 5.2: Model performance for Test Case 7 showing the errors (absolute value of difference between calculated and experimental  $\log K_d$  values) for datasets 1 and 2 with GC-1 models (without humic acids)

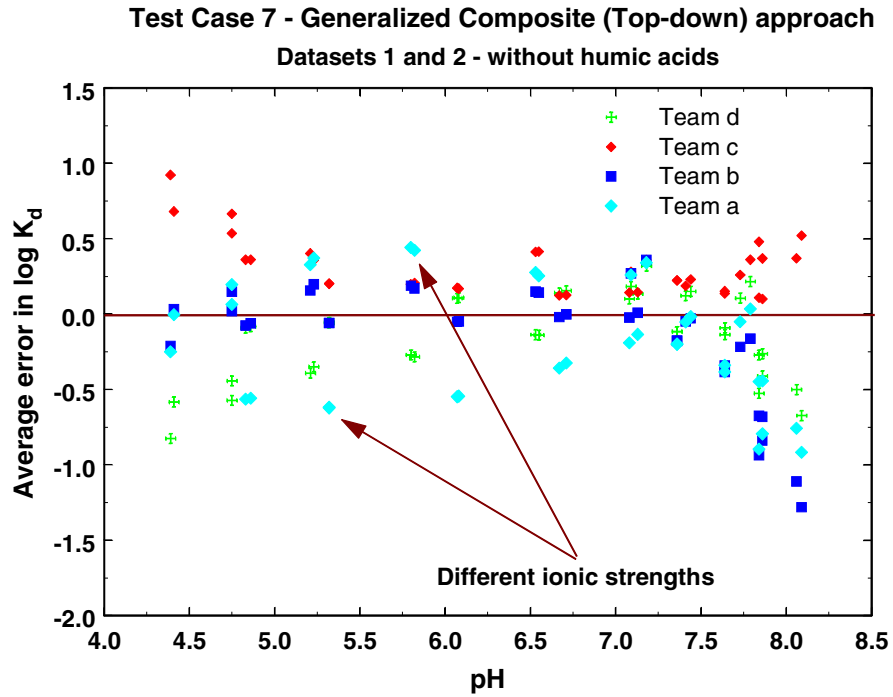


Figure 5.3: Model performance for Test Case 7 showing the errors (absolute value of difference between calculated and experimental  $\log K_d$  values) for datasets 1 and 2 with CA-2 models (without humic acids)

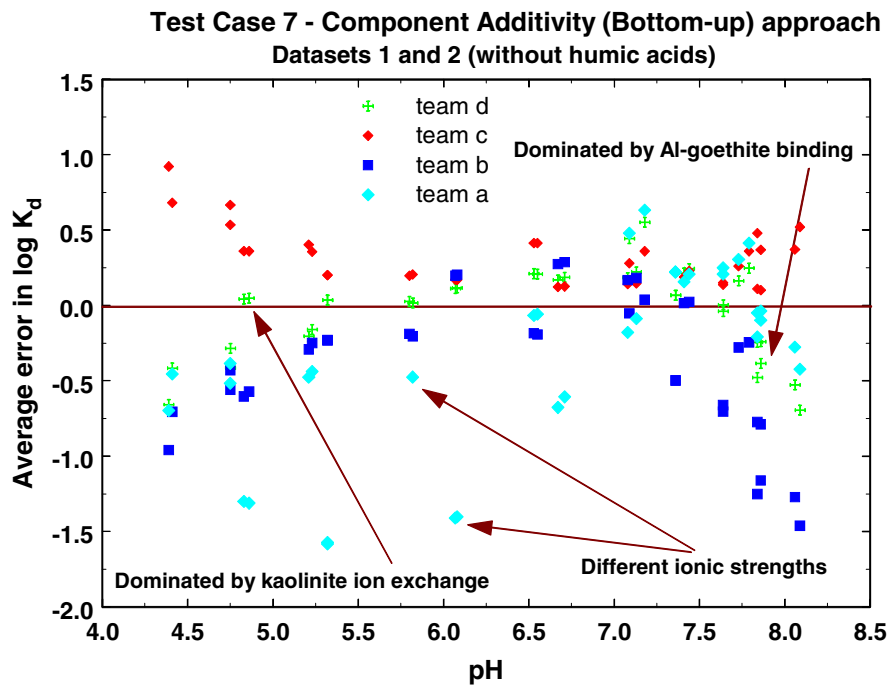
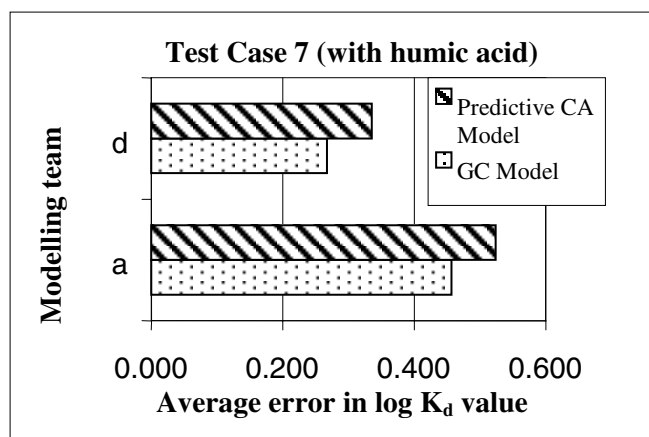


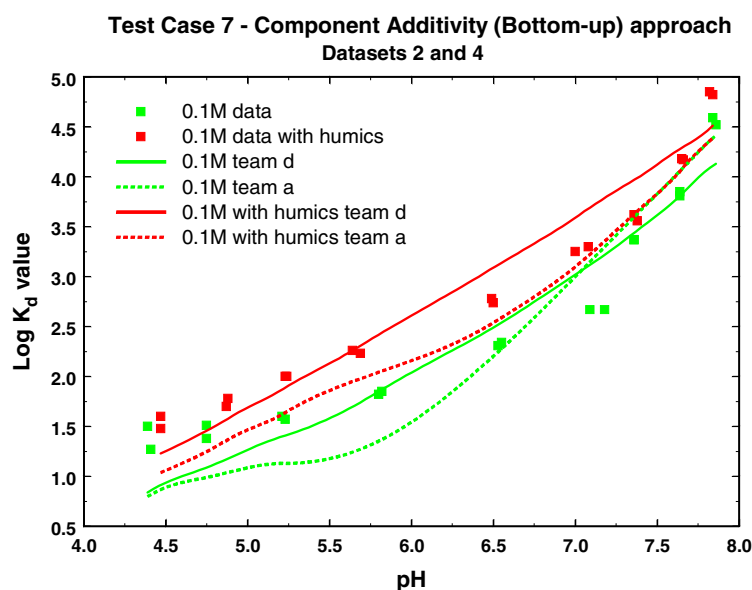


Figure 5.4: **Model performance for Test Case 7 (datasets 3 and 4, with humic acid) showing the sum of the errors (absolute value of difference between calculated and experimental  $\log K_d$  values) divided by the number of data points**



It can be seen in Figure 5.5 that the addition of humic acids increased Co(II) sorption. This occurred despite the fact that Co(II) formed strong aqueous complexes with the humic acid ligands. The increase in Co(II) sorption occurs because the humic substances are strongly sorbed in the lower pH range, and Co(II) associates with the humic substances due to strong binding by the carboxyl groups. Note that although Teams a and d each modeled the humic-Co interactions in very different ways, each achieved a reasonable fit to the Co(II) sorption data. Team a treated the humic substances as a solid colloidal phase that could sorb Co(II) and neglected any aqueous phase complexation of Co(II) with the humic ligands. Team d used a more complex modelling approach that considered both aqueous phase complexation between Co(II) and the humic acids and ternary surface-humic-Co complexes (reactions 7-9, 7-14, 7-19, and 7-32 in Table 5.5).

Figure 5.5: **Model performance for Test Case 7 showing the errors for datasets 2 and 4 with CA models (with and without humic acids)**



## 6. KEY ISSUES IN MODELLING COMPLEX SUBSTRATES (TEST CASES 6 AND 7)

### 6.1 Calibration and extrapolation

It is important when attempting to draw conclusions regarding the modelling outcomes to distinguish between features that are generic to the modelling approaches and those that are specific to the particular case studies considered in the two examples. The basic strategy underlying the modelling undertaken in Test Cases 6 and 7 is to calibrate models using one, or several, sets of experimental data and then extrapolate them to another set of experimental conditions or another substrate. The CA modelling strategy is, in essence, comprised of a sequence of such steps.

When modelling sorption data on various complex materials, the major methods of extrapolation used by the modelling teams were:

- a) extrapolation without variation of input parameters;
- b) parameter estimation from measured properties, such as BET surface area or extractable Fe content;
- c) optimisation.

The first method of extrapolation is appropriate for examples when a single substrate is used (i.e. the model is calibrated and applied on only one material). In general, all types of SC models worked well in this mode, particularly the GC models. This can be seen most clearly in the extrapolation to the elevated  $p\text{CO}_2$  data in Test Case 6 (Figure 4.6). Here both the CA and the GC models were able to predict the changes in U sorption with a variation of  $p\text{CO}_2$ . While the GC models provide a better simulation the data under the different experimental conditions, this can be partly traced to the higher degree of parameter optimisation in the GC models. However, it is also due to the fact that the basic GC models provide a simpler representation of the data using generic surface reactions. In contrast, the CA models are constrained to surface reactions found with model substrates.

A case where extrapolation without variation of parameters was less successful is seen in Figure 4.7 (where the simplest type of single-site GC sorption model failed for the example with higher total U concentration).

The second method of extrapolation is appropriate when a different substrate is modelled and the model can be calibrated according to measured substrate properties. Typical examples of this approach involved the BET surface area, mineralogy from elemental composition or extraction data (see Test Case 6). The success or failure of this approach is determined by the validity of the extrapolation procedure (see Figure 4.10). In this example, one modelling team incorrectly interpreted Fe-extraction data resulting in a large over-estimate of the effective sorbing surface.

The last method of extrapolation (re-optimisation) is not really an extrapolation method at all. In effect, a new model was generated with a different set of optimised parameters. While this was

undertaken by some teams, it is not recommended as a defensible method of transferring models between datasets. Indeed, re-optimisation has a negative effect in that it makes it impossible to assess the transferability of the model. Presumably it can be used to obscure model shortcomings.

The limited pH example in the GC modelling of Test Case 6 (see Figure 4.9 and related discussion) highlights some of the problems which can arise from attempted extrapolations. The GC models tended to be valid over a wide pH range and the focus on a narrower, environmentally significant pH range did not require significant model changes. In some cases models could even be simplified for the limited pH data (Table 4.11). In contrast, the CA models tended to fail when applied across wider pH ranges and would have needed re-calibration to simulate the limited pH data. This can be seen by the curved nature of the error curves for almost all the CA models in Test Case 6. This indicated the presence of a systematic pH dependent error.

As a note of caution, the modelling in Test Case 6 indicates that provision of experimental data across a wide pH can lead to a focus on pH extremes. These are probably less relevant to performance assessment and tended to negatively impact the models (particularly the CA models). Furthermore, it is likely that the processes occurring at these pH extremes may not be similar to those at moderate pH values, perhaps involving mineral dissolution. As a result, the data and models may be of limited value in these pH regimes. These shortcomings must be balanced against the fact that performance across a wide range of conditions provides rigorous test of the models.

## 6.2 Sources of parameter values

Some of the failures in model 0 in the CA modelling (Test Case 6) can be ascribed to the fitting of the sorption edges using FITEQL and similar equations. FITEQL focusses on the sorption edge (in terms of percentage sorption) and tends to reduce the accuracy of  $K_d$  predictions at high sorption pH regime. This is demonstrated by Figure 4.2, where the maximum is substantially over-predicted.

The input data for model development in the CA case requires prior models for all postulated component minerals. All of the 7 teams that attempted the CA modelling in Test Case 6 utilised a model for the U sorption data on ferrihydrite (based on the model of Waite *et al.*, 1994). Four of these seven teams also required a model for the U sorption on kaolinite. These teams fitted the supplied sorption data adjusting sorption constants. The modelling teams reported satisfactory results with fitting the model mineral sorption data. However, none of the CA modelling teams used any alternative data for U sorption on any other minerals which may have been relevant.

In modelling surface reactions, there was a tendency for inappropriate mixing of data from various sources. For example, there was a general tendency to rely on *either* the Waite *et al* (1994) or Dzombak and Morel (1991) modelling approach for ferrihydrite. However, one team (in Test Case 6) obtained some of their model constants from each of these sources. The model combined some acidity constants from the Waite *et al.*, (1994) model with some phosphate/sulphate sorption constants from Dzombak and Morel (1990). That is remarkable considering the site density in the two models is different, and so are the surface acidity constants. These mixes of models would be expected to become incorporated into erroneous log K values.

Site densities and types were mostly pre-assumed in the modelling undertaken in Test Case 6. In some cases the amount of sorbing sites was manipulated by changing the amount of sorbing surfaces, but the site densities were not changed. The resulting models enable us to assess the status of the assumption that ferrihydrite plays a major, even dominant role in the U sorption on the complex material. In general this simple assumption was only adequate to a limited extent. Ferrihydrite is a very strongly adsorbing phase, but is not an ideal model sorbent. A major problem is normalising the

sorption data for ferrihydrite, which has a high surface area and high apparent site density. In combination these factors mean that the ferrihydrite tends to dominate models for the natural substrates, particularly if generated by the CA approach. This is seen in the curved shapes of the error distributions of the CA models. There was evidence that models that used site density as a fitting parameter resulted in site densities well below that predicted on the basis of a ferrihydrite dominance.

The modelling demonstrated the value of multiple datasets. The inadequacy of datasets used for model calibration tends to be glossed over in many published journal papers. For example, there are insufficient experiments where several experimental parameters (pH, ionic strength, total radionuclide concentration, ionic strength,  $p\text{CO}_2$ ) are systematically varied. It is particularly important in the CA approach that the models for the component minerals are calibrated across a wide range of chemical conditions. The present exercise required simulation of a wide range of experimental data – it is possible that the component models themselves were not sufficient to handle such a range.

### **6.3 Top-down (GC) and bottom-up (CA) modelling approaches**

#### **6.3.1 *Complexity and model performance***

The Test Case 6 and Test Case 7 examples both indicated that the GC approaches provided better simulations of the reference dataset with less complexity. For Test Case 6, it may be argued that the modelling teams were different and self-selecting – in other words, some chose the CA approach and some the GC approach. But teams were not requested to follow both approaches. However, in TC7, all teams attempted both types of modelling. In this test-case the errors were substantially smaller for the same team using the GC model.

The complexity of the CA models may be greater, because they may include several surface species that are carried across from component models and play an insignificant role in the model for complex materials. These extra species make the models more complex and raises the question of whether it is warranted to delete them. While this would simplify the model, such species may be needed under some circumstances.

On the other hand, the top-down approaches tend to have the “principle of parsimony” (simplicity) built into them and usually incorporate only a minimum number of species. This makes them appear simpler.

#### **6.3.2 *Problems in assembling CA models from models for component minerals***

Non-additivity refers to the possibility that the behaviour of a complex solid phase cannot be adequately represented by the summing the behaviour of component phases. This may be because the properties of the individual minerals may be different in the complex material. If there is significant non-additivity of sorption phenomena, the CA approach is much more negatively impacted than the GC modelling.

Most modelling teams utilised some degree of optimisation in the CA approach, justifying this on the basis the properties of the phase in the mixture differed from the pure mineral. This raises another potential difficulty with the CA models which decreases their predictive capability. Both the extent to which the complex substrates are non-additive and the amount to which their surfaces differ from pure component minerals are serious potential sources of error in the CA approach which are absent in GC modelling.

A problem in the CA was the assumed dominance of ferrihydrite, to the extent that 4 of the 7 CA teams (in Test Case 6) did not include kaolinite sites. However, it was demonstrated the properties

of kaolinite were in some respects more similar to the mixed substrate (Figure 4.3). Furthermore, the teams that optimised site densities (both the CA and GC groups) concluded that site-densities were much lower on the complex material than for ferrihydrite (Figure 4.1). This could imply that the modelling of the natural materials would be facilitated if several other types of surface sites could be incorporated.

However, the teams that did include kaolinite tended to be able to improve their models by increasing the assumed role of the kaolinite above that expected on the basis of its weight fraction and assumed surface properties. The GC modellers were not as constrained by the assumed model minerals and many assumed a different surface reaction stoichiometry for the Fe-oxide surface. Most of the GC modelling teams in Test Case 6 assumed a significant ligand effect or a role for kaolinite (or both).

### **6.3.3 Extrapolation ability of GC and CA models**

The CA models assume that it is possible to accurately simulate sorption on a material given enough knowledge of its components. However, the source of a failure of a model based on the CA approach is difficult to determine. In some cases this could be traced to deficiencies in the component model – e.g. failure for a high U concentration or particular pH range. However it could also arise because the method of normalising the component model was inadequate or the properties of the phases altered or due to interactive effects. Unscrambling the many potential sources of failure in a CA model may be quite difficult.

The modelling outcomes raised the issue of whether the extrapolation ability of a CA model is potentially greater than a GC model. There is some evidence that this is the case, with the CA models possibly performing equally well as the GC models when extrapolated outside their calibrated ranges. While this may not appear a strong commendation, it does to some extent reduce the apparent advantages of the GC models on a calibrated dataset. Another factor supporting this is that only two of the GC models were carried across to the other substrates without parameter changes in Test Case 6. Of the other GC cases, at least one was sensitive to parameter variation in that the non-optimised model failed on a different substrate. Indeed the sensitivity of GC models to the values of in-built parameters may be a problem. While parameters can easily be optimised, the models may be useless if their performance is highly sensitive to the values of optimised parameters.

While the extrapolation ability of the models may be similar, the predictive power of the CA models is certainly greater. In a sense, the GC models have no predictive power beyond the datasets on which they are calibrated.

Several conclusions can be drawn from the predictive modelling exercise in the CA approach (model 0 in Test Case 6).

- 1) The modelling always produces the humped shape of the sorption curve (i.e. both upper and lower pH edges). Furthermore, the effect of the presence of elevated CO<sub>2</sub> can be accurately simulated for most models. This is a positive outcome of the modelling.
- 2) The magnitude of the sorption maximum tends to be poorly estimated and this may in some cases be due to the way FITEQL operates in optimising the pH edge in terms of % sorbed versus pH.
- 3) The number U sorption datasets for the component minerals is very limited which restricts the application of the predictive CA approach.

- 4) The question of non-additivity of sorption behaviour needs further investigation before the CA approach can be thoroughly assessed.
- 5) Methods of parameterisation differed, but no predictive models were completely satisfactory in terms of satisfying the error criteria.
- 6) There exists a strong possibility of significant differences between simple substrates and the mineralogical components of the complex materials. This may limit the CA approach even when numerous U sorption datasets for component minerals were available.



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## **APPENDICES**



## *Appendix 1*

### TEST CASE SUMMARIES

#### TEST CASE 1 Neptunium(V) Sorption on Hematite

##### *Data source*

Kohler, M., Honeyman, B. D., and Leckie, J.O., 1999, *Radiochim. Acta*, v. 85, p. 33-48.

Original raw data available from M. Kohler.

##### *Summary of the experimental study*

Np(V) sorption onto a laboratory preparation of pure hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) was studied in solutions containing the electrolyte sodium perchlorate (NaClO<sub>4</sub>) at a temperature of 20-22°C. Sorption was studied as a function of pH (6.5-9.0), NaClO<sub>4</sub> concentration (0.005-0.1M), the partial pressure of carbon dioxide gas (<5 ppm-1.95% CO<sub>2</sub> gas), and the solid/water ratio (10-1000 mg/L). A reaction time of 12 hours was used to reach sorptive equilibrium under all the conditions studied.

Acid-base titrations of the hematite suspension were conducted at 25°C as a function of NaClO<sub>4</sub> concentration (0.01-0.27M) to measure the proton surface charge and the point-of-zero charge (pH = 9.4). Carbonate adsorption on the hematite suspension was measured as a function of pH for one set of chemical conditions in a closed system containing a known amount of total carbonate. For comparison, adsorption of Np(V) was also measured as a function of pH onto a laboratory preparation of goethite and a cleaned commercial quartz powder.

X-ray diffraction confirmed the crystalline identity of the hematite and no impurities were detectable. Specific surface area (14.4. m<sup>2</sup>/g) was measured by BET nitrogen gas adsorption. Preliminary kinetic studies suggested that 12 hours reaction time was sufficient to achieve a steady-state concentration of dissolved Np(V) in the hematite suspensions.

##### *Objective of the Test Case*

The K<sub>d</sub> values for Np(V) sorption on hematite are shown in the report (Kohler *et al.*, 1999) to be significantly dependent on pH and the partial pressure of carbon dioxide. The goal of the test case is to determine whether the dependence of the K<sub>d</sub> values for Np(V) sorption on these chemical variables can be described with surface complexation models. In particular, the importance of fitting the selected data with and without an electrostatic correction term to the surface complexation reactions will be examined. The models developed by the Participants will be compared to determine the level of complexity that is required in order to fit the sorption data well. The results will be evaluated by the TDT to examine the advantages and limitations of different modelling approaches, including issues such as data requirements, model plausibility, and model development. See the section on Criteria in the main report for further discussion.

## TEST CASE 2 Se Sorption on Goethite

### *Data source*

Hayes, K.F. Equilibrium, Spectroscopic and Kinetic Studies of Ion Adsorption at the Oxide/Aqueous Interface:

<http://www.library.unsw.edu.au/~thesis/adt-NUN/public/adt-NUN20001215.143254/>.

PhD Thesis. Stanford University. 1987.

Original raw data is on pages 144 to 146 of this thesis.

### *Summary of the experimental study*

Goethite was synthesised according to a standard procedure. Selenium sorption was studied across a range of pH. Experiments were undertaken with both selenate ( $\text{SeO}_4^{2-}$ ) and selenite ( $\text{SeO}_3^{2-}$ ). The surface area of the goethite was  $52 \text{ m}^2/\text{g}$ .

- Experiments with selenate were carried out at two mass loadings of goethite: 3 g/L and 30 g/L. Background electrolyte was  $\text{NaNO}_3$  at various ionic strengths: 0.01, 0.1 and 1.0M  $\text{NaNO}_3$  (In addition, 0.001 M  $\text{NaNO}_3$  was also used for the 30 g/L goethite loading only). Total selenate was fixed at 100  $\mu\text{mol}$ .
- Three pH edges were obtained with 100  $\mu\text{mol/L}$  selenite with a goethite loading of 30g/L. The ionic strengths were 0.005, 0.1 and 1.0M.

Acid base titration data were obtained and will be provided in the spreadsheet.

EXAFS measurements were undertaken and the conclusion was that “selenite forms an inner-sphere co-ordinative complex at the goethite surface, whereas selenate retains its hydration sphere upon adsorption.” Some information about the structure of the selenite surface complex was obtained, with a binuclear structure (i.e. selenite bonding to two surface Fe atoms) appearing most likely. However it should be noted that the concentration of Selenium in the EXAFS samples was 50 times higher than that used in the sorption experiments.

A subsequent EXAFS study in the goethite/selenate system concluded that “the selenate oxyanion forms an inner sphere surface complex on goethite” (Manceau and Charlet, *Journal of Colloid and Interface Science*, **168**: 87-93 (1994). This is a different conclusion to that reached by Hayes (1987) and it is the modeller’s option how to reconcile these studies and model the sorption data of Hayes (1987).

## TEST CASE 3 U(VI) Sorption on Quartz

### *Data sources*

1. Kohler, M. and Davis, J.A., US Geological Survey, unpublished data, manuscript in preparation.
2. Pabalan, R.T., Turner, D.R., Bertetti, F.P., and Prikryl, J.D., 1998, in *Adsorption of Metals by Geomedia*, E.A. Jenne (ed.), Academic Press, Chap. 3, pp. 99-130.

Original raw data available from M. Kohler and R.T. Pabalan.

### *Summary of the experimental studies*

1. Kohler *et al.* (in preparation): U(VI) sorption onto a cleaned and sized commercially-obtained quartz powder (Min-u-Sil, Pennsylvania Glass Sand Corporation, Pittsburgh, PA, USA) was studied in solutions containing the electrolyte sodium nitrate (NaNO<sub>3</sub>) at a temperature of 20-22°C. Sorption was studied as a function of pH (4-9), NaNO<sub>3</sub> concentration (0.005-0.1M), the total concentration of uranium(VI) (10<sup>-8</sup>M to 10<sup>-5</sup>M), the partial pressure of carbon dioxide gas (ambient air -7.76% CO<sub>2</sub> gas), the concentration of fluoride (0-0.5 millimolar), and the solid/water ratio (10-100 g/L). A reaction time of 18 hours was used to reach sorptive equilibrium under all the conditions studied.

Base titrations of the quartz suspension were conducted at 22°C as a function of NaNO<sub>3</sub> concentration (0.004-0.1M) to measure the proton surface charge.

X-ray diffraction confirmed the crystalline identity of the quartz and no impurities were detectable by XRD. Specific surface area (0.33 m<sup>2</sup>/g) was measured by BET krypton gas adsorption. SEM micrographs showed that the grain size ranged from 8 to 30 μm. Preliminary kinetic studies suggested that 20 hours reaction time was sufficient to achieve a steady-state concentration of dissolved U(VI) in the quartz suspensions.

2. Pabalan *et al.* (1998): U(VI) sorption onto a cleaned and sized commercially-obtained quartz powder (Wedron #510, Wedron Silica Co., Wedron, IL, USA) was studied in solutions containing the electrolyte sodium nitrate (0.1M NaNO<sub>3</sub>) at a temperature of 18-22°C and equilibrated with the ambient atmosphere. Sorption was studied as a function of pH (2.5-8), the total concentration of uranium(VI) (2 x 10<sup>-8</sup>M to 2.15 x 10<sup>-6</sup>M), and the solid/water ratio (2-50 g/L). The specific surface area was measured as 0.03 m<sup>2</sup>/g using BET nitrogen gas adsorption. A reaction time of 10 days was used to reach sorptive equilibrium under all the conditions studied.

### *Objective of the Test Case*

The K<sub>d</sub> values for U(VI) sorption on quartz are shown in the report (Kohler *et al.*, in preparation) to be significantly dependent on pH, the concentration of U(VI), the concentration of fluoride, and the partial pressure of carbon dioxide. The goal of the test case is to determine whether the dependence of the K<sub>d</sub> values for U(VI) sorption on these chemical variables can be described with surface complexation models. The models developed by the Participants will be compared to determine the level of complexity that is required in order to fit the sorption data well. In particular, the necessity of an electrical double layer in the model will be examined.

In addition, the ability of the models calibrated with the Kohler data will be tested for their ability to predict the U(VI) sorption data of Pabalan *et al.* (1998) without any manipulation of model parameters.  $K_d$  values for U(VI) sorption on quartz from the two data sources (Pabalan *et al.* and Kohler *et al.*) differ by an order of magnitude. However, much of this difference may be due to the different surface areas of the two samples used by these investigators. In principle, this difference in surface area should be accommodated in the predictions of surface complexation models without any change in fitted model parameters. In addition, the data of Pabalan were also collected under different chemical conditions than those of Kohler (e.g. low partial pressures of carbon dioxide), and the test case will examine the ability of the calibrated model to predict U(VI) sorption under different chemical conditions than that for which the model was calibrated.

## TEST CASE 4 Nickel Sorption on Clays

### *Data sources*

1. Baeyens, B., and Bradbury, M.H. (1997), A mechanistic description of Ni and Zn sorption on Na-montmorillonite. Part I: Titration and sorption measurements, *J. Contam. Hydrol.*, 27, 199-222. (Modelling in: Bradbury, M.H., and Baeyens, B. (1997), A mechanistic description of Ni and Zn sorption on Na-montmorillonite. Part II: modelling, *J. Contam. Hydrol.*, 27, 223-248.) The content of these papers is described in more detail in PSI-reports 95-10 to 95-12 by the same authors.
2. Bradbury, M.H., and Baeyens, B. (1997), Modelling the sorption of Zn and Ni on Ca-montmorillonite, *Geochim. Cosmochim. Acta*, 63, 325-336.
3. Lothenbach, B., Furrer, B., and Schulin, R. (1997), Immobilisation of heavy metals by polynuclear aluminium and montmorillonite compounds, *Environ. Sci. Technol.*, 31, 1452-1462.
4. Tachi, T and Shibutani, T. (1999), JNC Technical Report.

Original raw data are available for all four studies.

### *Summary of the experimental studies*

1. Baeyens and Bradbury (1997): Ni sorption onto purified, size-fractionated and well characterised SWy-1 Na-montmorillonite was studied in NaClO<sub>4</sub> solutions at room temperature (20-22°C) under a N<sub>2</sub> atmosphere (< 5 ppm CO<sub>2</sub> and O<sub>2</sub>), using solid/water ratios of about 0.2-2 g/L. A reaction time of one to several days was used to reach sorptive equilibrium under all the conditions studied (demonstrated in preliminary experiments).

Sorption of Ni was studied as a function of:

- pH (3-10.5), at Ni concentrations < 3.7•10<sup>-7</sup>M,
- NaClO<sub>4</sub> concentration (0.01, 0.03, 0.1M), and
- the total concentration of Ni (about 10<sup>-9</sup>M to 10<sup>-4</sup>M), at constant pH values of 4.7, 5.1, 5.9, 7.0, 7.7, 8.2 (in 0.1 M NaClO<sub>4</sub>).

Additional sorption data are provided for Zn, Mn, Mg and Ca, which are contained as impurities in the purified montmorillonite:

- Zn sorption was studied as a function of pH (2-9.5) and as a function of added Zn concentration at constant pH values of 5.6 and 7.
- Ca sorption was studied as a function of pH (2-12) and of NaClO<sub>4</sub> concentration (0.01, 0.03, 0.1M).
- Mn and Mg sorption were studied as a function of pH (2-12).

Batch acid-base (back)titrations were conducted at two ionic strengths (NaClO<sub>4</sub> concentrations of 0.1 and 0.5M) to measure the proton surface charge. The concentrations of Zn, Mn, Ca, Mg, Fe, Al and Si were measured in the titration experiments. Specific surface area was measured by BET-N<sub>2</sub> gas adsorption. The mineralogical composition of the montmorillonite sample was measured with XRD. Strong acid and



D-C-B extractions were carried out to quantify extractable Fe and total inventories of reactive Zn, Mn, Ca and Mg. The CEC was measured by isotopic dilution.

2. Bradbury and Baeyens (1999): Ni sorption onto purified and well characterised Ca-montmorillonite (purified from SWy-1 Na-montmorillonite) was studied in CaNO<sub>3</sub> solutions at room temperature (20-22°C) under a N<sub>2</sub> atmosphere (< 5 ppm CO<sub>2</sub> and O<sub>2</sub>), using solid/water ratios of about 0.3-1.3 g/L. A reaction time of ≥ 2 days was used to reach sorptive equilibrium under all the conditions studied (demonstrated in preliminary experiments).

Sorption of Ni was studied as a function of:

- pH (3-10), at Ni concentrations < 3•10<sup>-8</sup>M,
- CaNO<sub>3</sub> concentration (0.003, 0.03 M), and
- the total concentration of Ni (about 10<sup>-8</sup>M to 10<sup>-4</sup>M), at constant pH values of 7.0 and 8.1 (in 0.03 M CaNO<sub>3</sub>).

All other experimental data on the montmorillonite sample (mineralogy, acid-base characteristics, CEC, inventories of different trace elements etc.) was used as given in reference (1).

3. Lothenbach *et al.* (1997): The sorption of Ni and other heavy metal ions (Zn, Cu, Cd) onto size-fractionated SWy-1 montmorillonite converted to the Na form was studied at room temperature (20-22°C). All experiments were carried out in 0.1 M NaClO<sub>4</sub> solutions, using a solid/water ratios of about 2 g/L. Experiments were done in batches under an Ar atmosphere, *p*CO<sub>2</sub> in the vessels is estimated as 9•10<sup>-9</sup> atm after 4 weeks, and as 6•10<sup>-6</sup> atm after 30 weeks.

Sorption of Ni was studied as a function of

- pH (4-9.5), at a single Ni concentration of 100 μM
- reaction time (2, 4, 30 and 60 weeks)
- Ba<sup>2+</sup> concentration (0, 33 mM), as Ba(ClO<sub>4</sub>)<sub>2</sub>.

For Zn, essentially the same set of experiments as for Ni was carried out.

Specific surface area was measured by BET-N<sub>2</sub> gas adsorption. The CEC was measured by the BaCl<sub>2</sub> method. Additional information is given in the appendix of a Ph.D. thesis by B. Lothenbach (Diss. ETH No. 11837, Zürich, Switzerland), which will be made available for the Sorption Project: Continuous acid-base titrations were conducted at 3 ionic strengths (NaClO<sub>4</sub> concentrations of 0.01, 0.1 and 0.5M) to measure the proton surface charge; dissolved Si and Al was measured at the end of each experiment The concentrations of Mg, Al and Si dissolving from the montmorillonite were measured as a function of pH (2-10) after 4 and 60 weeks reaction time. The mineralogical composition of the montmorillonite sample was measured with XRD.

4. JNC (Tachi and Shibusani, 1999; JGC, 1991): The sorption of Ni onto crude (natural) bentonite was studied at 25°C, using solid/water ratios of 10 and 20 g/L and a reaction time of 30 days throughout. All experiments were carried out under air; i.e. in or near

equilibrium with atmospheric CO<sub>2</sub>. Unlike the above studies (1)-(3), these measurements were aimed at generating data for a mechanistic investigation, but at determining a limited set of K<sub>d</sub> values for PA. No systematic sorption edges or isotherms were measured. A total of 18 K<sub>d</sub> values is available, covering the following conditions:

- pH 4.6-11 (adjusted using HCl or NaOH),
- initial Ni concentrations of 10<sup>-4</sup> and 10<sup>-6</sup>M,
- background electrolytes: water only, 0.001M and 0.1M NaCl, sea water.

Additional relevant information is given in several publications and JNC Technical Reports. This information will be collected and summarised in tables, which will be made available for the Sorption Project. We expect to be able to provide the following data:

- specific surface area (BET-N<sub>2</sub>),
- CEC,
- mineralogy of the bentonite, determined by XRD and in leaching experiments (about 50% smectite, 40% quartz, 0.5-3% feldspar, zeolite, pyrite, calcite and dolomite, about 0.4% gypsum, and traces of salts),
- exchangeable ions on the clay surface,
- development of pH, as well as sulphate, Na, Ca concentration in supernatant solutions as a function of time (up to ca. 150 days),
- acid-base titrations of a pure smectite separate at different ionic strengths.

## TEST CASE 5 Np(V) Sorption on Montmorillonite

### *Data sources*

1. Turner, D.R., Pabalan, R.T., and Bertetti, F.P., 1998, Neptunium(V) sorption on montmorillonite: An experimental and surface complexation modelling study, *Clays and Clay Minerals*, v. 46, p. 259-269.

Original raw data are available from D. Turner.

2. Gorgeon, L., *Contribution à la modélisation physico-chimique de la rétention de radioéléments à vie longue par des matériaux argileux*.

This work includes Np sorption on bentonite study.

### *Summary of the experimental study*

Np(V) sorption onto a laboratory preparation of Na-montmorillonite was studied at fixed initial Np(V) concentration ( $\approx 1 \times 10^{-6} \text{M } ^{237}\text{Np}$ ) in solutions containing the electrolyte sodium nitrate (0.1 molal  $\text{NaNO}_3$ ) at room temperature ( $20 \pm 2 \text{ }^\circ\text{C}$ ) over a pH range of about 4 to 11. Four sets of sorption experiments were conducted with different  $p\text{CO}_2$ : trace  $\text{CO}_2$ , atmospheric  $\text{CO}_2$  (forward and reverse) and no  $\text{CO}_2$ . A reaction time 14 days was used to reach sorptive and pH equilibrium under all the conditions studied. The reaction time was so long mainly to relatively slow mass transfer of  $\text{CO}_2$  between the gas and aqueous phases.

The Na-montmorillonite was obtained natural Ca-smectite (SAz-1) by conversion with NaCl solution and purification. The measured ( $\text{N}_2$ -BET) specific surface area was  $97 \pm 2 \text{ m}^2 \text{ g}^{-1}$ . X-ray powder diffraction analyses performed at different phases of preparation showed the interlayer spacing consistent of ion exchange of Na for Ca.

### *Objective of the Test Case*

Fit the selected data with a mass action model. Then extend the model in a predictive fashion to bentonite with chemical conditions provided by TDT. The models developed by the Participants will be compared to determine the level of complexity that is required in order to fit the sorption data well. The results will be evaluated by the TDT to examine the advantages and limitations of different modelling approaches, including issues such as data requirements, model plausibility, and model development. See the section on Criteria in the main report for further discussion.

## TEST CASE 6 U Sorption on Koongarra Weathered Schist

### *Data source*

Payne, T.E., Uranium (VI) Interactions with Mineral Surfaces: Controlling Factors and Surface Complexation Modelling. PhD Thesis, University of NSW, 1999. Available on the web at:

<http://www.library.unsw.edu.au/~thesis/adt-NUN/public/adt-NUN20001215.143254/>

Original raw data is on pages A1-14 to A1-18. This dataset will be duplicated in the spreadsheet of the test case.

### *Summary of the experimental study*

Koongarra is a uranium deposit in Northern Australia that has been the subject of intensive study to attempt to understand and model the mechanisms of U migration. Experimentally, U(VI) sorption was studied with a fine particle fraction separated from Koongarra weathered schist by sedimentation. Variables included:

- pH (3-10);
- contacting gas-air and elevated  $p\text{CO}_2$  (1%);
- effect of extraction of Fe-minerals using DCB reagent;
- mass loading of 4 g/L and 20 g/L;
- U concentration. Many experimental data were obtained using tracer addition of  $^{236}\text{U}$  (therefore the U content being dominated by natural U in the samples) but some with elevated total U such as 100  $\mu\text{mol/L}$ ;
- ionic strength – data were obtained in  $\text{NaNO}_3$ , typically 0.1M. Other concentrations from 0.02M to 2.5M were used for both low and high pH edges;
- added Mg (had little effect on U sorption);
- 4 different solid materials.

The samples were characterised in terms of their natural U content and its partitioning amongst various mineral phases, using sequential extractions and other techniques. Particular emphasis was placed on assessing the labile (accessible) pool of U using isotope exchange. The samples were examined by SEM/EDX. The BET surface areas were measured.

### *Objective of the Test Case*

The U(VI) sorption on the Koongarra materials was shown to be significantly dependent on pH, partial pressure of carbon dioxide, ionic strength (only at high pH values), and total amount of U present in the system. The sorption (expressed in percentage terms or as a  $K_d$ ) decreased with increasing U concentration.

The goal of the test case is to determine whether the dependence of the  $K_d$  values for U(VI) sorption on these chemical variables can be described with surface complexation models, considering either a limited (Part A) or full (Part B) dataset (see below). The models developed by the participants will be compared to determine the level of complexity that is required in order to fit the sorption data adequately.

There has been a previous attempt to model the U sorption data using the “component additivity” approach and the “generalised composite” approach (Waite *et al.*, 2000). While promising, both of these methods (as implemented in the cited paper) tended to provide model pH edges that were too steep. In other words, sorption in the mid-pH range of high uptake was over-predicted, whereas the uptake at high and low pH extremes was under-predicted. Thus the goal would be to use the SCM to obtain an improved simulation of the sorption data. The modellers would have the option of using the approaches of Waite *et al.* (2000) or entirely different modelling procedures. It would be essential to document the modelling strategy in detail.

**Data provided for both modelling cases**

Table 1: **U sorption datasets for Koongarra substrates**

Paragraph		Substrate	Mass loading	Gas phase	U added	NaNO <sub>3</sub>
PART A	PART B					
1,2	2,3,4	W2	4 g/L	air	trace	0.1M
3	5	W2	4 g/L	1% CO <sub>2</sub>	trace	0.1M
4	6	W2	4 g/L	air	100 µmol/L	0.1M
5	7	W2	4 g/L	air	trace	0.02, 0.2, 2.2M
6	8	W1	4 g/L	air	trace	0.1M
7	9	W1	20 g/L	air	trace	0.1M
7	9	W1	20 g/L	1% CO <sub>2</sub>	trace	0.1M
7	9	W1	20 g/L	Air	100 µmol/L	0.1M
8	10	W7	4 g/L	Air	Trace 1 µmol/L 100 µmol/L	0.1M

Table 2: **Summary substrate data (BET surface area, total U and extractable U content)**

Sample	BET (m <sup>2</sup> /g)	Total U (µg/g)	TAO- Extractable U (µg/g)
W1 (13.0-13.2m)	24.6	356	42.6
W2 (14.0-14.2m)	52.3	426	225.0
W7 (13.0-13.2 m)	51.9	10.4	1.0

**The following characterisation information was also be supplied:**

- a) Total elemental content by PIXE/PIGME.
- b) Qualitative XRD and SEM/EDX information indicating that the materials are weathered schist with main mineral components being quartz, kaolinite, crystalline Fe-oxides, amorphous Fe-oxides.

## TEST CASE 7 Co Sorption on Soil

### *Data source*

Zachara, J.M., Resch, C.T. and Smith S.C. 1994, *Geochimica et Cosmochimica Acta*, Vol. 58, No. 2., pp. 553-566. Influence of humic substances on  $\text{Co}^{2+}$  sorption by a subsurface mineral separate and its mineralogical components.

### *Summary of the experimental study*

$\text{Co(II)}$  ( $10^{-6}$  mol/L) sorption onto subsurface mineral materials was studied in absence and presence of a sorbed leonardite humic acid (LHA). The subsurface materials were a  $<2.0$   $\mu\text{m}$  size fraction of an ultisol saprolite (CP) and this same material treated with dithionite-citrate-bicarbonate (DCB) to remove Fe-oxides (DCP). Comparable experiments (with and without LHA) were also performed with mineral sorbents representing dominant phases in the CP separate (gibbsite, Al-goethite, and kaolinite) to evaluate their potential contributions to Co sorption.

The mineralogical composition of the CP was analysed. CEC for CP and DCP were analysed as a function of pH. Surface areas were measured both for CP and DCP.  $\text{Co}^{2+}$  complexation to LHA was determined in 0.01 and 0.1 mol/L  $\text{NaClO}_4$  over pH 4.5 to 8.0.

Cobalt complexation to LHA was determined in 0.01 and 0.1 mol/L  $\text{NaClO}_4$  over pH 4.5 to 8.0.

Cobalt sorption was measured on the CP and DCP isolates, KGAA-1, gibbsite and Al-goethite at  $I = 0.1$  and 0.01 in  $\text{NaClO}_4$  over the pH range 4.5 to 8.5. The sorption measurements were repeated with LHA-coated minerals.

Batch measurements of LHA on both the CP and DCP were employed (sorbents at 20-90  $\text{m}^2/\text{L}$ ; LHA-DOC at  $\approx 11$  mg-C/L) over a range in pH and ionic strength at  $I = 0.01$  and 0.1 in  $\text{NaClO}_4$ .

The sorption kinetics was experimentally tested for all measured systems and long enough equilibration times were used.

### *Objective of the Test Case*

The goal of the test case is to compare two approaches in the model fitting: first directly from measured sorption data and second by using the set of sorption models for each component minerals.



## *Appendix 2*

### **ACTIVITY COEFFICIENTS**

#### **Aqueous species**

For each test case, a standard set of thermodynamic data for aqueous species were provided as part of the instructions, so that differences between the model predictions for sorption would not be caused by the use of different thermodynamic data. Despite this, a few teams chose to modify the aqueous thermodynamic data by including additional aqueous species or changing the thermodynamic constants for aqueous species. The details are not provided here, but the reader should be aware that this occurred in a few cases.

In the modelling exercises presented in this report, the modelling participants were free to use whatever convention they wished for the correction of aqueous concentrations to activities. A convention is required both to extend the application range of SC models to higher ionic strength and to make the activity corrections consistent within other geochemical models (i.e. the same reference state for all species and an internally consistent correction method for all aqueous species). Almost all modelling participants used the Davies equation for this purpose in this project. Some did not report what convention was used. There were certain calculations (e.g. in Test Case 6) that needed to be completed at high ionic strength (>1M). Although it is known that the Davies equation does not apply at this high ionic strength, many still used the Davies equation while noting that it should not apply. However, some of the modelling teams left the high ionic strength system out of the model calibration steps in Test Case 6.

It is noted that the NEA recommends the SIT approach for determining aqueous activities, and it is recommended for consistency that future activities within the NEA Sorption Project require use of the SIT approach.

#### **Surface species**

A detailed discussion of the activities and reference states of surface species is beyond the scope of this project. Most modelling participants assumed that the activity coefficient for surface species were equal to one, or in the case of SC-EDL models, equal to the electrostatic term added to mass laws that describe the formation of the surface species (i.e. the activity of surface species is corrected by the electrostatic attraction/repulsion terms).

A few modelling teams applied activity corrections to the surface species using the Davies equation, as if the species were dissolved (the net charge of the surface species was computed and an activity coefficient was calculated based on the ionic strength in solution). This approach seems invalid and is not recommended. Of course, even with incorrect activity coefficients for surface species, it is possible to achieve a good fit to sorption data because the errors are subsumed into the



stability constants for the surface species during fitting. However, such errors likely make it more difficult to describe sorption data as a function of ionic strength.

## **Impact of ion activity model on the model results: Application to Test Case 2<sup>1</sup>**

### ***Introduction***

There are several ways of treating activity coefficients in the context of surface complexation models. One thing common to all papers which the author has come across is to apply a specified model to solution speciation. Surface chemical reactions have been treated accordingly, i.e. all aqueous species involved in a surface chemical reaction are corrected, but other suggestions exist applying no corrections based on aqueous chemistry to surface chemical reactions at all. Here, the effect of different aqueous activity correction models on surface complexation models is evaluated in an exemplifying way for the Se/goethite systems studied by Hayes (1987). Activity corrections, which have previously been used in a database for surface complexation on hydrous ferric oxide by Dzombak and Morel (1990), which are largely based on the Davies equation, have been used on the one hand and activity corrections, calculated from the specific ion interaction theory (SIT) have been applied for comparison. The two approaches have been applied to the selenium adsorption data obtained by Hayes (1987) in sodium nitrate solutions. In a first step the goethite acid-base data were analysed using both models as well. The data are interesting since for the conditions chosen by Hayes (1987) selenate adsorption as the one extreme exhibits a strong ionic strength dependence whereas selenite adsorbs virtually independently of ionic strength.

### ***Procedures***

1. From the given experimental data of the spread-sheets,  $\log H^+$  values were calculated using:
  - a) Tabulated activity coefficients based on Dzombak and Morel (1990), which will be referred to as a Davies-type approach, even though there are data which are outside the range of applicability of the Davies equation (the tabulated activity coefficients for  $I > 0.1M$  have been obtained elsewhere by Dzombak and Morel).
  - b) Calculated activity coefficients for the proton at the various sodium nitrate concentrations used in Hayes study based on the specific ion interaction theory (referred to as SIT in the following) as specified by Grenthe and Puigdomenech (1991), Chapter IX. The values were calculated using an EXCEL-spreadsheet and rounded values of the format a.b.c.d. were used. For the SIT, when no data for the selenium case were available, available sulfur parameters were used.

The data were added in the application input files in the format a.b.c.d. The optimisations were run with UCODE, using the same UCODE files for the two cases. Fits were done on molar concentrations of adsorbed Se, with the same kind of error weighting in all cases.

2. First the acid-base models for the goethite were obtained and these were then used for the Se adsorption data. In the evaluation of the titration data, data are fitted based on proton adsorbed. Since no internal determinations of the conditional  $pK_w$  are available for those data, an inconsistency is introduced by comparing the Davies and SIT results, i.e. different charge density/pH relationships may in principle be obtained. To insure internal consistency for both approaches this is accepted. In the present case with the relatively low values of ionic strength, the inconsistency does not become evident on a graphical representation of the data.

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1. This was contributed by Johannes Lützenkirchen, FZK-INE, D-70621 Karlsruhe, Germany.

3. The pertaining activity coefficients for the master species were calculated in an EXCEL-spreadsheet as described above for the SIT approach. The resulting values as well as the corresponding values from Dzombak and Morel (1990) are given in Table 1. One surprising difference is that with the 1M sodium nitrate concentration significant differences occur, which are most spectacular for the selenite and selenate, respectively. But also the sodium and nitrate values differ from the values given in Dzombak and Morel (1990).

Table 1: **Logarithm of the activity coefficients for the aqueous master species based on the Davies equation and the SIT approach**

<b>Ionic strength in M Master Species</b>	<b>1</b>	<b>0.1</b>	<b>0.03</b>	<b>0.01</b>	<b>0.005</b>	<b>0.001</b>	<b>Model</b>
<b>Proton</b>	-0.134	-0.102	-0.068	-0.044	-0.032	-0.015	SIT
	-0.140	-0.110	-0.070	-0.050	-0.030	-0.020	Davies
<b>Sodium</b>	-0.244	-0.113	-0.071	-0.045	-0.033	-0.015	SIT
	-0.140	-0.110	-0.070	-0.050	-0.030	-0.020	Davies
<b>Nitrate</b>	-0.244	-0.113	-0.071	-0.045	-0.033	-0.015	SIT
	-0.140	-0.110	-0.070	-0.050	-0.030	-0.020	Davies
<b>Selenite</b>	-0.896	-0.446	-0.283	-0.178	-0.131	-0.062	SIT
	-0.560	-0.440	-0.265	-0.180	-0.130	-0.060	Davies
<b>Selenate</b>	-0.936	-0.450	-0.284	-0.179	-0.131	-0.062	SIT
	-0.560	-0.440	-0.265	-0.180	-0.130	-0.060	Davies

## Results

### 1. Acid-base model

- The acid-base model is basically affected by three issues: (i) new  $\log H^+$  values, (ii) new surface charge densities, in particular at the higher pH values, where the  $pK_w$  value becomes important, (iii) the new value of the activity coefficient at 0.01M sodium nitrate.
- The combined effect of these three issues results in new electrolyte binding constants and a slightly different capacitance value (Table 2): The acid-base model performed thus slightly better with the Davies correction.

Table 2: **Acid-base model parameters for the 1-pK, Basic Stern charging model, evaluated on the basis of the Davies equation and the SIT approach**

	<b>anion binding</b>	<b>cation binding</b>	<b>capacitance</b>	<b>Goodness of fit</b>
<b>Davies</b>	0.344	0.430	0.604	0.0778
<b>SIT</b>	0.313	0.405	0.608	0.0797

### 2. Se adsorption model

- Selenite model:** this model is characterised by its simplicity. For the Davies framework an ideal charge distribution along with spectroscopic input leaves only one parameter to fit, namely the stability constant for the selenite bidentate, binuclear surface complex. Both

approaches yield similar stability constants, the goodness of fit being slightly better for the Davies case (Table 3).

Table 3: **Stability constants, evaluated on the basis of the Davies equation and the SIT approach, for the selenite/goethite system (ideal charge distribution assumed) based on the respective version of the 1-pK BS charging model (Table 2)**

	Stability constant	Goodness of fit
<b>Davies</b>	25.6	0.60
<b>SIT</b>	25.2	0.78

- b) **Selenate model:** this system is characterised by its pronounced ionic strength dependence. From spectroscopic investigations it is inferred that monodentate surface complexes form. Both inner- and outersphere surface complexes have been suggested. Based on a number of spectroscopic studies on other anions, it was assumed in the first modelling attempts that inner- and outersphere surface complexes are coexisting. Then more extensive calculations showed that actually the experimental data are not able to **conclusively** resolve parameters for both complexes. Thus in a subsequent step only one complex was assumed. Charge distribution factor and stability constant were optimised simultaneously. Correlation between the two was 0.76, which is not considered a high correlation. The results of the optimisation runs are summarised in Table 4. The parameters are quite close and goodness of fit is better for the Davies approach

Table 4: **CD-parameters and stability constants evaluated on the basis of the Davies equation and the SIT approach, for the selenate/goethite system (ideal charge distribution assumed) based on the respective version of the 1-pK BS charging model (Table 2)**

	Stability constant	CD-factor	Goodness of fit
<b>Davies</b>	9.79	-0.682	2.9
<b>SIT</b>	9.84	-0.679	3.6

### Summary

The present report compares two different activity correction models with respect to surface complexation modelling in the goethite acid/base, the selenite/goethite and the selenate/goethite systems. For the first approach, unspecific activity coefficients were used, whereas with the SIT model activity corrections at sufficiently high ionic strength will differ for different ions of the same charge. For the SIT not all parameters were available, which are required for the application of the SIT to the different selenium species, and those parameters missing were replaced by the analogous values for sulfur species. With the derived activity coefficients it became evident that for the highest value of ionic strength used in the calculations the activity coefficients obtained from the SIT approach could significantly differ from the ones obtained from Dzombak and Morel (1990). Thus a first conclusion is that the use of more accurate approaches such as SIT is certainly preferable.

With both approaches the data can be reasonably described. Parameters differed slightly, but in the context of surface complexation modelling by no means significantly. Surprisingly, for all cases the goodness of fit was always better for the Davies-type approach, whereas one might have expected rather a random behaviour of the goodness of fit parameter. However, due to the limited data investigated, this should not be overinterpreted or even generalised.

In principle the SIT approach is easily coupled with surface complexation models. It would be highly desirable to have a self-consistent speciation code including the SIT. This would avoid the complex procedure of calculating the activity coefficients in a separate spread-sheet. I plan to some programming in the course of this year on the FITEQL code and I will try to incorporate the SIT as an option.

### ***References***

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### *Appendix 3*

## DEFINITION OF “FITTING PARAMETER”

### **What is a fitting parameter**

In the course of our evaluation of the various modelling contributions, it turned out that the definition of “fitting parameter” is not in all cases as straightforward as one might expect. Since the distinction between fitted and independent parameters is important with regard to the quantitative evaluation of model complexity, a brief discussion of fitting parameters for a thermodynamic radio-nuclide sorption model is given here.

### *Equilibrium constants*

The most obvious case of a fitting parameter is an *equilibrium* constant for a surface complexation or ion exchange reaction involving the RN of interest that is being fitted to the experimental dataset under consideration. Further obvious fitting parameters include surface protolysis constants, or surface complexation constants of other competing elements, if they are fitted to the particular experimental data. The number of fitting parameters for such auxiliary species can become very large when one has to deal with complex electrolytes:

- The use of outer-sphere surface species in a BSM or TLM may require the definition of constants for each electrolyte species.
- Modelling of ion exchange of a RN requires the ion exchange constants of all major cations.

If such constants are taken from independent pieces of literature (evaluated from independent sets of experimental data, see Section on parameter transferability), they are counted not as fitted but as independent parameters.

Note that independent literature does not include previous interpretations of exactly the same dataset. Since all test cases of this exercise were based on data that had previously been modelled (for reasons already explained at an early stage of this project), this distinction is important for the assessment of model complexity:

- If e.g. surface protolysis constants for the sorption of Ni on montmorillonite are fitted from the provided dataset (Bradbury and Baeyens, 1997), they are counted as fitting parameters.
- If these constants are taken from e.g. the study of Wanner *et al.* (1994), they are counted as independent parameter, not as fitting parameter. Note that all SC constants in a model need to correspond to the same setup (see Section on parameter transferability); i.e. the constants by Wanner *et al.* (1994) would have to be used in conjunction with a one-site SCM/DLM, the respective edge site density and surface area, etc.

- If, on the other hand, protolysis constants are taken directly from Bradbury and Baeyens (1997), they are being counted as fitting parameter, because they had originally been developed in conjunction with the Ni sorption data under consideration.

In this context, each surface species is counted as model parameter. I.e. the formation of two different RN species (e.g.  $\text{SOHNpO}_2^+$ ,  $\text{SONpO}_2$ ) at a given surface site is counted as 2 fitting parameters. Likewise, the formation of a certain RN species at 2 different (e.g. strong and weak) surface sites (e.g.  $\text{S}^{\text{w}}\text{ONpO}_2$ ,  $\text{S}^{\text{s}}\text{ONpO}_2$ ) is counted as 2 fitting parameters. The same holds for any auxiliary surface species.

### ***Other parameters***

Basically, all other adjustable parameters are treated in the same fashion as stability constants. These include:

- site densities;
- surface areas;
- EDL parameters such as capacitance values and charge densities;
- CEC values.

If these values are based on independent data (e.g. if the surface area is set equal to the BET surface area), they are counted as independent and not as fitted. In several cases modelling teams used independent measurements to (narrowly) constrain such parameters, but in the end still felt that minor adjustments had to be made. In these cases, the slightly adjusted parameters still were counted as fitting parameters.

### ***Parameters in extrapolations***

In several test cases, extrapolations of calibrated models to different conditions or different substrates were required. While all surface equilibrium constants were to be used as derived in the model calibration, a few of these cases required the definition of some additional parameters. Examples include:

- Surface area of clay edges: This was not counted as fitting parameter if the BET area was used or if the same fraction of the BET area as in model calibration was used.
- Site densities at clay edges: This was not counted as fitting parameter if the same site density as during calibration was kept (in micromoles/m<sup>2</sup> if an EDL model was used, or in micromoles/unit mass in case of an NEM that did not use surface area). It is also possible to use a fix relation between CEC and edge site density, keeping the ratio of weak/strong or SiOH/AlOH sites constant, if applicable.
- Ion exchange constants of additional cations (e.g. Ba-Ni in TC4): Most teams solved this by setting equal the equilibrium constant for the half reaction of Ba and Ca with the surface.

Where case-specific adjustments were made (e.g. if the ratio of weak/strong sites changed) that were not prompted by independent experimental evidence, the respective parameters were counted as fitted.

### *Special cases*

There were several cases where modelling teams made adjustments which, strictly speaking, were not within the rules laid out in the instructions to test cases:

- In several instances, stability constants for solution species or solids were used that differed from the provided data. These were counted as additional fitting parameters.
- In some cases,  $p\text{CO}_2$  was varied to achieve better fits and was also counted as additional fitting parameter.





## *Appendix 4*

### **UNCERTAINTY AND ERROR ANALYSIS**

Fitting of data to some model or function is quite a common task in scientific work, and has been studied much and deeply. Fitting might also be called optimisation (of parameter values), because in many systems of interest it is possible only to try to minimise the difference between observed and calculated values. If we have, after years of scientific work, a fundamental theory good enough for some phenomenon, just one measurement might enable the application of the theory to a whole class of connected phenomena. If we do not have such a theory, but just a model or hypothesis, both the model fitting and especially extrapolation becomes much more difficult. Chemical thermodynamics has been quite a successful theory, but still nowadays almost all of its applications include some model (set of reactions relevant for the studied system), which is fitted to some experimental data. I.e. it is difficult to obtain direct molecular-level data regarding the existence of some aqueous or surface species; however, if the macroscopic data is well described by a model, the respective species are assumed to exist. In the NEA sorption test cases surface complexation models were applied and fitted, and it has not been proved yet that adsorption may be completely modelled by SCM models and that we already have found the best reactions describing the systems. This means that not only the experiments but also models include errors, and that this modelling error may be of a deeper nature than the experimental error.

Optimisation may be classified as:

1. linear optimisation, LP;
2. linear integer optimisation LPI;
3. non-linear optimisation NLP;
4. non-linear, integer optimisation NLPI.

Both non-linearity and integer parameter values make the optimisation considerably more complicated. Most chemical systems including surface complexation models are non-linear and integer valued. Non-linearity follows from the different form of mass action and mass balance equations, the latter being typically linear. Optimisation of non-linear systems is most often based on local linearisation of equations, which may cause the finding of only local optimum or minimum; there is no general method of knowing if the real global minimum is reached (sometimes change of parameter values of initial guess may show it). Some new methods like Monte-Carlo simulations and genetic algorithms try to avoid this problem by generating either randomly or systematically new models (new parameter sets), which are then tested against some criteria like also in more traditional methods. Ideally these new methods should be better in finding good parameter sets, because they are doing the search by globally varying parameters in a broader range. The application of these new methods consumes much calculation power and there might be some convergence problems when the “artificially” generated parameter values are outside the limits of application of the studied model. In NEA Test Case 2, Monte-Carlo simulations were applied, but in no case were genetic algorithms applied.

Integer optimisation means method that can handle non-continuous changes in parameter values like changing from release of one proton to reaction where two protons are released. Apparently no one applied any integer optimisation method in NEA test cases. This is of course closely related to chemical plausibility, which means that only certain types of reactions are acceptable. On the other hand chemical plausibility quite often means that good fits have been observed by those chemically plausible models. Larger application integer optimisation methods might produce some new good fits, of which some may be chemically plausible. One possibility to extend the model is to use continuous rather than integer valued parameters (like in charge distribution models, which were applied by some modelling teams). Of course, integer optimisation was done in this exercise, but mainly manually based on:

1. chemical plausibility;
2. searching of simplest models;
3. testing of different models, and selecting those for final modelling that gave the best fit;
4. subjective perception (based on experience, published approaches, etc.).

The use of surface complexation modelling limits already the possible trial function for fitting quite significantly, and chemical plausibility consideration still more. The fitting needs some criteria: What is optimal? How is a good model characterised? Many teams relied either totally or partly on “fitting by eye”, which might be very efficient but not very quantitative. Fitting by eye may be very sensitive to differences in some narrow range – causing implicit data weighting. On the other hand it is not so simple to give a definition of a good fit in the case when we cannot assume that our model goes inside the experimental points (only random experimental error). If we have such a case, in a certain range the experimental errors may be much bigger than in other ranges, and forcing the model too tightly to the data in such a range might cause serious fitting problems. It is possible to solve this problem either by using experimental error estimates, which is already possible in common fitting programs like FITEQL, or to modify the experimental data so that errors are closer to each other in different ranges (e.g. applying  $K_d$  or  $\log K_d$  instead of per cent sorbed). Some comparisons based on Test Case 3 are given below.

Most codes (including FITEQL) use squared differences as their error estimates, which is natural because it is an extension of calculating length of vectors in our three-dimensional space, but other good mathematical methods are available as well. Any error estimate using values from the total fitted range are global in the sense, that models overestimating or underestimating systematically at neutral pH, but giving errors in other direction at low or high pH, may be equally good. It may be difficult to force the model for over/underestimation just by data weighting. Another problem with the global error is the large effect that one single point may cause, especially if the difference is squared; examples of this phenomenon may be found in TC6. In such a case data weighting may help. An even simpler approach might be to treat such a data point as outlier, especially if the point is at the extreme of a pH-range.

### **Impact of choice of the form of experimental data on the model results and goodness of fit: Application to Test Case 3<sup>1</sup>**

#### ***Introduction and preliminary remarks***

There are several ways of using adsorption data in fitting parameters to surface complexation models. The standard procedure is to use some version of FITEQL, or some other

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1. This was contributed by Johannes Lützenkirchen, FZK-INE, D-70621 Karlsruhe, Germany.

chemical speciation program for fitting experimental data. From the description in the manual one would calculate from the measured values of the adsorbing entity in solution the free master species concentration and use this master species as the type II component on which the optimisation is based (i.e. for this component both free and total concentrations are known). Since this is rather awkward, more often a dummy type II component is introduced, whose free concentration is set equal to one and whose total concentration is set equal to the concentration adsorbed. The same can be done with the actual values of the component concentration remaining in solution (i.e. non-adsorbed). Often adsorption data are published as percentage or fraction adsorbed or in the form of distribution coefficients. These data cannot be directly used in FITEQL. Depending on which data are used for the optimisation runs a different weighting of data series and data points may be occurring. Thus data with different “properties” may be governing the optimisation results. This is not an objective way to obtain best fit parameters. The most elegant way is most probably to achieve a weighting of the experimental data (i.e. the data that are actually measured) via the respective point by point experimental errors. Unfortunately, experimental errors are rarely specified in a detailed way. Errors can be distinguished on different levels. One is the laboratory level: on this level, the experimental errors occur on fixed procedures that are applied in one specified laboratory. On a more general level, errors appear when certain procedures vary among laboratories. Such procedural differences may be very subtle. To give a few examples, one might mention pH-measurements, which in the literature are found to be carried out before or after solid-liquid separation. The quality of solid-liquid separation may significantly affect the outcome of adsorption experiments. Another relevant issue (e.g. for surface charge data or comparisons of adsorption data on a (surface) specific basis) may be the measurement of specific surface area. Therefore, it is hard to judge to what extent it is advisable to make a model fit all data points, when so little is known about the experimental errors.

Weighting is important in data fitting and should be done based on good error estimates. The ideal situation is to use the actual measurements in the optimisation runs and attribute reasonable weights to them. Working with literature data, the published data often need to be used, since the original data cannot be obtained. Often they can be recalculated though. The choice of the form of the data used may be influenced by other aspects. One is what is actually feasible with the available software. Another is what the goodness of fit criterion in judging the model actually is. For the NEA sorption project the logarithm of the distribution coefficient had been selected as the criterion, but the usual fitting programs will not allow executing fits on that variable.

Here, different options for input data are used to evaluate their potential effect on the outcome. All data are always used without objective weighting. In all cases a weight of unity is attributed to all data points.

The data from Test Case 3 were chosen for various reasons:

- first data from Test Case 2 (Hayes 1986) were considered; however, the total concentration of Se was the same in all datasets; i.e. no differences were obtained in terms of percentage and Se adsorbed; also for some selenite data a range of data were at nearly 100% adsorbed which can have easily been affected by experimental errors (e.g. only slightly incomplete separation would result in 98.7% instead of 100% adsorbed) and the precision of the experimental data themselves may strongly affect  $K_d$  values.
- for Test Case 3 as given in the EXCEL spreadsheets a variation of total U over three orders of magnitude was available; the data close to 100% of adsorption are restricted to a narrow pH range and there are not so many data points with more than 90% adsorption as compared to the total number of data points.

The aqueous speciation scheme was taken from the spreadsheet provided by NEA, but obvious errors were corrected for. The aqueous speciation is a basis for the application of the surface complexation model. In the case of uranyl/quartz there is a potential uncertainty about aqueous uranyl/silica complexes. Not only are these not studied in much detail. Also data on the dissolution of quartz in this complex system must be available for a full understanding of the aqueous speciation. This, in turn, would require a pre-equilibration of the quartz to reach equilibrium with the aqueous phase and measurement of Si in solution at the end of each experiment.

For the experimental data no errors in pH measurements and aqueous U concentrations are available. Therefore assumptions are required for the data weighting. Temperature was set to 298.15 K, although the data were collected at 20-22°C in the case of the adsorption data. Temperature for the surface charge data was not specified.

It was not attempted to push the model to its limits, i.e. to decrease the goodness of fit parameters by adding more species than those reported here. This would be hardly justifiable since on the one hand the above mentioned uncertainties of aqueous speciation exist, and since on the other hand the errors for objective weighting are not available.

Also this exercise serves as an example. The extent to which the discussed features may affect optimisations in other cases or to which the observations may be transferred from one system to another is not clear.

### **Procedures**

- a) From the given experimental data of the spread-sheets,  $\log H^+$  values were calculated using tabulated activity coefficients based on Dzombak and Morel (1990). The optimisations were run on specific surface charge density vs.  $\log H^+$  data with UCODE coupled to a modified version of FITEQL2.1. The electrostatic model chosen was the basic Stern model. The site density was fixed at 4.6 sites/nm<sup>2</sup>. The log of the stability constant for the deprotonation of the singly coordinated groups was fixed at -7.9 (Hiemstra *et al.* 1996). Sodium binding constant ( $\log K = 0.97$ ) and capacitance (1.44 F/m<sup>2</sup>) were optimised.
- b) The acid-base model was then used with the U adsorption data. Different models were tested. Based on the results presented at the workshop, a model with two sites and monodentate surface complexes was tested first. Subsequently a one-site model with bidentate bonding was tested and turned out to be better. This first evaluation was done on data in the form percentage adsorbed vs.  $\log H^+$  (option 1). This allows a smearing out in the fitting procedure, i.e. all data range from 0 to 100 independent of the total amount of U in the system. Once the model was considered to be sufficient for the subsequent calculations the parameters from this model were chosen as the starting values in the optimisations on:
  - molar concentrations of adsorbed U (option 2);
  - molar concentrations of aqueous U (option 3);
  - $\log K_d$  values (option 4);
  - $K_d$  values (option 5).

Optimisations were always done using a modified version of FITEQL2.1 allowing for output of the above 5 quantities. This application was coupled to UCODE. All 113 data points of model set A were fitted simultaneously. Options 2 and 3 can be used with standard FITEQL by specifying the respective dummy components.

- c) Three surface species were used for the U surface speciation scheme:
- a bidentate  $(\text{SiO})_2\text{UO}_2$  – complex, with ideal charge distribution (i.e. 2 of the 7 coordinations of  $\text{UO}_2^{2+}$  go to the surface plane),  $\log K_1$ ;
  - a bidentate  $(\text{SiO})_2\text{UO}_2\text{OH}^-$  – complex, with ideal charge distribution (i.e. 2 of the 7 coordinations of  $\text{UO}_2^{2+}$  go to the surface plane),  $\log K_2$ ;
  - a bidentate  $(\text{SiO})_2\text{UO}_2\text{CO}_3^{2-}$  – complex, with ideal charge distribution (i.e. 2 of the 7 coordinations of  $\text{UO}_2^{2+}$  go to the surface plane),  $\log K_3$ .
- d) The results were treated in a EXCEL spreadsheet in the following way:
- The parameters resulting from the five options were summarised in a table.
  - The sum of squared residuals divided by the number of data points was calculated. For  $\log K_d$  this corresponds to the criterion fixed for the NEA test cases.
  - The goodness of fit parameters were summarised in a table, where for the options 1 to 5 the various goodness of fit parameters are given, calculated according to the above statement. The diagonal of the matrix yields the self-consistent values, where the same data were used for fitting as for calculating the goodness of fit.

## Results

Table 1 shows the results for the stability constants. Obviously the various options result in different optimum values for the adjusted parameters (all fits started from the same initial parameter guesses). However, the variation is well within the range of uncertainty which one should attribute to stability constants in suspensions.

Table 1: **Logarithm of the stability constants for the three U containing surface complexes and options 1 to 5**

fit based on	Log $K_1$	Log $K_2$	Log $K_3$
Uads	-1.97	-7.38	-10.30
Uaq	-2.05	-7.49	-10.20
U%ads	-1.92	-7.30	-10.30
Log $K_d$	-1.89	-7.44	-10.10
$K_d$	-1.90	-7.23	-10.50

Table 2 shows the matrix for the goodness of fit parameters obtained for the different options and applied with the respective output (e.g. the goodness of fit for the percentage adsorbed output obtained with fit on  $\log K_d$  was calculated in the same way as that for percentage adsorbed output obtained with fit on percentage adsorbed).

In the best outcome for the respective options bold and underlined figures should coincide. However, this clearly is not the case for adsorbed concentration,  $\log K_d$  and  $K_d$ . For 4 of 5 options the fit on the aqueous concentrations (i.e. the truly measured values) is best.

Table 2: **Goodness of fit matrix (as described in the text). The bold figures show the diagonal, i.e. the evaluation of the goodness of fit and the data for the optimisation have the same basis. The underlined figures show the best fit for the respective option**

fit based on	Goodness of fit calculated for					calculated goodness of fit parameter
	Uads	Uaq	U%ads	logK <sub>d</sub>	K <sub>d</sub>	
Uads Option 2	<b>2.37E-13</b>	<u>1.66E-13</u>	3.03E-13	4.99E-12	4.60E-13	based on sum of squared residuals for Uads
Uaq Option 3	2.37E-13	<b><u>1.67E-13</u></b>	3.03E-13	4.78E-12	4.60E-13	based on sum of squared residuals for Uaq
U%ads Option 1	102.84	116.57	<b><u>99.33</u></b>	301.88	110.18	based on sum of squared residuals for % adsorbed
LogK <sub>d</sub> Option 4	0.1531	<u>0.1527</u>	0.1606	<b>0.3067</b>	0.1788	based on sum of squared residuals for log K <sub>d</sub>
K <sub>d</sub> Option 5	2.69E+05	<u>1.51E+05</u>	4.02E+05	2.39E+05	<b>5.38E+05</b>	based on sum of squared residuals for K <sub>d</sub>

### Summary

Clearly, this exercise shows that the use of different input data with optimisation routines results in different best fit parameters. Comparing the goodness of fit shows that for a different option chosen, the best fit in terms of the respective kind of data is not necessarily optimal. The observations can be explained by different weighting of the data points. As an example, for percentage adsorbed and adsorbed concentrations, it is expected that an improvement of the fit is predominantly obtained for data with nearly 100% adsorption in all datasets (first case) independent of total U, whereas for the second case it is predominantly obtained for the data with nearly 100% adsorption for those datasets with the highest total U concentration. For aqueous and adsorbed concentrations it is expected that the best fit is more strongly focussing on data with little adsorption and high total U concentration (former) or on data with strong adsorption and high total U concentration (latter). These statements hold for unit weighting. Using objective weights, it is expected that weighting will be independent of the form of the experimental data (i.e. the errors used for the weighting are calculated to correspond to the experimental data used in the optimisation routine). This statement stresses that for these kind of optimisation problems weights are important.

As for the separate parameter sets obtained from the different options, it is noted that for the present case no dramatic variations occur, if one realistically considers the uncertainties associated with experimental data in suspensions.

### References

- D.A. Dzombak, F.M.M. Morel (1990) Surface complexation modelling: Hydrous Ferric Oxide. John Wiley, New York.
- K.F. Hayes (1987) Equilibrium, spectroscopic, and kinetic studies of ion adsorption at the oxide/aqueous interface. Ph.D. thesis, Stanford University.
- T. Hiemstra, P. Venema, W.H. van Riemsdijk (1996), Journal of Colloid and Interface Science, 184: 680-692.

## Part 3

This part contains additional data plots that form the basis for Parts 1 and 2; in particular, graphical comparisons of experimentally determined and model-derived  $K_d$  values as well as the corresponding quantitative assessments of fits.

This additional information is provided for test cases, 1, 3, 4, 5 and 7. In case of test cases 2 and 6 it is deemed that the plots given in Part 2 suffice to illustrate the performance of the various models.





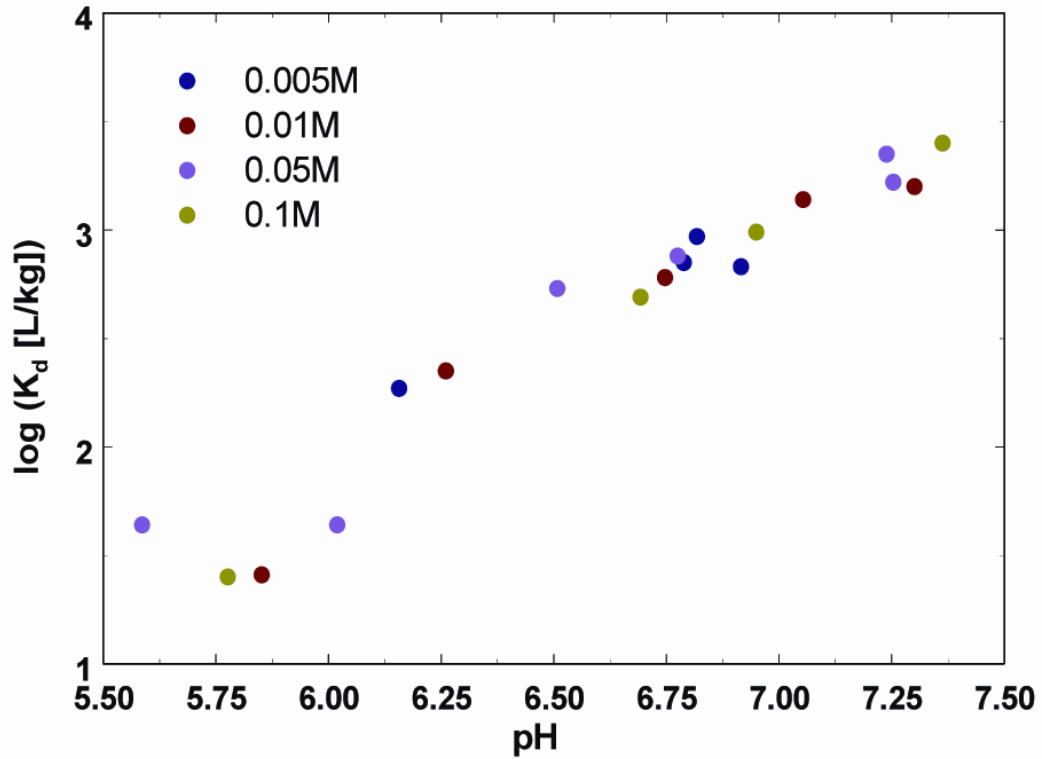
## **Test Case 1:**

### **Np(V) adsorption on hematite**

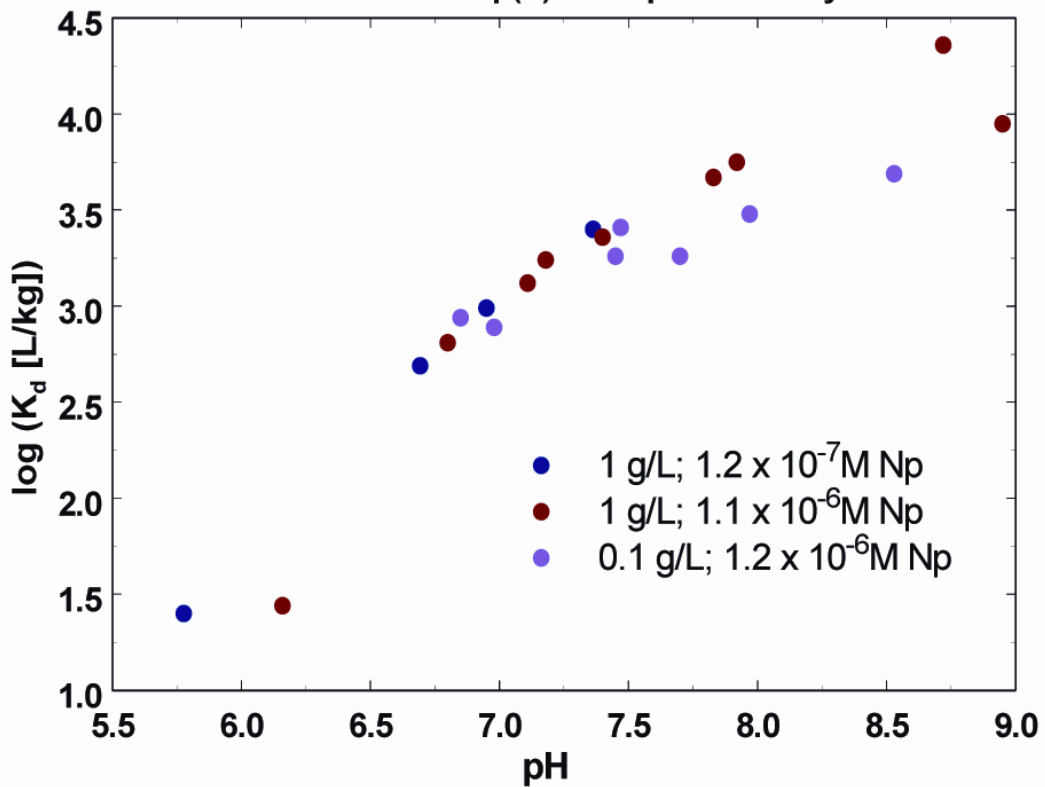


Experimental data Kohler et al. (1999)

Effect of  $\text{NaClO}_4$  concentration

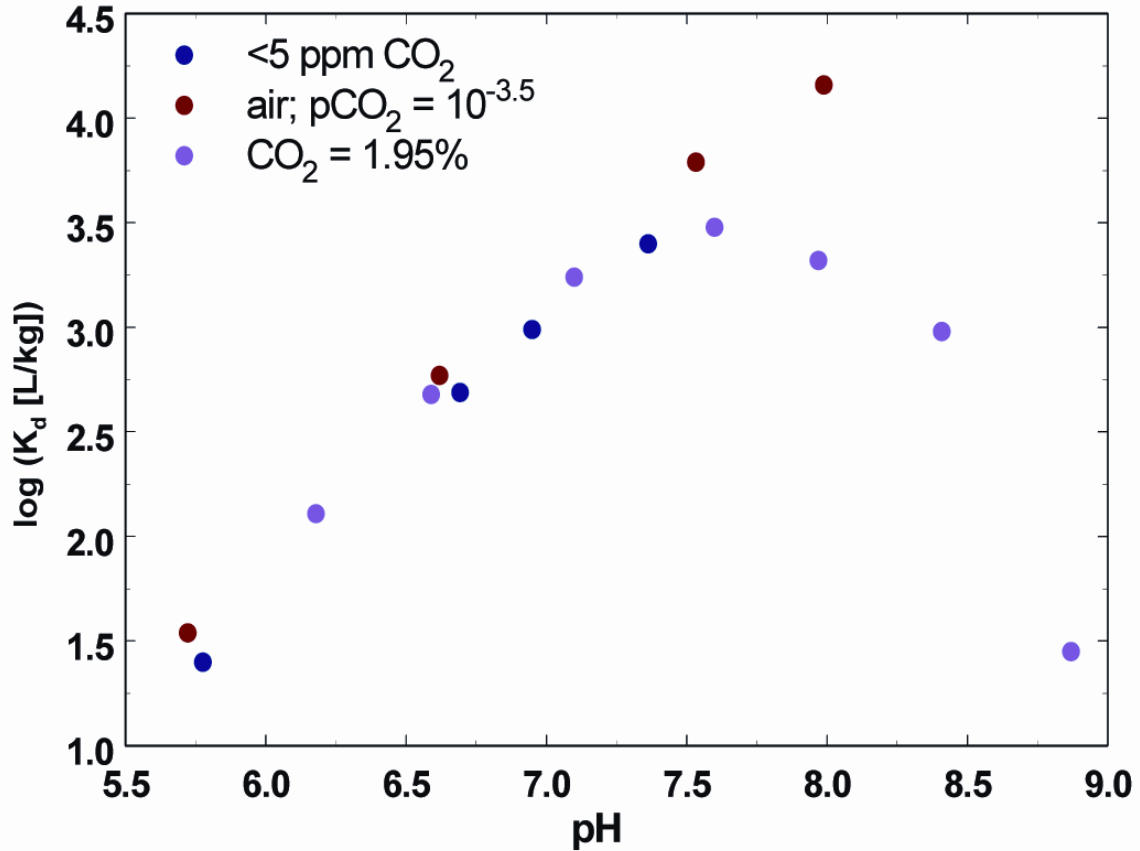


Effect of Np(V) adsorption density

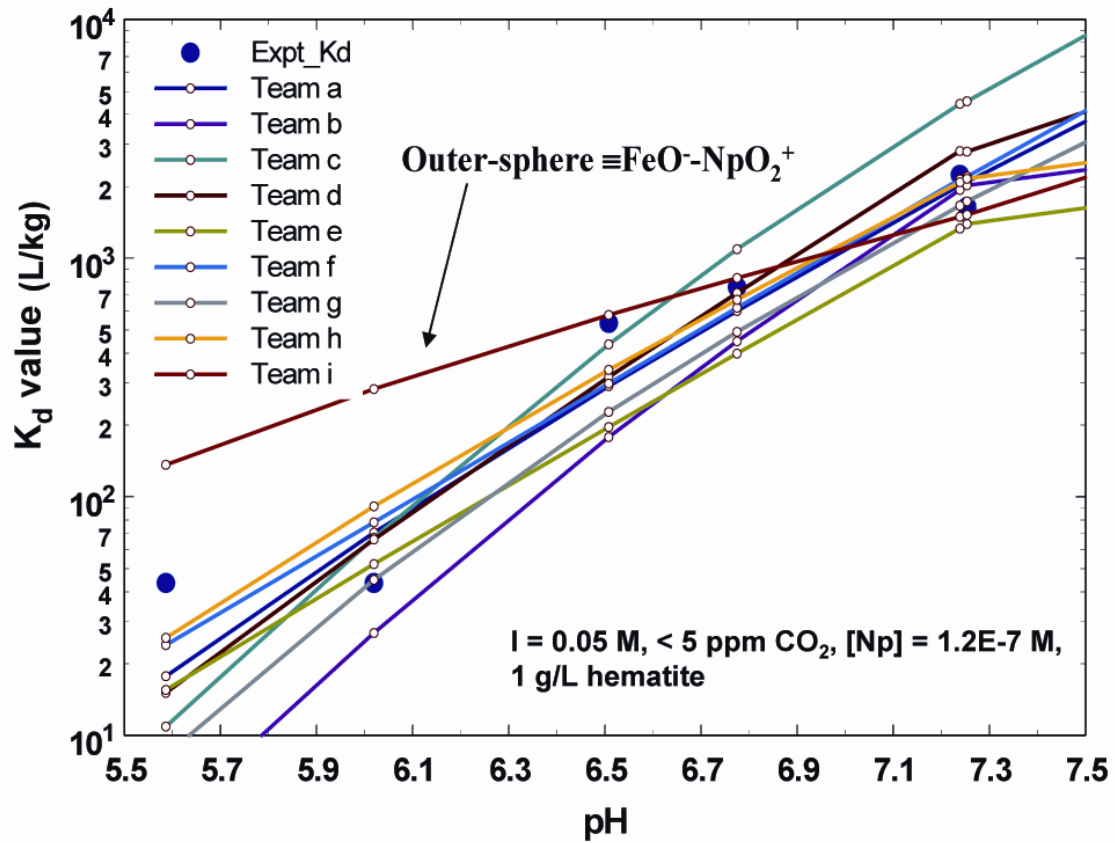
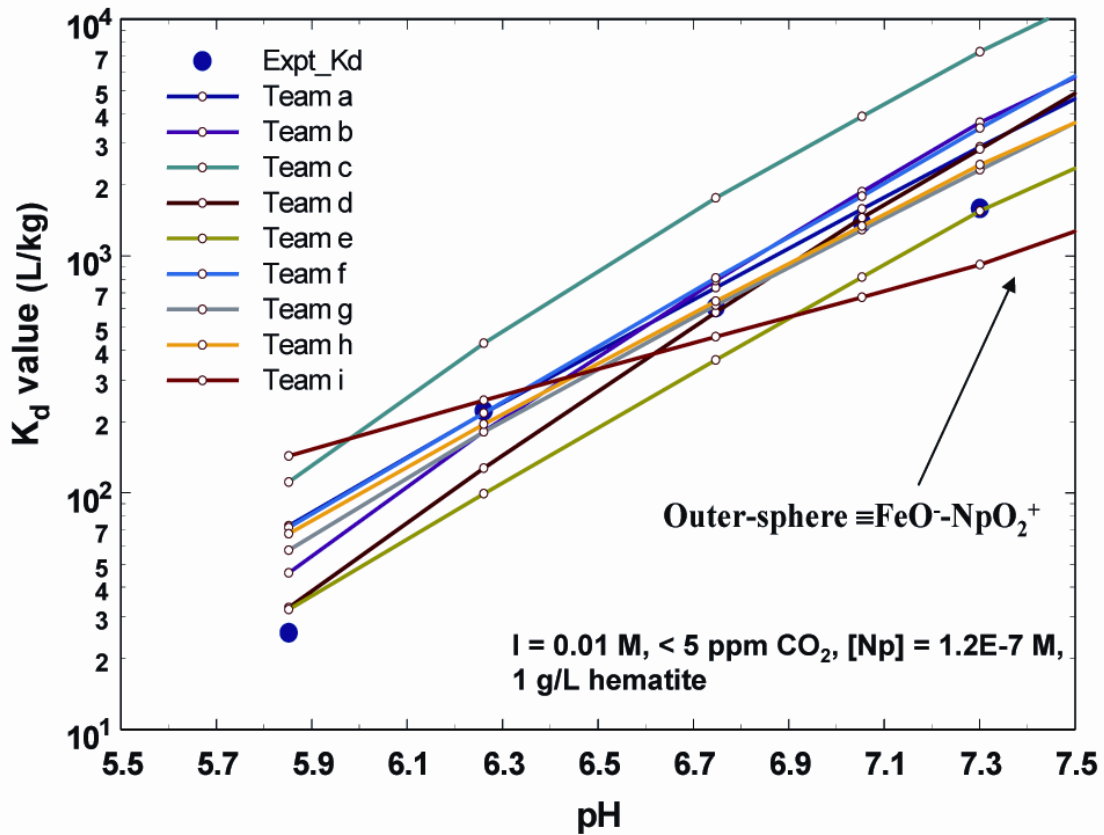


Experimental data Kohler et al. (1999)

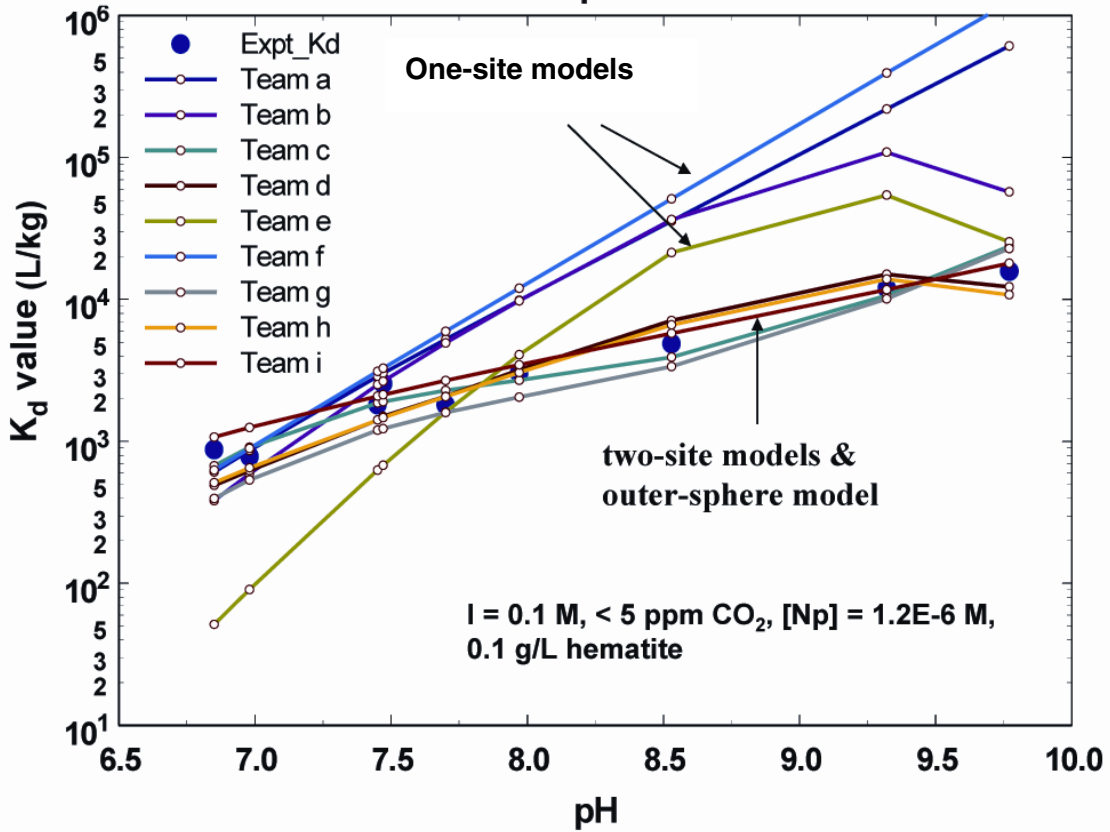
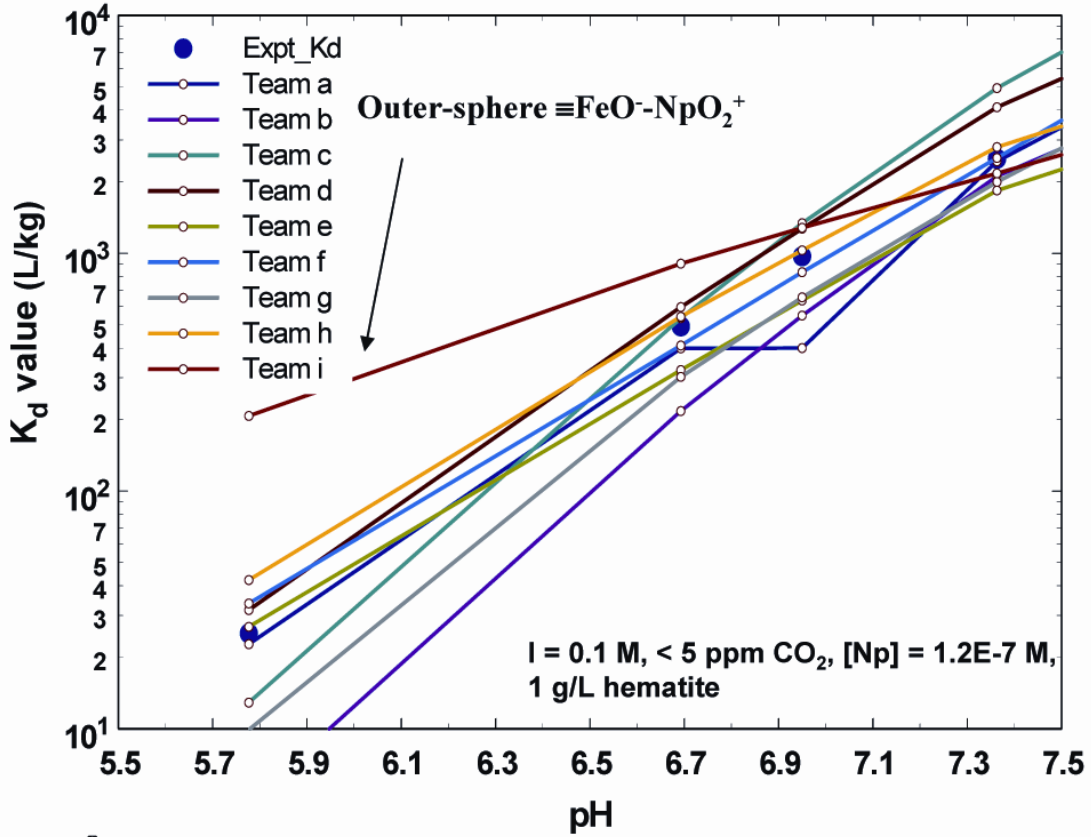
### Np(V) adsorption on hematite Effect of partial pressure of CO<sub>2</sub>



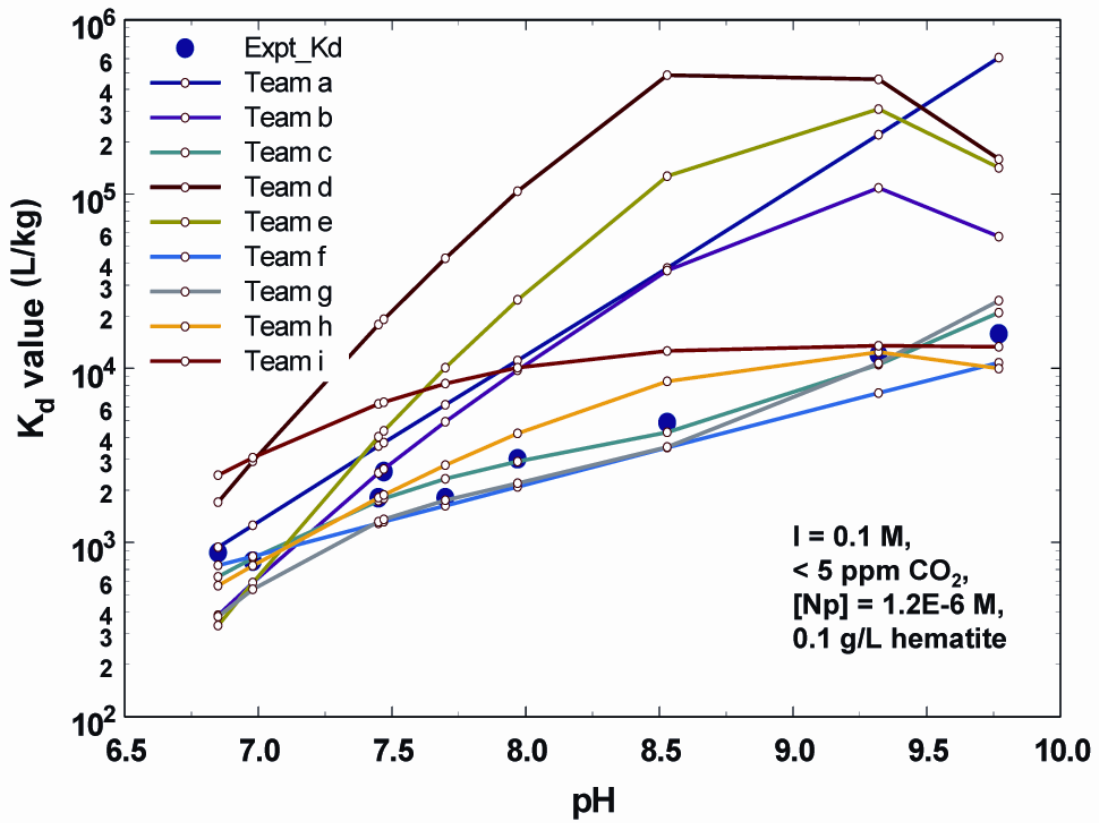
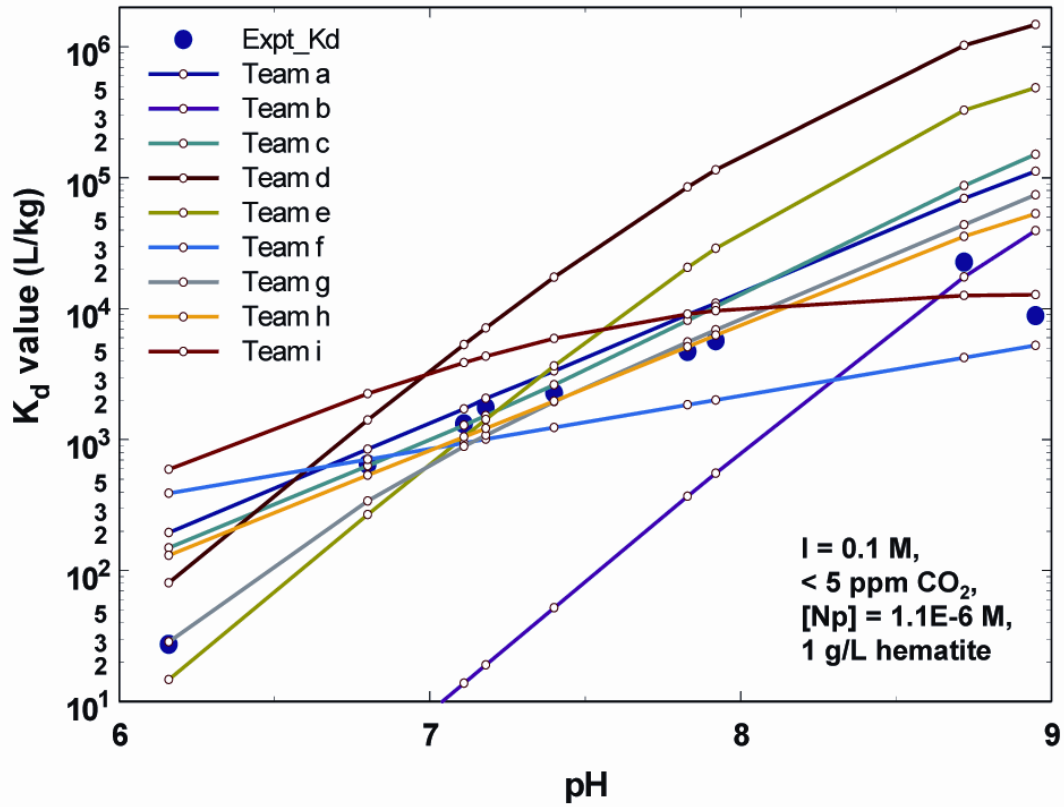
### Model calibration: EDL models



### Model calibration: EDL models

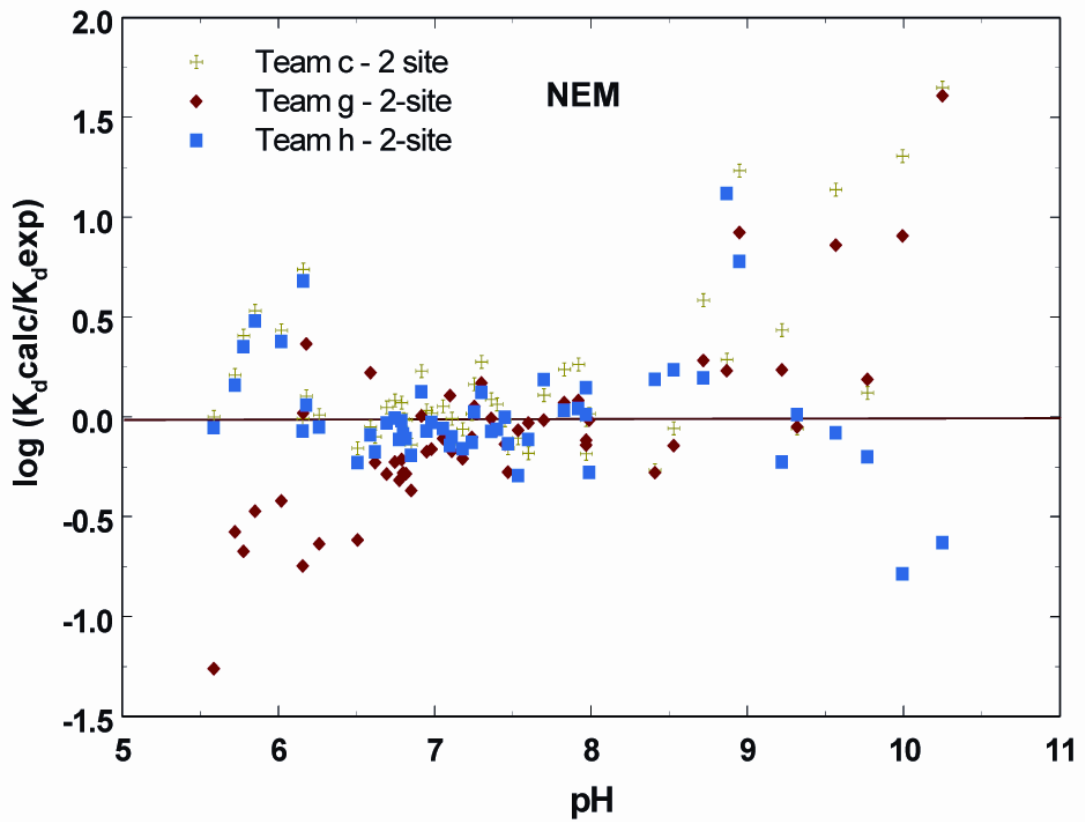
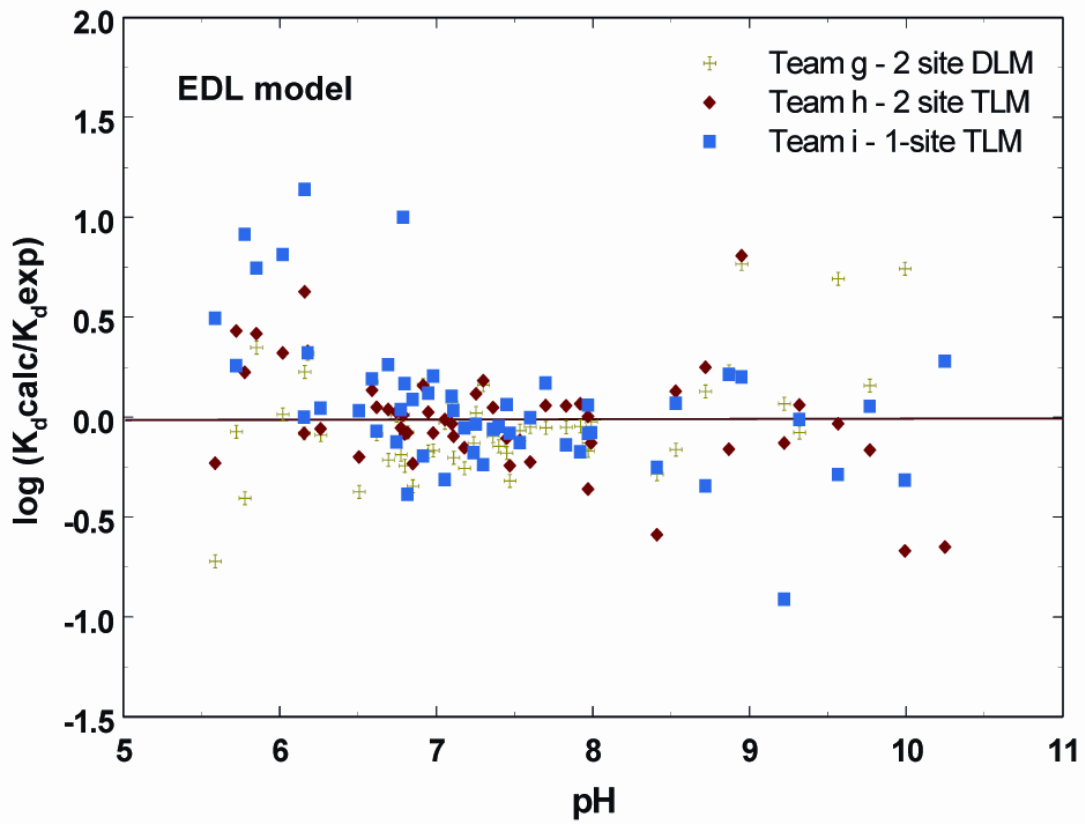


### Model calibration: NEMs

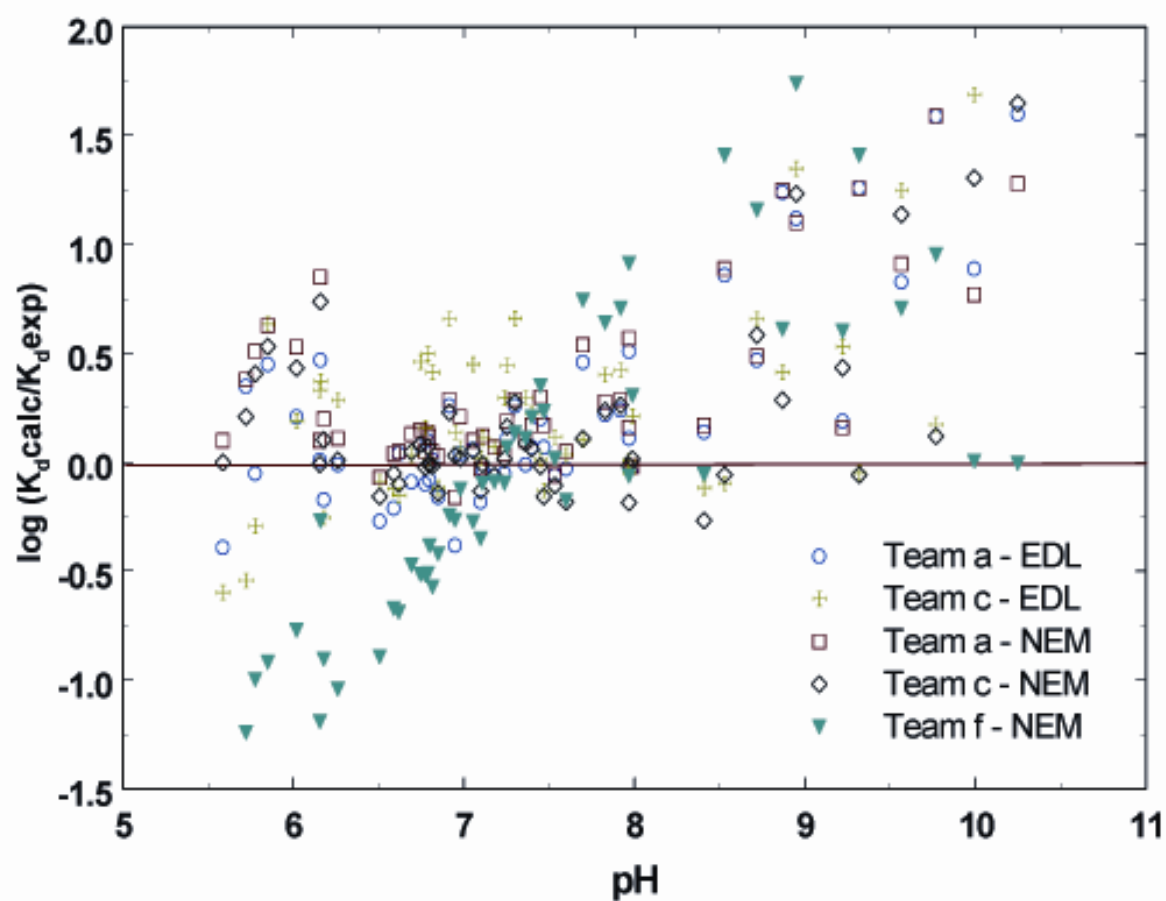




### Model calibration: EDL vs. non-electrostatic models



## Model calibration: Omission of ternary surface Np-carbonato complexes





## **Test Case 3:**

# **U(VI) adsorption on quartz**

### **Explanation**

#### References:

- a) Kohler, M. and Davis, J.A., U.S. Geological Survey, unpublished data, manuscript in preparation.
- b) Pabalan, R.T., Turner, D.R., Bertetti, F.P. and Prikryl, J.D., 1998, in Adsorption of Metals by Geomedia, E.A. Jenne (ed.), Academic Press, Cahp. 3, pp. 99-130.



## EXPLANATION

**Part A: Model calibration based on reference (a)**  
**Model 1: SC-EDL model, Model 2: SC-NEM**

<b>Original U(VI) sorption on quartz - reference (a)</b>				
All experimental points are for 100 grams/L of quartz				
Dataset	Tot U(VI) (mol/L)	NaNO <sub>3</sub> (mol/L)	gas phase	NaF (mol/L)
Ax.1	1,0E-08	0,01	air	none
Ax.2	1,2E-07	0,01	air	none
Ax.3	1,0E-06	0,01	air	none
Ax.4	1,0E-06	0,01	air	5,00E-04
Ax.5	1,0E-05	0,01	air	none
Ax.6	1,0E-08	0,01	7.5% CO <sub>2</sub> /92.5% N <sub>2</sub>	none
Ax.7	1,0E-07	0,01	7.5% CO <sub>2</sub> /92.5% N <sub>2</sub>	none
Ax.8	1,0E-06	0,01	7.5% CO <sub>2</sub> /92.5% N <sub>2</sub>	none
Ax.9	1,0E-05	0,01	7.5% CO <sub>2</sub> /92.5% N <sub>2</sub>	none

## EXPLANATION

**Part B: Application of models 1 & 2 to data by reference (b)**

All samples equilibrated with a gas phase of air			
All samples suspended in 0.1M NaNO <sub>3</sub> solution			
Dataset	Quartz (g/L)	Total U(VI) (mol/L)	Total U(VI) (mol/g)
Bx.1	2,1	2,1E-07	1,0E-07
Bx.4	21	1,9E-08	9,2E-10
Bx.2	21	2,1E-07	1,0E-08
Bx.5	51	2,0E-06	4,0E-08
Bx.3	54	2,0E-07	3,8E-09

## EXPLANATION

### Labelling of plots

#### Model calibration

A1.1 - A1.9 and A2.1 - A2.9 →  $K_d$  values calculated by models 1 & 2 for datasets 1-9 of reference (a)

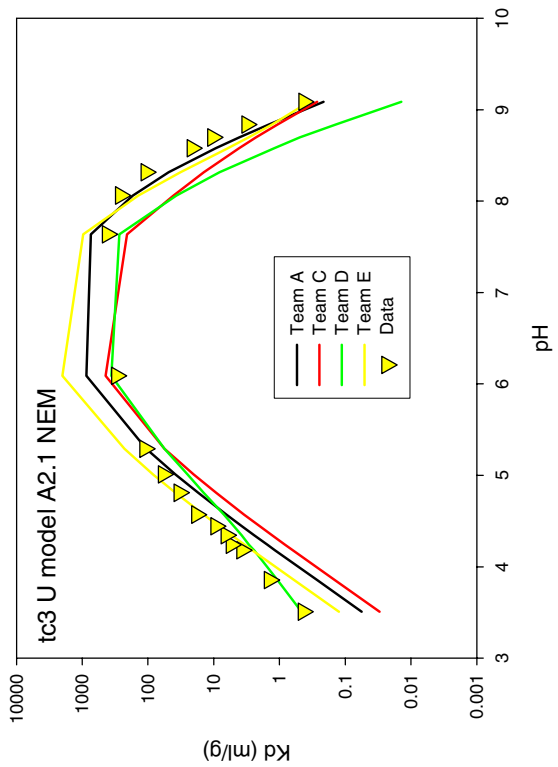
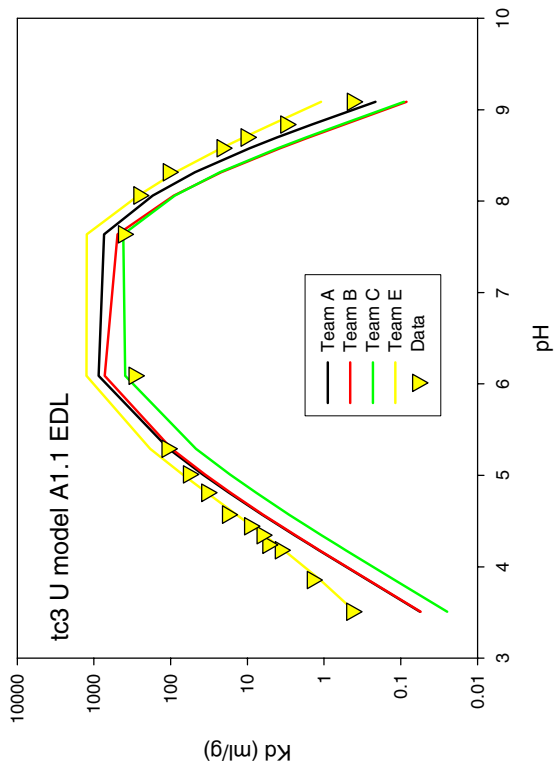
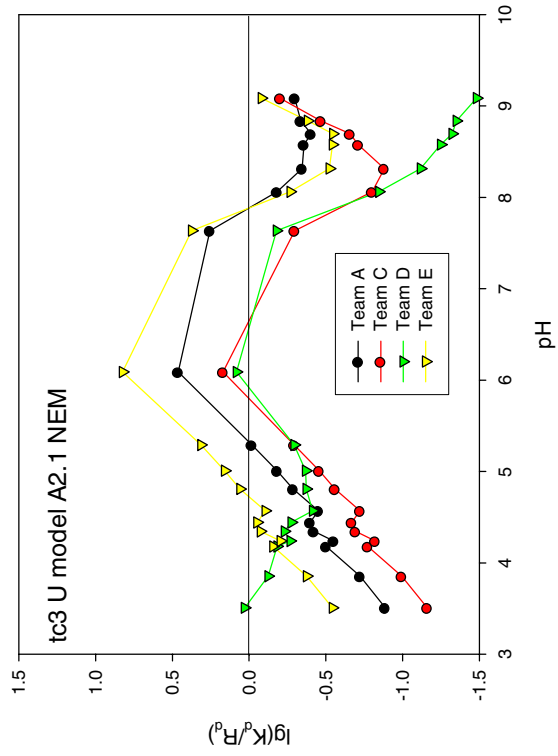
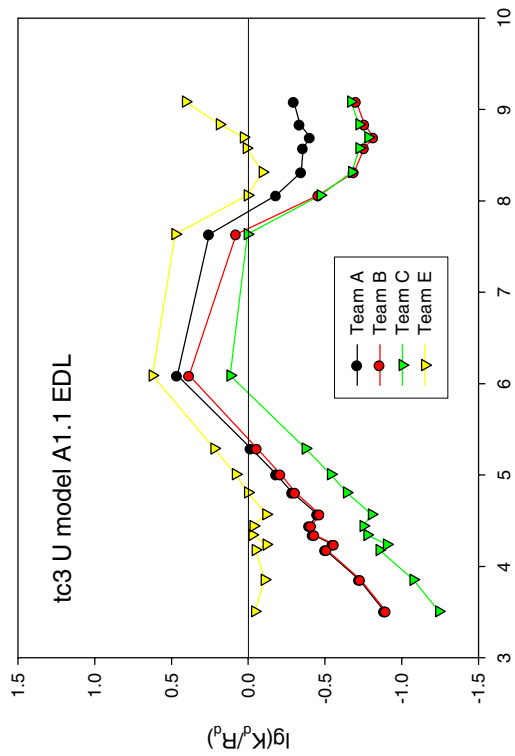
#### Model application (prediction)

B1.1 - B1.5 and B2.1 - B2.5 →  $K_d$  values calculated by models 1 & 2 for datasets 1-5 of reference (b)

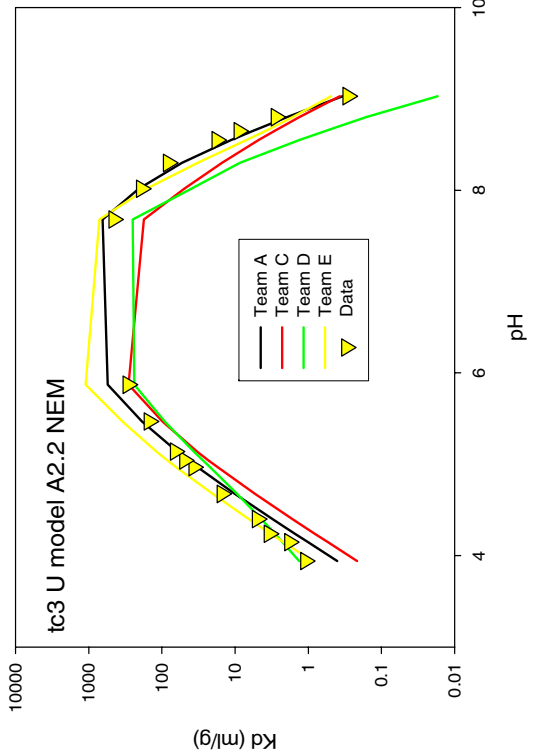
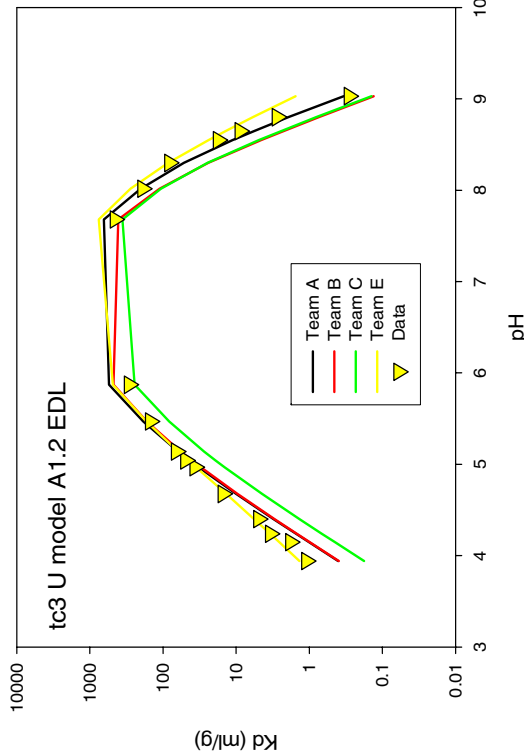
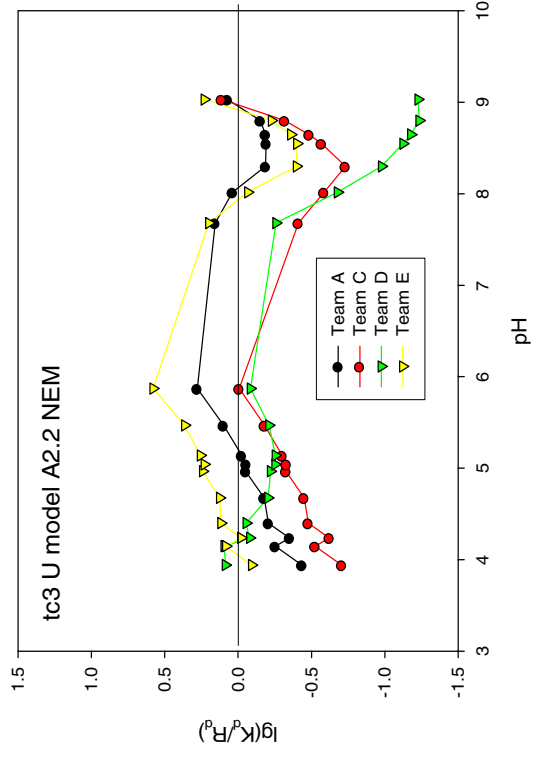
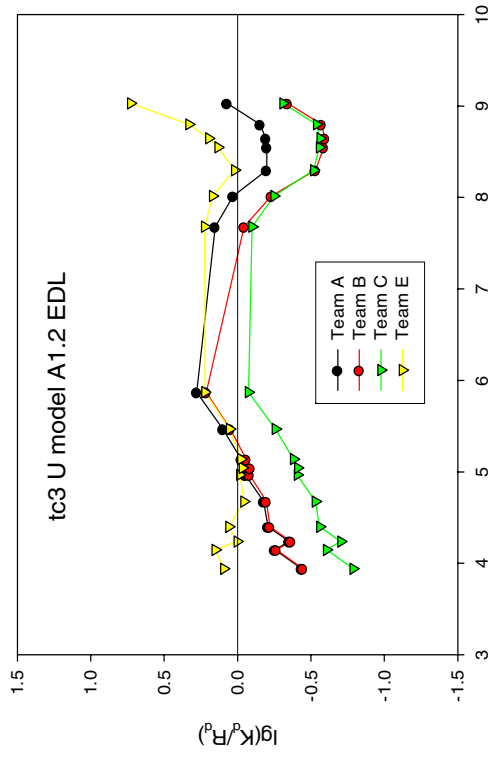
error plots:

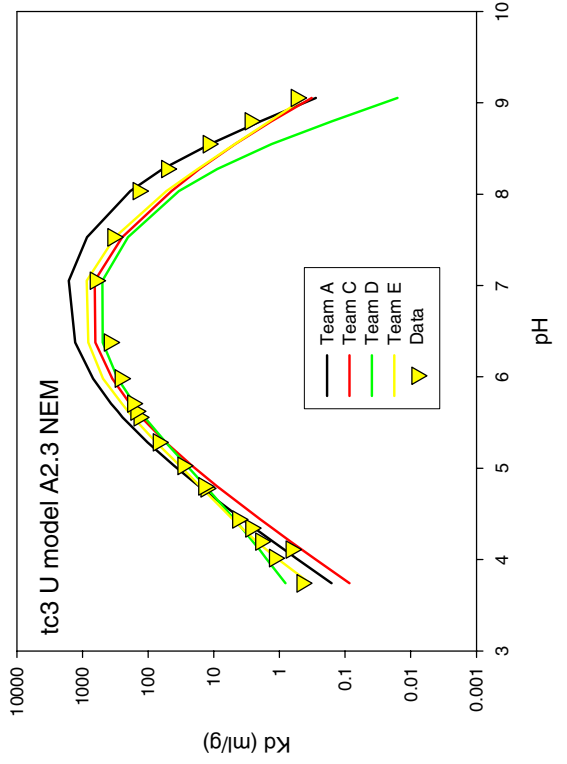
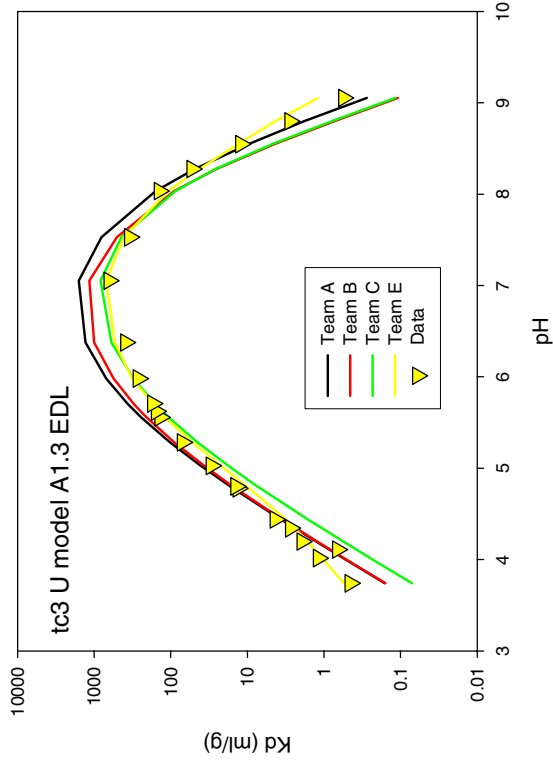
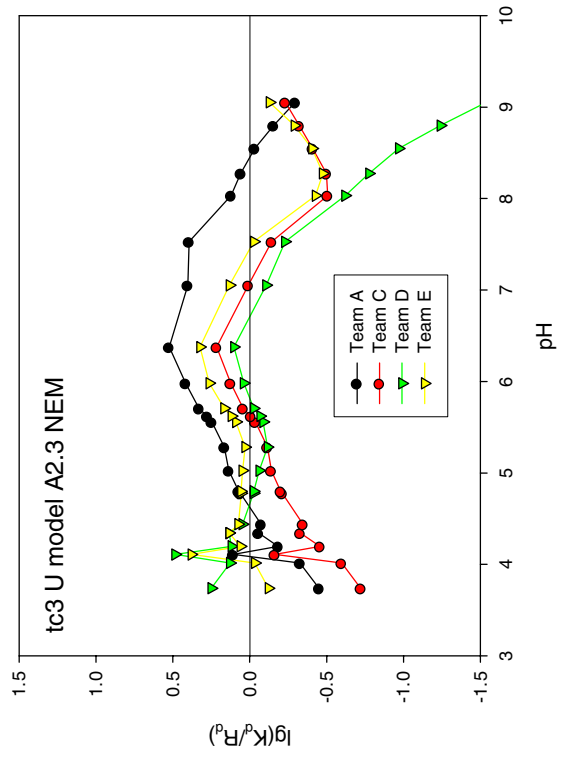
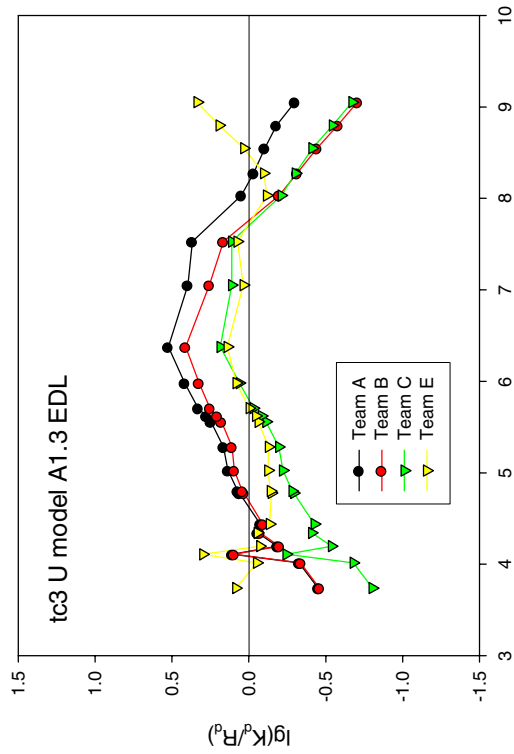
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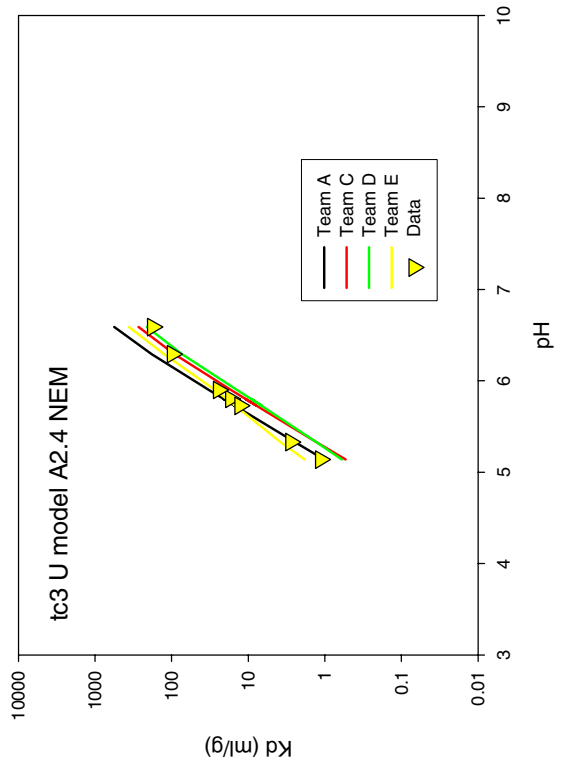
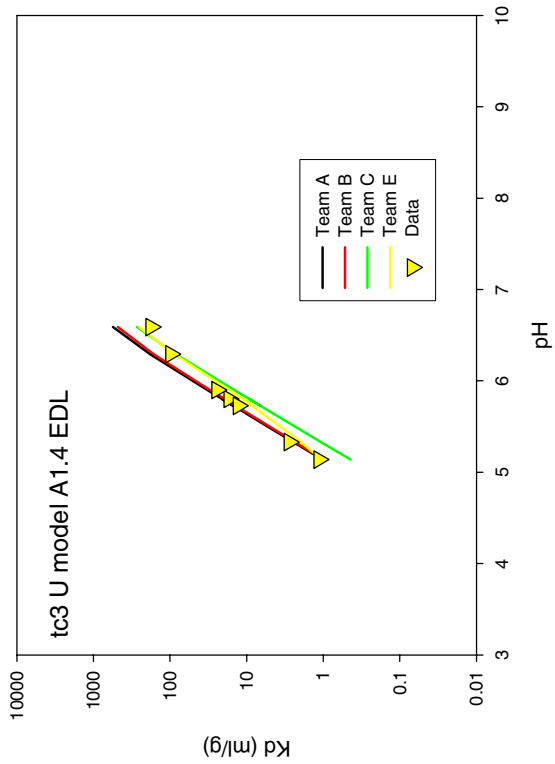
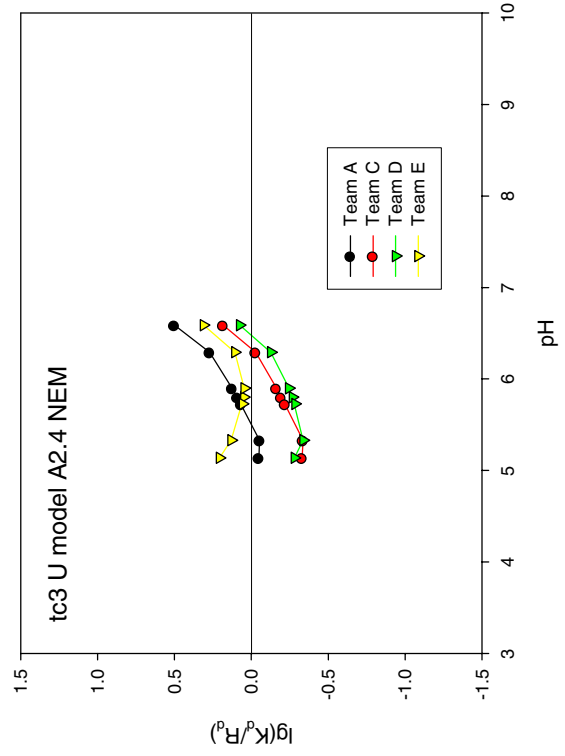
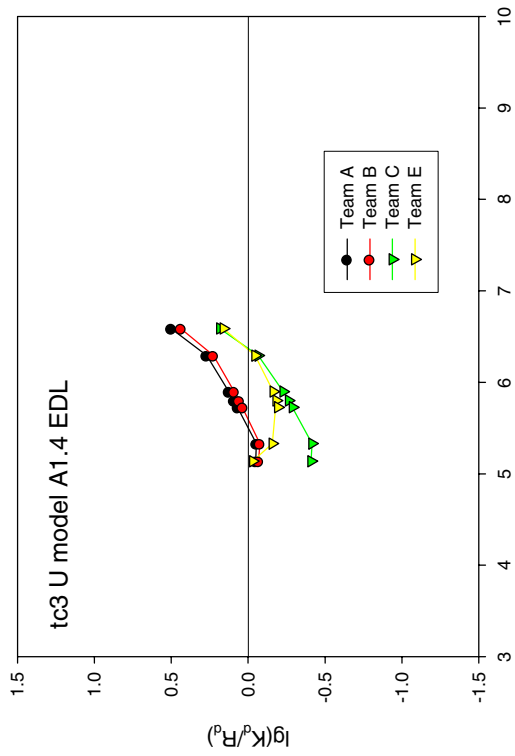
$R_d$  = experimental value

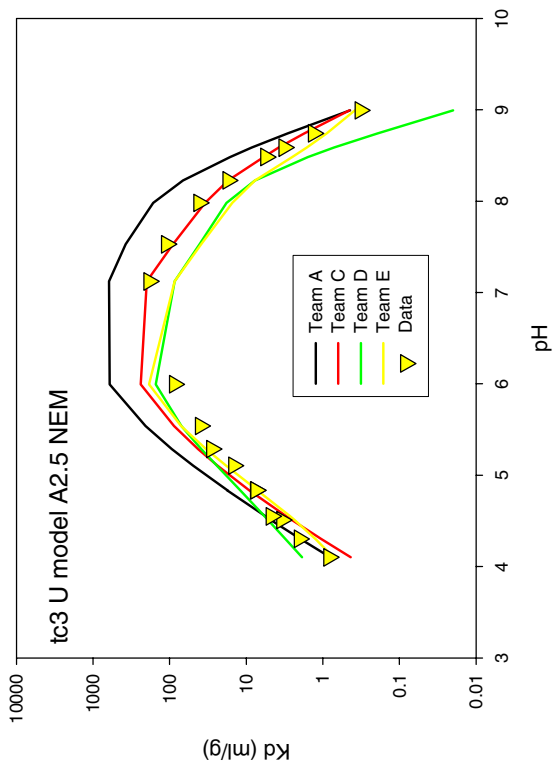
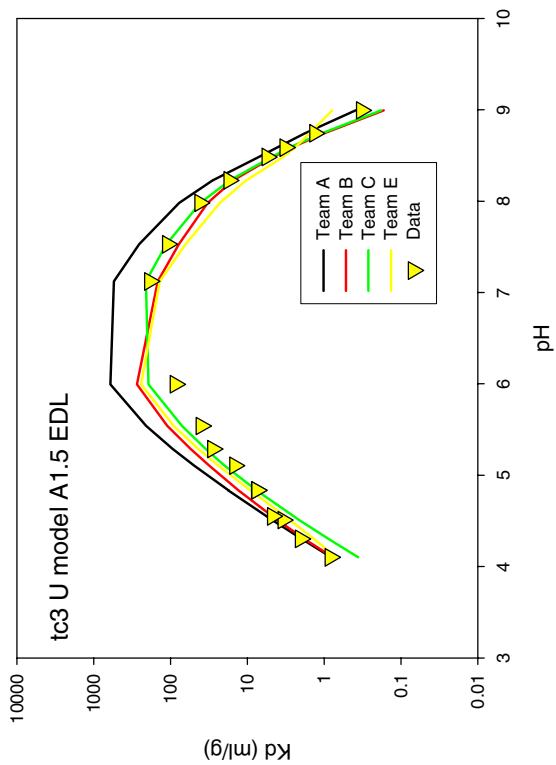
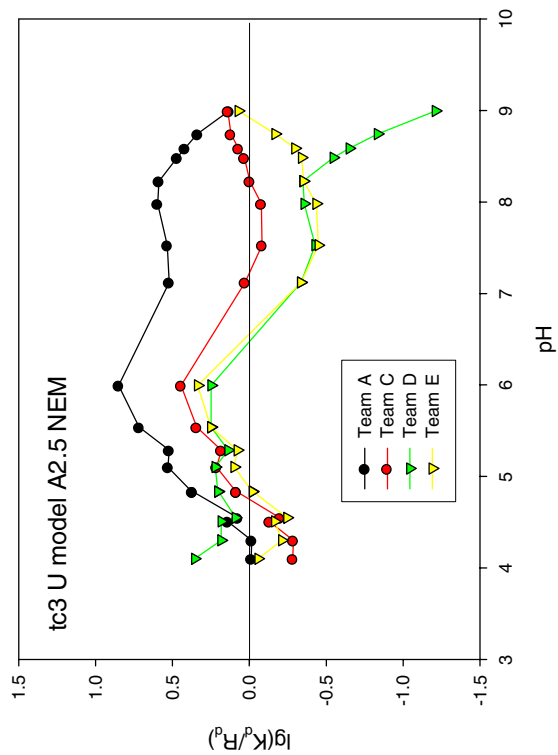
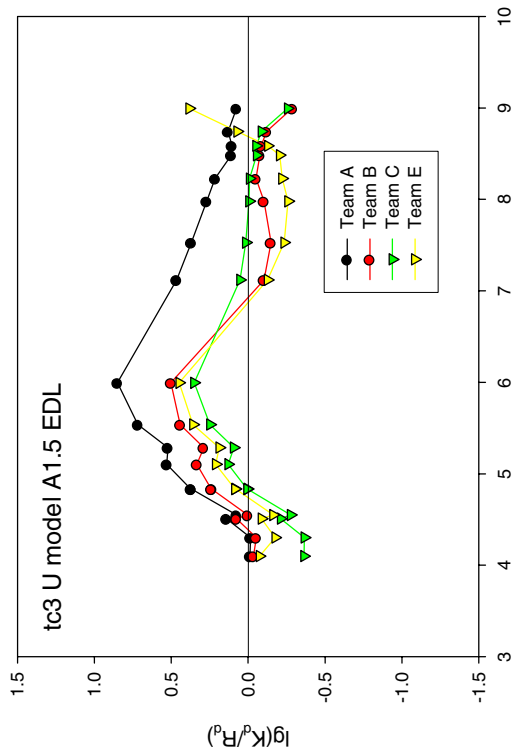


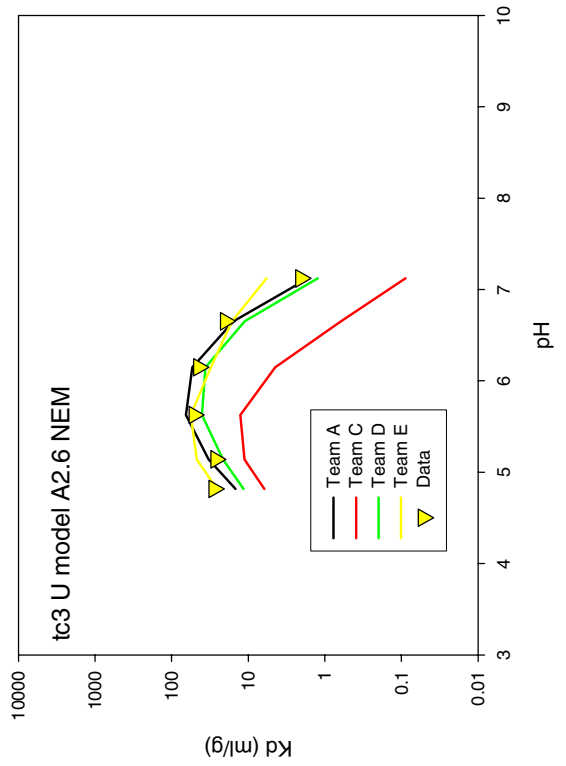
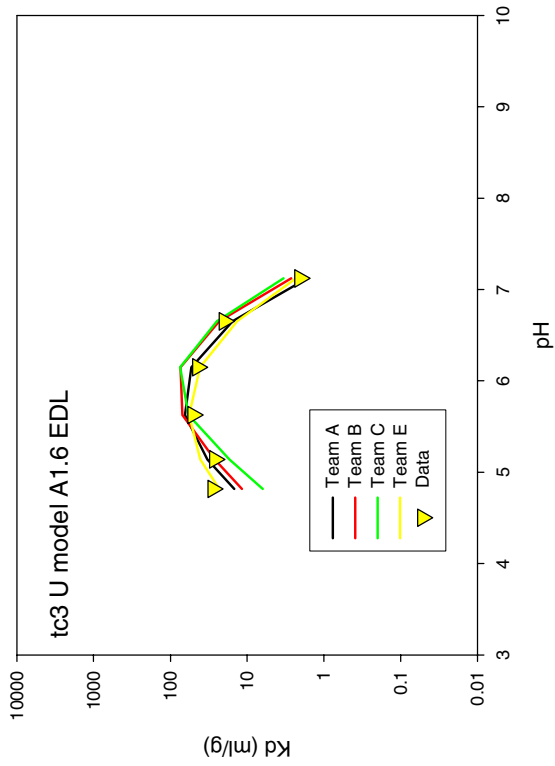
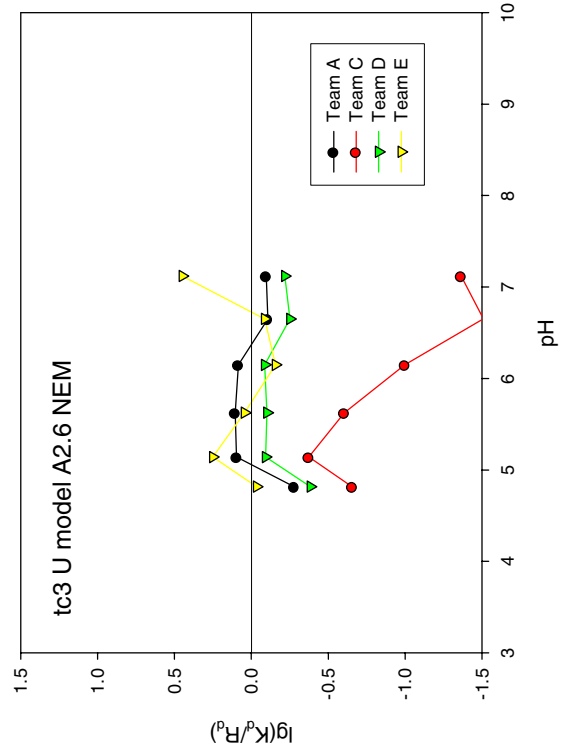
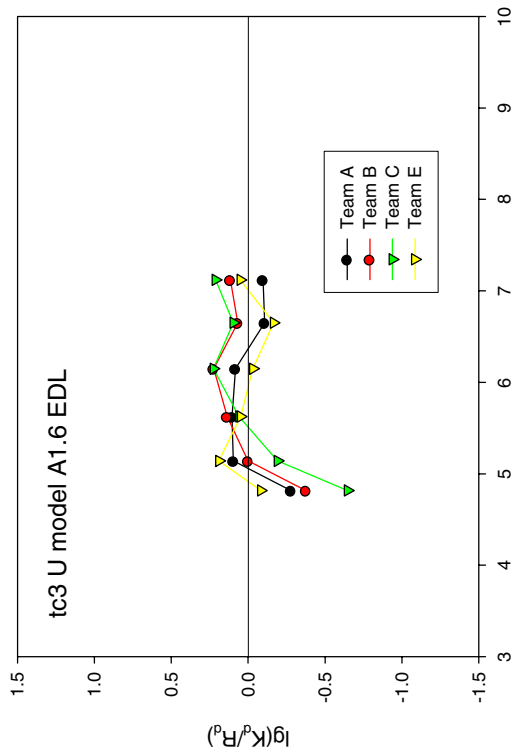


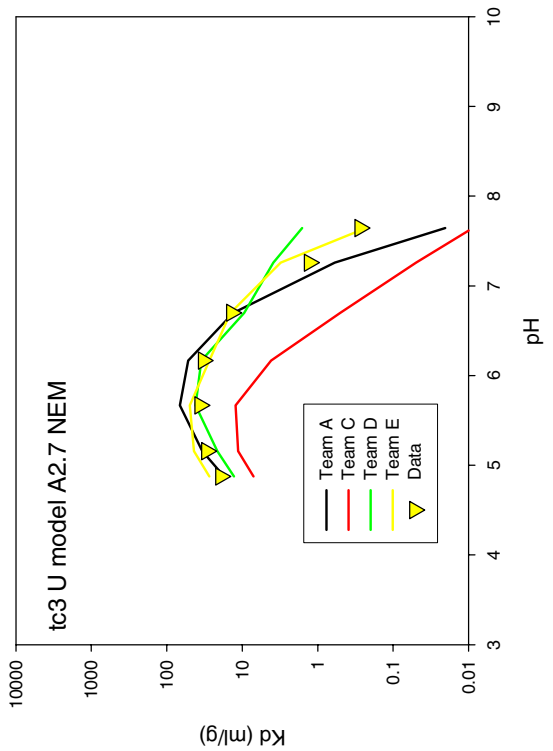
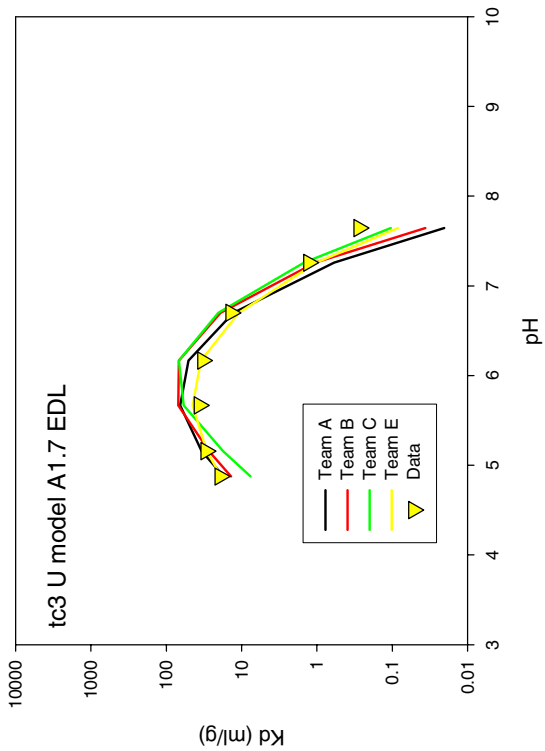
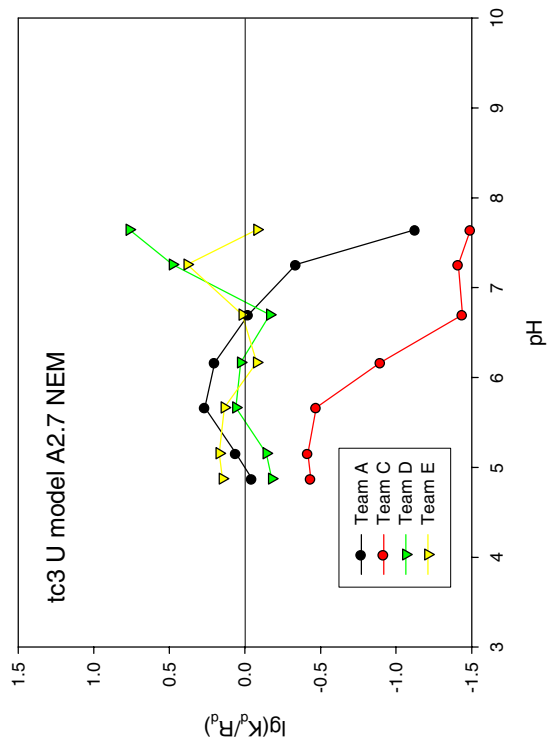
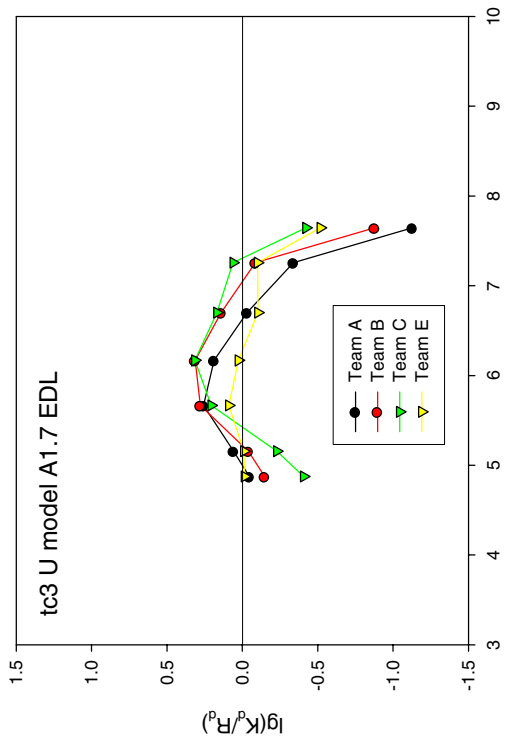


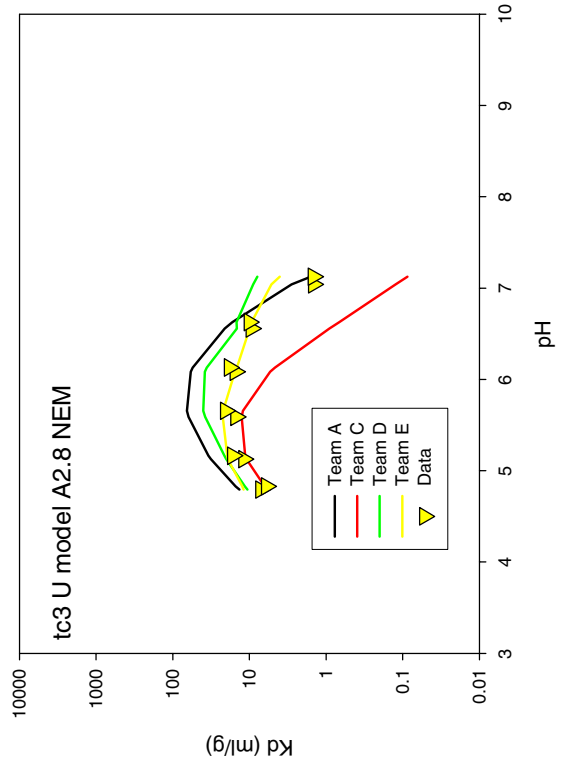
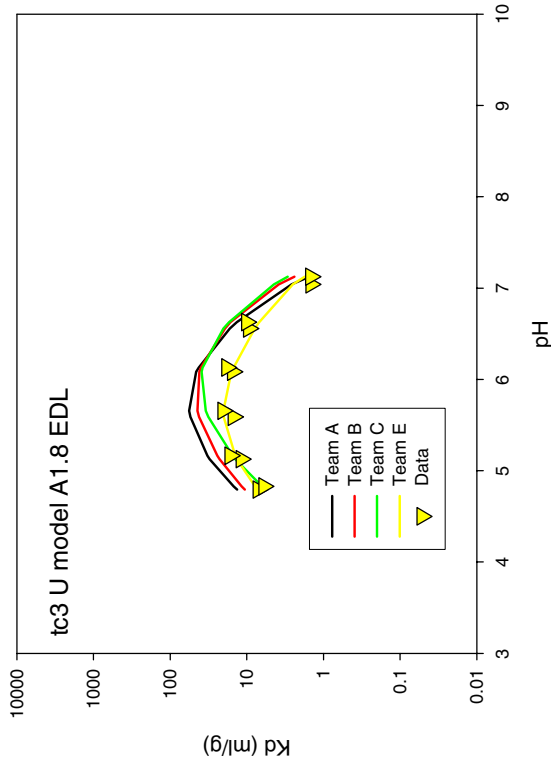
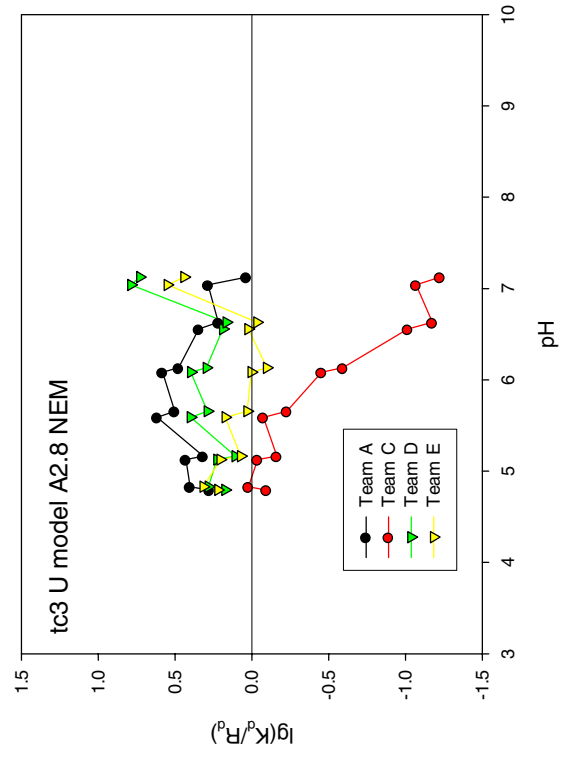
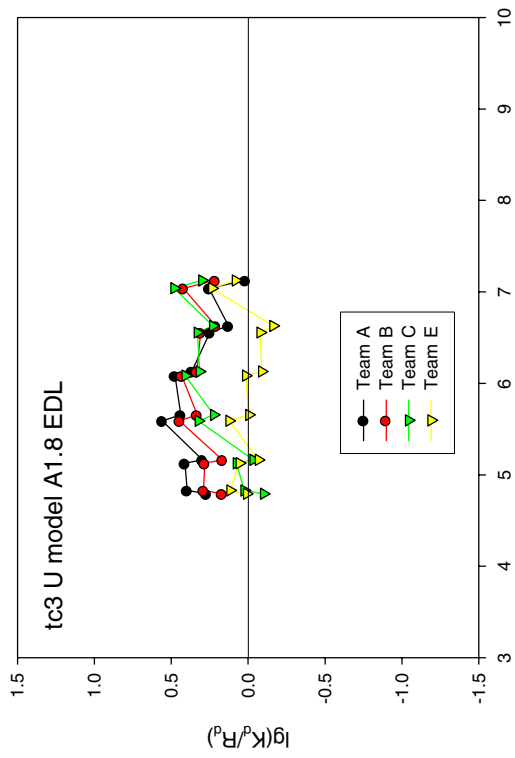


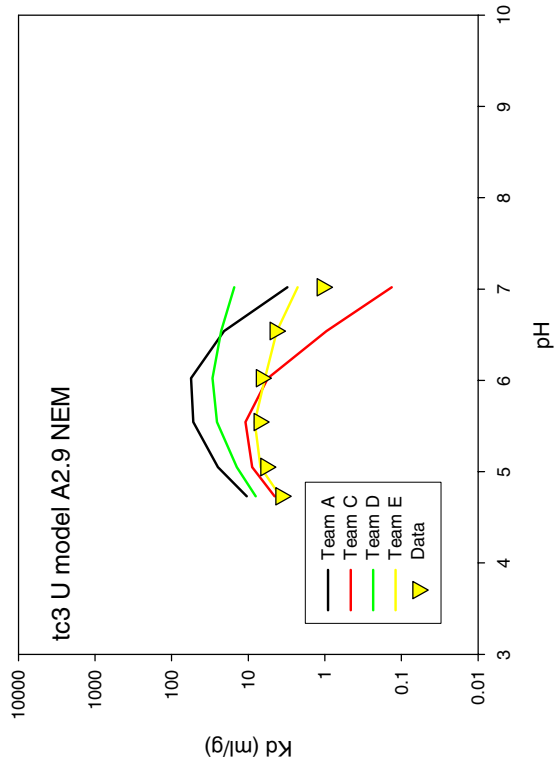
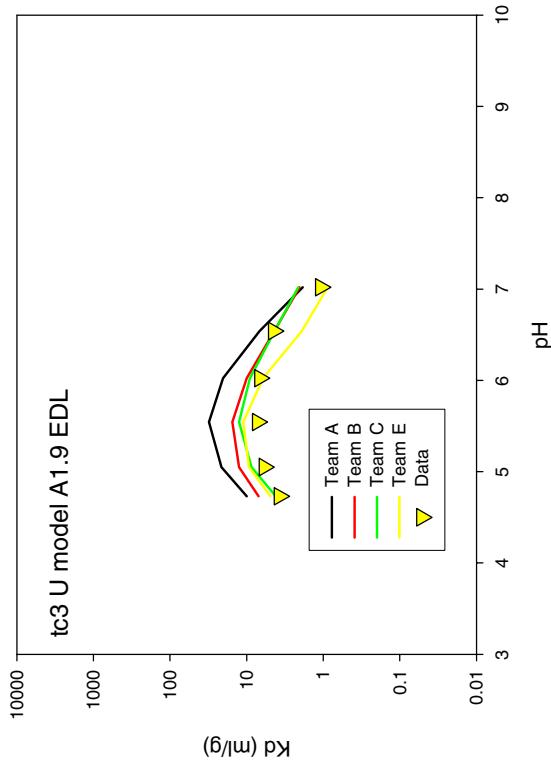
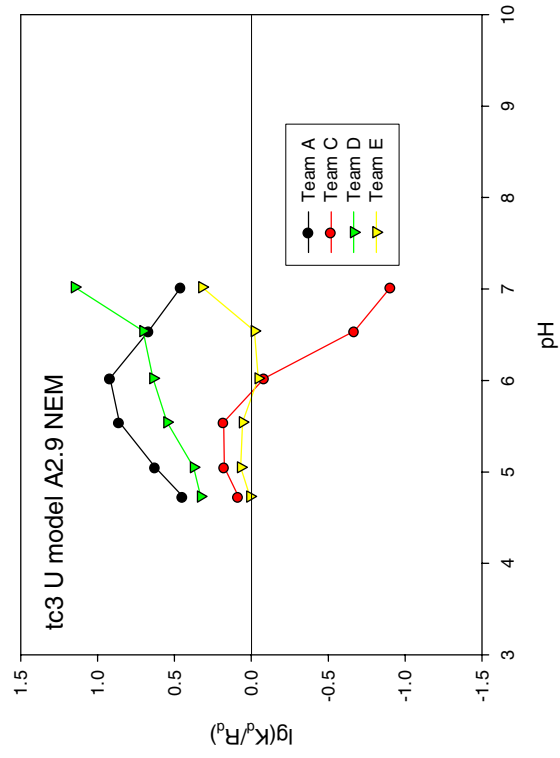
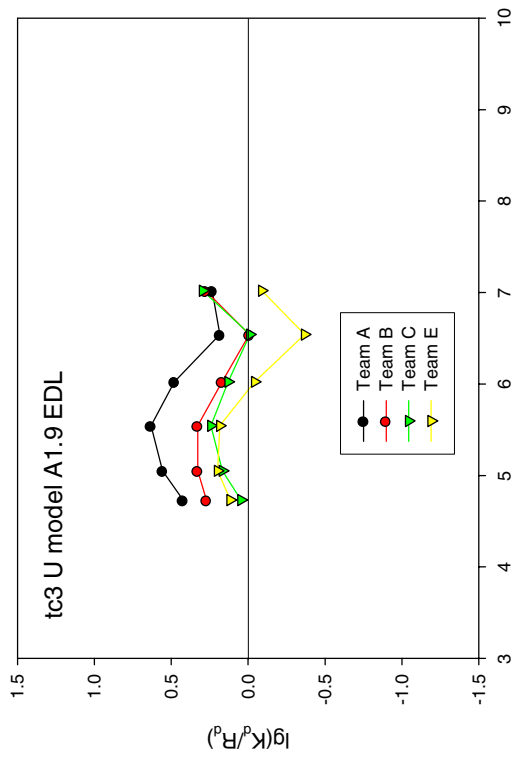




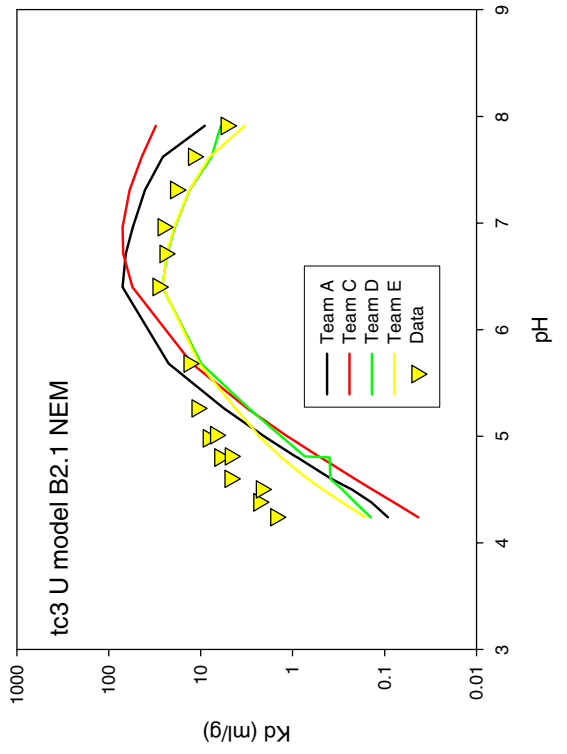
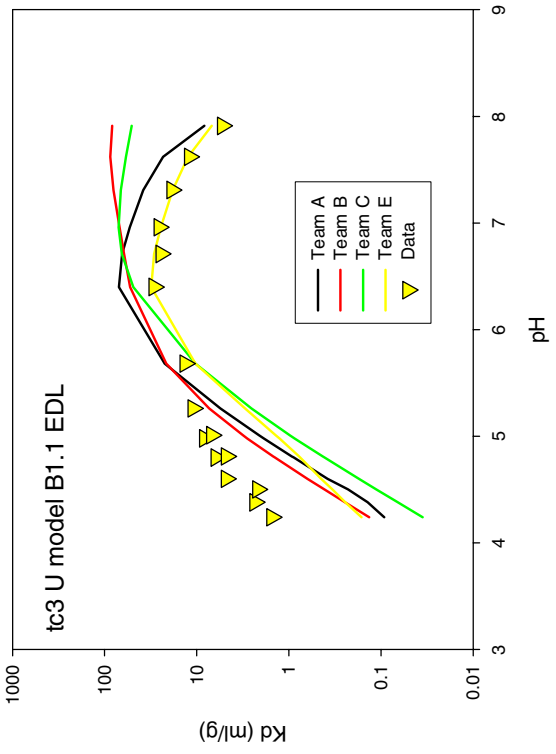
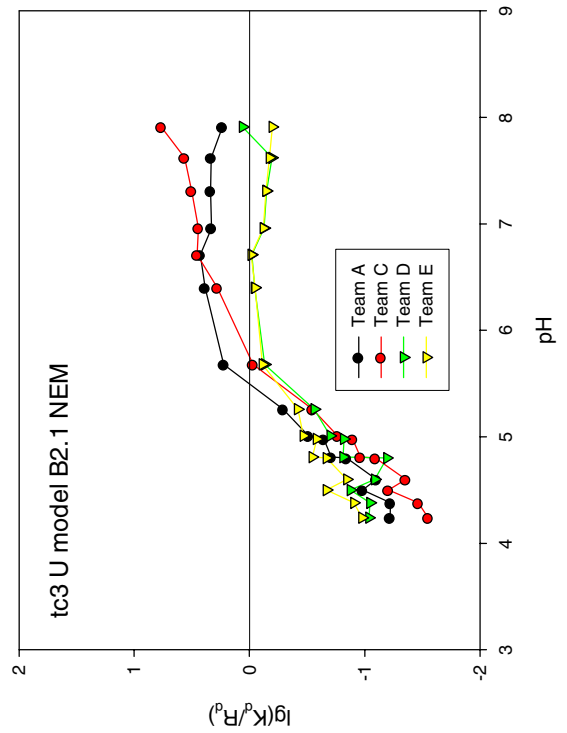
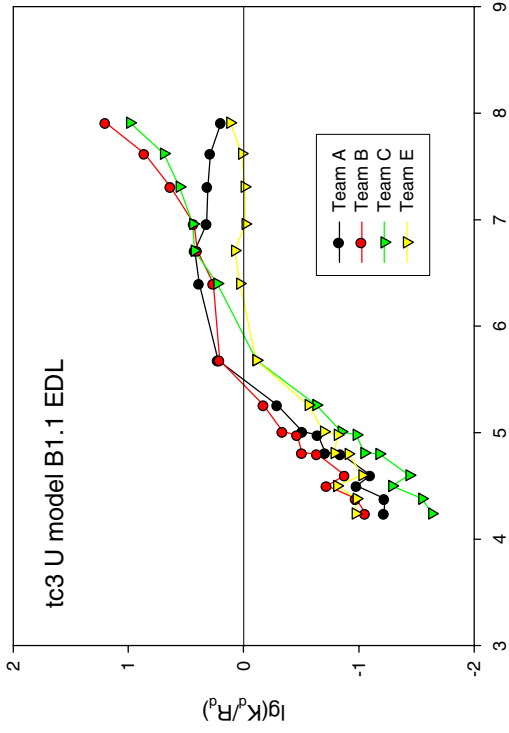


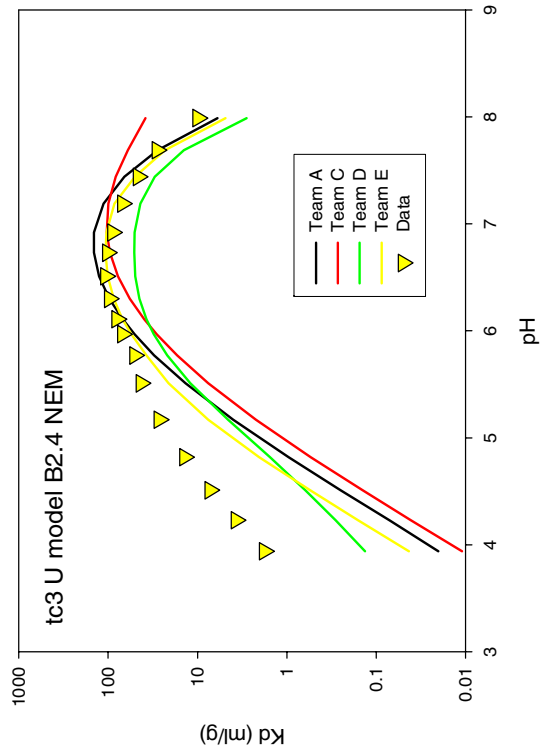
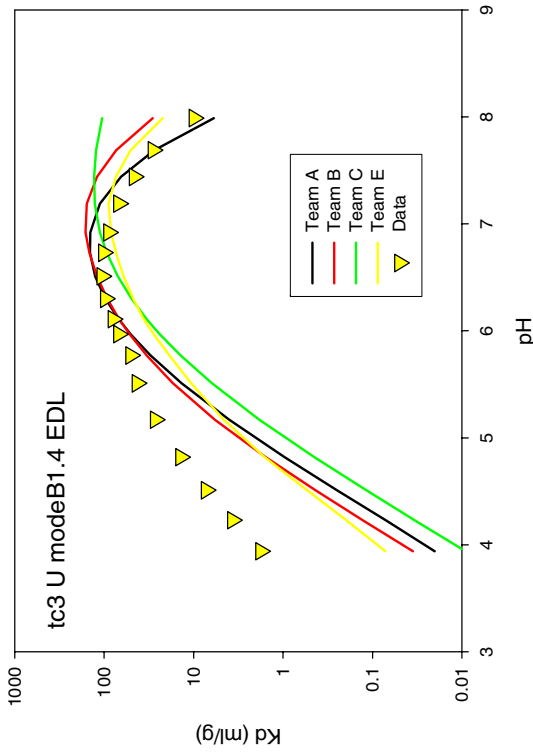
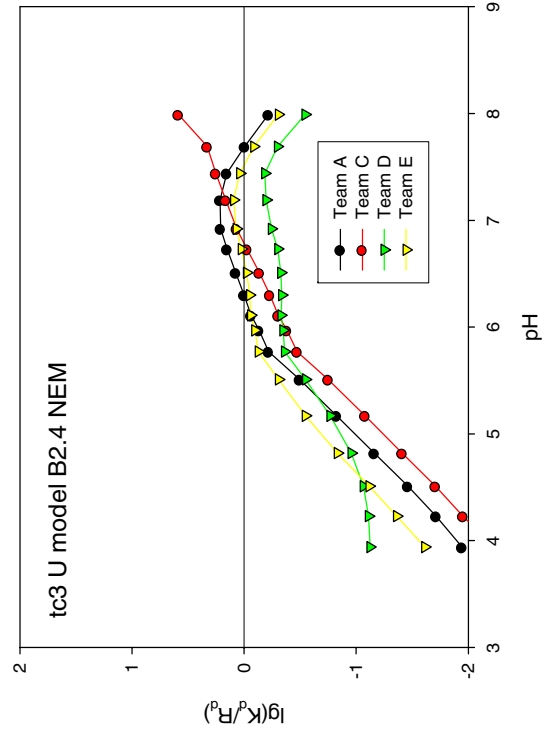
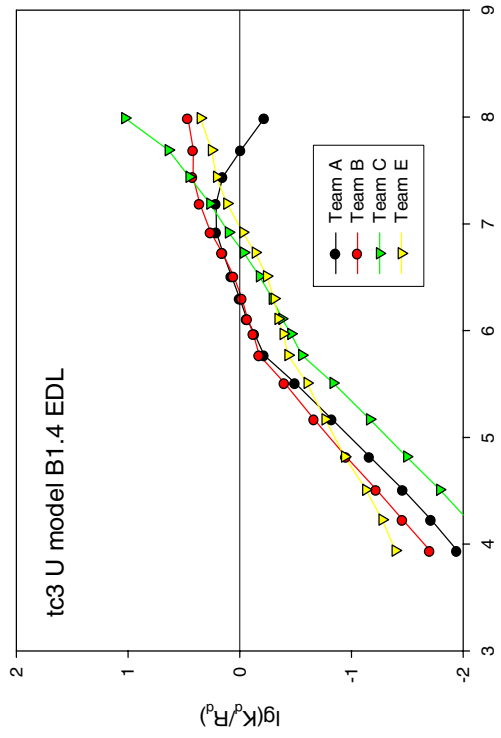


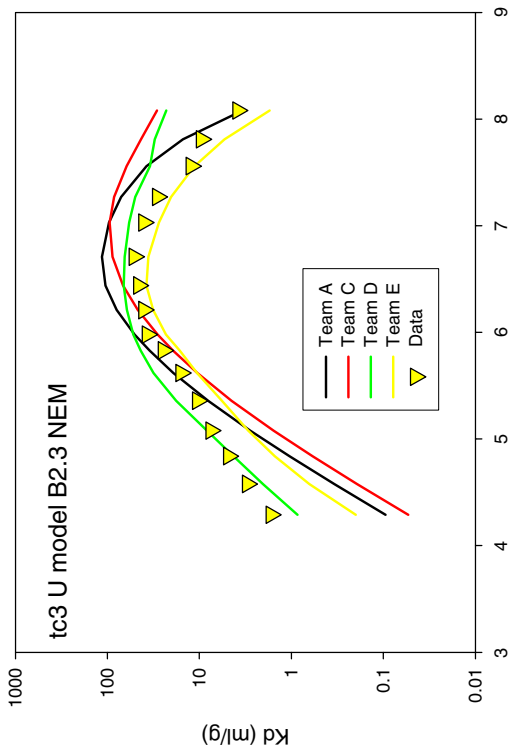
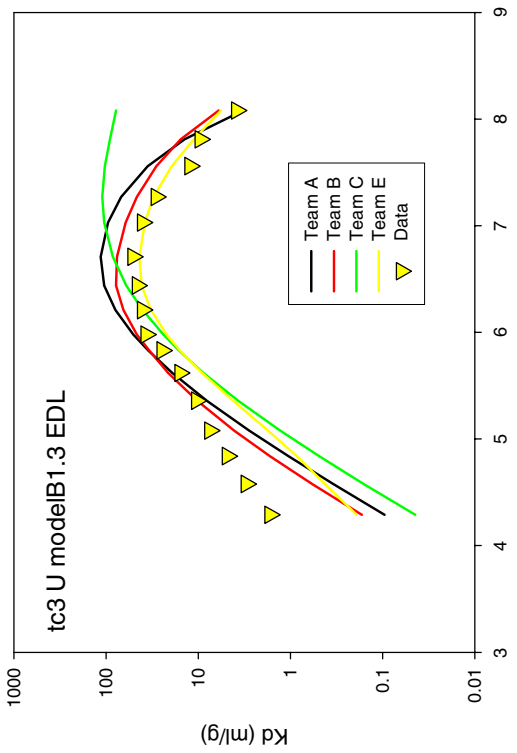
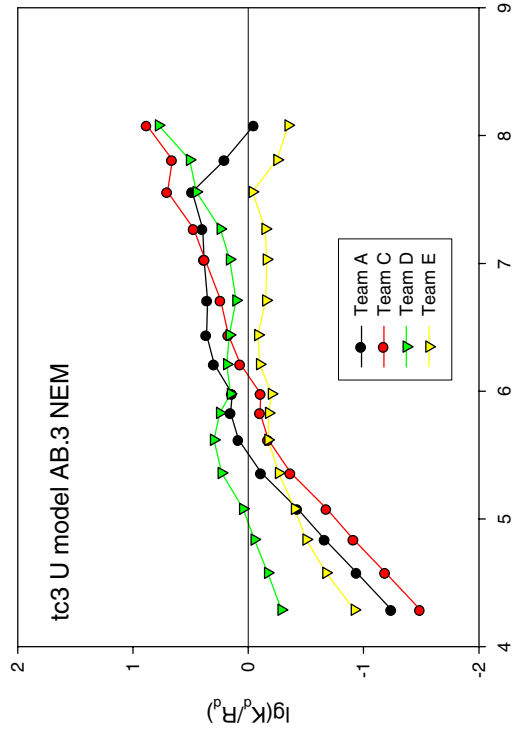
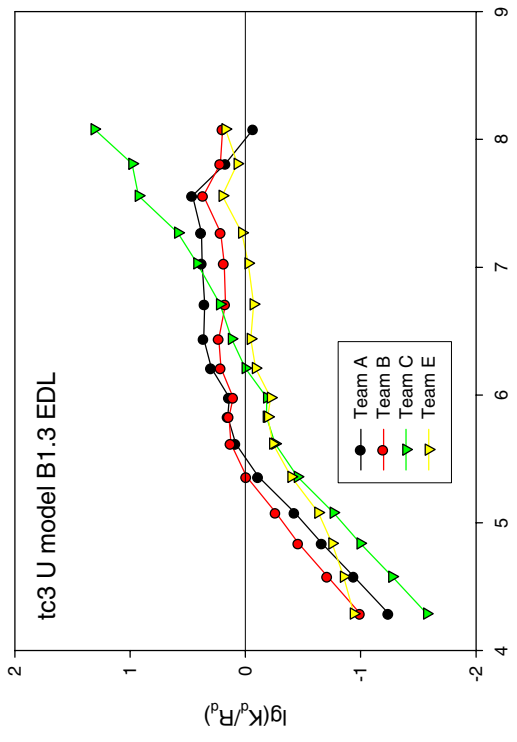


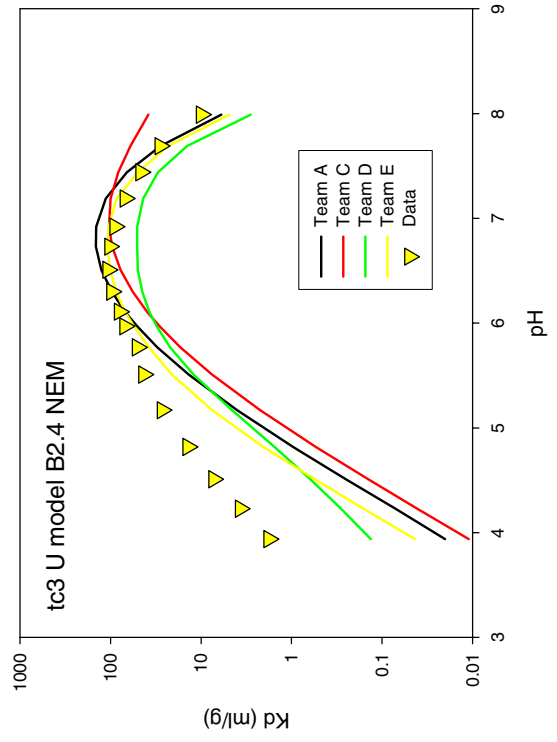
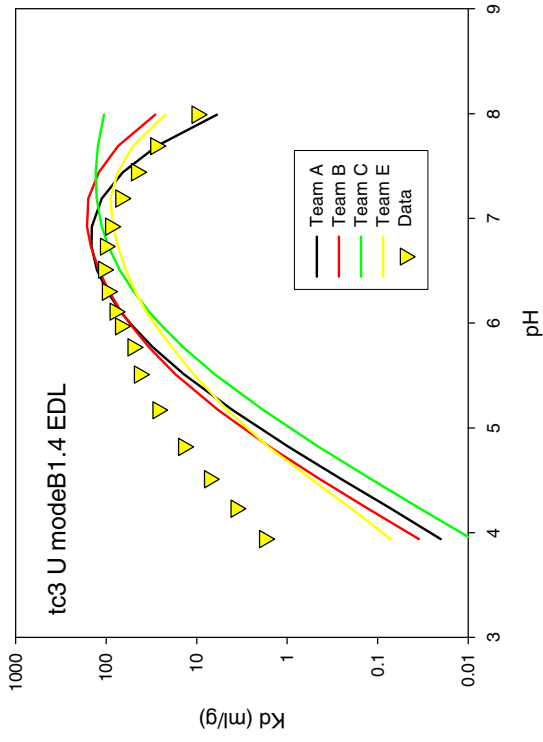
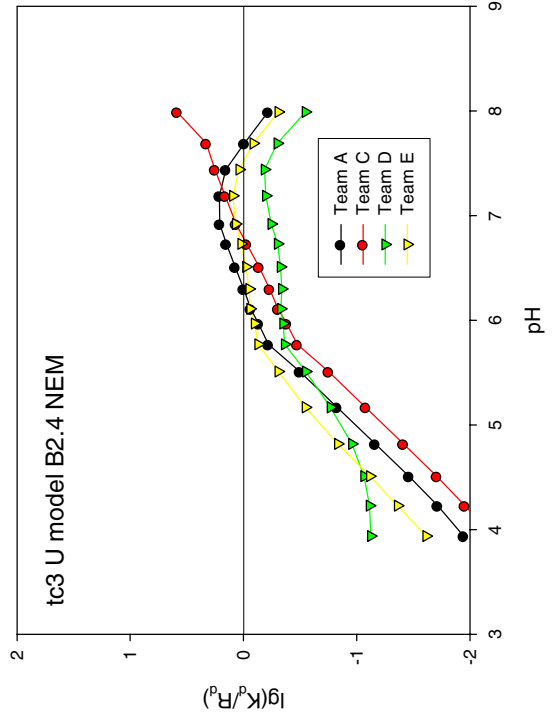
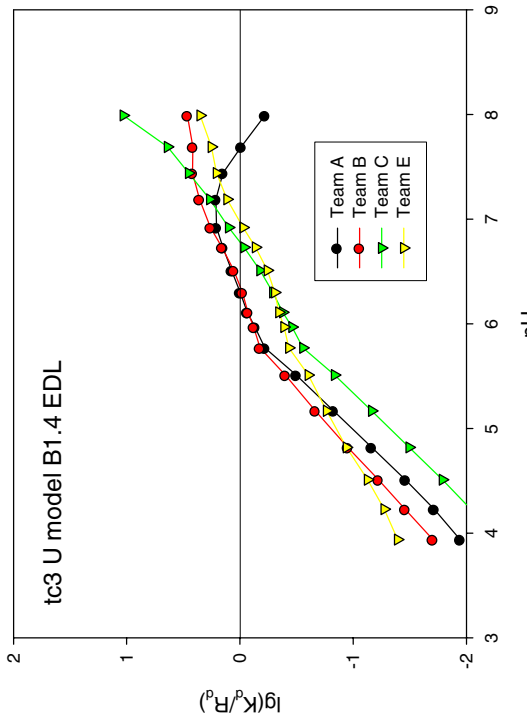


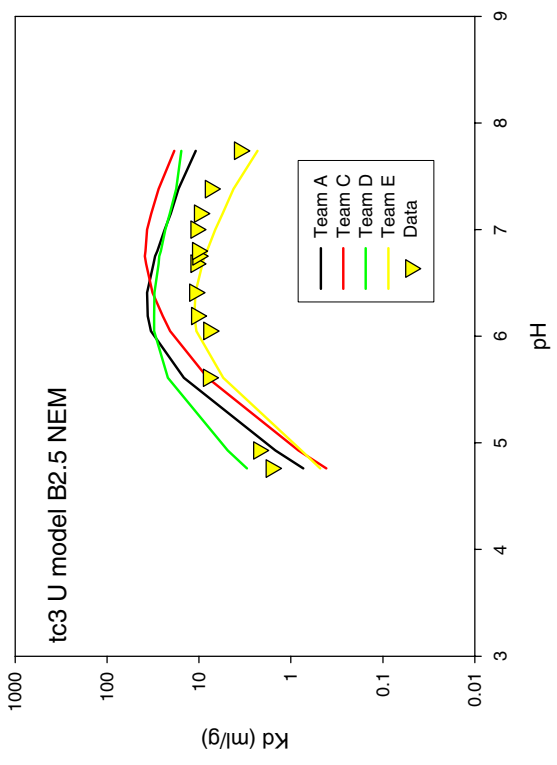
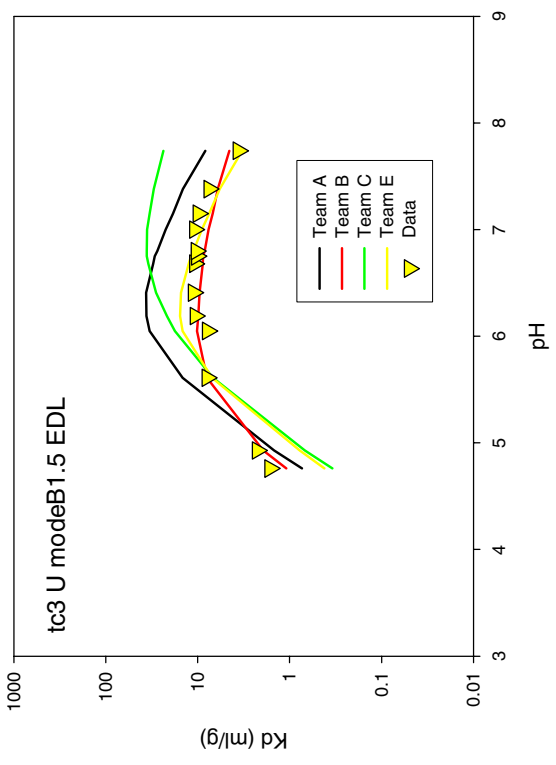
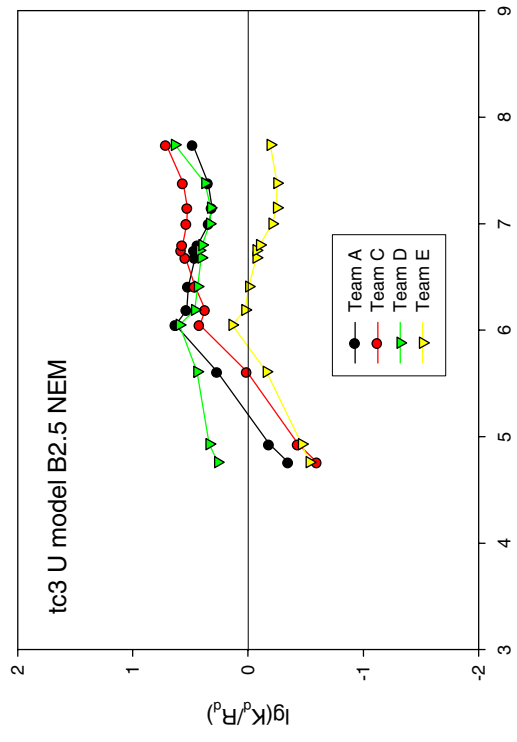
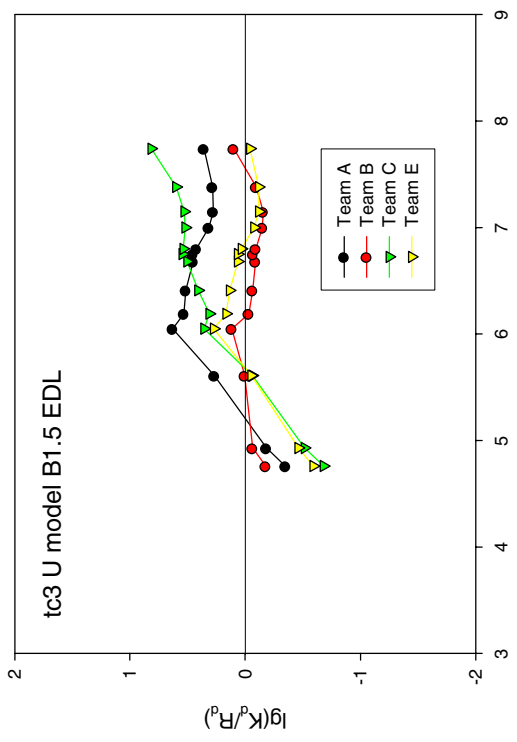










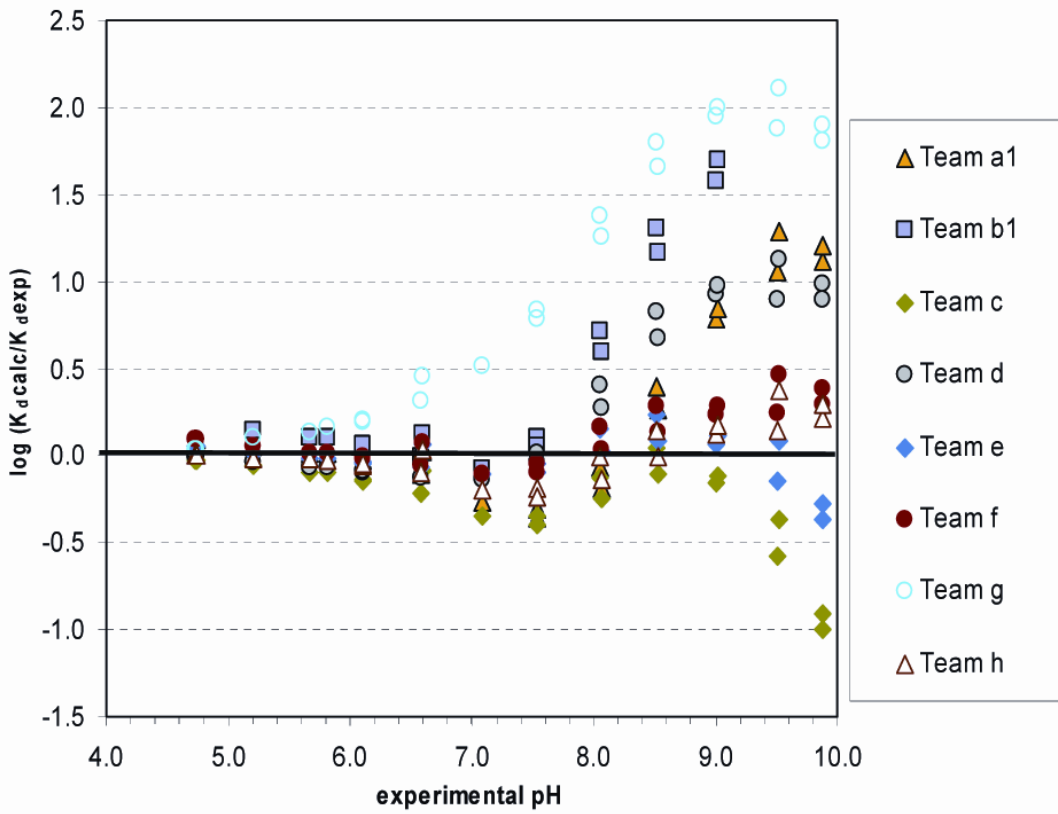
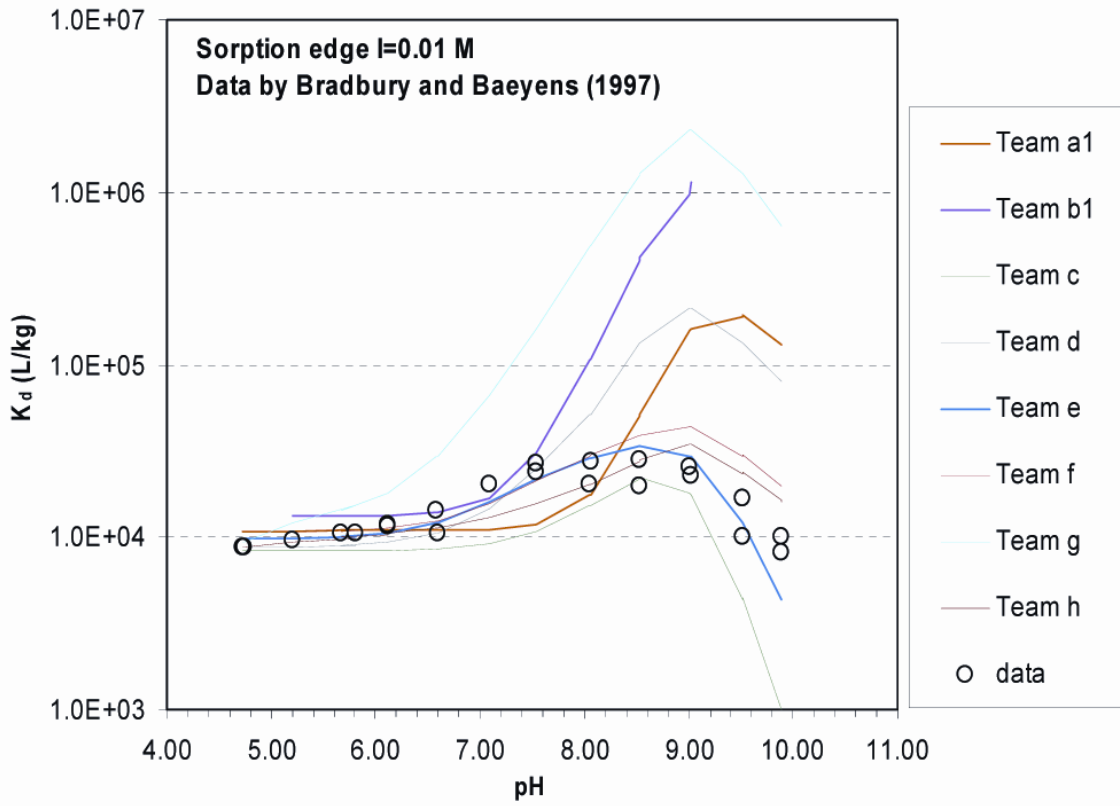


## **Test Case 4:**

### **Ni Sorption on clays**

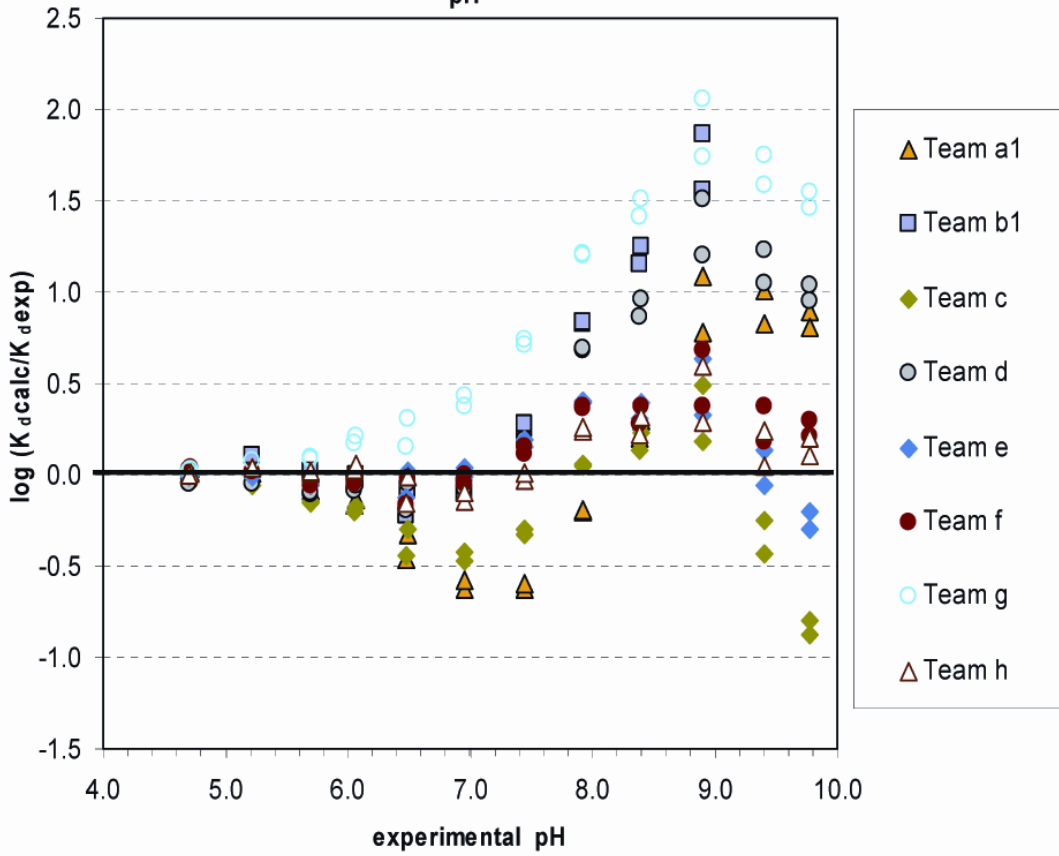
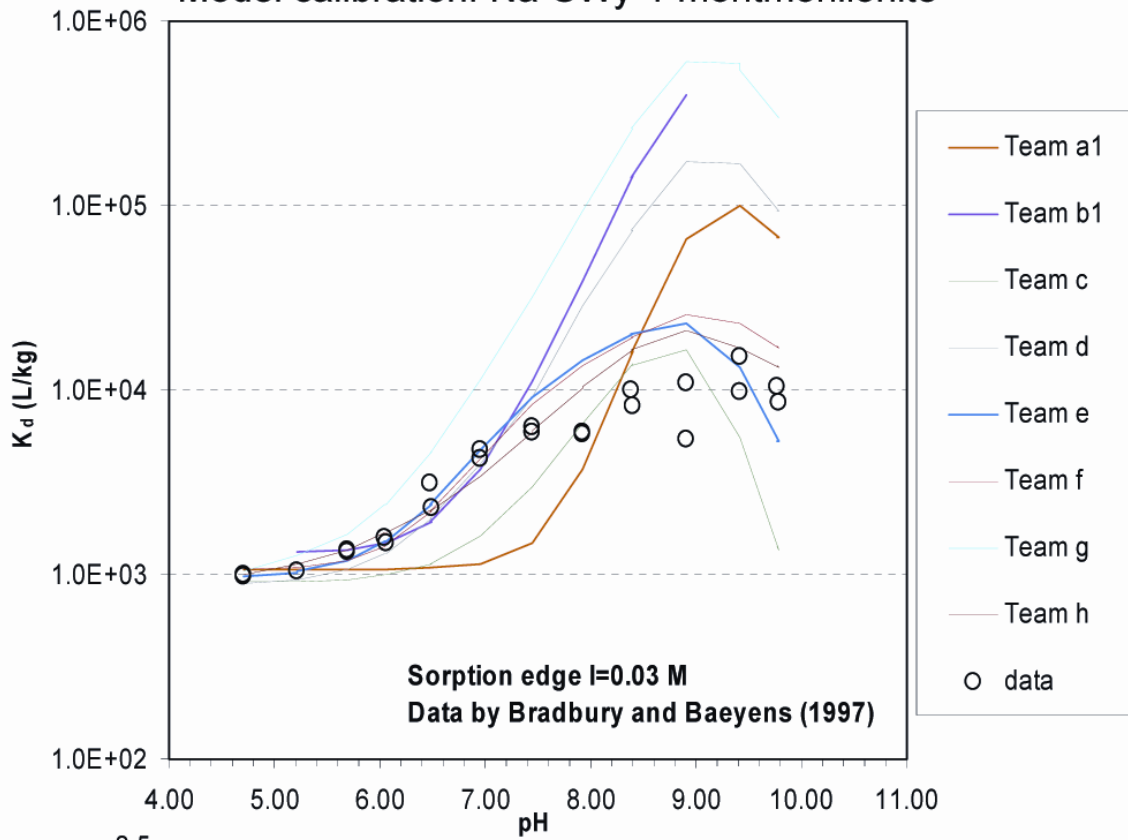


### Model calibration: Na-SWy-1 montmorillonite

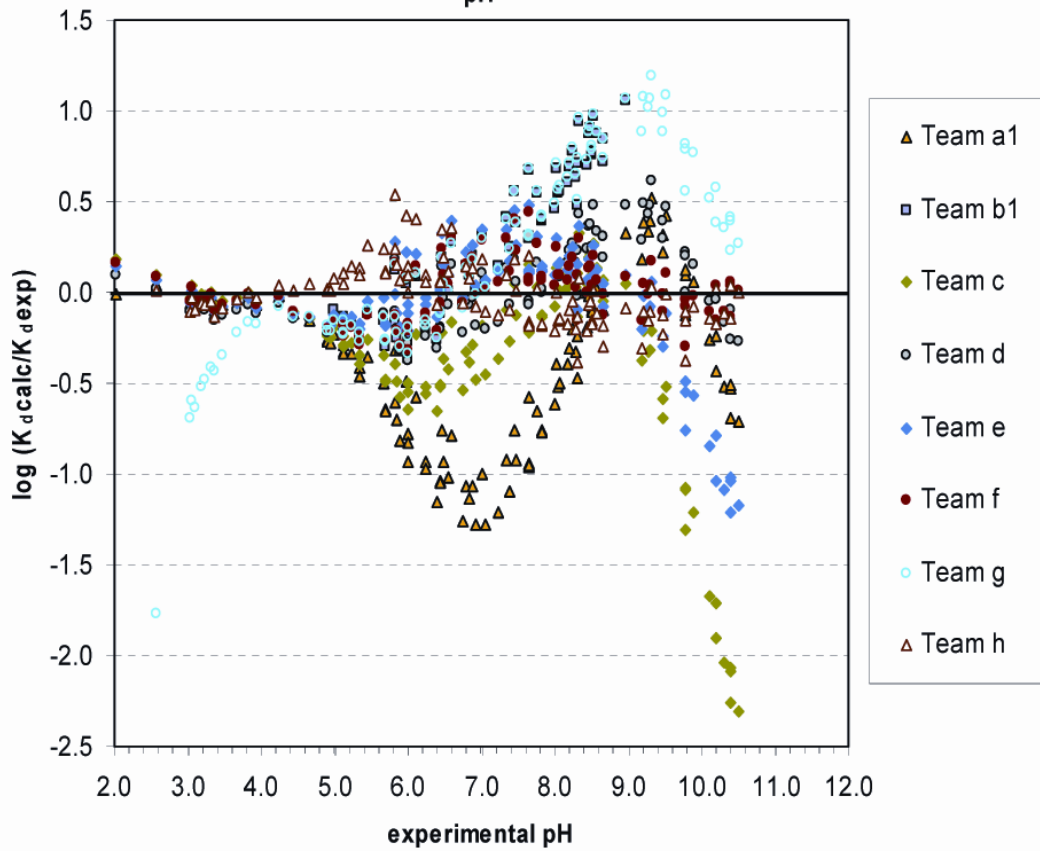
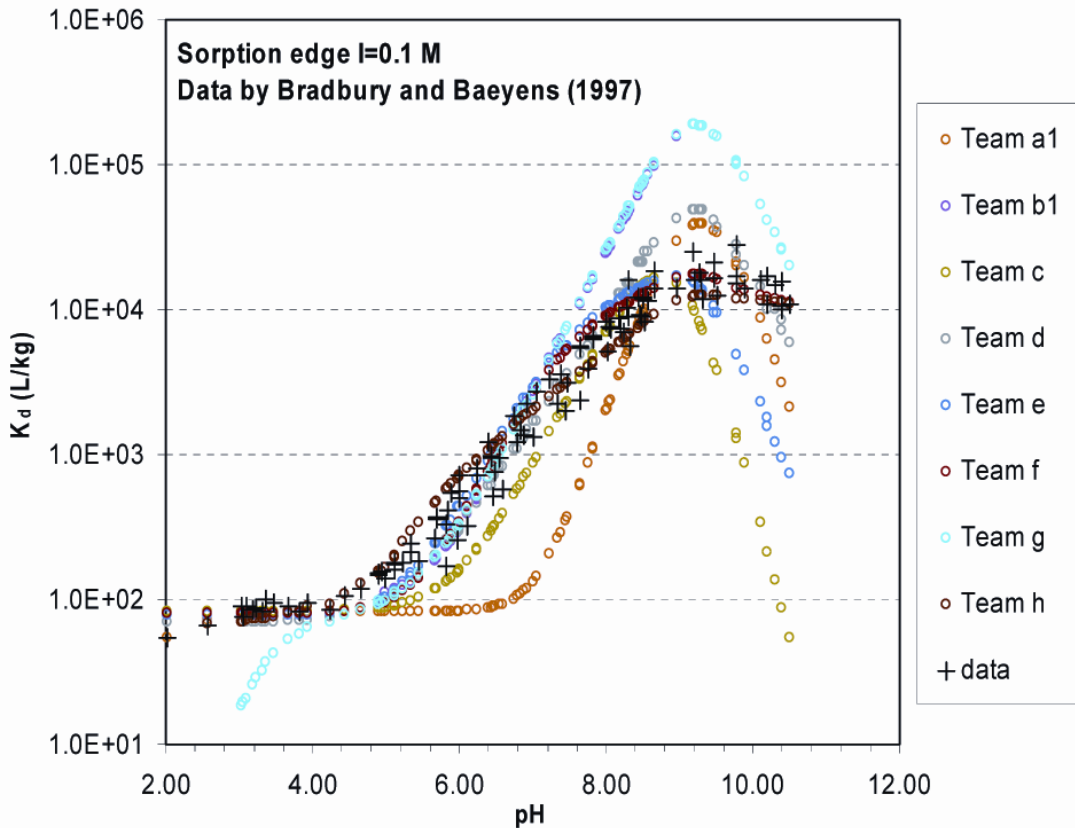




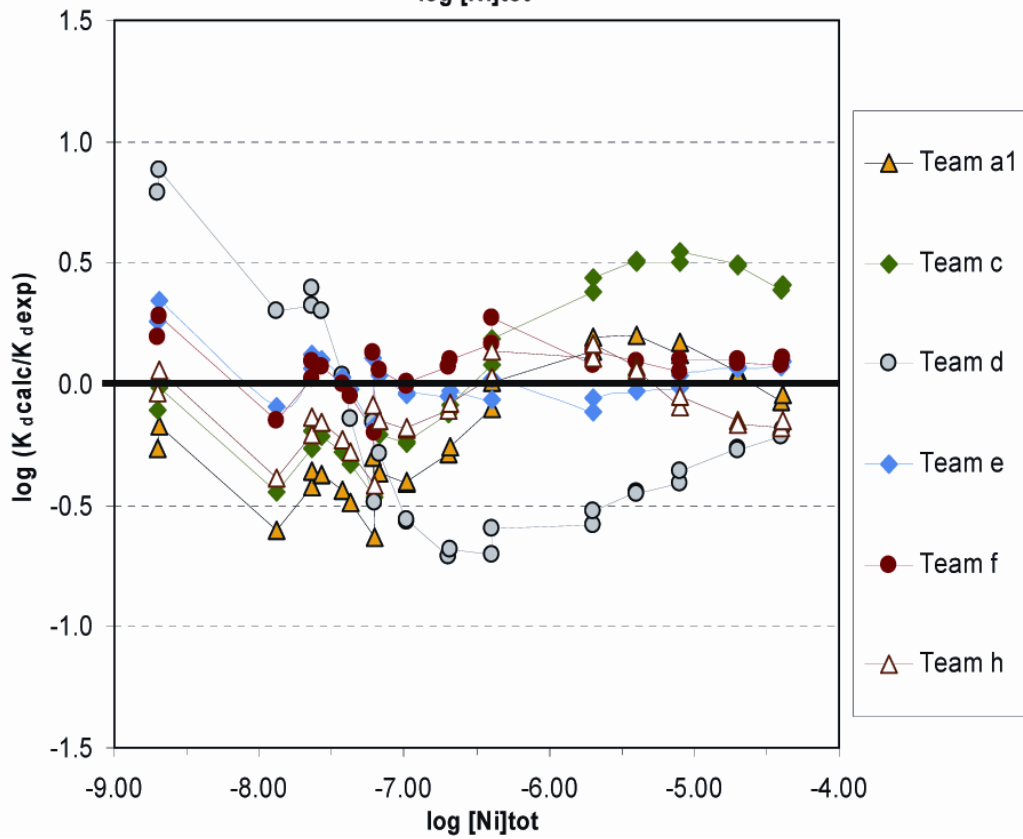
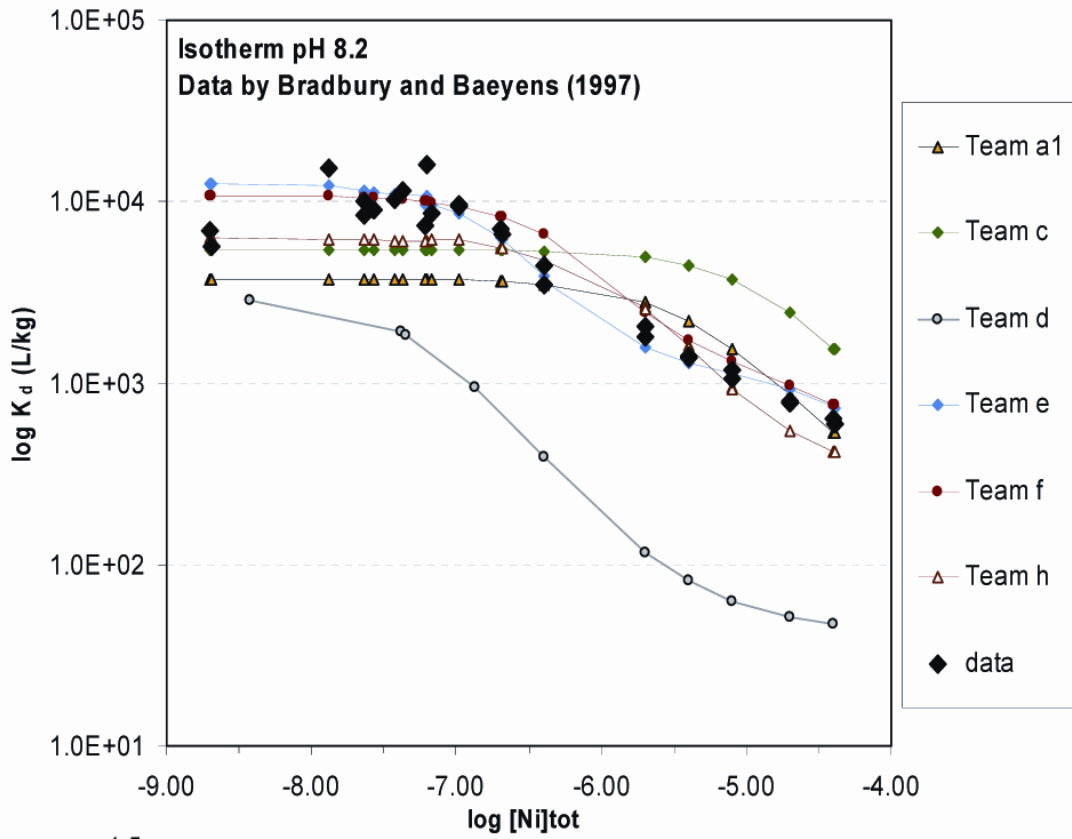
### Model calibration: Na-SWy-1 montmorillonite



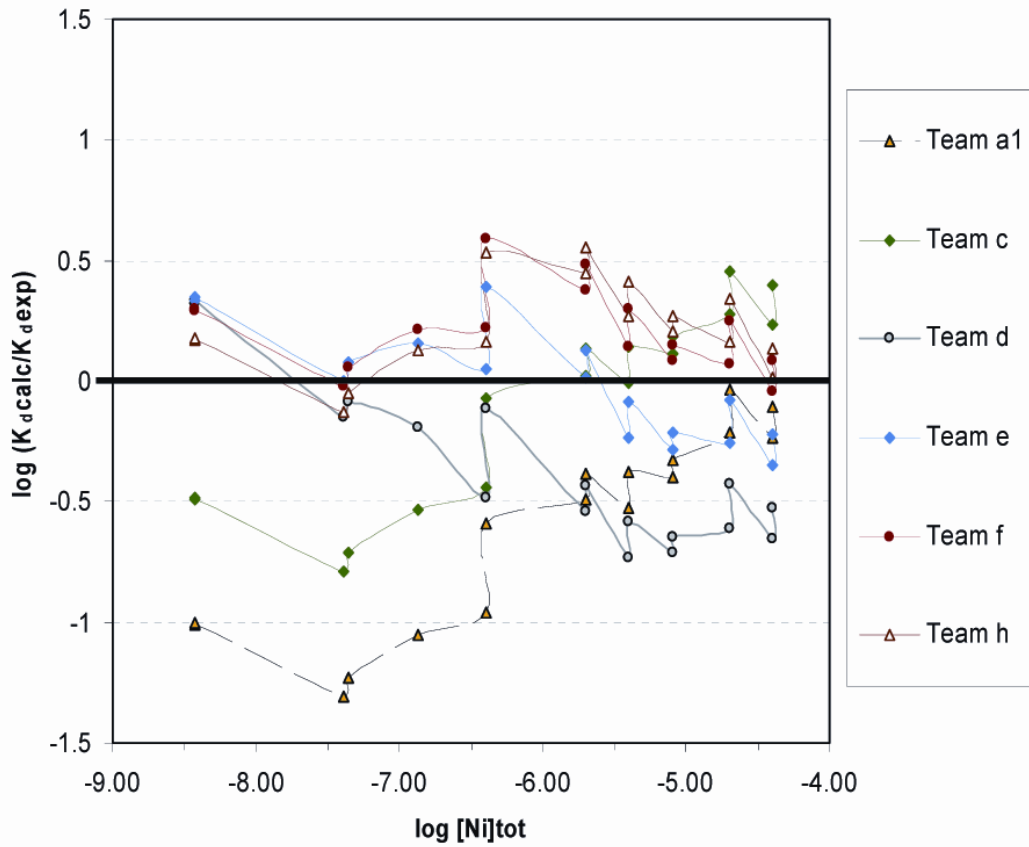
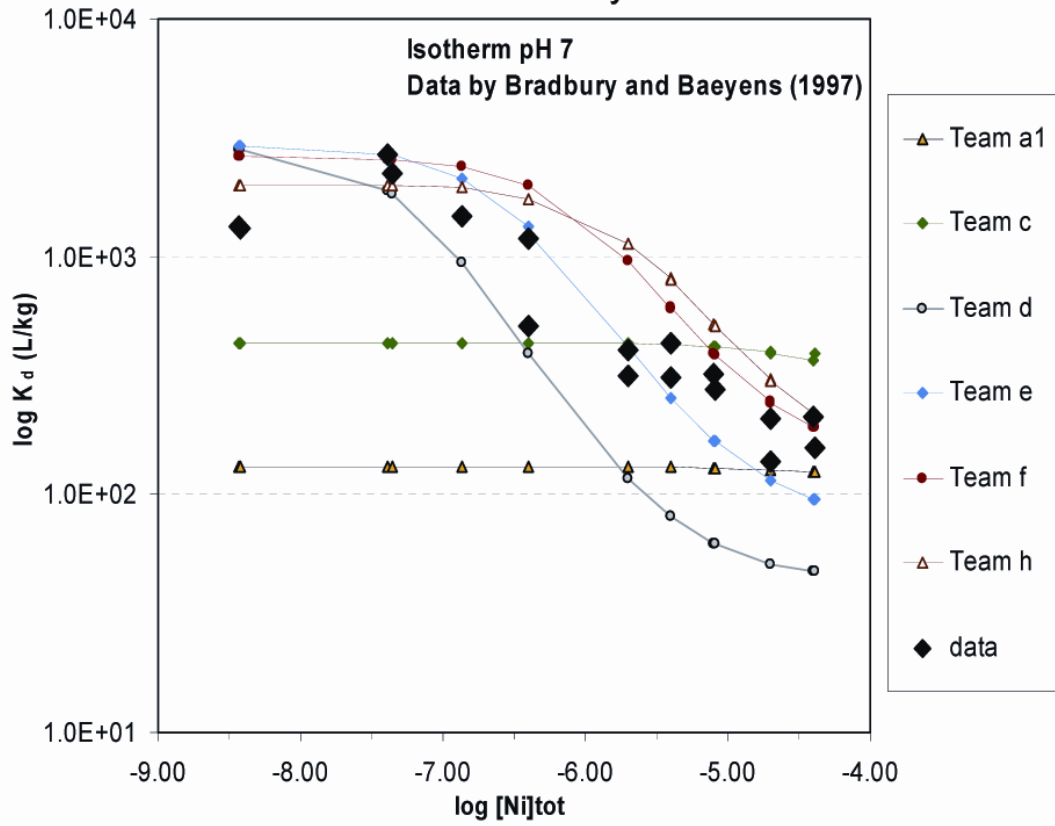
### Model calibration: Na-SWy-1 montmorillonite



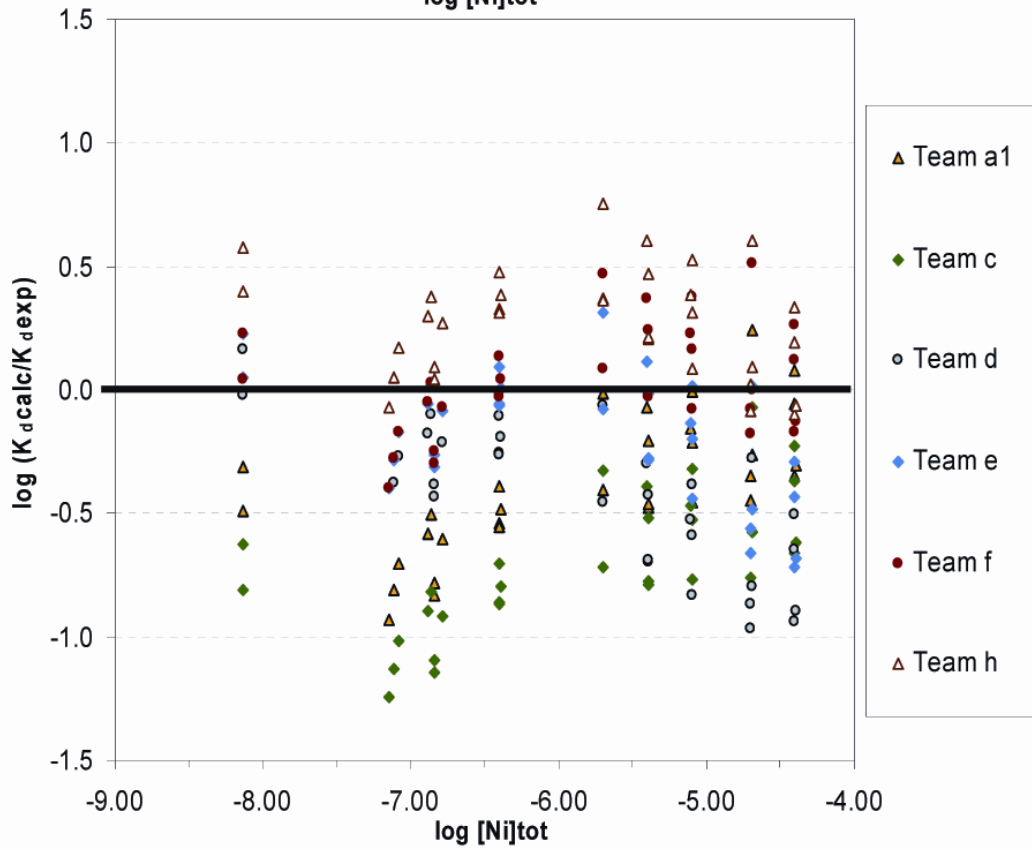
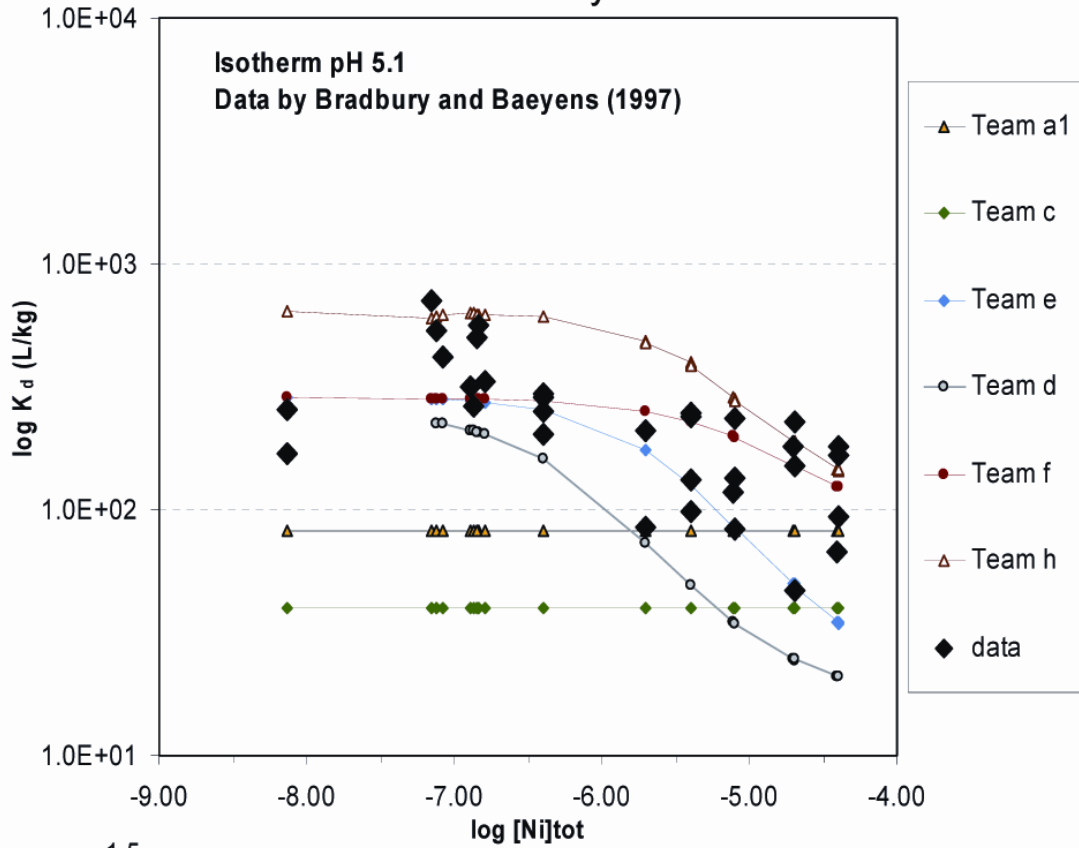
### Model calibration: Na-SWy-1 montmorillonite



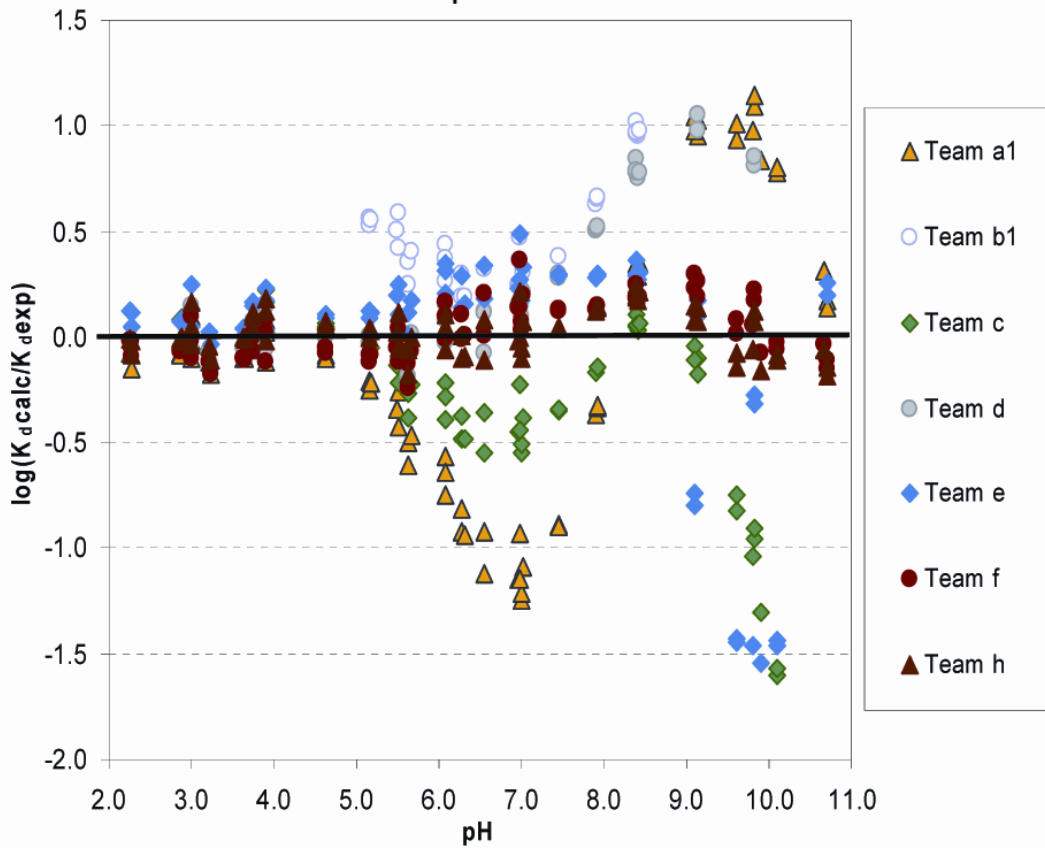
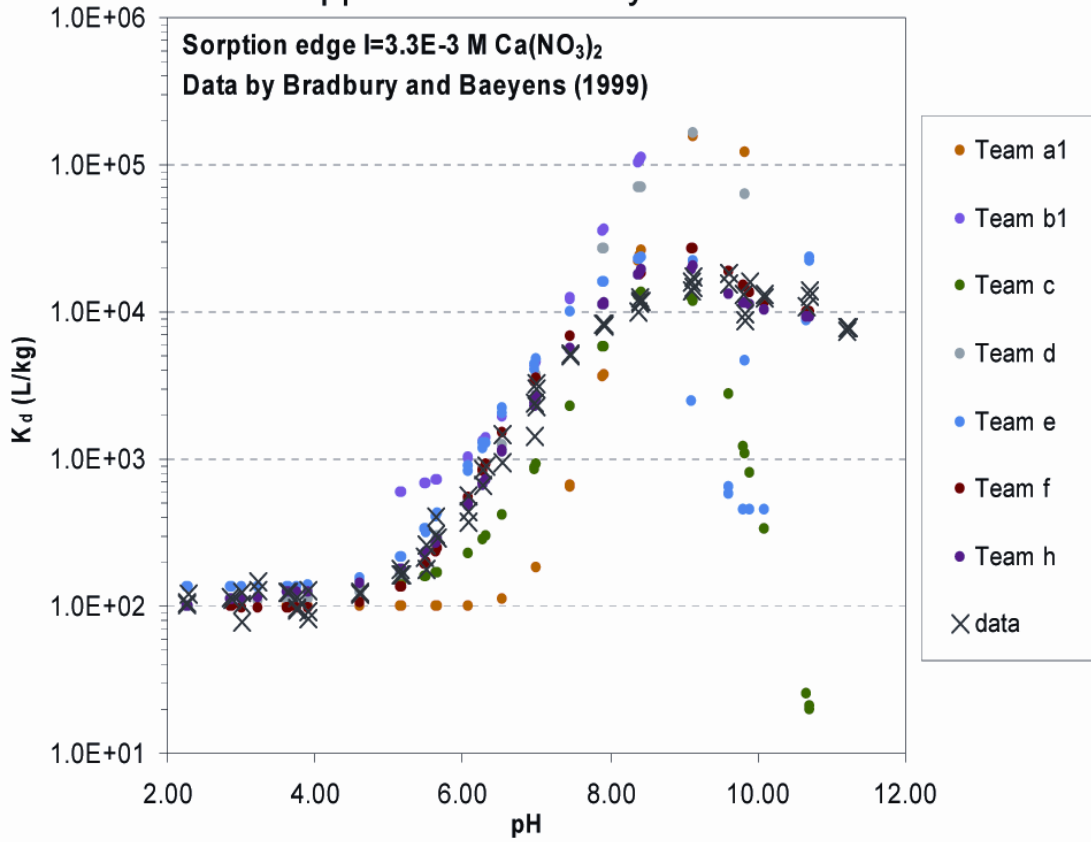
### Model calibration: Na-SWy-1 montmorillonite



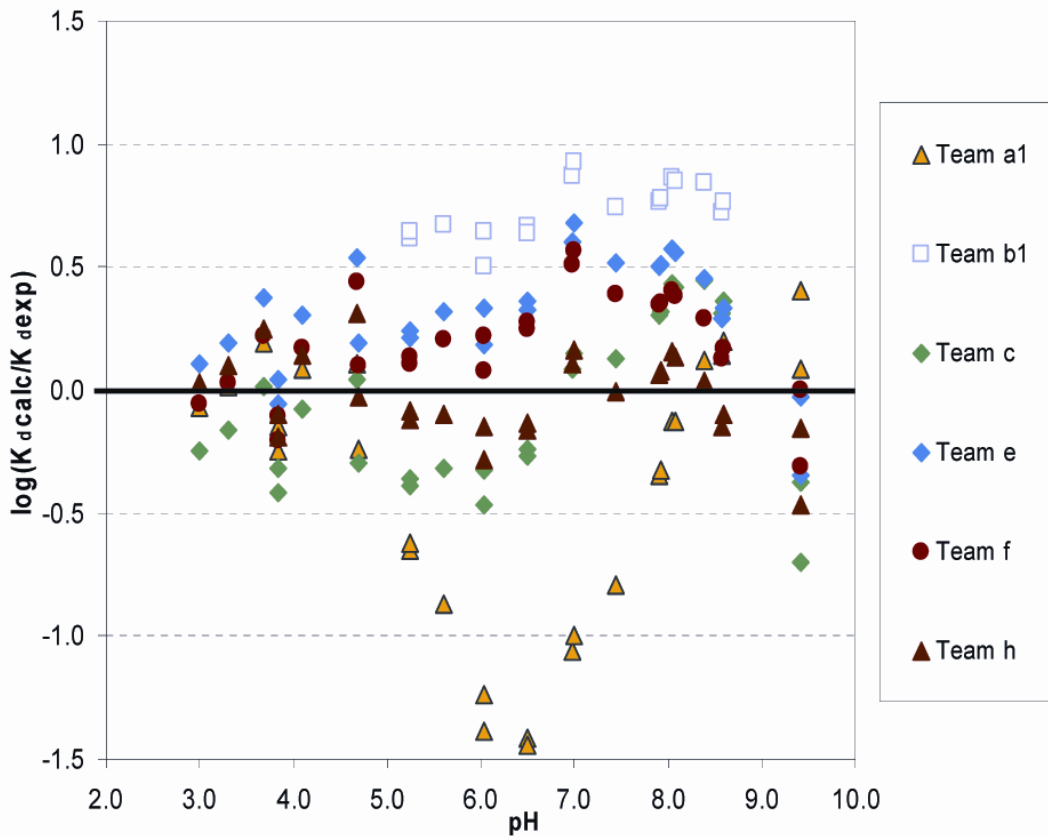
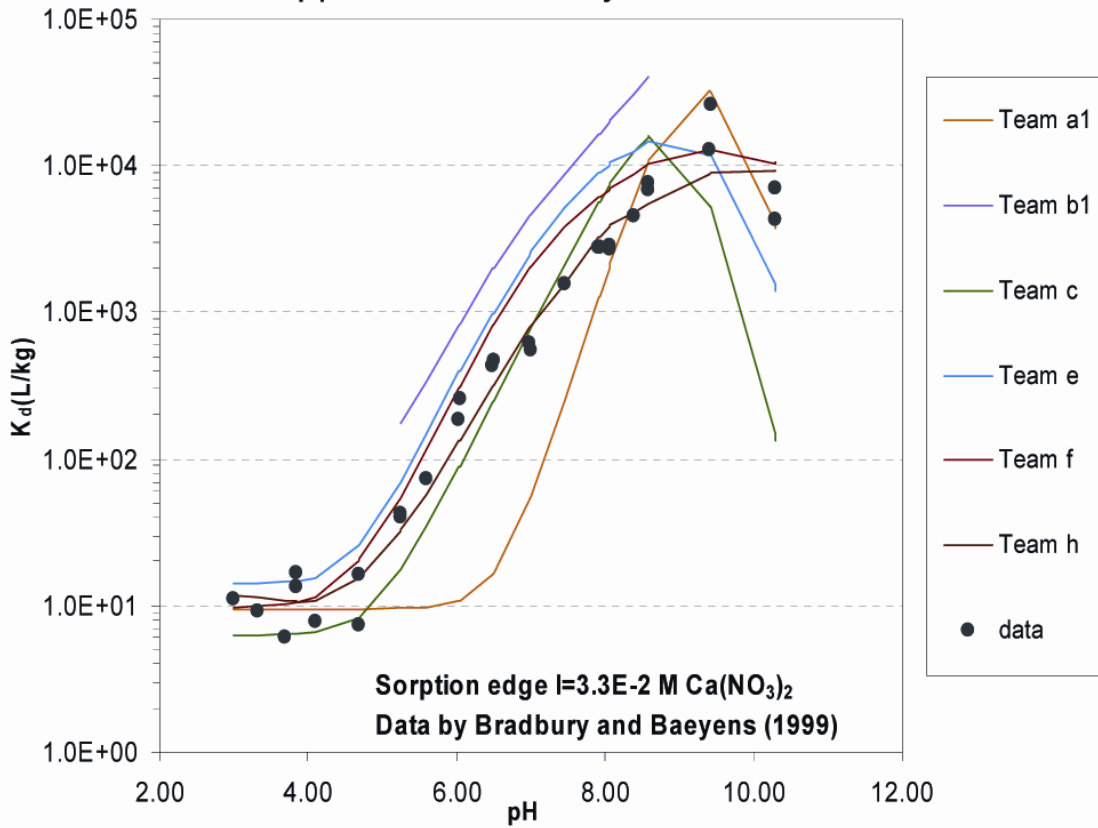
### Model calibration: Na-SWy-1 montmorillonite

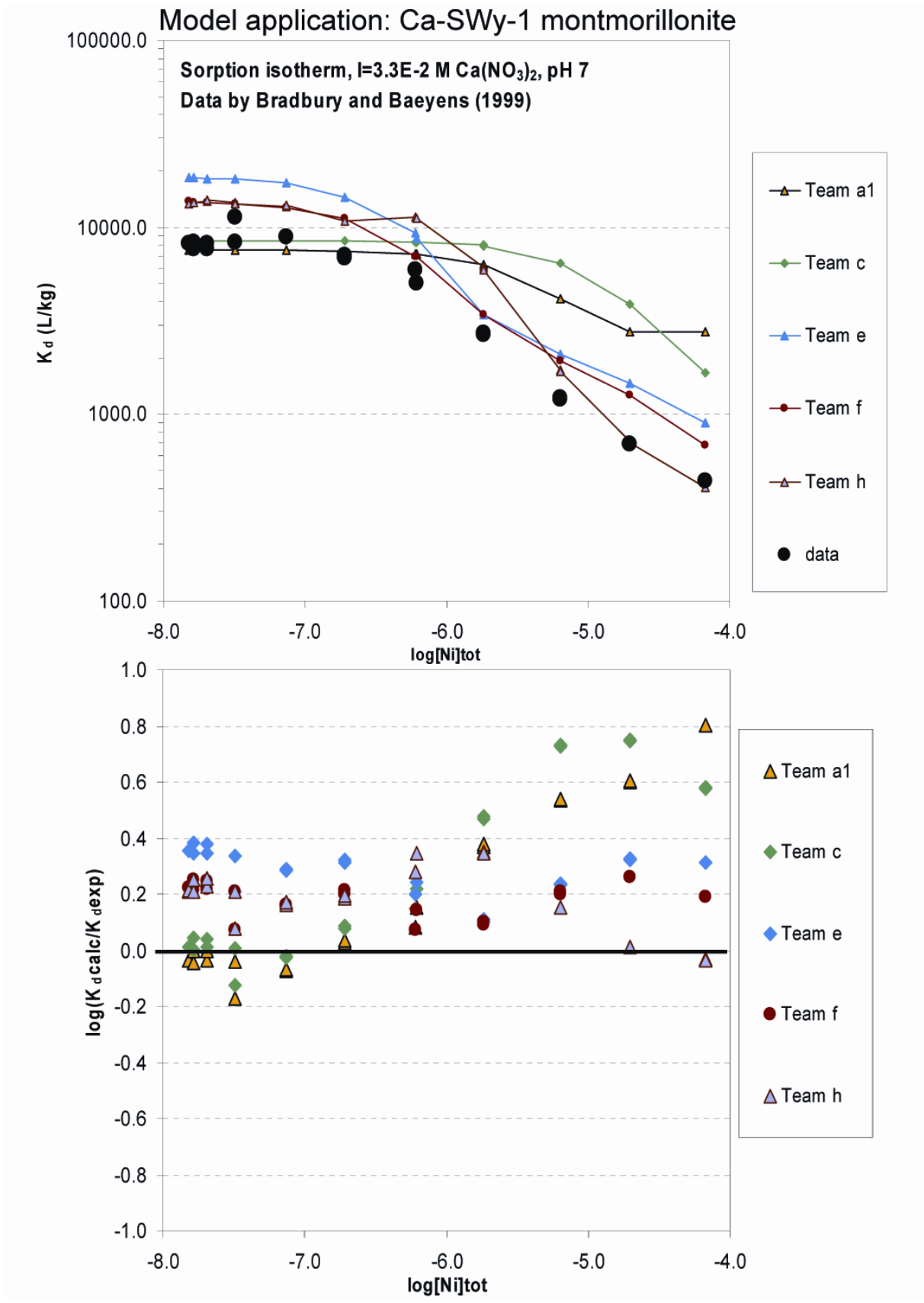


### Model application: Ca-SWy-1 montmorillonite



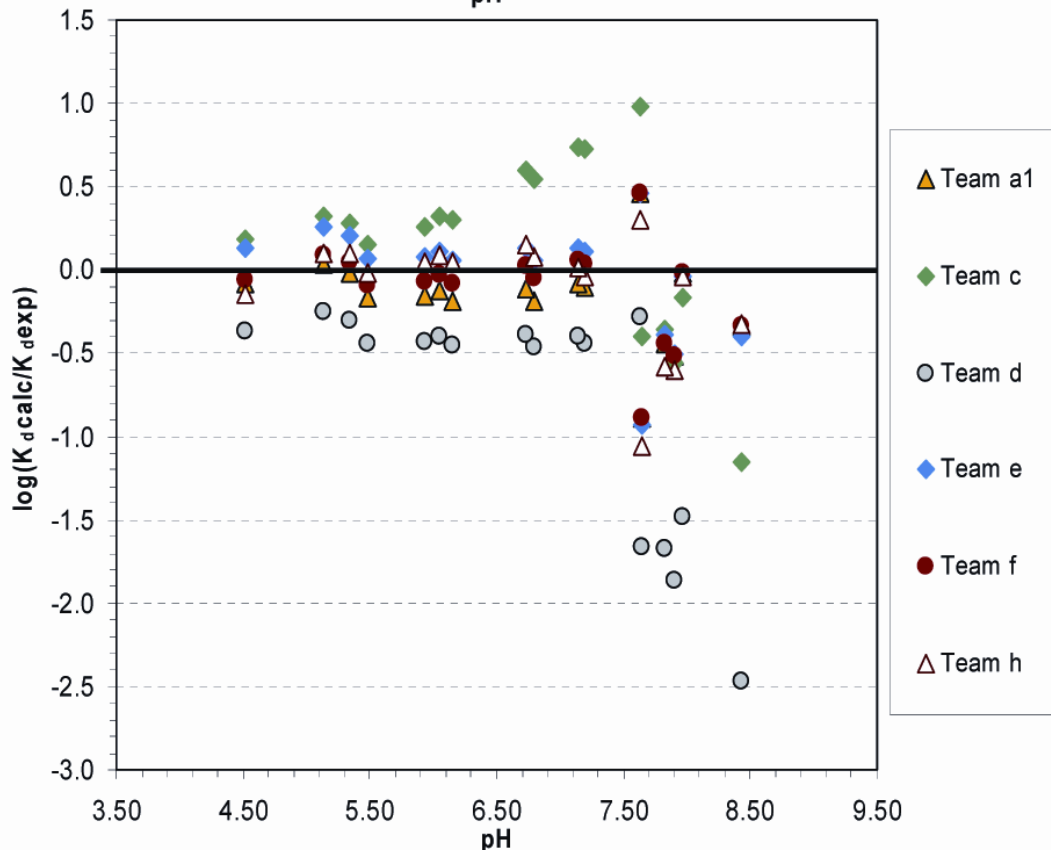
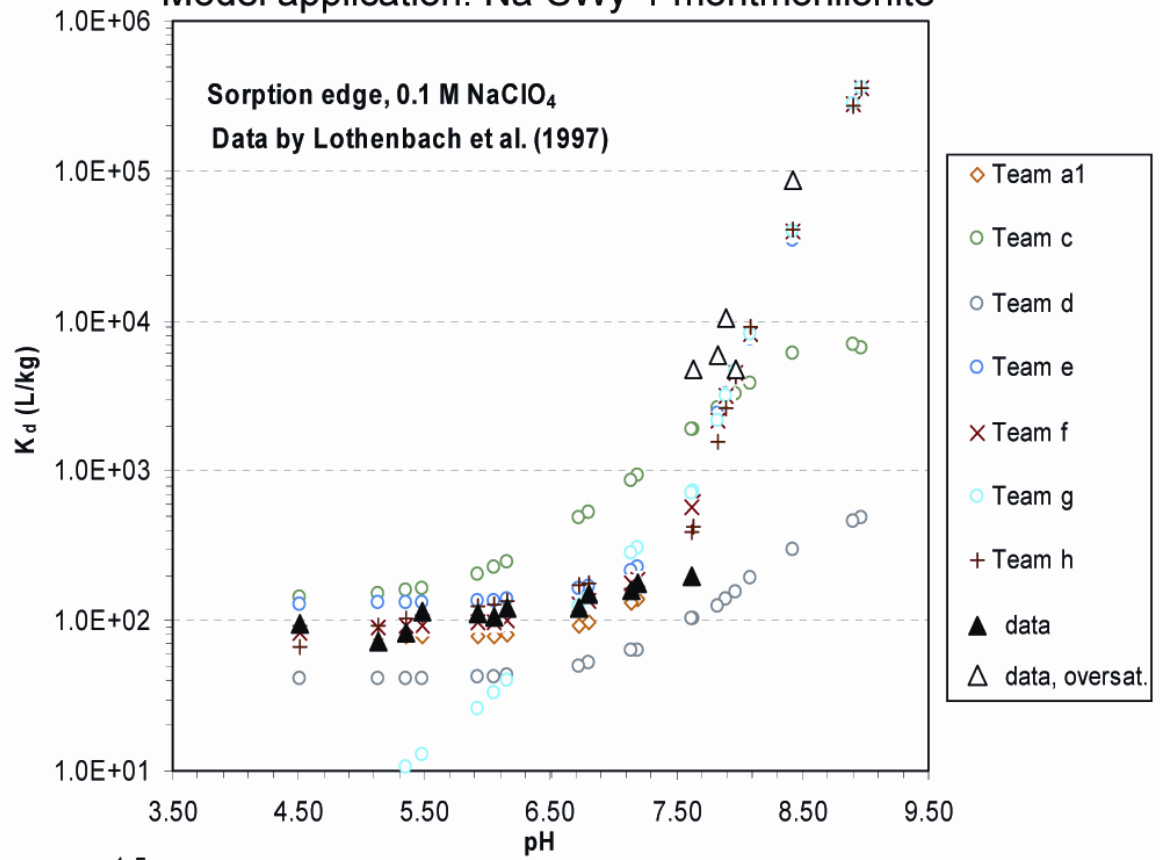
### Model application: Ca-SWy-1 montmorillonite



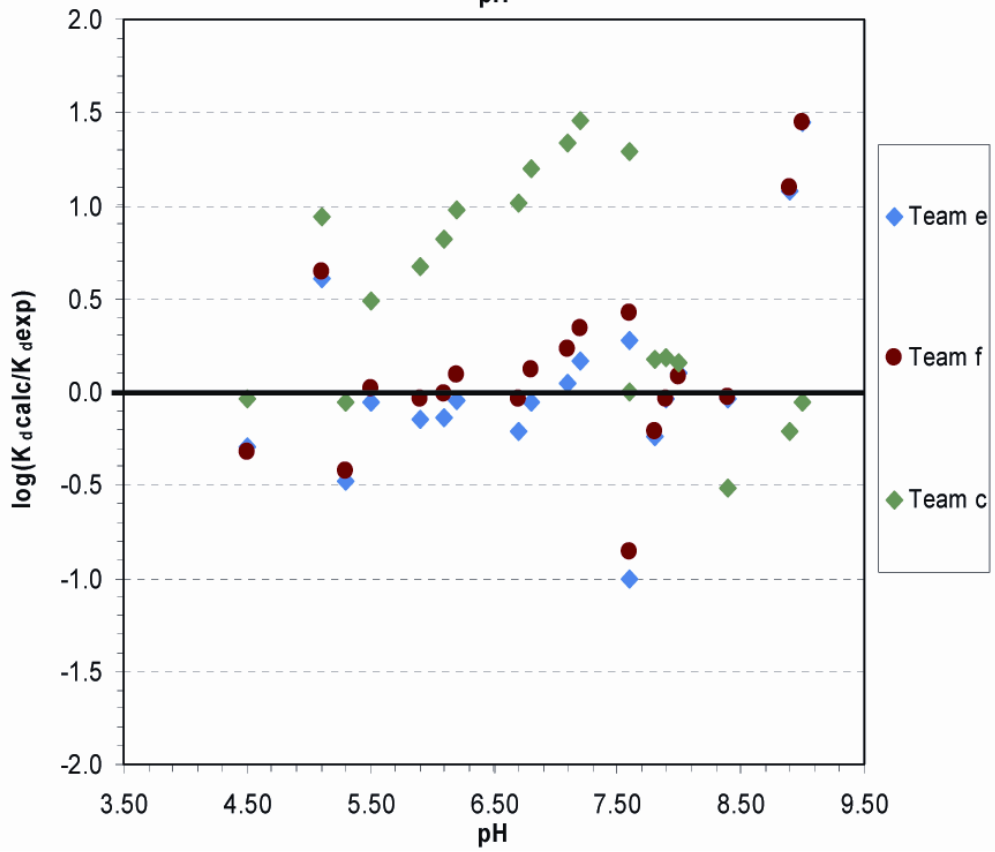
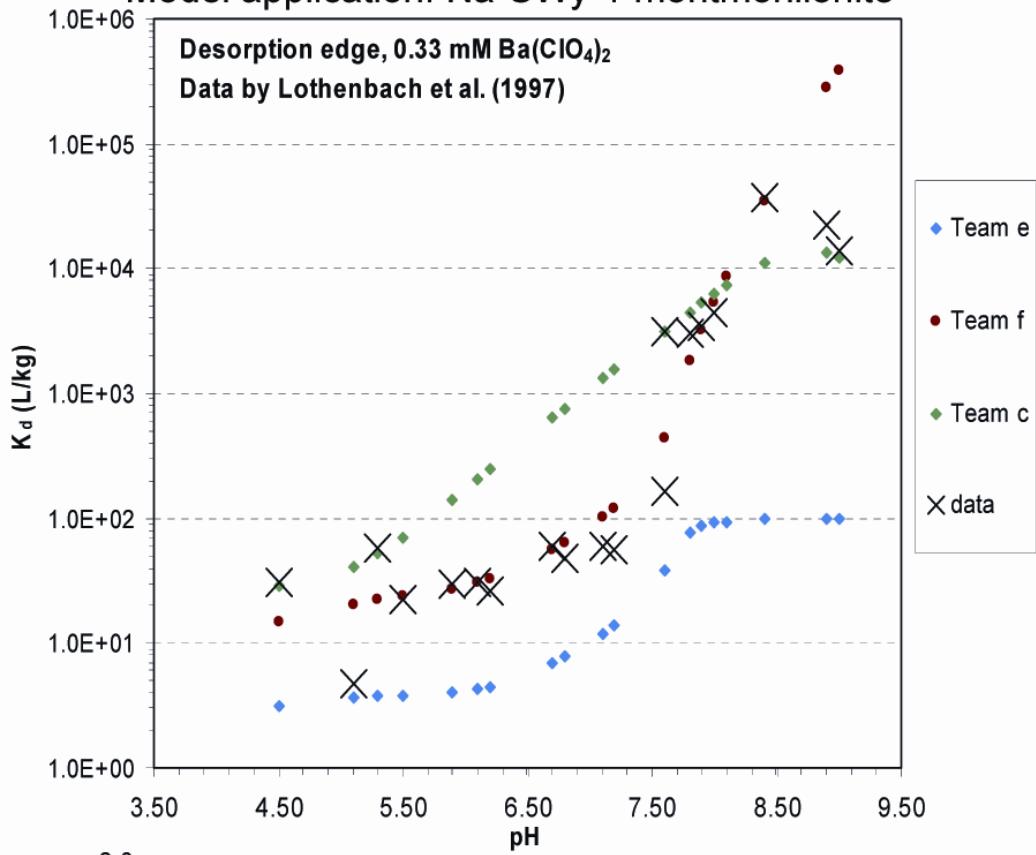




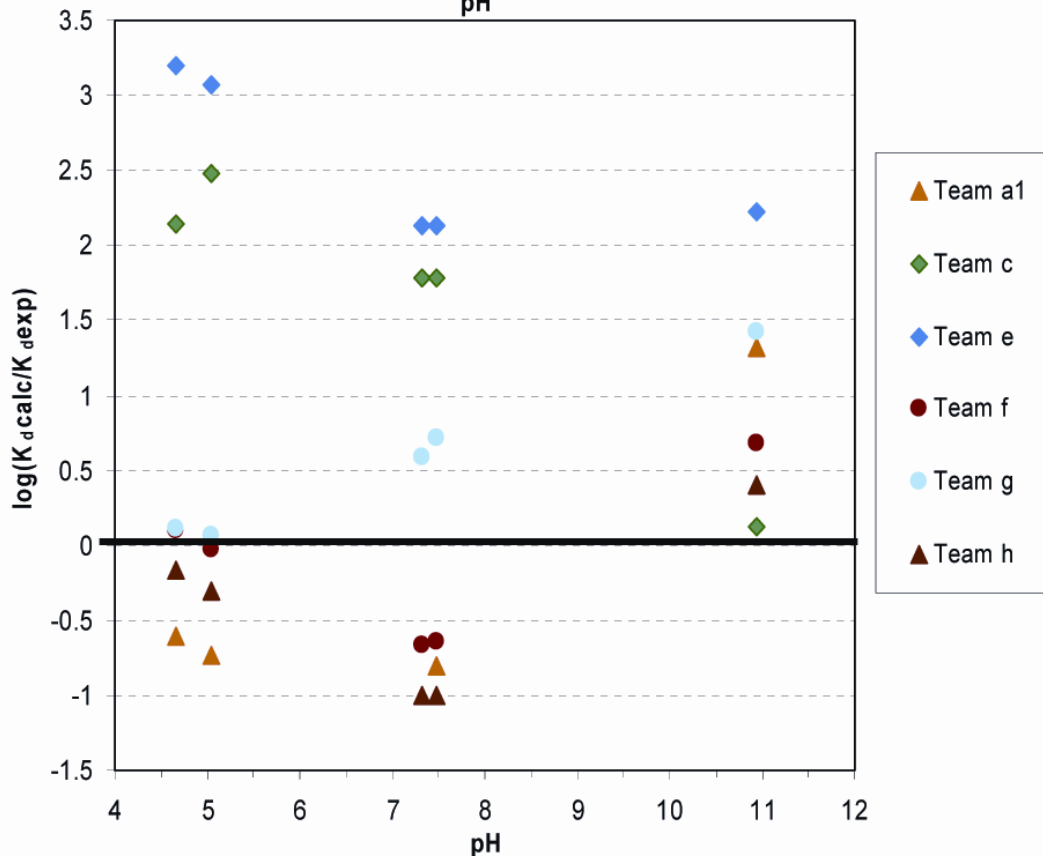
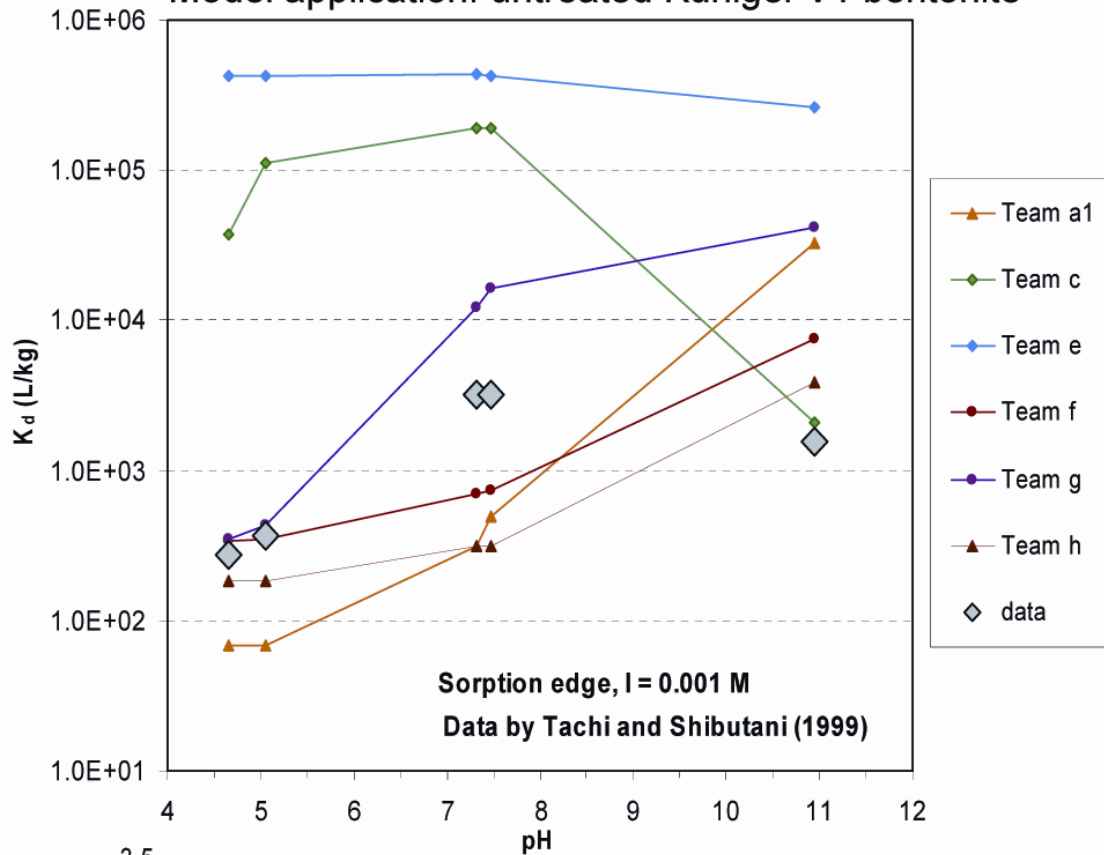
# Model application: Na-SWy-1 montmorillonite



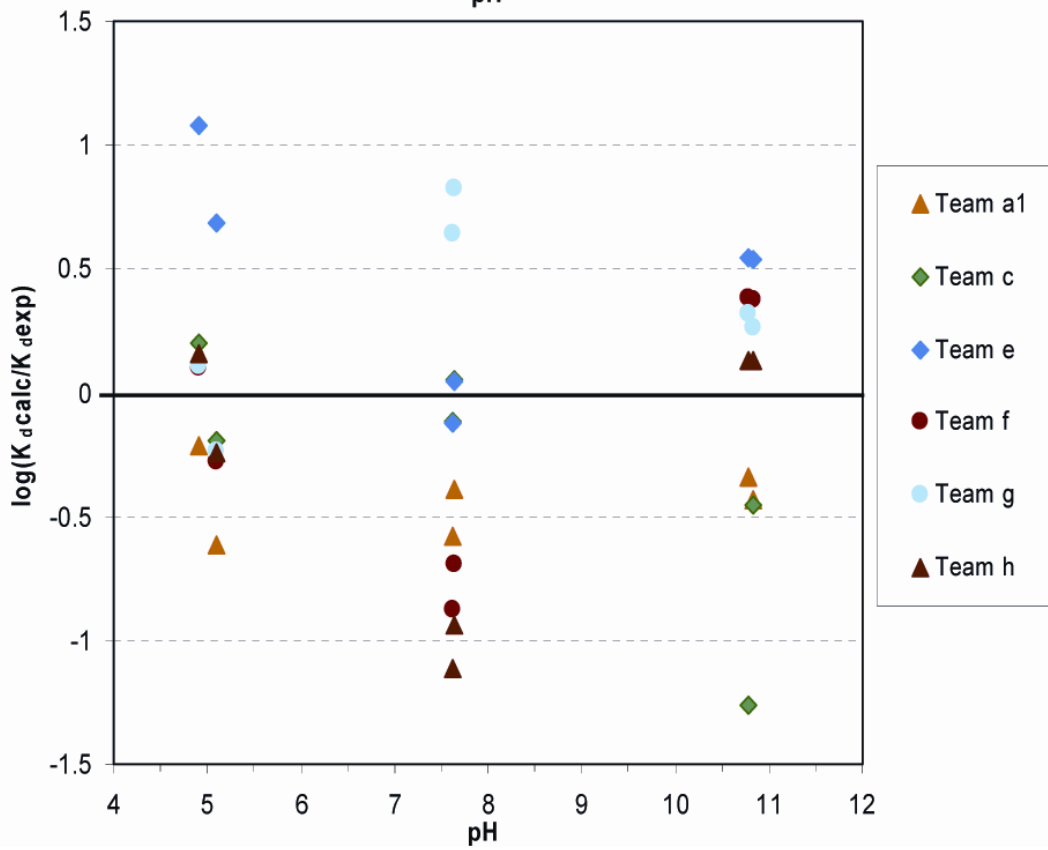
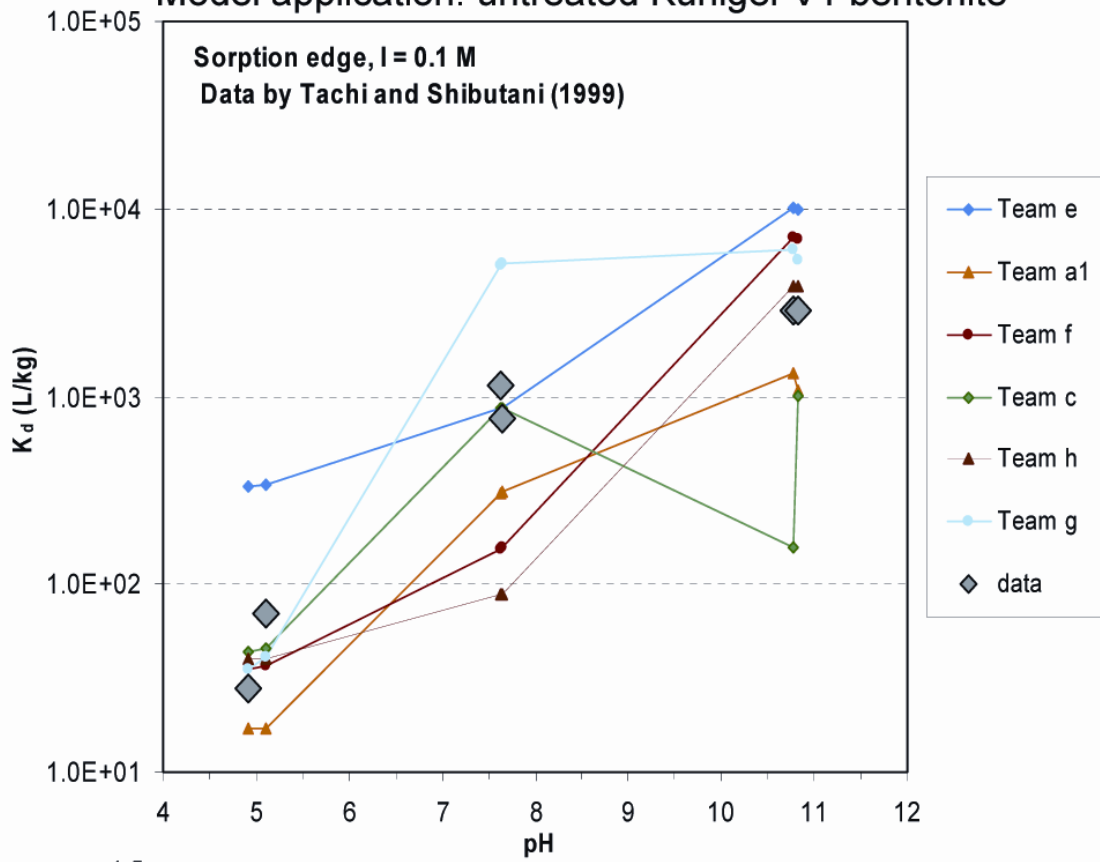
### Model application: Na-SWy-1 montmorillonite



### Model application: untreated Kunigel-V1 bentonite



### Model application: untreated Kunigel-V1 bentonite



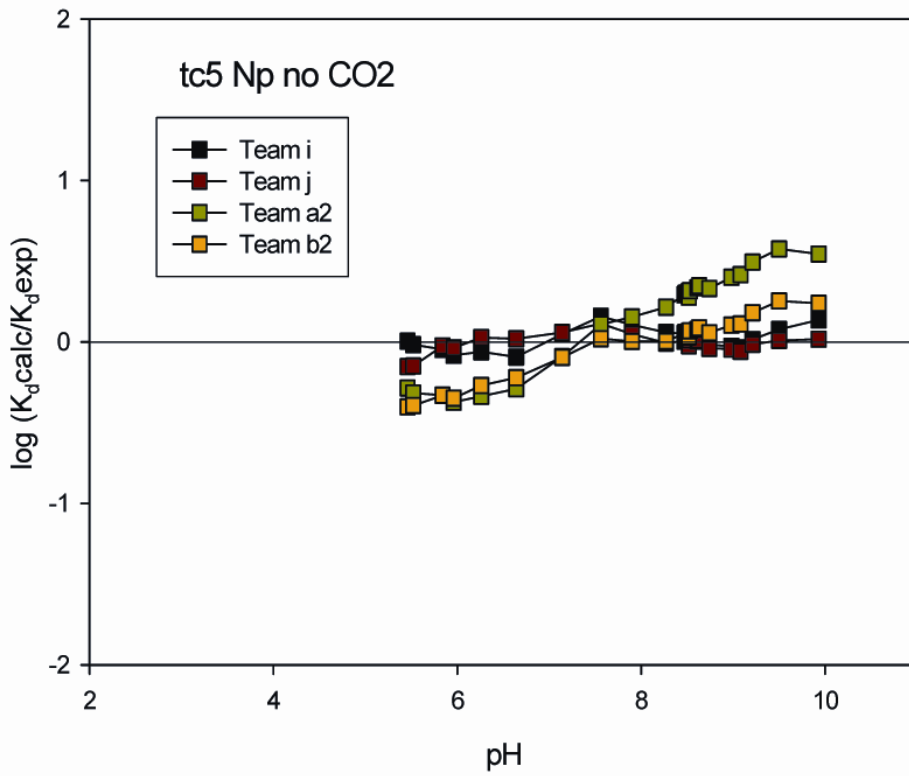
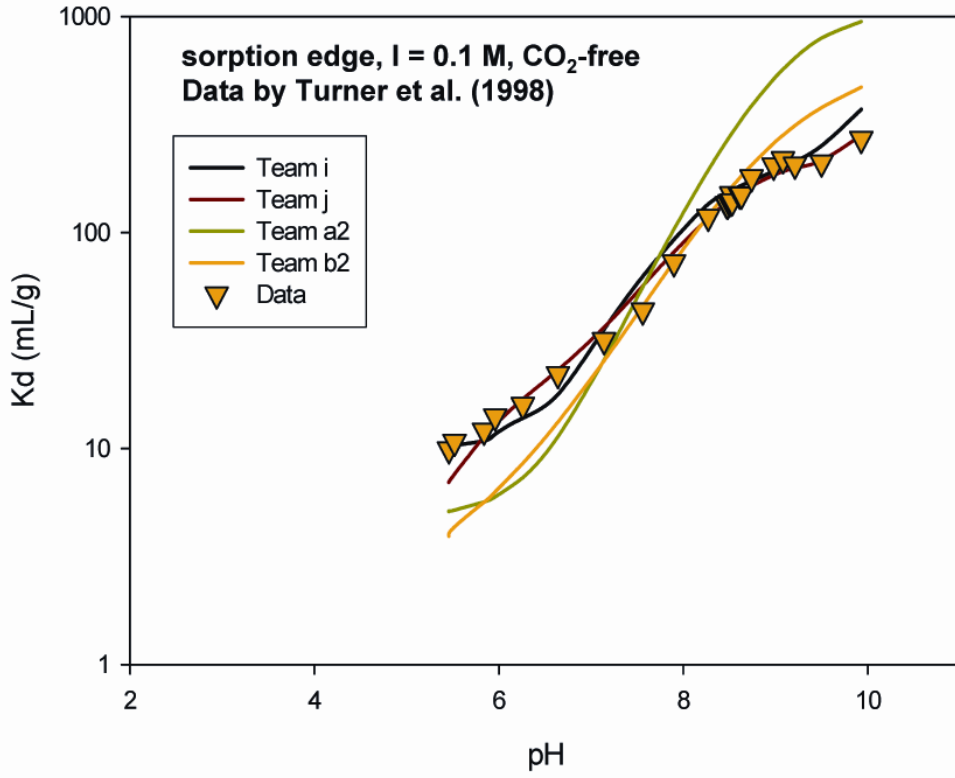


## **Test Case 5:**

### **Np(V) Sorption on clays**

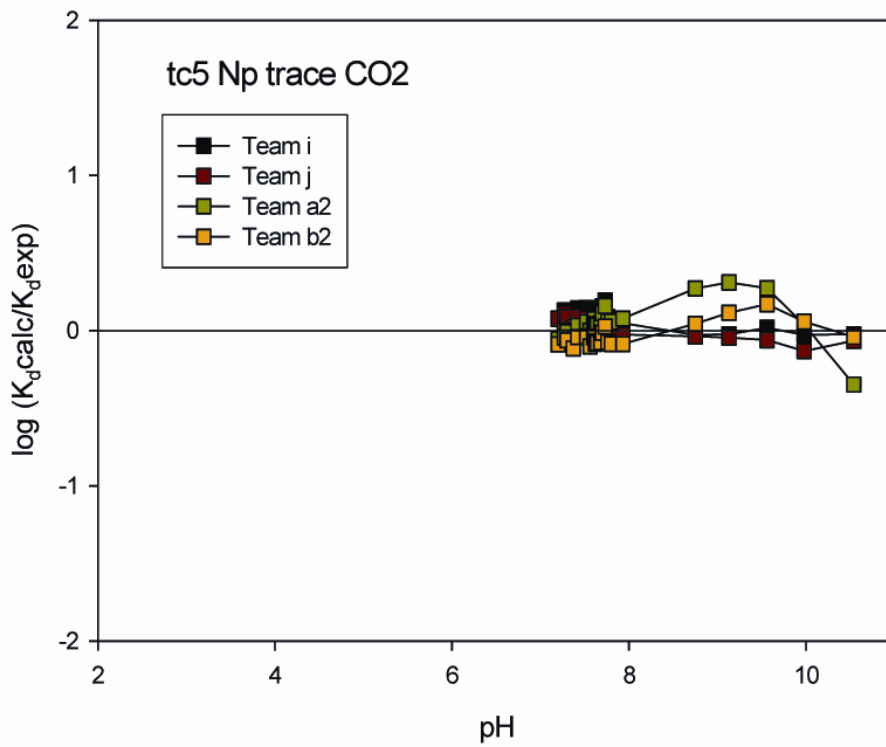
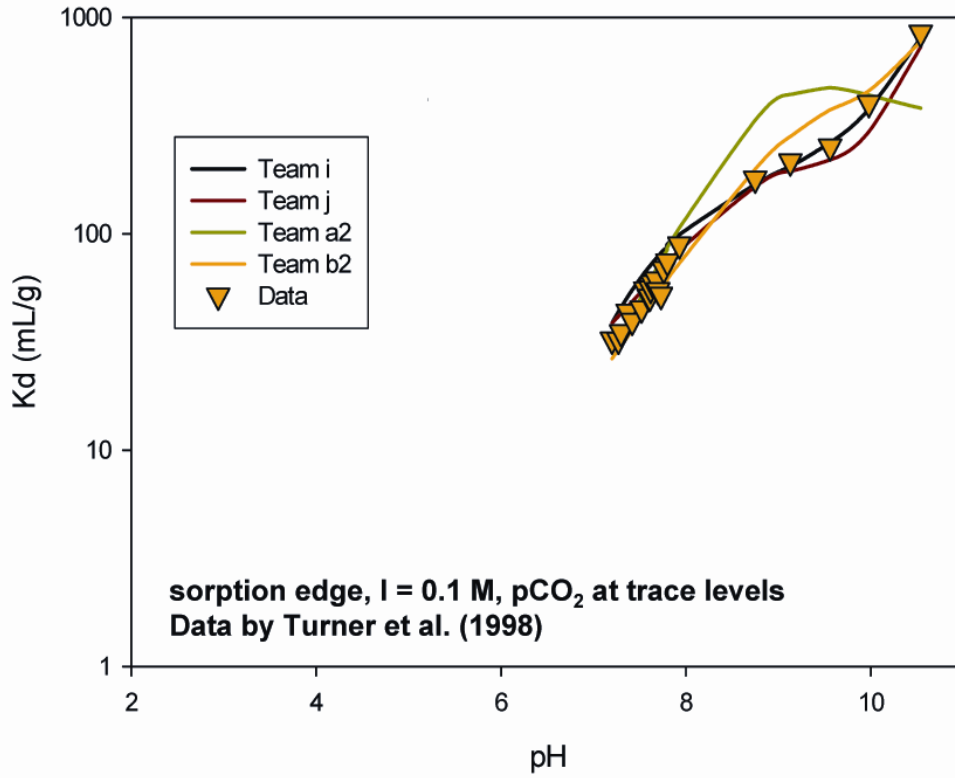


### Model calibration: Na-SAz-1 montmorillonite



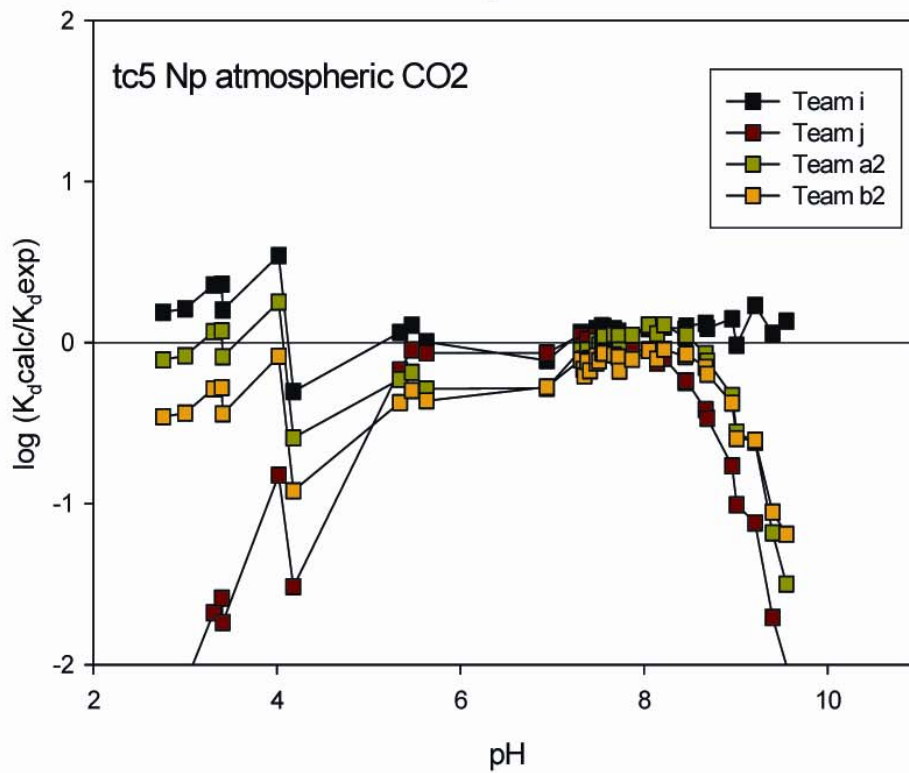
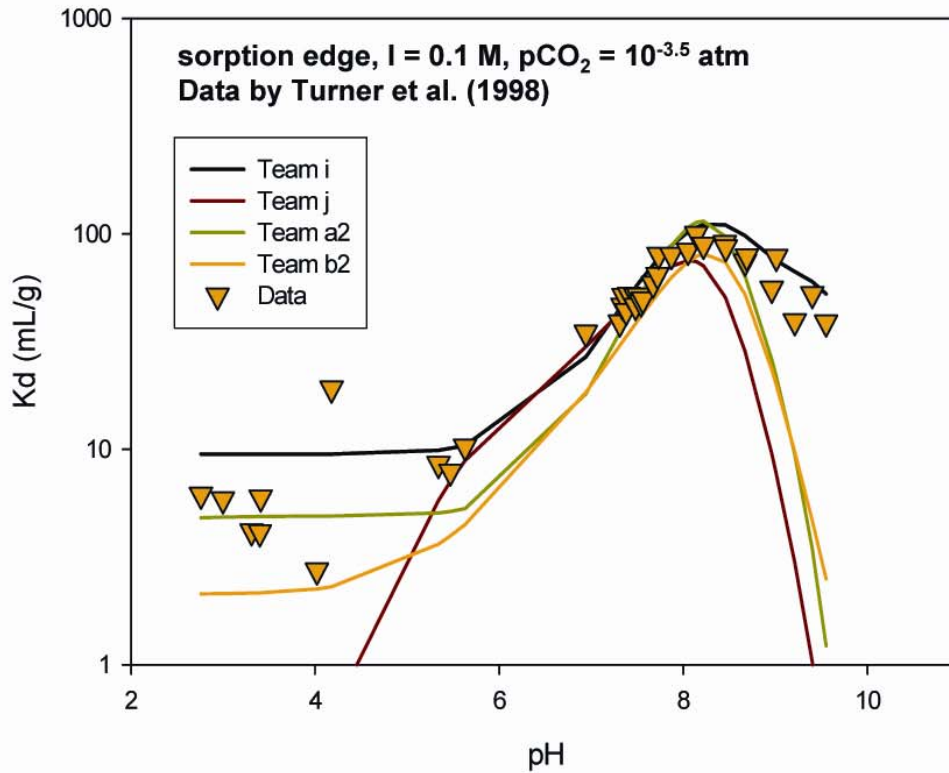


### Model calibration: Na-SAz-1 montmorillonite



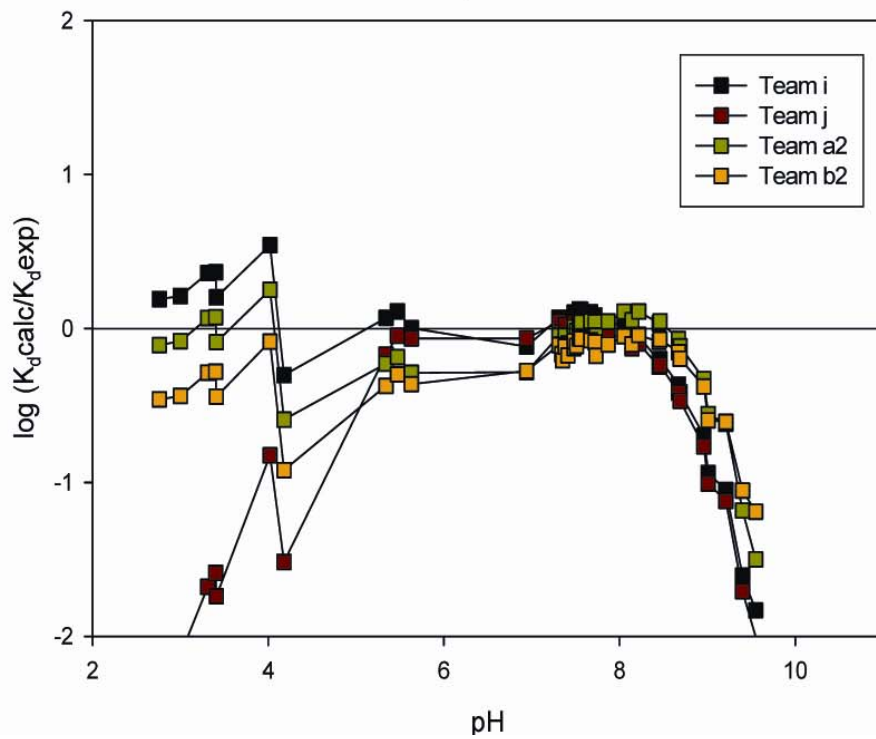
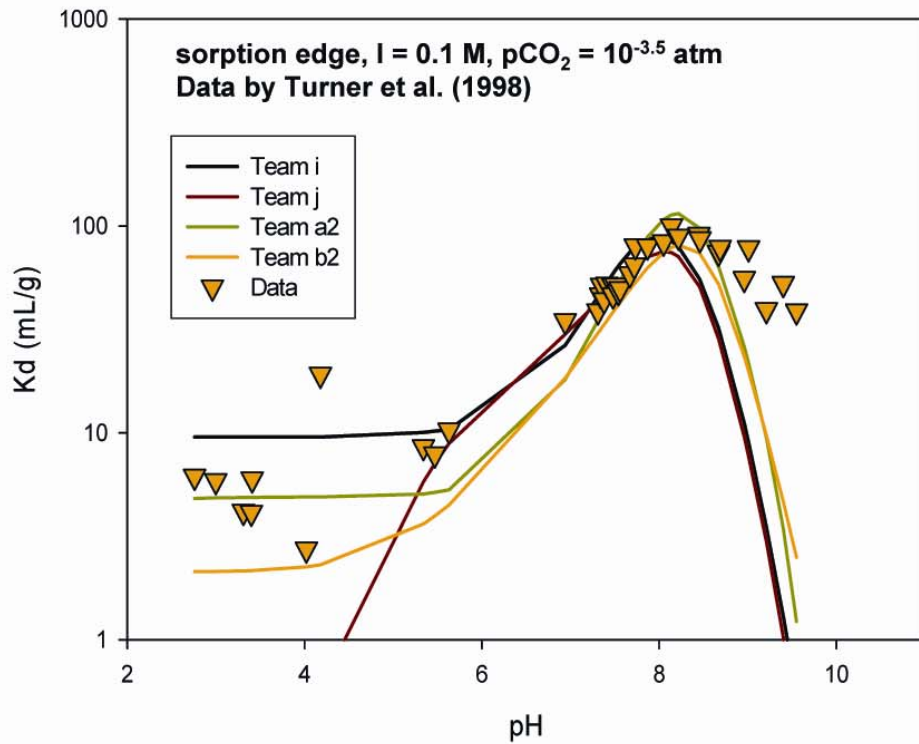
## Model calibration: Na-SAz-1 montmorillonite

a) the model of Team i includes a ternary Np-carbonato surface comp

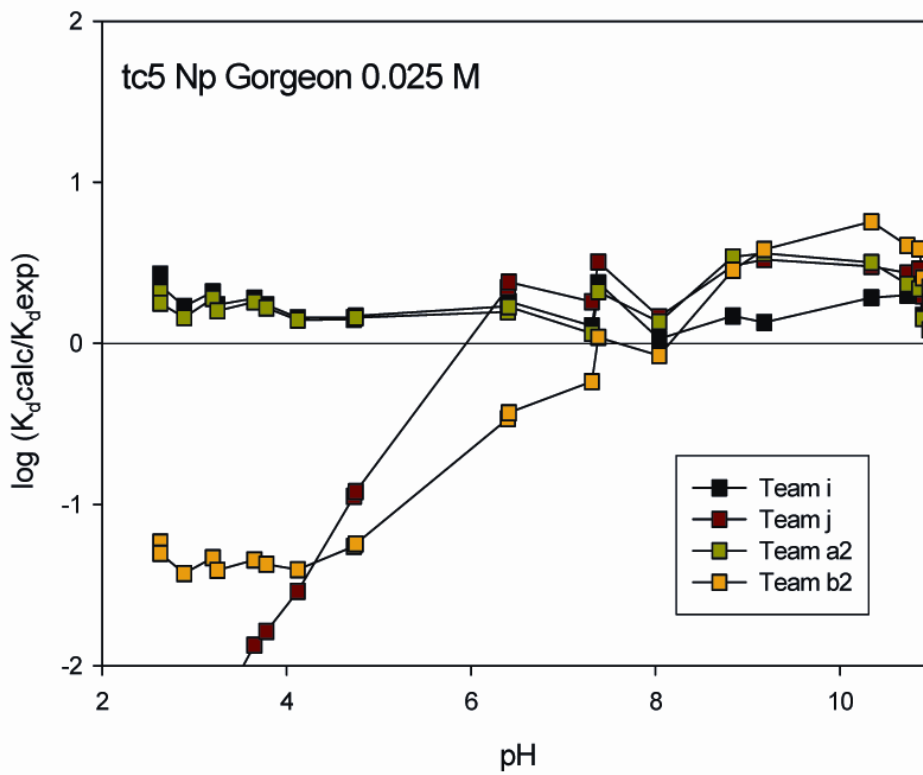
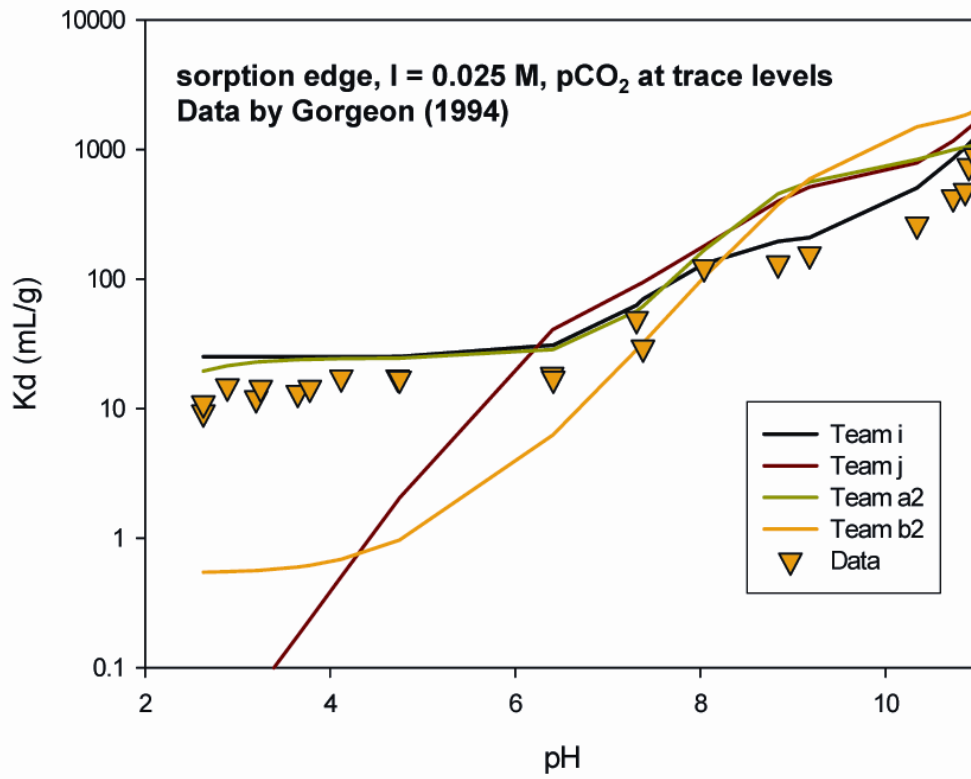


## Model calibration: Na-SAz-1 montmorillonite

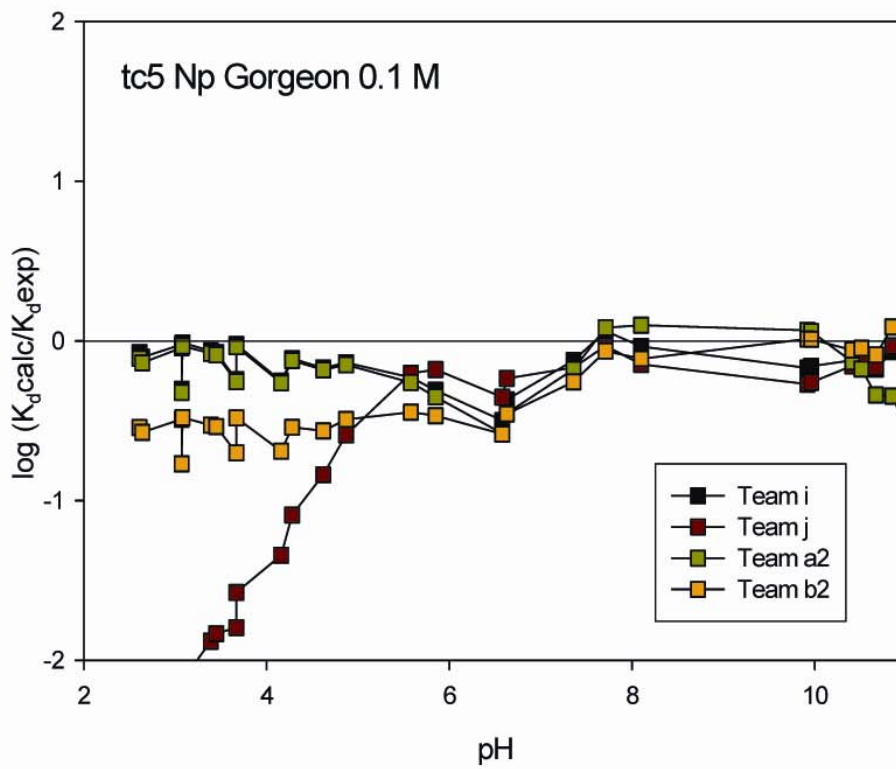
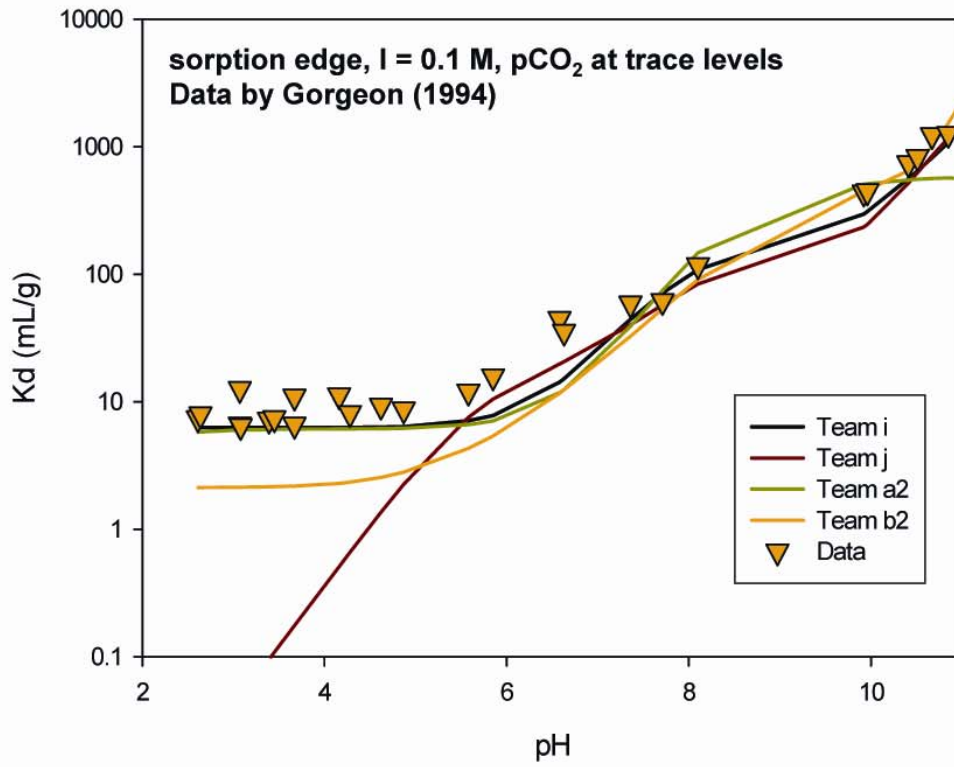
b) the model of Team i does not include a ternary Np-carbonato surface complex



## Model application: purified Wyoming bentonite



### Model application: purified Wyoming bentonite



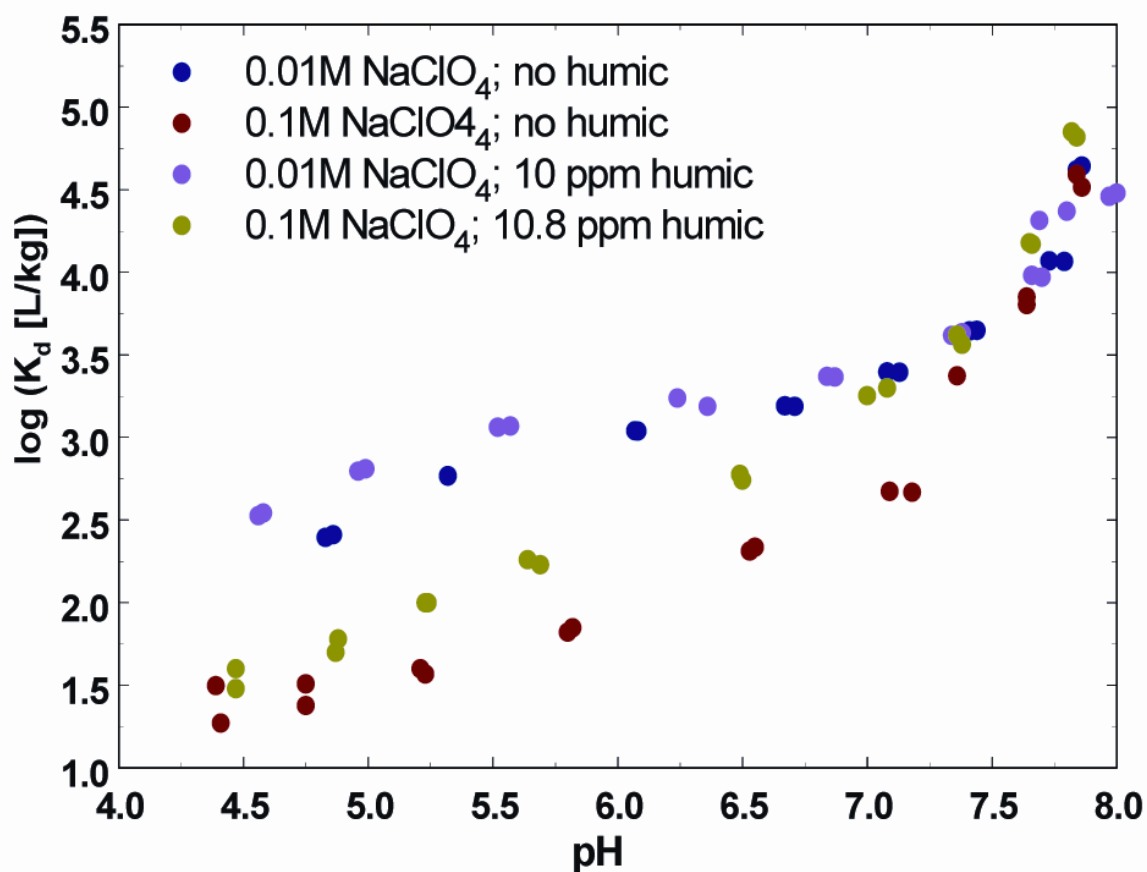
## **Test Case 7:**

### **Co(II) Sorption on a soil and its component element**



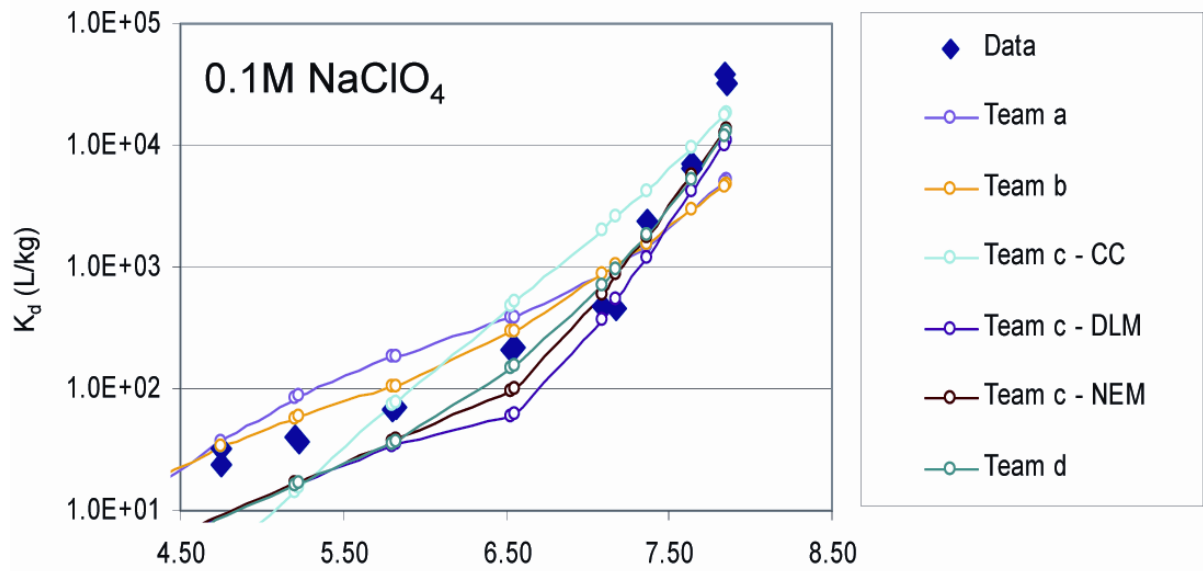
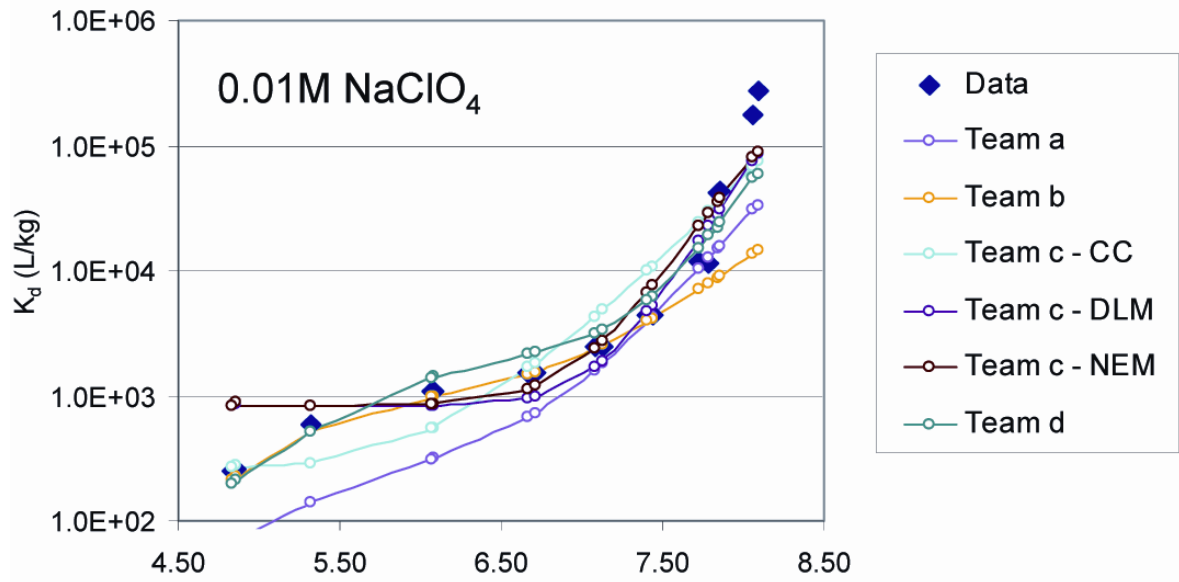
Experimental data: Zachara et al. (1994)

### Effect of $\text{NaClO}_4$ and humic acid concentration

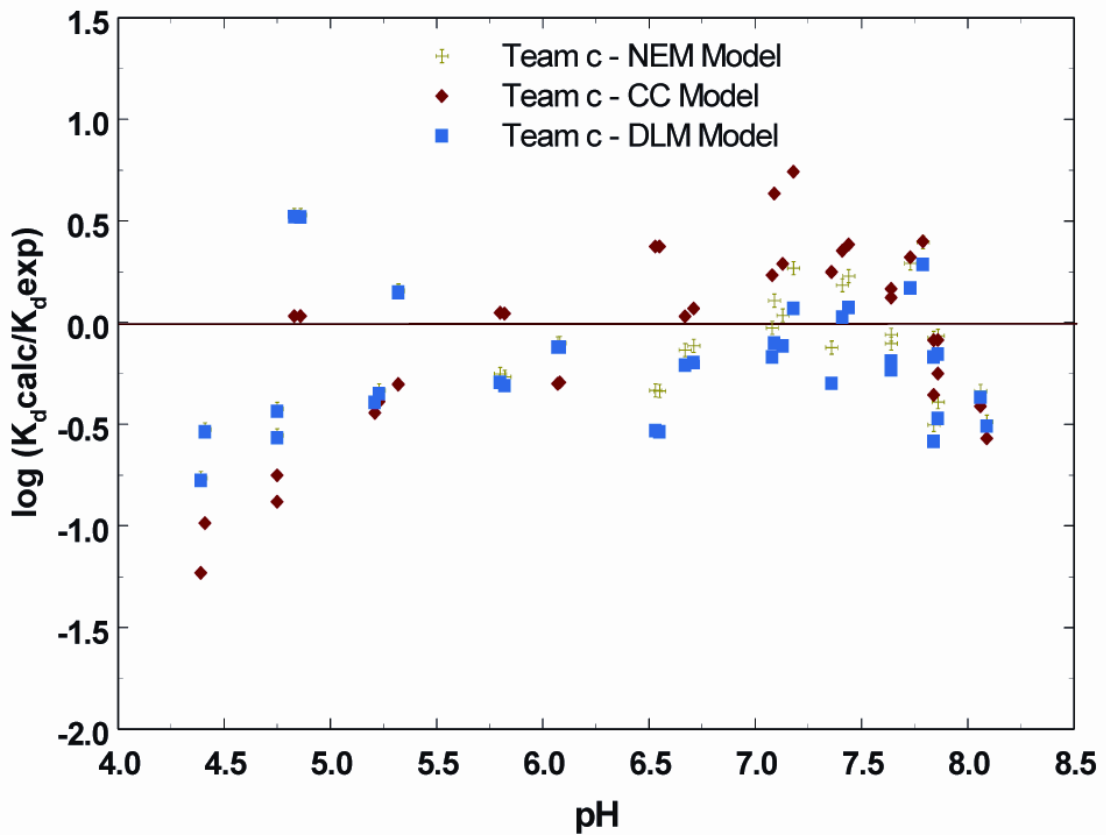
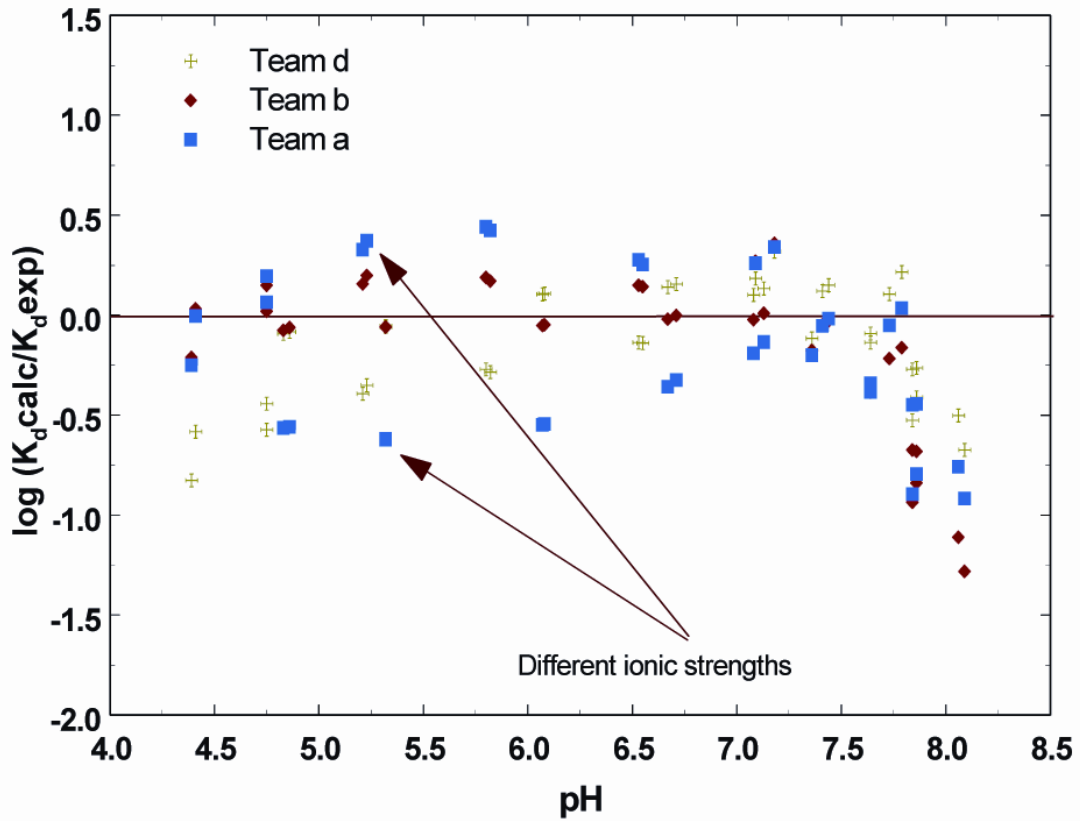




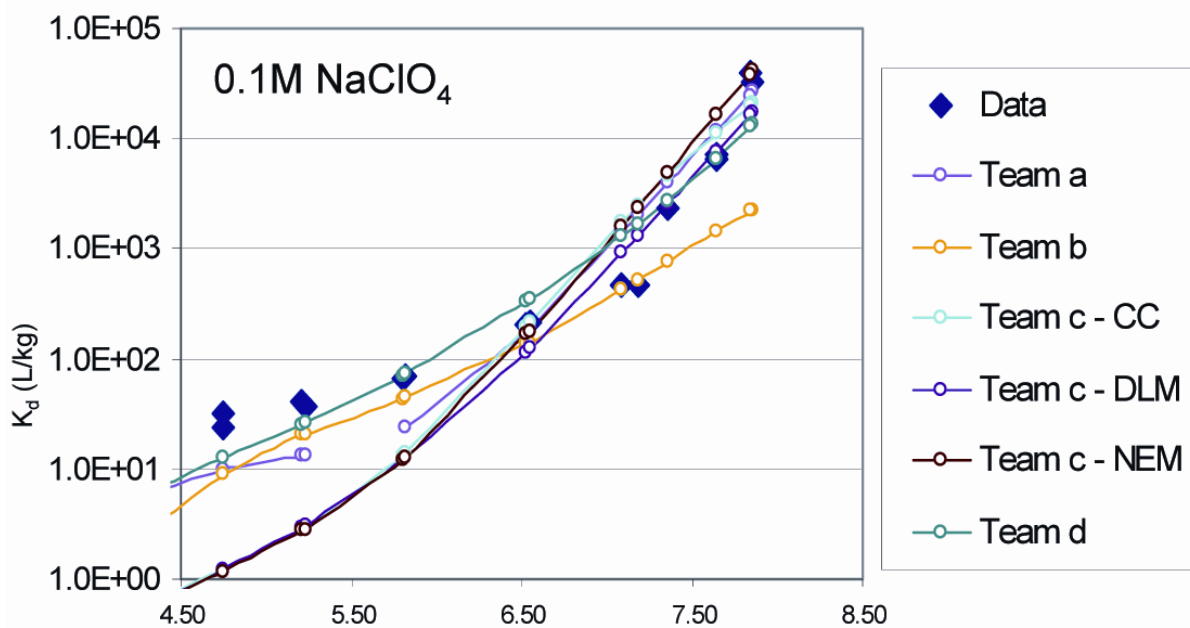
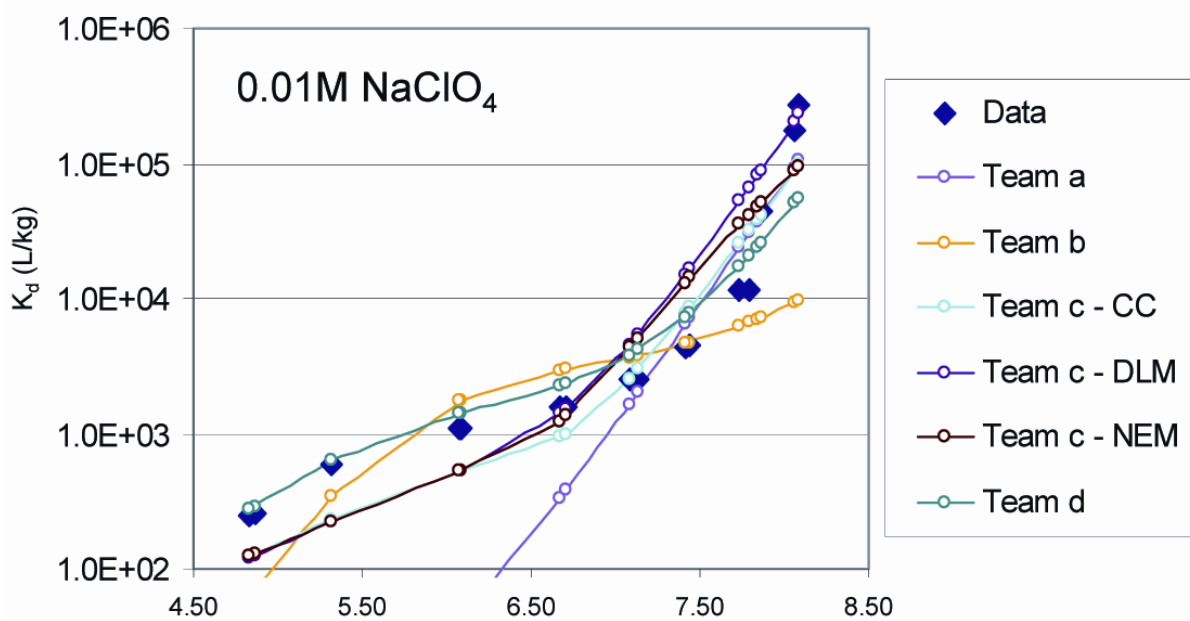
### Generalised composite (top-down) approach

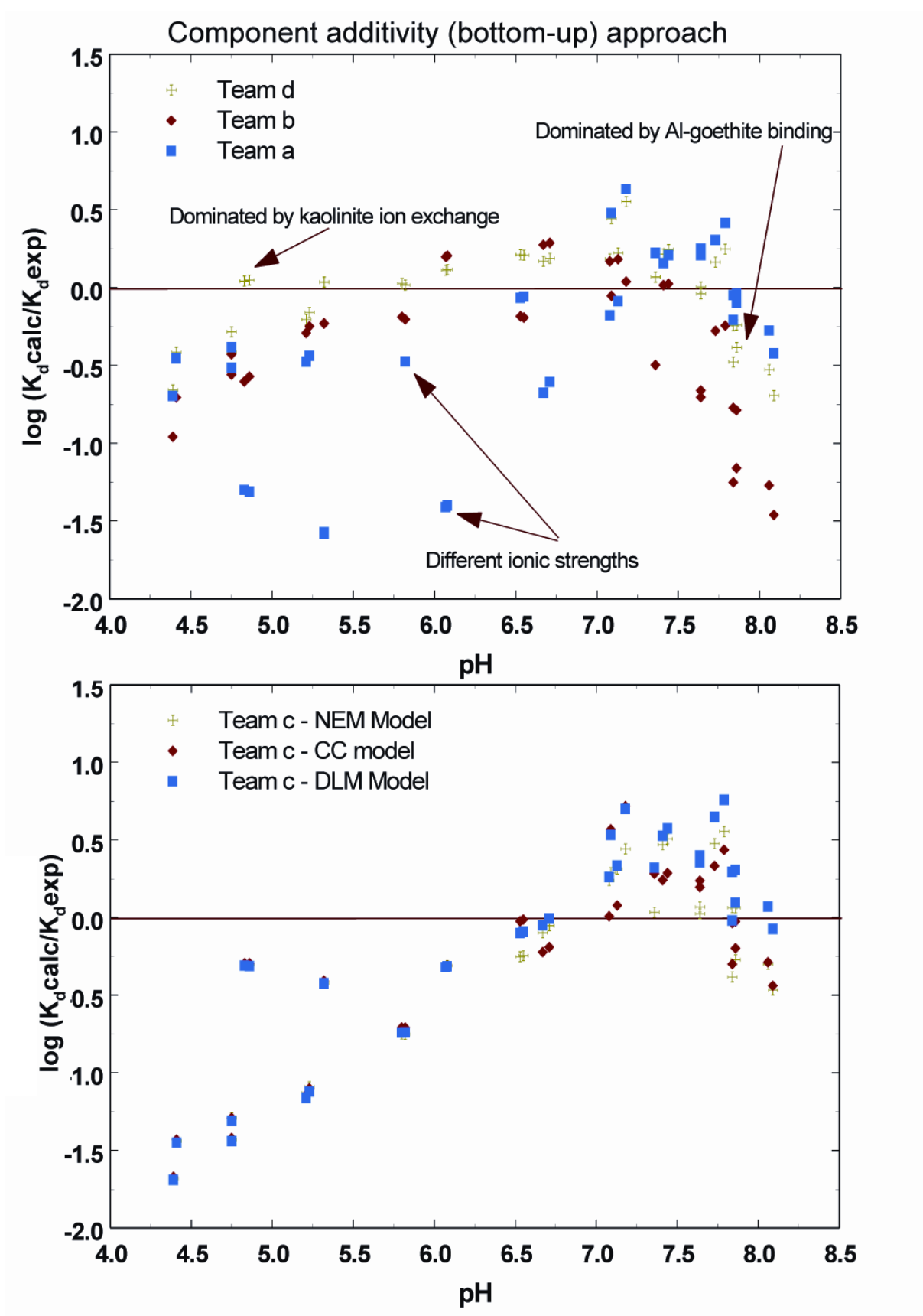


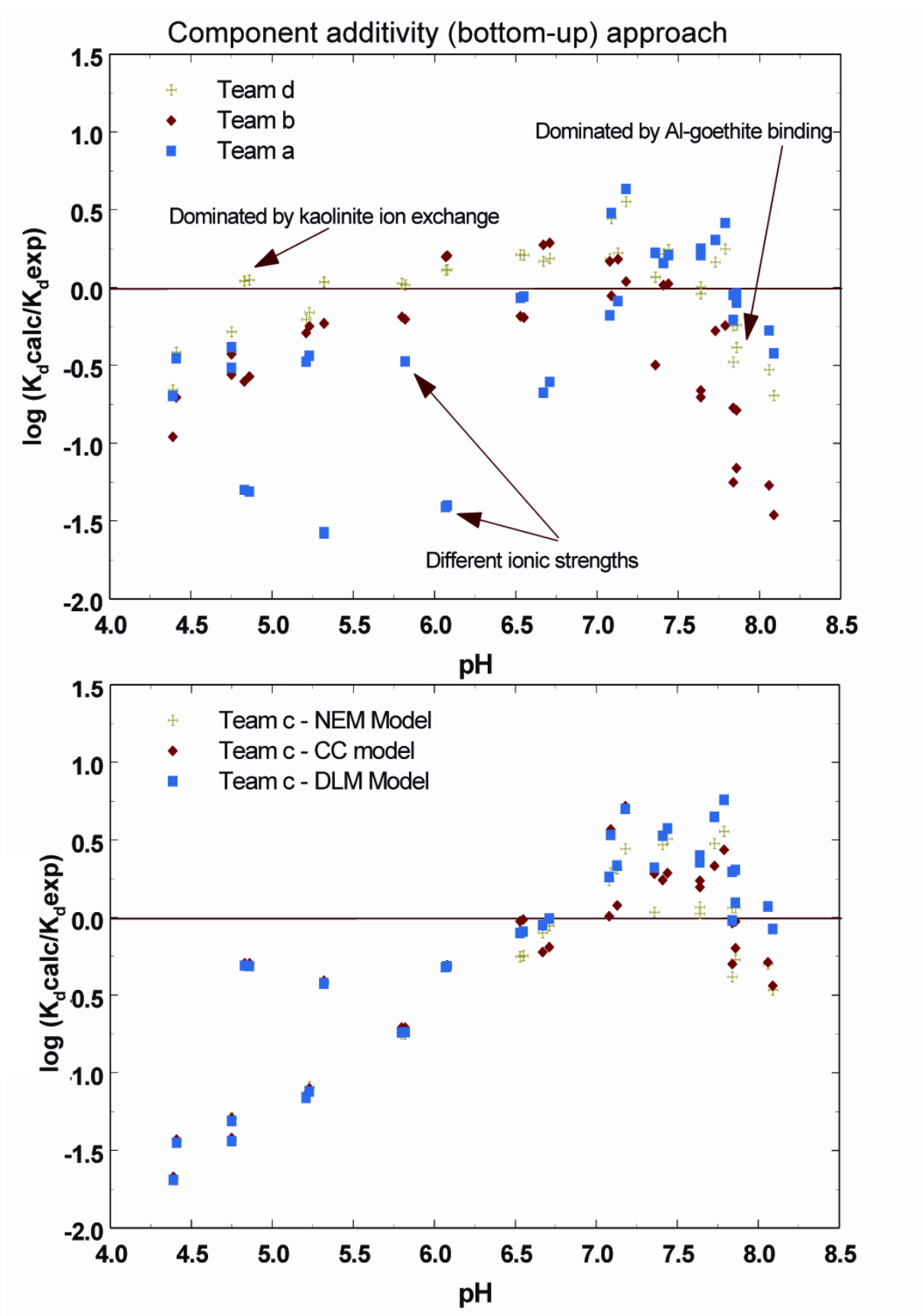
### Generalised composite (top-down) approach



### Component additivity (bottom-up) approach

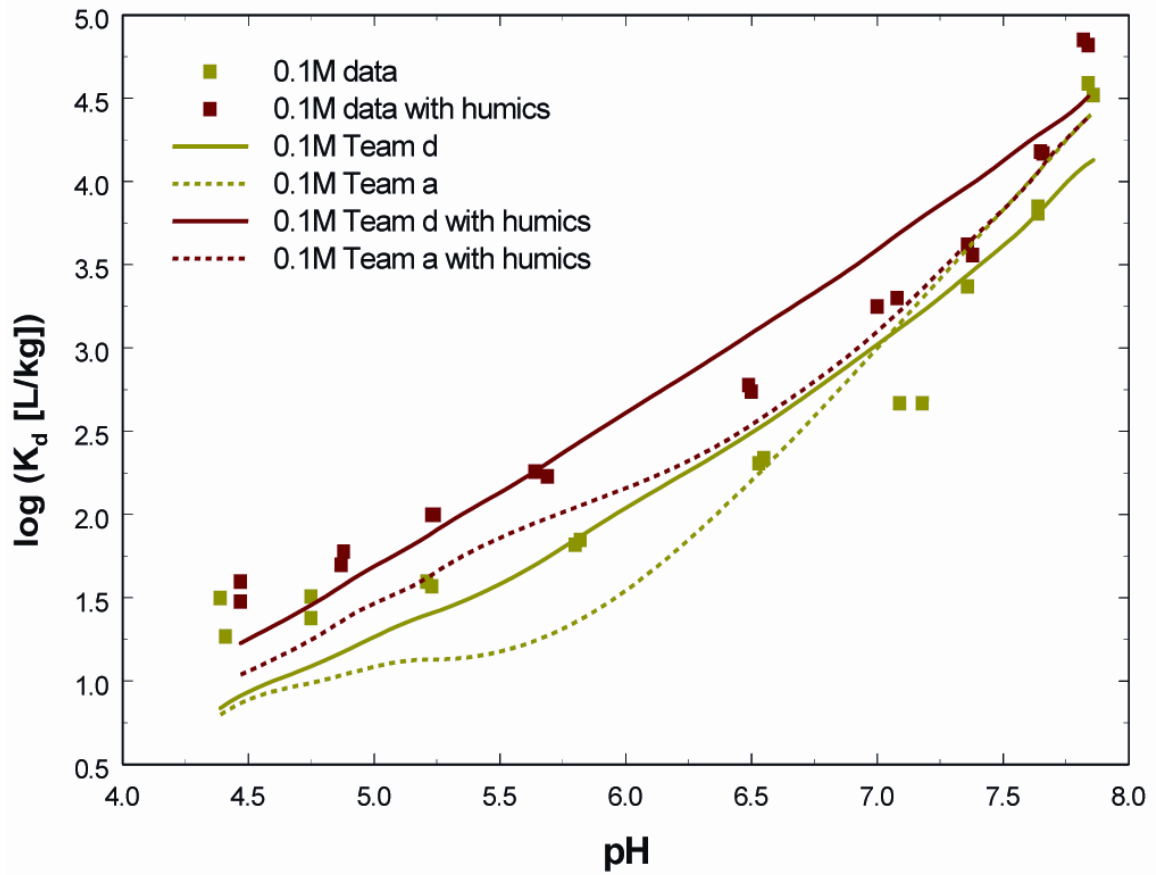




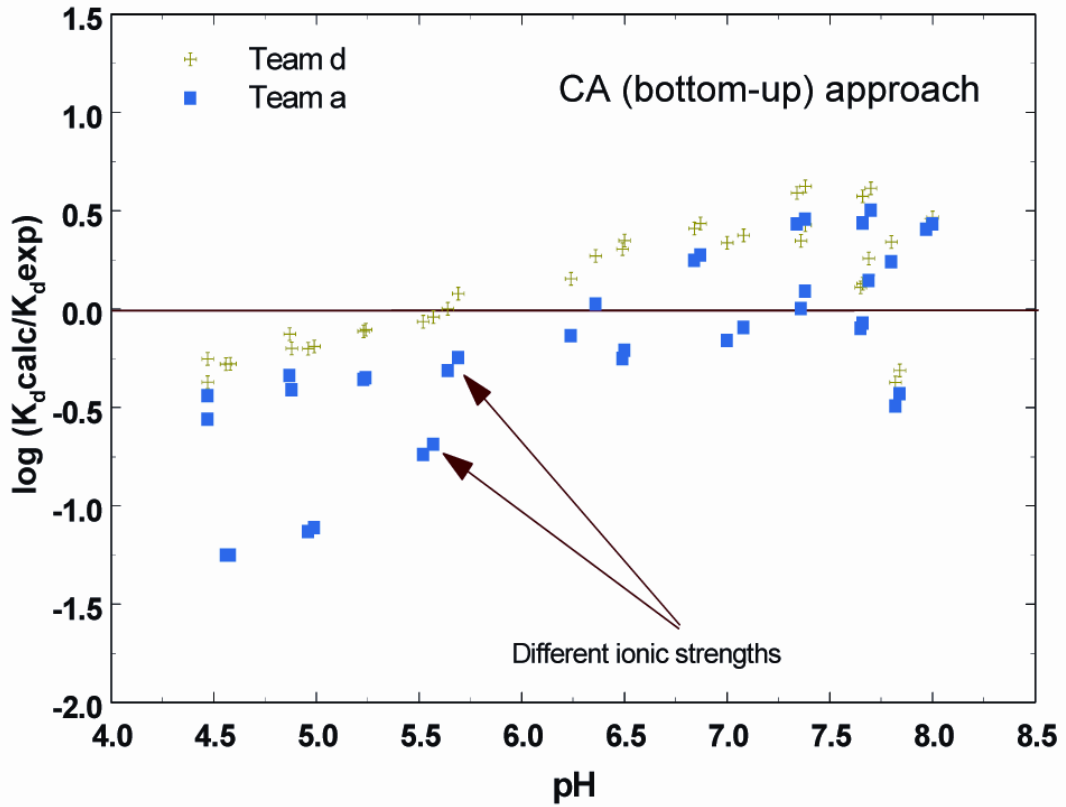
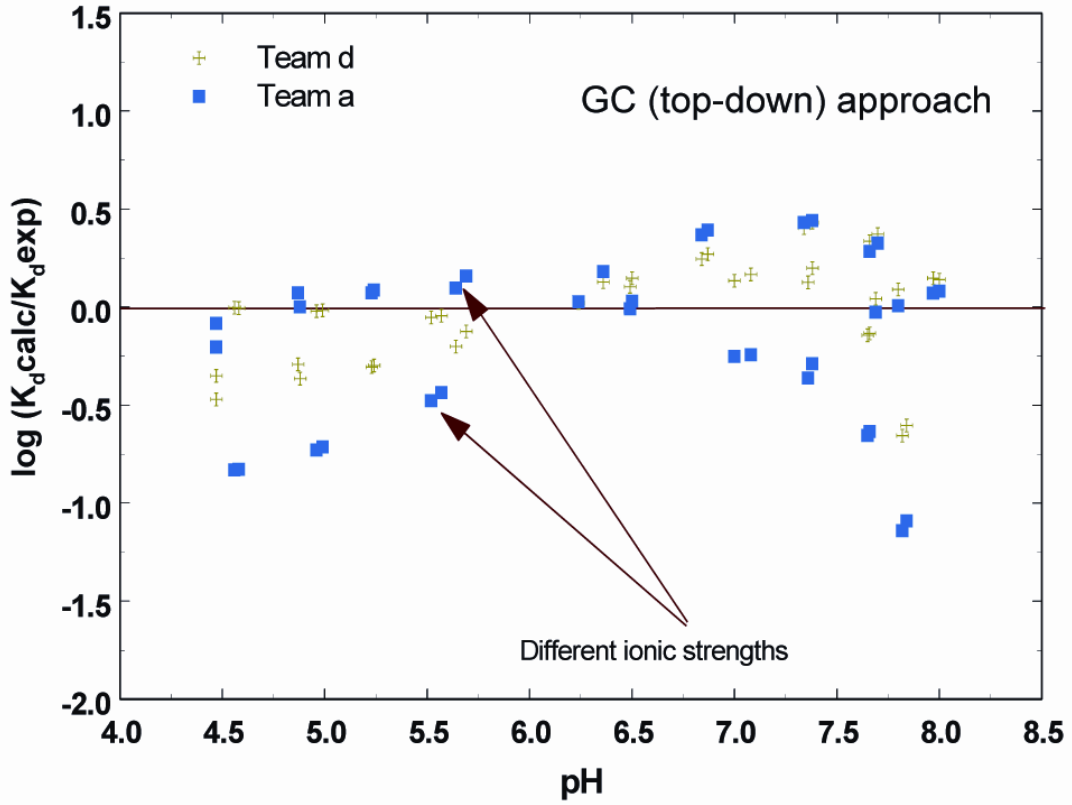


## Sorption in the presence of humic acid

### Component Additivity (Bottom-up) approach Humic acid added



### Sorption in the presence of humic acid



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