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**NUCLEAR ENERGY AGENCY
THERMOCHEMICAL DATABASE PROJECT - PHASE IV**

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**Radioactive Waste Management Committee
Nuclear Science Committee**

From Thermodynamics to the Safety Case

Symposium Proceedings

Karlsruhe, Germany

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FOREWORD

The NEA Thermochemical Database (TDB) Project and Sorption Project share a common interest - improving the quality and traceability of the results of thermodynamic modelling of radionuclide speciation (dissolved, adsorbed) for use in support of a safety case for the long-term management of radioactive waste. The TDB Project aims to make available a high-quality thermodynamic database to meet the needs of those performing safety assessments for the disposal of radioactive wastes. The project has published reviews of chemical thermodynamic data for the main actinide elements and those elements present in fission or activation products as well as guidance (or state-of-the-art) reports. The Sorption Project aims to study the development of chemical thermodynamic models of sorption mechanisms to aid the prediction of long-term sorption behaviour of radionuclides in a radioactive waste repository.

The symposium "From Thermodynamics to the Safety Case" held on 17-19 May in Karlsruhe, Germany, hosted by the Karlsruhe Institute of Technology, was organised jointly by the NEA TDB and Sorption Projects. The last NEA TDB Symposium "The Use of Thermodynamic Databases in Performance Assessment" was held in Barcelona 29-30. May 2001. Since then substantial amount of work has been undertaken in the TDB II, TDB III, and TDB IV phases of the project. A large number of reviews and updates have been completed and published. In addition the Waste Management Organisations (WMOs) have undertaken a number of Performance Assessment (PA) exercises which have required the use of thermodynamic data to a varying extent. These exercises have identified critical chemical data which may require a new approach to the development of thermodynamic databases. This has triggered internal efforts from the various WMOs to acquire and/or estimate relevant thermodynamic data. Regardless of all these efforts, there are a number of critical areas of chemical and thermodynamic data which are still missing.

The objective of the NEA symposium From Thermodynamics to the Safety Case was to present and discuss the principal outcomes of these two projects with interested communities (academic institutions, technical support organisations, waste management organisations, regulatory bodies). Emphasis was placed on illustrating and discussing the successful use and key challenges when applying thermodynamic models and underlying databases to problems of interest to the waste management community as a whole.

The objectives were:

- to present the progress achieved in the NEA TDB Project
- to present the current thermodynamic database development projects performed by the various WMOs to meet their requirements
- to identify the current critical gaps in thermodynamic data needed for the PA of radioactive waste management
- to present and discuss the various approaches to fill in the current gaps.

The symposium was divided into four sessions:

- Focus on databases
- Using thermodynamic models
- Focus in the Sorption Project

- How thermodynamics underpins a safety case-using the models.

The symposium was attended by 75 delegates from 16 countries (including China). These proceedings contain extended abstracts of the papers delivered by the invited speakers as well as summary records of the session discussions. The main conclusions on the future work under the TDB and Sorption Projects and recommendations made during the wrap-up session are also summarised at the end of the volume.

Acknowledgement

The organisation of the symposium and the preparation of the proceedings have benefitted from the support from the following organisations, in the framework of the NEA TDB IV and Sorption III projects:

ANSTO, Australia	JAEA, Japan
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On behalf of all the participants the NEA would like to express its gratitude to Karlsruhe Institute of Technology (KIT) for acting as hosts for the symposium. The NEA also acknowledges the contributions of the programme committee for the symposium:

Bernhard Schwyn, Nagra, Switzerland

Scott Altmann, ANDRA, France

Bernhard Kienzler, KIT – INE, Germany

Patrick O’Sullivan, OECD NEA

Cherry Tweed, NDA-RWMD, UK

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Finally thanks are extended to those who provided oral or poster presentations and to all delegates for their active engagement at the symposium.

TABLE OF CONTENTS

FOREWORD.....	2
WORKSHOP SYNTHESIS: MAIN THEMES OF SESSIONS	8
Session I. Focus on Databases	9
Session II. Using Thermodynamic Models.....	12
Session III. Focus on the Sorption Project.....	14
Session IV: How Thermodynamics Underpins a Safety Case	17
CONCLUSIONS AND RECOMMENDATIONS	24
APPENDIX A - ABSTRACTS OF PRESENTATIONS	26
From Thermodynamics to the Safety Case	27
The OECD Nuclear Energy Agency (NEA) Thermochemical Database Project	30
Example of a TDB Review	32
From TDB to a Workable DB -Development of the PSI/Nagra TDB	35
From TDB to a Workable DB – The Case of JAEA-TDB	36
High pH Systems	38
Using Thermodynamic Models: Saline Systems	41
Principles and Limitations of Thermodynamic Modelling of Redox Sensitive Systems	42
Radionuclide Solubility Control in Solid Solution – Aqueous Solution Systems	43
Taking Thermodynamics to Real Systems.....	44
Theoretical and Experimental Basis of Thermodynamic Sorption Models	45
Applications of Thermodynamic Sorption Models (TSMs) to Real Substrates.....	47
Impact of Model Choices and Parameter Uncertainty on K_D Representation	49
How Thermodynamics Underpins a Safety Case	51
APPENDIX B - LIST OF PARTICIPANTS.....	53

INTRODUCTION

A key activity in the development of a safety case for the disposal of radioactive waste is modelling of the behaviour of radionuclides in the environment. In geological disposal the most likely route for radionuclide migration is in groundwaters. It is therefore important have confidence in predicted reactions between radionuclides and the surrounding rocks and engineered barrier materials. This requires calculation of the stability of complexes and solid compounds forming under the relevant conditions, which relies on chemical thermodynamic data.

The TDB Project was initiated, with the purpose of making available a comprehensive, internally consistent, internationally recognised and quality assured chemical thermodynamic database, which meets the specialised modelling requirements for safety assessments of radioactive waste disposal systems. As ground waters and porewaters are the transport media for radionuclide and other waste components, the knowledge of the thermodynamics of the corresponding elements in waters of various compositions is of fundamental importance. The reviews of thermodynamic data published for the most important elements by the TDB Project put weight on the assessment of the low-temperature thermodynamics in aqueous solution and make independent analyses of the available literature in this area. This also includes the elaboration of a standard method for the analysis of ionic interactions between components dissolved in water. This method allows the general and consistent use of the selected data for modelling purposes, regardless of the type and composition of the groundwater, within the ionic strength limits given by the experimental data used for the data analyses in the present review. The TDB database contains only data that have been evaluated from the original experimental data. The data are selected through critical review by teams of experts and the selection process is documented in the reports. Reviews of the inorganic species of the actinides uranium, neptunium, plutonium, americium and thorium have been published. Some elements of importance as activation or fission products technetium, selenium, nickel and zirconium have also been reviewed. Also included in the series of publications are data for compounds and complexes of these elements with selected organic ligands. Finally, additional books have been published with a different aim to that of the review books; these are either a guidance report ("Modelling in aquatic chemistry", 1994) or a state-of-the-art report (Solid solution).

The Thermochemical Database Project has been an integral part of the OECD Nuclear Energy Agency activities and is currently in its fourth phase. The activities up to the third phase have concentrated on the publication of review books, on uranium, americium, technetium, neptunium and plutonium, nickel, selenium, zirconium and thorium as well as on compounds and complexes of these elements with selected organic ligands. Two other reviews (on Tin and Iron) will soon be published. Phase IV was initiated in 2008, with the purpose of addressing the requirements as identified in Phases I to III and considering the new requirements for thermochemical data stemming from the progress experienced in the design and safety assessment of underground radioactive waste disposal concepts.

The OECD NEA Sorption Project was launched to study the potential of chemical thermodynamic models for improving the representation of sorption phenomena in the long-term safety assessment of radioactive waste repositories. The project was established to address the proposition that:

- the uncertainty associated with K_d values used in safety cases derives largely from the necessity to transfer K_d values from laboratory experiments to the expected conditions corresponding to different safety case scenarios;
- thermodynamic sorption models (TSMs) are suited to the transfer of K_d values in a fully quantitative and traceable manner, because of their ability to describe sorption under variable geochemical conditions.

The project is currently in its third phase. Phase I was focussed on a workshop held in Oxford, UK in 1997 and a guidance report was produced on using thermodynamic sorption models for informing the selection of K_d values. The second phase took the form of a benchmarking exercise to interpret well-characterised datasets for the sorption of radionuclides onto complex materials. From Phase II the following requirements were identified:

- guidelines for TSM development
- elaborating of up-scaling criteria (moving from laboratory scale to field scale) and
- educating modellers and those involved in the development of safety cases on the proper application of thermodynamic sorption modelling to relevant systems.

The NEA TDB and Sorption Projects share a common interest - improving the quality and traceability of the results of thermodynamic modelling of radionuclide speciation (dissolved, adsorbed) for use in support of a safety case for the long-term management of radioactive waste. The objective of this symposium is to present and discuss the principal outcomes of these two projects with interested communities (academic institutions, technical support organisations, waste management organisations, regulatory bodies). The symposium was also an opportunity to gather views from the delegates on the future direction of the two projects.

Sessions I to III were organised with presentations from invited speakers and a symposium format allowed for discussion after each presentation. The themes of these sessions were 'Focus on databases', 'Using thermodynamic models' and 'Focus on Sorption Project'. Session IV took a different format and considered the topic of 'How thermodynamics underpins a safety case'. The session opened with a scene-setting talk, after which delegates were divided into five working groups, with each of the groups reporting back to the plenary session. The groups were asked to discuss the questions:

- How accurate is my thermodynamic calculation?
- How representative is my sorption model?
- How relevant are thermodynamics in a world ruled by kinetics?

This was followed by an open discussion on the future of the two projects.

The symposium synthesis section of these proceedings is structured around the main sessions of the symposium. For sessions I to III a brief summary is given of the content of each of the presentations and along with details of the subsequent discussions. For session IV the 'rapporteurs' reports from each of the discussion groups are summarised, followed by details of the open discussion on future of the TDB and Sorption Projects. A summary of the main outcomes of the symposium also is given. Speakers were asked to provide an extended abstract summarising their presentations and these are provided in Appendix A. A list of the participants is given in Appendix B.

WORKSHOP SYNTHESIS: MAIN THEMES OF SESSIONS

The welcome address on behalf of the hosts was given by Horst Geckeis, Institute for Nuclear Waste Disposal (INE) of the Karlsruhe Institute of Technology. This was followed by opening remarks from Cherry Tweed detailing the aims of the conference and the structure of the presentations and discussions groups.

Bernhard Schwyn (Nagra, Switzerland) presented a scene-setting talk which gave a general introduction to the NEA TDB and Sorption Projects. The talk highlighted how an understanding of chemical processes, in particular the migration of radionuclides from a repository into the biosphere, is an essential part of a safety case. Often disequilibrium may exist and a careful assessment is needed to check if thermodynamic equilibrium can be assumed, though in some cases the assumption of equilibrium may be conservative. The TDB Project and the Sorption Project share some common themes, but there are also some important differences in their approaches. The TDB Project selects only high quality data, so estimated values and data of insufficient quality are excluded. Consequently, there are gaps in the NEA TDB and therefore it cannot be used directly for thermodynamic modelling. The aim of the Sorption Project is to provide guidance on the development of tools for performance assessment, to allow the prediction of K_d values in systems that are evolving chemically. This approach is more flexible than use of experimentally derived K_d values that are relevant only for the specific chemical conditions at which they were measured. Thermodynamics play an important part in providing an understanding of chemical processes, and this understanding underpins the safety case. A sound thermodynamic dataset is essential in the modelling of radionuclide solubilities and the modelling of porewater compositions and radionuclides speciation is prerequisite for thermodynamic sorption modelling.

There was some discussion after this presentation, regarding predications on which safety cases are based and how their reliability over long time scales can be assessed. It was noted that the models used in the safety case give predictions and these models can be compared with complex real systems which may allow gaps or inconsistencies to be highlighted. The models give confidence that the concepts behind the safety case are valid and that the long-term behaviour will be consistent with the assessed ranges of potential evolutions.

Session I. Focus on Databases

This session considered the development chemical thermodynamic databases for use in performance assessment. The topics addressed were:

- the background and history of the NEA TDB Project
- the processes undertaken by the TDB review teams
- the development a 'workable' database from the NEA TDB review publications.

Cynthia Atkins-Duffin (LLNL, USA) presented an overview of the TDB Project and the main achievements over its 25 year history. The objectives of the TDB Project are to produce a database:

- that contains data for elements of interest in radioactive waste disposal systems
- that is based on original experimental data, rather than compilations or estimates
- that is internally consistent
- that documents the sources of data and the reasons for selections
- that treats all solids and aqueous species of the elements of interest for nuclear storage performance assessments.

All selected data are for 25°C, 0.1 MPa and corrected to zero ionic strength and have uncertainties given at 95% confidence. CODATA values are used as primary auxiliary data.

The review process comprises a technical review which critically analyses experimental data and selects data for inclusion and is followed by a peer review, which is separate from the technical review and has the function of ensuring that the review procedures were followed. The review procedures are published in a set of guideline documents. Reviews have been published for:

- inorganic species of the actinides U, Np, Pu and Am
- inorganic species of Tc, Se, Ni and Zr
- compounds and complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with selected organic ligands.

Following this presentation there was some discussion on the review process. Particular mention was made of the small pool of experts available to carry out reviews and how to balance this with the desire to avoid using a reviewer on more than one project simultaneously. Given the relatively small number of available reviewers there was agreement on the need to maintain skills and experience in both the use of thermodynamic data in modelling and the experimental skills which lead to an understanding of how data of the required quality is produced.

There was also mention made of how CODATA values are used as a primary source of auxiliary data and changes in CODATA could affect values in the database. It may be that for small changes, for example of 0.1 in a log value, the effort in changing all related values may not be justified.

Robert Lemire (Deep River, USA) presented an overview of the process and challenges involved in producing the TDB review, which drew upon his experience as chair of the iron review team. The iron review was divided into two parts because it was recognised early that the review would take more effort than initially anticipated. Part 1 (in peer review at the time of the workshop) covers Fe, simple ions, chlorides, selected other halide solids and complexes, sulphates, carbonates, simple Fe-Si-O solids, and aqueous sulphides. Part 2 (currently at the data review stage) comprises of data for phosphates, arsenates, nitrates, sulphide solids, and the remaining halido complexes.

The process involved firstly an effort to review all relevant literature and to reassess the primary data. Assessment was made of uncertainties and checks made for consistency, with adjustments made where

required. It was necessary to consider many of the values together as part of thermodynamic cycles in order to maintain internal consistency. The main challenges included:

- the limited data on Fe(II)/Fe(III) couple as a function of the ionic medium
- the reliability of some SIT interaction coefficients and
- derivation of data from studies that used natural minerals compositions.

It is also becoming a more complicated process to search the literature with access to Chemical Abstracts more difficult and modern studies published in a more diverse range of journals and web-based media.

Discussions on the Fe review at first focussed on the data gaps in Fe(II) chemistry, in particular for Fe(II) complexation with sulphate and fluoride. As Fe(II) chemistry is critical to aspects waste assessment, it was felt that this is an important area to investigate, despite the problems in studying Fe(II) experimentally due to the difficulties in maintaining the required redox conditions. It was pointed out that iron corrosion studies are not generally useful for obtaining thermodynamic data because the phases studied are not well defined (for example green rust). There are also gaps at temperatures 300-350°C.

Wolfgang Hummel (PSI, Switzerland) and **Akira Kitamura (JAEA, Japan)** gave presentations addressing the development of workable databases based on data from the NEA TDB. The criteria for selection of data in the TDB series of publications ensure that only high quality data from experimentally derived values are selected. Consequently, there are gaps in these datasets for species that may be of importance in assessment calculations, but for which there is either no data or the available data are not of sufficient quality. However, these ‘missing species’ need to be considered in thermodynamic calculations – it is preferable to have a value with a high uncertainty rather than have no value at all. Therefore, for a workable database the problem of filling these data gaps needs to be addressed.

In the Nagra/PSI TDB values are classified based on the source of the data:

- Coredata values are taken from CODATA and other universally accepted data for groundwater modelling
- Recommended data are NEA selected values, values from widely accepted compilations such as IUPAC and USGS, and values derived from critical ‘in house’ reviews
- Supplementary data are taken from NEA reviews where data are suggested for ‘scoping calculation’, but not selected in the NEA TDB or are estimated data.

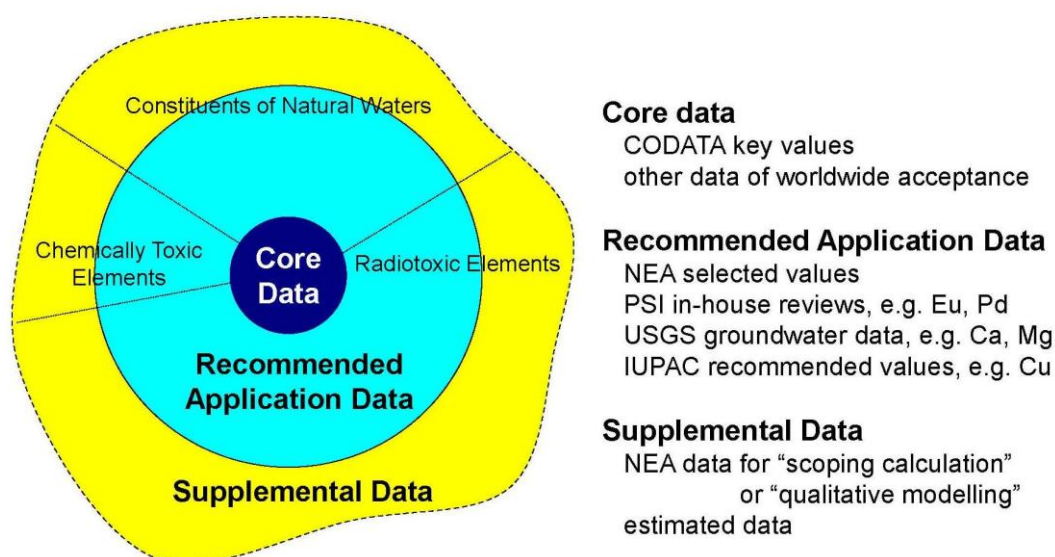
The NEA TDB reviews give details of data considered, but not recommended, so this can be a valuable source for filling data gaps. If no data is available then estimation by comparison with chemically similar elements can be performed.

The JAEA TDB has been developed for performance assessment of geological disposal of HLW and TRU. Twenty-five elements were identified as being of importance to the performance assessment and selected for inclusion in the database. Data from NEA publications were reviewed and in most cases accepted for inclusion. For some elements additional data was required to fill gaps, for example hydroxide-carbonate complexes of actinides. For some elements, for example actinium and protactinium there was very little reliable experimental data and in these cases chemical analogy with other actinides was applied to estimate values.

Following the two presentations, the problems associated with filling gaps in the data were discussed at some length. Particular mention was made of gaps in the NEA recommended data for the hydroxide-carbonate complexes of some actinides. Under certain conditions these may be major aqueous species and

it is therefore important that data for these species are included for calculations, because even data with a high uncertainty will give more accurate predictions than if data is not included. Also discussed were missing citrate complexes of Np^{3+} , Np^{4+} , U^{4+} and Pu^{4+} . Mention was made of the danger of some users taking the NEA recommended data and being unaware of the gaps and so arriving at misleading answers when performing calculations. The question was raised as to whether the data gaps should be flagged or whether it is the users' responsibility to make sure that they understand the applicability of the database. It was generally felt that while raising an awareness of the data gaps would be beneficial, the TDB Project should not recommend values for the missing species. The criteria for recommended data are clear and publishing data to fill gaps has the potential to cause confusion as to the status of this additional data, which could eventually come to be thought of as 'NEA recommended'.

Figure 1: Classification and sources of data in the Nagra/PSI TDB (after oral presentation by W. Hummel)



In filling data gaps it was acknowledged that there is usually a tendency to be conservative in estimates *i.e.* to choose values that give the highest solubility. However, it was pointed out in the discussions that being conservative for some radionuclides may not be conservative overall when daughters are considered. If the solubility of the parent is actually lower, it remains in the repository longer and daughters are concentrated over a smaller area, thus increasing their impact. Comment was made on the necessity to make sensibly conservative assumptions, in order to avoid unnecessary effort. General coherency checks are also useful to evaluate if the output looks sensible.

It was also noted in the discussions that europium is often used as an analogue for other elements with valence III. Europium is a lanthanide that is fairly easily reduced so may be a special case. It was suggested that it may be useful to look further at potential problems with the use of analogues and carry out investigations of the less well-studied lanthanides.

Session II. Using Thermodynamic Models

Session II focused on how thermodynamic models are used in 'real situations' related to radioactive waste management. The topics examined included:

- high-pH systems
- saline systems
- redox sensitive systems
- solid solutions
- source terms for radionuclide release from vitrified waste.

Steve Williams (NDA-RWMD, UK) gave a presentation on the particular problems in modelling the solubility of certain elements in high pH systems. Hydroxyl complexation controls the behaviour of some important elements in cement systems at high pH, for example Th, U(IV), Pu(IV) Np(IV) and Am, whose solubility is controlled by equilibrium with the radionuclide oxide or hydroxide phase. However, the cement porewater composition will change over time which affects aqueous speciation. Also longer-term cement mineralisation reactions can incorporate radionuclides in a number of more stable phases.

There are some apparent inconsistencies in reported values of the solubility for certain elements at high pH. For example for Tc(IV) there are differences of up to two orders of magnitude in the measured solubility above pH 12. This is a particularly difficult system to study and suggested reasons for the discrepancies are differences in the crystallinity of the solid phases or the presence of small quantities of Tc(VII).

Tin solubility is high in pH 12 sodium hydroxide solutions, but experimental studies with calcium hydroxide or cement porewaters give much lower solubility. The solubility limiting phase has been identified as burtite $\text{SnCa}(\text{OH})_6$. Similarly, from limited data on niobium complexation thermodynamic modelling predicted high solubility at high pH, but measured solubility in cement porewaters were much lower. This was partly resolved by studies of the effect of calcium on niobium solubility and identification of a poorly crystalline phase by XRD, with a probable composition of $\text{CaNb}_4\text{O}_{11}\cdot 8\text{H}_2\text{O}$.

Nickel solubility in cement systems is not well represented by the simple hydroxide system. The low solubility at high pH is possibly due to incorporation of nickel in the cement as Ni-Al double layer hydroxides.

The modelling of the evolution of cement phases is an important area in understanding the evolution of high pH systems with time. The modelling of C-S-H continues to develop, but the thermodynamics of these systems are difficult to study as their structure and composition tends initially to be fairly amorphous and develops over time.

In discussion on this presentation it was noted that there is evidence that at high pH the hydroxyl ions provide competition for the binding of tetravalent ions with other ligands. For example, some organic ligands only have an effect on radionuclide solubility if they are in high concentration.

Donald Reed (Los Alamos National Laboratory, USA) focused on experiences of the safety case development for the WIPP facility as an example of a saline system. The facility has been operating since 1999. The role of thermodynamics in the safety case covered actinide speciation and solubility calculations, corrosion and reactions of the waste materials and the effects of microbial activity. As the site is in salt formations, with ionic strength greater than 3.5, the Pitzer method is the only option for activity corrections. A considerable amount of work has gone into the gathering of Pitzer parameters, with

selection justified empirically by comparison with experimental data. At present there are no data for temperature corrections to Pitzer parameters.

Naturally occurring microbes are indigenous to the site and their effects need to be considered. To counteract the effects of carbon dioxide generation by microbial activity, magnesium oxide is emplaced with the waste. Due to high uncertainty in the effects of microbial action, a very conservative assumption was made that all organic carbon will be converted to carbon dioxide and the precautions to remediate this form a significant part of the costs. Bioreduction may also be important in controlling redox conditions and, therefore, the solubility of multivalent elements.

There are some differences between NEA publications and the WIPP database, which have had to be justified to the regulators. The selected actinide carbonate species for example are different for the WIPP application.

The subject of the availability of Pitzer data was raised in discussions following this presentation. A decision was made at the start of the TDB Project to use SIT (Specific Ion Interaction Theory) for extrapolation to zero ionic strength and SIT interaction parameters are given in the reviews. However, the SIT method is not applicable for very high ionic strength solutions. It was noted that Pitzer parameters can be difficult to measure and that measurements for some metal complexes have to be made in high ionic strength solutions, making extrapolation to zero ionic strength difficult.

Jordi Bruno (Amphos 21, Spain) gave a presentation focusing on the principals of thermodynamic modelling of redox sensitive systems. In many natural water systems several redox states can co-exist, in apparent disequilibrium. This occurs because the kinetics of redox reactions are often very slow (in the absence of a catalyst or microbial action) compared to the residency of redox components in an open system. The measurement of redox potential in the field is also complicated by perturbations caused by sampling and drilling in hydrogeological characterisation. However, in a waste repository, certain wastes and engineered barriers have a strong reducing capacity and in the unperturbed system a global or local equilibrium may occur. The solubility and sorption behaviour of many important radioelements is dependent on redox state, so it is necessary to consider Eh as a master variable in assessments of anoxic repository conditions.

At present, the NEA-TDB Project provides thermodynamic data, for many redox sensitive species, but some important redox data are missing, such as iron. There are also challenges in the modelling, because calculations tend to produce very sharp redox fronts. These can create instability in models and require a large amount of computing power.

The problems of measuring redox in the laboratory were raised in discussions. The slow kinetics can make the establishment of redox equilibrium difficult, for example the uranium(IV)/ uranium(VI) system. In redox studies of manganese, the addition of aluminium oxide has proved necessary to catalyse reactions.

Dirk Bosbach (Research Center Juelich, Germany) gave a presentation on solid solutions and how they can play an important role in controlling the solubility of some elements. In natural systems most minerals are solid solutions, rather than pure minerals. In many cases solid solutions are thermodynamically more stable than mixtures of pure minerals due to a negative Gibbs excess energy of mixing and the formation of solid solutions may have important effects on the control of radionuclide aqueous concentrations. For example, radium uptake by barite results in lower solution concentration than would be predicted by the solubility of pure radium sulphate. The kinetics of radium incorporation into barite can be slow. The evidence shows that initially the surface comes into equilibrium with the solution, the bulk solid having much lower radium concentration but, over time, a uniform composition is reached.

The thermodynamic concepts of the behaviour of solid-solution-aqueous-solution systems are well developed. The challenge is to derive thermodynamic data from experiments at relatively low temperatures, where the achievement of equilibrium is complicated by the potential formation of metastable states.

In discussions on this presentation, a question was raised regarding the achievement of equilibrium in solid solution/ aqueous solution systems. It was accepted that experimental observations may not represent complete equilibrium and in some cases, it is more likely that dissolution and re-precipitation at the surface is occurring. Activation energies may be too high for direct incorporation and in these cases, mechanistic models need to be used.

To conclude this session, **Bernd Grambow (Subatech, France)** gave a presentation entitled 'Taking thermodynamics to real systems' which provided examples of the application of thermodynamics to calculate source terms for radionuclide release. He described the two main types of thermodynamic control on the release of radionuclides from vitrified wastes, the thermodynamic constraints on the dissolution of the glass matrix and solubility of the encapsulated radionuclides. The glass matrix does not come into equilibrium with solution, but equilibrium between the glass surface and the solution can exist. The glass matrix dissolution can be described in models similar to SiO₂ solubility (the 'affinity rate law'). However, although models based on simple phases rather than solid solutions are largely successful in reproducing experimental results, a complete thermodynamic description is still not available.

Factors controlling the release of radionuclides from spent fuel are:

- the stability of the fuel matrix
- release at grain boundaries, which are fast enough to be effectively regarded as instantaneous and
- the solubility of individual radionuclides.

Under reducing conditions the fuel matrix is more stable and dissolutions tend to be controlled by thermodynamics. Radiolysis can lead to more oxidising conditions and kinetic control is more important here.

Thermodynamic constraints on porewater compositions have been investigated in laboratory experiments and thermodynamic models have been developed. The models need to be qualified for the time scales for which they are valid. Key responses can be reproduced by the models but in some cases certain components need to be removed, for example, dolomite in clays. Perturbations often require large mass transfers and therefore in 'real systems' timescales may be long.

In discussion after this presentation a question was raised on how the affinity rate law is used. It was explained that the affinity law is one factor considered to ascribe dissolution rates in the model of glass dissolution mechanisms.

Session III. Focus on the Sorption Project

Presentations in Session III described the work of the Sorption Project, with particular emphasis on the key messages from the Phase III guidance document, which was in preparation at the time of the symposium. The aim of this document is to address the key issues of concern in using thermodynamic sorption models to support safety cases for the disposal of radwaste. The topics addressed in this session included:

- an overview of the sorption project and its goals
- the theoretical and experimental basis of TSMs

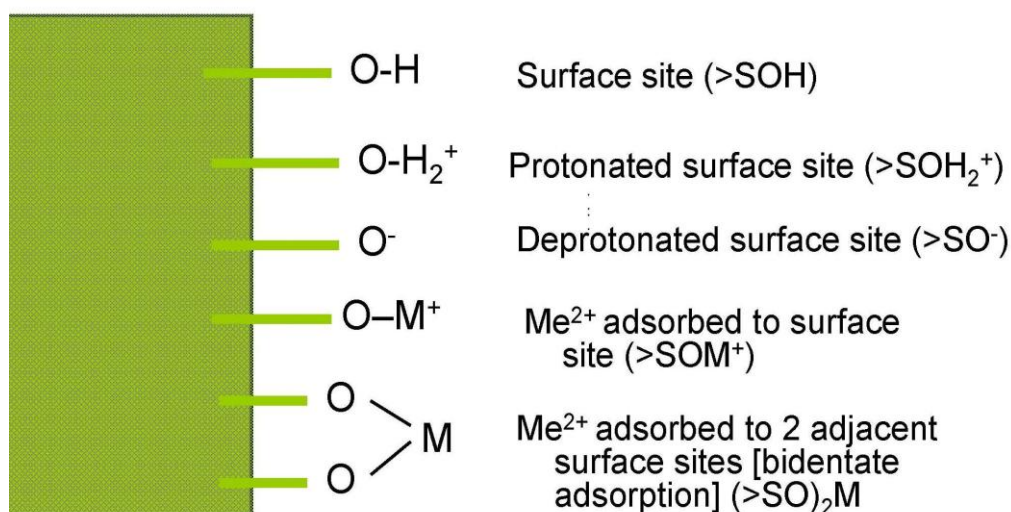
- an illustrative example for a 'simple' case focussing on experimental determination of parameters and constraining of model choices
- the applicability of TSMs to real substrates
- impact of model choices and parameter uncertainty on K_d representation
- effect of chosen representation of sorption on TSM parameterization
- key recommendations.

Scott Altmann (ANDRA, France) and **Michael Ochs (BMG Engineering, Switzerland)** opened the session with an introduction to the Sorption project, which described the background to the development of thermodynamic sorption models (TSMs) and the project's goals. Sorption and transport need to be coupled in performance assessment to predict migration. The main transport mechanism for most radionuclides is by diffusion/advection. Thermodynamic sorption models can well characterise radionuclide sorption on pure, single minerals. Most sorption data is in the form of experimentally derived partition coefficient (K_d) values. The Safety Case will be strengthened if K_d values used can be explained in term of the underlying physical/chemical mechanisms. The principal challenge for the TSM Project is the development of models for the complex, heterogeneous systems of interest to the Radwaste community. The TSM Project has been running since 1995 and is now in Phase III. The main objective of Phase III is the production of a guideline book for the development of TSM models.

Tim Payne (ANSTO, Australia) and **Johannes Lützenkirchen (KIT-INE, Germany)** gave a presentation considering the theoretical and experimental basis of TSMs. The thermodynamic concepts underlying the TSM approach are similar to those used in modelling aquatic chemistry. The difference with sorption models is the presence of surface sites, which can interact with aqueous species to form surface complexes. The chemical components of the model can combine to form aqueous and surface species. One or more types of surface sites are included as chemical components as illustrated in Figure 2. Each of the species is defined relative to its components by chemical equations. Mass balance constraints are applied and the activities of all species involved in reactions are related by equilibrium constants. Activity corrections of surface species are defined by reference to electrostatic equations and there are a number of alternative electro-static models available. It is worth noting that where equilibrium constants are derived from sorption models their values are dependent on a range of model assumptions and therefore are not thermodynamic quantities that can be readily applied to other sorption models.

The main parameters are surface areas and site populations, surface site hydrolysis reactions, radionuclide surface reactions and electrical double layer parameters. Parameters may be determined by sorption experiments, fitting of experimental data or estimated by the re-evaluation of existing data. Advanced analytical techniques such as Extended X-ray Absorption Fine Structure (EXAFS) and Time Resolved Laser Fluorescence Spectroscopy (TRLFS) can provide data on surface species. Phase III of the TSM Project has achieved an increased consensus among experts on methods for the development of TSMs, with the conclusions presented in the draft report.

Subsequent discussions focussed on the conditions required for obtaining good quality data from sorption experiments. One issue raised was the potential alteration of solids, for example under some pH conditions iron minerals may not be stable and could dissolve. Also discussed was the observation that the preparation of samples for batch sorption experiments usually involves the crushing of intact rocks and the possibility that this process will introduce secondary sites.

Figure 2: Surface complexation reactions (after oral presentation by T. Payne and J. Lützenkirchen)

The problems of distinguishing between sorption and incorporation were also highlighted, with the example given of iron reactions with clay minerals. It is recognised that these process can occur, but at present a full representation is beyond the scope of the TSM Project.

Another point raised was that the time taken to achieve equilibrium is something that needs to be considered when performing radionuclide sorption experiments. Similarly, time dependency in titrations to measure surface hydrolysis is a factor that may affect the quality of results.

Thermodynamic sorption models use mass balance constraints and the activities of species are related by equilibrium constants for reactions. The question was raised as to whether the solid surface is assumed to be at a reference state and the work of Sverjensky relating to standard states of activities for surface sites was cited as addressing this point ⁽¹⁾.

Michael Ochs (BMG Engineering, Switzerland) and **Jim Davis (US Geological Survey, USA)** described the applications of TSMs to real substrates. The challenge in developing TSMs for use in a safety case is related to the ability to predict radionuclide sorption for ‘real’ materials of relevance to disposal scenarios. These materials are composed of a number of solid phases and therefore more complex than the pure, single minerals used in many laboratory experiments. Further complexity may arise from the non-additivity of sorption contributions of individual phases, physical effects relating to the compaction of materials and the poor characterisation of the solid phases.

The sorbing components in compacted clays are often well defined component phases, and the contribution to sorption can be combined in an additive way. However, complications arise because the composition of porewater in clays cannot be measured directly and it is therefore necessary to derive this information from modelling. A further issue in developing TSMs for clays is whether assumptions about electrostatic effects based on disperse systems are valid for the narrow pore spaces. A number of experimental studies are suggesting that the approach is feasible.

⁽¹⁾ D.A. Sverjensky, 2003, Standard states for the activities of mineral surface sites and species. *Geochimica et Cosmochimica Acta*, Vol. 67, No. 1, pp. 17–28

Following the presentation the question was raised of the importance of microbiology on sorption properties for some sub-surface applications. In compacted clays, microbial action is thought to be limited. Biological materials are a component of the 'real' samples examined, but there are uncertainties about how representative each sample is and how biological component may change over time. A general point was also made about the importance of the quality of data in the thermodynamic database, for example, the uranium-hydroxyl-carbonate solution species discussed during Session I.

Vincenz Brendler (FZ Dresden-Rossendorf, Germany) and **Johannes Lützenkirchen (KIT-INE, Germany)** gave a presentation on the impact of model choices and parameter uncertainty on K_d representation and how the choice of sorption representation in a model affects its parameterisation. Thermodynamic sorption models are complex and rely on a large amount of input data. It is important to understand the impact of uncertainty in the models. Uncertainties may be derived from analytical errors, sampling errors, container wall adsorption, drifts of temperature, pH or E_h . Other errors are more difficult to quantify, such as inadequacies in analytical methods, undetected phase alteration, the precipitation of secondary phases during experiments and contamination of samples. To investigate uncertainties a number of specific sorption models have been examined under the NEA Thermodynamic Sorption Project.

Following on from the presentation the question of how can conceptual uncertainty in the model be accounted for was put forward, for example, where a mechanism may involve not just surface sorption, but precipitation or ion-exchange. In such cases it is necessary to go back to the original experimental data and compare the results of different conceptual models. Spectroscopic techniques may also be useful in identifying species formed. Reference was also made to the forthcoming Phase III publication which will provide recommendations for development of models. These will cover the areas of:

- acquisition of sorption data and TSM parameters
- TSM parameterization
- suitability and adequacy of models
- model applications.

Questions were also raised about how impurities in the substrate can affect experimental results and how this can be assessed. An example was given of silica impurities in selenium experiments having altered results by a factor of up to 10. This question will be addressed in the Sorption Project's Phase III publication which will contain recommendations on the characterisation of samples and reactions in experiments.

Session IV: How Thermodynamics Underpins a Safety Case

This structure of this session was different to the first three. It opened with a scene setting talk after which the delegates were divided into of working groups to discuss a number of key questions. The groups reported their discussions to the plenary session. The workshop concluded with an open discussion which allowed delegates to put forward opinions on the future direction of the TDB and Sorption projects.

Hans Wanner (ENSI, Switzerland) gave the scene setting talk in which he considered how thermodynamic models are used to support safety cases. Geological disposal aims to isolate waste from the biosphere, but complete isolation is not achievable and some radionuclides will eventually migrate from the repository. Therefore, assessment of migration is an essential part of the safety case. In the waste packages the limitation of solubility is the important mechanism in controlling the migration of many radionuclides. The prediction of radionuclide solubilities in the relevant aqueous solution is one of the key uses of thermodynamic modelling for the safety case.

In the backfill and the geosphere it is sorption that is most important in limiting radionuclide migration. Batch sorption experiments generate K_d values, but thermodynamic sorption models can provide a better understanding of the chemical processes involved and so increase confidence in predictions. They are also of value in aiding the assessment of the long-term evolution, due to processes such as the migration of high-pH plumes, carbonation and groundwater ingress.

Discussion groups

Five small working groups were convened to consider relevant aspects of the following questions:

- 1) How accurate is my thermodynamic calculation?
- 2) How representative is my sorption model?
- 3) How relevant are thermodynamics in a world ruled by kinetics?

although discussions were not limited to these issues.

The objectives of the working group sessions included ensuring that all of the symposium participants had a chance to express their views on technical issues and develop and discuss suggestions regarding directions of future work. A rapporteur assigned to each group reported back to the plenary session on the results of the group discussions.

Working Group A focussed mainly on Question 2 relating to sorption, but also considered some aspects of Question 1 relating to thermodynamic data.

The working group noted that the importance of sorption in radioactive disposal depends to a great extent on the disposal system under consideration, including the nature of the host rock and the materials of the engineered barriers.

The group considered that the success (or failure) of thermodynamic sorption models to provide a 'good' representation of radionuclide sorption in a particular system depended strongly on three factors:

- The simplicity or complexity of the system being modelled, and particularly whether the sorbing substrate was a single 'pure' mineral or a more complex rock.
- The radionuclide of interest.
- The location in the disposal system where sorption might be occurring.

For example, various detailed research studies have developed successful sorption models which do have some predictive capability for simple systems, but there is still considerable uncertainty associated with sorption models for more complex systems involving real rocks and groundwaters. For these systems, the predictive capability of sorption models remains fairly low.

With respect to the radionuclide of interest, it was noted that some systems were chemically easier to represent and model than others. For example, models of caesium sorption may be more accurate or representative than models of the sorption of radionuclides such as plutonium or selenium, which exhibit several redox states and form a wide range of aqueous and surface species or complexes.

Similarly, it is easier to develop appropriate sorption models for parts of the disposal system that are relatively more stable (*e.g.*, the centre of a clay host rock formation) than it is for regions at the interfaces between materials (*e.g.*, in a clay host rock near to a cementitious engineered barrier) where various dynamic chemical evolution processes may occur over time. Although thermodynamic sorption models are coupled relatively easily within reactive transport models and such coupled models can be applied to

investigate the interface regions, there is often considerable uncertainty in the conceptual model of the geochemical alteration processes that may occur and this hampers accurate quantification of radionuclide sorption in such regions. The working group identified iron-bentonite and cement-bentonite interactions as particular issues of interest, as well as the effects of an influx of glacial groundwaters. A key uncertainty relates to the fact that in evolving situations, the identity of the solid phase (on which sorption might occur) is often uncertain.

The need to understand the geochemical evolution of such evolving systems and to support sorption models with reliable core and auxiliary thermodynamic data, led the working group to support a suggestion for continued work in an international forum on thermodynamic data.

It was stressed that there are potentially significant savings to be made if the waste management organisations can continue to collaborate on work on thermodynamic database development. It was further suggested that international collaboration on this topic is necessary because there is a lack of sufficiently experienced radio-chemists and thermodynamicists in any one country.

Discussion of what future international work on thermodynamic databases might include, focussed on the need for an electronic database (*e.g.*, containing the NEA thermodynamic data) with a modern (possibly internet-based) interface. The work could also sensibly involve review of proposals for thermodynamic data collection activities in individual OECD member states, and the provision of advice to increase the overall coherence of the programmes. It was noted that there might be a need to have more than one dataset to deal with both low and high ionic strength systems.

The working group considered that it would not be sensible to continue databases of sorption distribution coefficients (K_d s) because such databases have been compiled in the past and are of very limited utility. Instead, the group suggested that it would be sensible to undertake a critical review of the literature with the aim of selecting a set of highly reliable sorption data that would provide an example of best practice in sorption investigations and which might be used in the derivation of appropriate reference values for certain sorption parameters.

Finally, it was suggested that some well-defined sorption tests cases could form the basis for a future international study to assess the ability to model sorption on certain systems. It was envisaged that this might involve different modelling teams undertaking some ‘blind prediction’ work with subsequent comparison of their results against existing experimental data on real clay samples taken from relevant national programmes. Clays were suggested as at present these are the materials best understood by TSMs.

The discussions of **Working Group B** focussed on questions 1 and 2 and considered in particular:

- the effects of conservatism
- characterisation of solid phases and surfaces
- the problems of scaling up laboratory experiments.

The group discussed the problem raised in some of the previous sessions, of how only high-quality experimentally-derived data is selected in the NEA TDB and as a consequence some important species may be omitted. There were suggestions that the quality selection criteria could be relaxed to allow more data to be included, but the group did not come to a consensus on this issue. The group felt there may be a tension between the scientific rigour of the TDB compliers and the practical needs of safety case assessors and that the NEA can play a role in bringing together the requirements of these two parties.

Where there is a high degree uncertainty for important species, this leads to necessarily conservative values being assigned in performance assessment. The effects of this conservatism need to be understood

in order to make judgements on where resources for new work can be most effectively used, but the group recognised that in some aspects these decisions will be driven by the requirements of specific repository sites and disposal concepts.

The group also discussed the requirements for a sorption database. In common with Working Group A, it was felt that efforts should not be directed towards simply compiling sets of parameter values, but rather that descriptions of liquid-surface interactions would be more useful. It was noted how constant improvements in technology are driving what can be achieved in the characterisation of species. For example, techniques such as EXAFS are allowing detail of surface species to be examined.

The challenges of translating data from relatively small scale laboratory experiments to models of repository scale volumes and the issues of understanding the representative elemental volume (REV) were highlighted. An REV may be conceptualized as the smallest volume of porous or fractured medium for which the parameters or processes of a model are representative of the whole. It was felt that these issues may not have been fully resolved. There are challenges in representing sorption for areas where the surface chemistry is gradually changing, such as the near field / far field interface, particularly over timescales relevant to geological disposal.

The question of the importance of kinetics was considered at the very end of the group's discussion time. An issue that may require further investigation is inhomogeneity of solid surfaces due to alteration over time. Although the thermodynamics of aqueous solutions are in many cases well understood, there are uncertainties in the behaviour of metastable phases and their changing sorption properties over time.

Working group C's discussion at first concentrated on the question of the importance of thermodynamics compared to that of kinetics. The main conclusion was that although kinetics are important in the understanding of laboratory experiments, over long time scales thermodynamic considerations tend to be more important. Thermodynamic equilibrium gives a definition of limit past which a reaction will not proceed

The group then moved on to discuss the importance of ensuring the completeness of the thermodynamic database used to support performance assessment. The work done by the NEA TDB project was acknowledged as a crucial foundation, but two significant omissions were identified. The first of these was the lack of Pitzer parameters, which are required for the accurate modelling of high-saline systems. Secondly it was pointed out that significant gaps exist in the data needed for performing calculations at temperatures other than 25°C.

The group noted that each national waste-management organisation maintains its own thermodynamic database, tailored for particular waste inventories and specific disposal sites. It was emphasised in the working group's discussions that there are benefits in saving time and effort, if the exchange of experience and data between organisations is maintained.

Finally suggestions for future work in the TDB and Sorption projects were discussed. These included more detailed guidance notes for users of the TDB and procedures on best practice in experimental techniques for obtaining thermodynamic data. The group felt it was important to provide updates to the current database, to minimise divergence of the data used by member organisations. A maximum of 5 years between updates was suggested.

Working Group D concentrated on discussions of the future direction of the TDB and Sorption projects and identified a number of areas that it felt should be the focus of further work. In many cases these suggestions echoed points raised by other groups.

There is a need amongst many of the TDB users for the modelling of high ionic strength environments, which requires the use of Pitzer parameters. It was pointed out that in some cases Pitzer parameters for ion interactions with Na^+ and Cl^- may not be sufficient and other major ions may need to be considered, for example Ca^{2+} or SO_4^{2-} . There may also be interest in the combination of Pitzer with sorption models. The group also recognised the need for more data for modelling at temperatures other than 25 °C.

There was also interest expressed in:

- verification of temperature extrapolation methods
- identification of species formed at higher temperatures
- sorption modelling at higher temperature.

It was also suggested that the flagging of species that only form in high temperature or high pressure environments would aid the user. Other suggested areas for further work were:

- the review of data for additional actinide elements
- the review of ligands and mineral phases
- the investigation of radiolysis effects.

The group also discussed the use of thermodynamic models in the safety case and how they provide an understanding of the underlying systems. The main conclusion was that thermodynamics is a valuable tool for assessing the impact of changes in a system and provides a framework for more detailed studies of other important aspects such as kinetics and redox.

Working group E first considered the question ‘How accurate is my thermodynamic database?’, the principal points made were that:

- A prerequisite for accuracy is the identification of all species involved
- It is also necessary to understand the effects of uncertainties.

The group then moved on to discuss issues related to sorption modelling. It felt that there would be benefits in development of procedures for conducting sorption experiments, which are generally not as well defined as those for aqueous chemistry. A suggestion was also made that the compilation of sorption data requires an approach similar to that of the TDB Project, with critical assessment of the experimental methods used to derive a set of key values. It was argued that the compilation of sorption data by an internationally recognised body, such as the NEA, would ensure that the methods and underlying assumptions have endorsement. This proposal received some support, but it was questioned whether sorption is sufficiently well defined to allow this sort of approach to be used.

The use of ‘component additivity’ in sorption models was also discussed, with a particular focus on cement systems. ‘Component additivity’ considers the sorbing surface as the sum of individual component mineral phases. The group felt that this approach has its merits in developing an understanding of sorption mechanisms, but also noted that a simple composite model (which treats the bulk surface as a homogenous whole, with one set of parameters) also has its advantages, especially for more complex systems.

On the kinetics versus thermodynamics question, it was felt that it is important to understand how kinetics and thermodynamics should combine, but that at present there is no clear answer.

Following the presentations from the working groups there was a plenary discussion session. Discussions on the Sorption Project first focussed on the form of a sorption database. The TDB Project publishes sets of recommended values for thermodynamic data. In contrast, in thermodynamic sorption modelling it is possible to choose different models to describe the same processes. Therefore, the sorption

database would consist of high quality sorption data from experimental studies that can be used for the development of models. Currently the main source of uncertainty in TSMs tends to be the scatter in experimental data and not the choice of sorption model. A critical review of the available data should aid in reducing these uncertainties and provide high quality data as the basis for the development of models.

A significant challenge for sorption modelling remains the transfer of models for single minerals to the representation of complex systems.

The issue of gaps in NEA TDB was considered in presentations at the symposium (Hummel, Kitamura) and in general discussions. At the moment, each organisation tends to use its own data for filling gaps. There was general agreement that the TDB Project could have a role in building a consensus on approaches to filling data gaps. One option is for the publication of 'augmenting data' by the NEA. However, this option has the drawback that estimated or uncertain data values could become confused with recommended values from the NEA TDB and there was no clear consensus among the delegates on this proposal. Another option suggested was for the NEA to host a forum (possibly web-based). This would allow workers to collaborate on problems associated with filling data gaps and to define areas of common interest.

There was also discussion of the modelling of saline systems and the need for sets of relevant Pitzer parameters. This is of particular interest to those programmes using salt environments for disposal, such as the USA and Germany. A further suggestion on this issue was the production of a thematic document on modelling saline systems. The issues associated with temperature effects were also highlighted as an area requiring further study, but it was generally considered a lower priority than Pitzer parameters and was recognised as requiring a long-term programme.

Mention was also made of the potential problems caused by the inclusion of amorphous and crystalline forms of some solids in the TDB. It may be appropriate to publish guidance on the appropriate form to choose.

Opinion was gauged from the delegates on the priorities for future programmes. On the TDB Project there was most interest in the following points.

- Publication of state of the art volumes.
The topic of most interest was: methods for estimation of case specific data.
Other topics suggested were:
 - databases for cement systems, rock-forming minerals and clay-forming minerals
 - kinetics.
- High ionic strength systems, extrapolation/interpretation methods for the coefficients of the Pitzer activity model.
- Temperature effects on the relevant species, verification and extrapolation of data.
- Making available the database files in an electronic format.
- Education of younger staff to maintain capability.
- Filling of gaps in data.

Other suggested areas included:

- missing ligands
- missing complexes (ternary)
- other elements (generally there appears to be no strong call for data on other elements to be added to the database after the Fe and Sn volumes are published)
- update of the element volumes
- update of the organic volume
- update of the U, Am, Np, Pu, Tc second time
- development of a more user friendly database interface
- the establishment of user groups on
 - the exchange of data sets
 - guidelines on data base use
 - vetting of proposed estimates
- a list of experts who can aid in filling gaps or add insight
- guidance on the impact of changes to key values.

The main topics of interest for future work on the Sorption Project were:

- Compilation of high quality raw data sets for sorption on well-defined solid phases, for single key sorbents. It was suggested that the focus should initially be on one key element (*e.g.* uranium), a single EDL and data for a number of solid phases.
- A procedure for developing high quality data sets.
- Blind Prediction Test.
- The education of TSM users.

CONCLUSIONS AND RECOMMENDATIONS

The presentations at the workshop demonstrated the advances made in the field of thermodynamic modelling applied to the problems of radioactive waste management. Over the 25 years of its existence the TDB has become recognised as a key source of thermodynamic data and there is now a far greater degree of agreement across organisations in the data values used and approaches.

The main conclusions on the future work under the TDB Project were:

- Addressing of the issue of gaps in the data. The criteria for data selection ensure that only high-quality data are included, so that where there are no data of sufficient quality values are omitted. There was broad agreement that the project should only publish data that met its strict quality criteria, although this would result in data gaps. To achieve a useable database it is necessary to fill the data gaps in and it was suggested the NEA should explore the option of providing a forum (possibly web-based) for TDB users to collaborate on this issue.
- There was demand from some users for Pitzer parameters. Due to the high ionic strength of solutions in saline systems, the only option for activity correction is use of the Pitzer method. The requirement for data on temperature effects was also highlighted. The role of the TDB Project in the compilation of Pitzer parameters and data on temperature effects was discussed.
- There is interest in the production of review documents, particularly on the subject of estimation methods, although some guidance is given in previous NEA publications ⁽²⁾. Other suggestions included 'state-of-the-art' publications on cements systems, rock-forming minerals, clay-forming minerals and kinetics.
- It is recommended that updates of current volumes should continue as required, to prevent a divergence of the data values used. There is no strong requirement expressed for further elements to be included in future publications, after the iron, tin and molybdenum volumes.
- The release of the TDB as electronic database file format should be considered.

Similarly, since the inception of the Sorption Project in 1997 there is a greater acceptance of the TSM approach for describing sorption and closer consensus on the methods for the development of TSMs. There are still challenges in transferring models for single minerals to the prediction of sorption behaviour of complex solids.

⁽²⁾ B. Allard, S. A. Banwart, J. Bruno, J. H. Ephraim, R. Grauer, I. Grenthe, J. Hadermann, W. Hummel, A. Jakob, T. Karapiperis, A. V. Plyasunov, I. Puigdomenech, J. A. Rard, S. Saxena, K. Spahiu, 1997, *Modelling in Aquatic Chemistry*. OECD Publications.

The main conclusions on future of the Sorption Project were:

- There is a need for the compilation of high quality raw data sets for use in the development of thermodynamic sorption models. This should concentrate on sorption on well-defined solid phases, for single key sorbents. A critical review of data should improve consistency and reduce uncertainties.
- The focus of the Sorption Project is fairly broad at present. There are arguments for concentrating effort on one key element (*e.g.* uranium), a single EDL and a number of solid phases.
- The development of high quality data sets will be aided by standard procedure on this subject. The procedure would cover recommendations on the acquisition of sorption data and TSM parameters as well as model parameterization.
- Blind prediction test can help gauge the consistency of TSM approaches.

There is also a need for both the TDB and Sorption Projects to develop and maintain skills. It is therefore recommended that the NEA continue to be a forum in which modellers, experimentalists, safety assessors and regulators can be brought together to improve technical competency and promote international discussion of thermodynamic modelling activities.

APPENDIX A - ABSTRACTS OF PRESENTATIONS

FROM THERMODYNAMICS TO THE SAFETY CASE

Bernhard Schwyn,

Nagra, Member of the Management Boards NEA-TDB and NEA-Sorption

This symposium was co-organised by the two NEA projects “Thermochemical Database” and “Sorption” to present thermodynamic approaches used to model chemical processes in a radioactive waste disposal system.

The understanding and quantification of chemical processes, in particular the migration of radionuclides, is an essential part of a safety case. “A safety is the synthesis of evidence, analyses and arguments that quantify and substantiate a claim that the repository will be safe after closure and beyond the time when active control of the facility can be relied on” (quoted from NEA, 2004).

The approaches to do a safety case may vary between different national programmes; the applied thermodynamic principles are however universal. The international platform of NEA is therefore ideal to compile corresponding databases and to develop methods jointly.

Geochemical features and processes are omnipresent in a disposal system; the most important ones are depicted in Figure 1. However, chemical equilibrium is often not reached which limits the applicability of thermodynamic principles. But also in cases of disequilibrium a sophisticated application of thermodynamics provides information about intermediate quasi equilibriums or the direction into which chemical reactions are driven. When thermodynamic modelling is used in performance assessment one has to check carefully whether equilibrium can be assumed. In some cases, however, the assumption of equilibrium is conservative in view of long-term safety.

In an equilibrium system all chemical processes are thermodynamically interconnected by definition. This implies that the different processes shown in Figure 2 such as porewater composition, solubility limits and sorption of radioelements need to be modelled consistently based on one consistent dataset.

To hold a conjoint symposium for the two NEA projects “Thermochemical Databases” and “Sorption” may be a venturesome undertaking since the philosophies of the two communities differ markedly:

The Thermochemical Database Project is committed to carefully review of the available literature and select basic thermodynamic data for elements relevant to radioactive waste management. The quality of the selected data has the highest priority; insufficient data quality and missing information leave gaps in the dataset. From the user’s point of view an incomplete dataset is disastrous and data of lower quality or estimated data would be the lesser evil. An important goal of this symposium is therefore to show how a consistent dataset can be obtained using and completing the data provided by the TDB Project. An equally important goal is to show how thermodynamic models can be applied to realistic situations of a disposal system.

The Sorption Project is strongly user oriented. It aims to provide the performance assessor with a tool based on thermodynamics (Thermodynamic Sorption Models) to derive sorption coefficients (K_d values) adaptable to various and chemically evolving systems. Without such models K_d values are purely empirical and only valid under conditions under which they were measured. Due to the complexity of mineral surfaces it is currently unrealistic to analyse radioelement sorption on minerals down to basic thermodynamic data. Instead, mass action laws are formulated for reactions of dissolved radioelement

species with mineral surfaces, and corresponding equilibrium constants are derived directly from sorption measurements on minerals with experimentally characterised surfaces.

From a performance assessment point of view a close co-work between the two communities is crucial to successfully underpin a safety case. A sound and complete thermodynamic dataset is necessary to model radioelement solubilities and other geochemical features and processes. The ability to model porewater composition and radioelement speciation is a prerequisite for the development of Thermodynamic Sorption Models. The latter, even if not directly used to derive sorption coefficients, increase confidence in radionuclide retention within a safety case.

NEA (2004): Post-Closure Safety Case for Geological Repositories, Nature and Purpose. ISBN 92-64-02075-6, OECD/NEA, Paris.

Figure 1: Geochemical features and processes of a disposal system

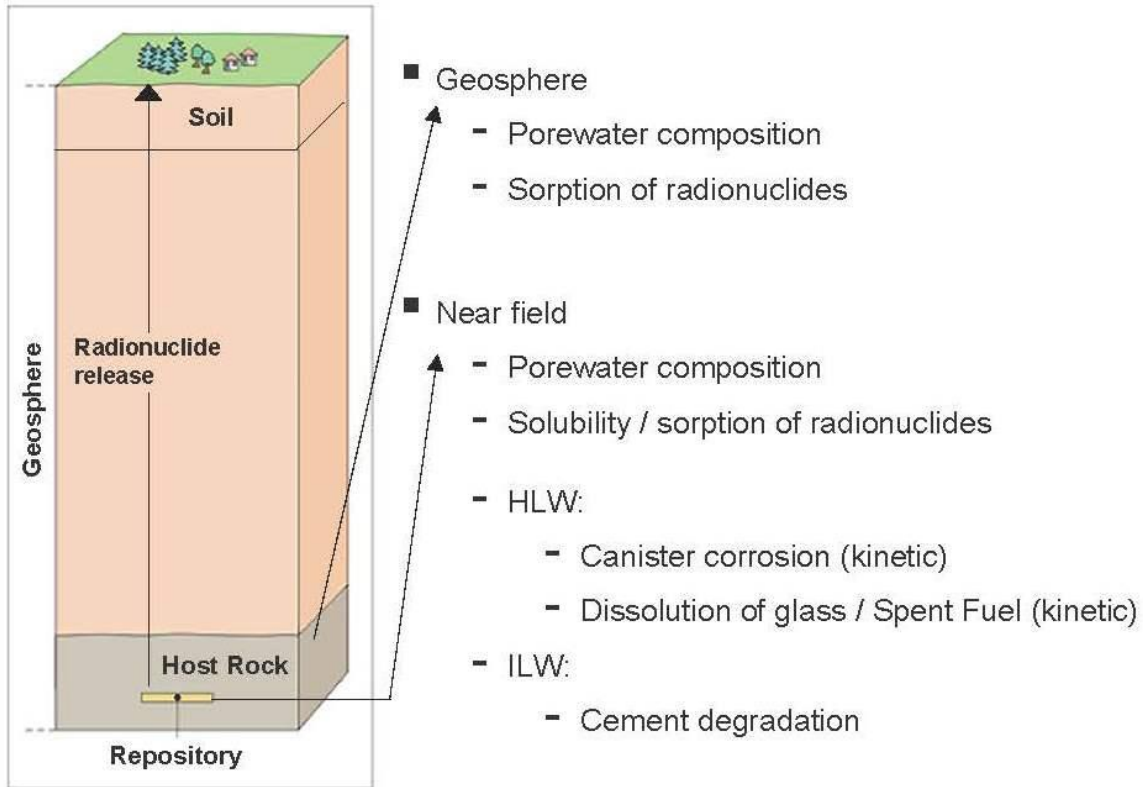
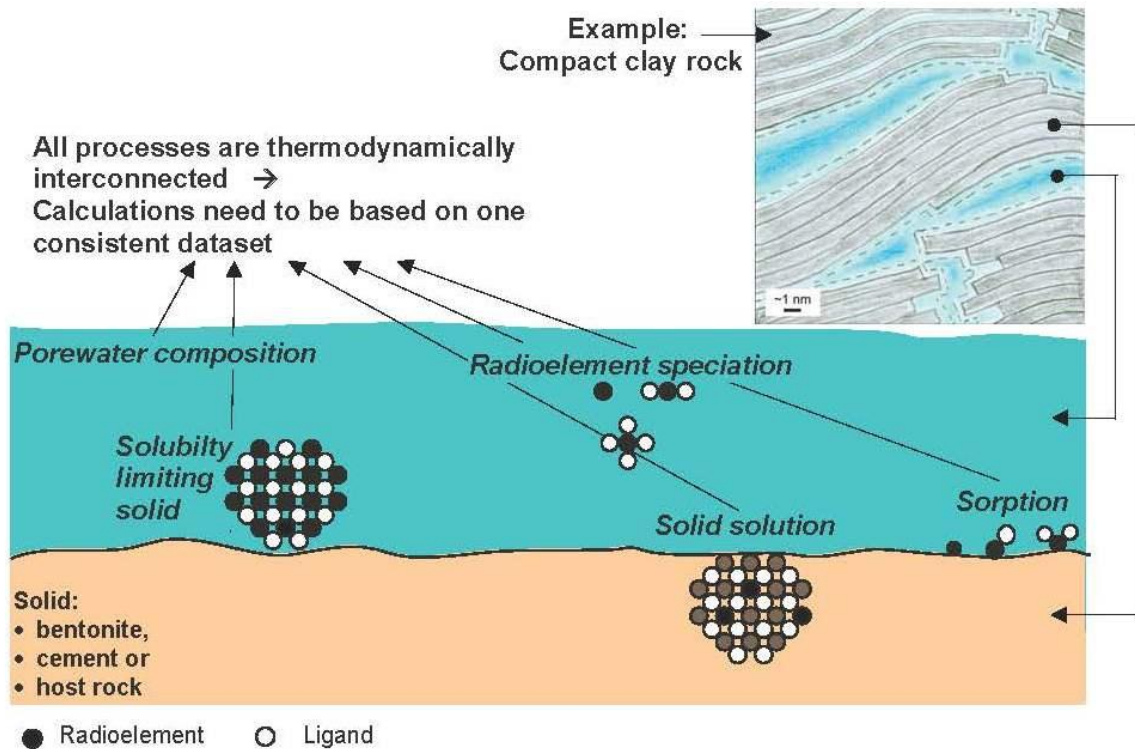


Figure 2: An example of consistent thermodynamic modelling



THE OECD NUCLEAR ENERGY AGENCY (NEA) THERMOCHEMICAL DATABASE PROJECT

Cynthia E. Atkins-Duffin,

on behalf of the NEA and the participants of TDB Project Phase IV

The goal of the OECD Nuclear Energy Agency (NEA) Thermochemical Database (TDB) Project is to make available a comprehensive, internally consistent and quality-assured chemical database of selected chemical elements. This database should meet the specialized modeling requirements for safety assessments of radioactive waste disposal systems.

The presentation will describe the evolution of the project from its inception in 1984 to the present organization as a semi-autonomous project under the aegis of the OECD NEA. While remaining true to scientific principles and project organization/structure, the 25 year effort has resulted in a series of major reviews on the chemical thermodynamics of inorganic species and compounds:

- I. Grenthe, J. Fuger, R.J.M. Konings, R.J. Lemire, A.B. Muller, C. Nguyen-Trung, H. Wanner, “Chemical Thermodynamics of Uranium”, Elsevier Science Publishers B.V., Amsterdam (1992)
- R.J. Silva, G. Bidoglio, M.H. Rand, P. Robouch, H. Wanner, I. Puigdomenech, “Chemical Thermodynamics of Americium”, Elsevier Science Publishers B.V., Amsterdam (1995)
- J.A. Rard, M.H. Rand, G. Anderegg, H. Wanner, “Chemical Thermodynamics of Technetium”, Elsevier Science Publishers B.V., Amsterdam (1999)
- R.J. Lemire, J. Fuger, H. Nitsche, P.E. Potter, M.H. Rand, J. Rydberg, K. Spahiu, J.C. Sullivan, W.J. Ullman, P. Vitorge, H. Wanner, “Chemical Thermodynamics of Neptunium and Plutonium”, Elsevier Science Publishers B.V., Amsterdam (2001)
- R. Guillaumont, T. Fanghanel, J. Fuger, I. Grenthe, V. Neck, D.A. Palmer, M.H. Rand, “Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium”, Elsevier Science Publishers B.V., Amsterdam (2003)
- H. Gamsjager, J. Bugajski, T. Gadjia, R.J. Lemire, W. Preis, “Chemical Thermodynamics of Nickel”, Elsevier Science Publishers B.V., Amsterdam (2005)
- A. Olin, B. Nolang, L.-O., E. Osadchii, E. Rosén, “Chemical Thermodynamics of Selenium”, Elsevier Science Publishers B.V., Amsterdam (2005)
- P.L. Brown, E. Curti, B. Grambow, C. Ekberg, “Chemical Thermodynamics of Zirconium”, Elsevier Science Publishers B.V., Amsterdam (2005)
- W. Hummel, G. Anderegg, I. Puigdomenech, L. Rao, O. Tochiyama, “Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with Selected Organic Ligands”, Elsevier Science Publishers B.V., Amsterdam (2005)

- J. Bruno, D. Bosbach, D. Kulik, A. Navrotsky, “Chemical Thermodynamics of Solid Solutions of Interest in Nuclear Waste Management”, OECD Nuclear Energy Agency, Paris (2007)
- M. Rand, J. Fuger, I. Grenthe, V. Neck, D. Rai, “Chemical Thermodynamics of Thorium”, OECD Nuclear Energy Agency, Paris (2009)
- “Chemical Thermodynamics of Tin, (in peer review)
- “Chemical Thermodynamics of Iron, part A”, (in peer review)
- “Chemical Thermodynamics of Iron, part B”, (review in process)
- “Chemical Thermodynamics of Molybdenum”, (review in process)
- “Chemical Thermodynamics of Ancillary Data”, (initiation report received)

In addition two workshops have been organized to better support the interface between the “data generators/reviewers” and the “data user community.”

- The Use of Thermodynamic Databases in Performance Assessment – Barcelona, SPAIN 2000
- From Thermodynamics to the Safety Case - Karlsruhe, GERMANY 2010

A related book is also of interest:

B. Allard, S.A. Banwart, J. Bruno, J.H. Ephraim, R. Grauer, I. Grenthe, J. Hadermann, W. Hummel, A. Jakob and T. Karapiperis, A.V. Plyasunov, I. Puigdomenech, J.A. Rard, S. Saxena, K. Spahiu, “Modelling in Aquatic Chemistry,” OECD Nuclear Energy Agency, Paris (1997)

EXAMPLE OF A TDB REVIEW

An overview of the iron review: process and challenges

Robert Lemire, Chairperson,

TDB Iron Team

For each of the TDB reviews, the key product should be a list of carefully assessed chemical thermodynamic values suitable for use as a database. The set of values should be as accurate as currently possible, but consistent, coherent, and appropriate to the needs for nuclear fuel waste management. The intent is to provide a framework to allow modellers to calculate what *can* happen in a certain scenario, not what *will* happen, as the latter is in the realm of kinetics (including surface science).

Work on the TDB Iron Review began in 2004/2005, and early-on it was recognized that this project would require an extensive effort. Therefore, the undertaking was divided into two parts: (1) as part of TDB Phase III: Fe, simple ions, chlorides, selected other halide solids and complexes, sulfates, carbonates, simple Fe-Si-O solids, and aqueous sulfides, and (2) as part of TDB Phase IV: phosphates, arsenates, nitrates, sulfide solids, and the remaining halido complexes. The initiation report covered both parts, and Iron Part 1 is now undergoing peer review. The TDB reviewers for Part 1 included Urs Berner (Fe(II) complexes), Robert Lemire (chairperson, initiation report, Fe metal, halide, sulfate and other solids, consistency calculations), Claude Musikas (Fe(III)/Fe(II) electrochemistry, Fe(III) carbonato, chlorido and sulfato complexes), Donald Palmer (hydrolysis species, interaction coefficients), Peter Taylor (oxides and hydroxide solids), and Osamu Tochiyama (sulfide aqueous species).

As usual, the process began with an attempt to review all of the relevant literature; then there was a reassessment of the available primary data. This is not a mechanical process, but requires the reviewer to consider the quality of each study and to assign his own estimate of uncertainties. Usually a discussion of the paper was prepared and documented in Appendix A of the review. In cases where than one source for a value was available, a best value and associated uncertainty were proposed.

In the iron review, values of many of the experimentally-determined quantities are related. To maintain database consistency it was necessary to consider many of these quantities together as part of the related chemical thermodynamic cycles (Figure 1). These included $\Delta_{\text{red}}G(\text{Fe}^{2+})$, $\Delta_{\text{red}}G(\text{Fe}^{3+})$, $\Delta_{\text{red}}S(\text{Fe}^{3+})$, $\Delta_{\text{ox}}H(\text{Fe}(\alpha))$, $\Delta_{\text{ox}}H(\text{Fe}^{2+})$, $S^{\circ}_{\text{m}}(\text{FeCl}_2(\text{cr}))$, $\Delta_f H^{\circ}_{\text{m}}(\text{FeCl}_2(\text{cr}))$, $\Delta_f H^{\circ}_{\text{m}}(\text{FeCl}_3(\text{cr}))$, $\Delta_f H^{\circ}_{\text{m}}(\text{FeBr}_2(\text{cr}))$, $\Delta_f H^{\circ}_{\text{m}}(\text{FeBr}_3(\text{cr}))$, $\Delta_{\text{sln}}G^{\circ}_{\text{m}}(\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{cr}))$, $\Delta_{\text{dehyd}}G^{\circ}_{\text{m}}(\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{cr}))$, $\Delta_{\text{sln}}H^{\circ}_{\text{m}}(\text{FeCl}_2(\text{cr}))$, $\Delta_{\text{sln}}H^{\circ}_{\text{m}}(\text{FeCl}_3(\text{cr}))$, $\Delta_{\text{sln}}H^{\circ}_{\text{m}}(\text{FeBr}_2(\text{cr}))$, $\Delta_{\text{sln}}H^{\circ}_{\text{m}}(\text{FeBr}_3(\text{cr}))$, $S^{\circ}_{\text{m}}(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}))$, $\Delta_f H(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}))$, $\Delta_{\text{sln}}H(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}))$, $\Delta_{\text{sln}}G(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}))$, $\Delta_{\text{sln}}G(\text{FeCO}_3(\text{cr}))$, $S^{\circ}_{\text{m}}(\text{FeCO}_3(\text{cr}))$, and $\Delta_{\text{decomp}}H(\text{FeCO}_3(\text{cr}))$. The associated assessed values for $S^{\circ}_{\text{m}}(\text{Fe}(\alpha))$ and $\Delta_f H^{\circ}_{\text{m}}(\text{Fe}_2\text{O}_3(\alpha))$ were not varied. After an initial consistency calculation, three of the experimental results were re-assessed, and minor adjustments were made to four other assessed uncertainties to generate a final consistent set of selected values.

There have been several challenges in assessing the data. Careful studies of the Fe(III)/Fe(II) couple as a function of ionic medium were surprisingly sparse, and most were rather dated. The value for $\alpha(\text{Fe}^{3+}/\text{ClO}_4^-)$ was found to be substantially more positive than expected, and values for $\Delta\varepsilon$ for reactions involving Fe^{3+} appeared to be non-linear when based on results for low ionic strengths. The amount of data on iron complexation with sulfate and Fe(II) complexation with fluoride also was only marginally adequate. Furthermore, some complexes that are very weak (essentially non-existent) at 298.15 K (*e.g.*, FeCl^+) are quite important at higher temperatures.

For solids, thermodynamic studies commonly have been carried out on non-stoichiometric compounds or on real minerals rather than pure end-member compositions (for example, accurate enthalpy of solution work was done using a sample of “amosite” with the composition $\{\text{Fe}^{2+}_{5.2766} \text{Fe}^{3+}_{0.12} \text{Mn}_{0.0825} \text{Mg}_{1.5209}\}$ ($\text{Si}_{7.9163} \text{Al}_{0.0837} \text{O}_{22.0363}\}$ $\{(\text{OH})_{1.9637}\}$). Also, many low-temperature heat capacity studies have been focused on physics aspects, and don't aid calculation of standard entropies at 298.15 K. For the common oxides and hydroxides, there are voluminous data with many discrepancies, and many of the phases are metastable. Wüstite (Fe_{1-x}O) was a particular challenge as it is not a stoichiometric solid (often $(1 - x) \sim 0.93$), is metastable with respect to $(\text{Fe}/\text{Fe}_3\text{O}_4)$ below ~ 840 K, but is an important stable phase at high temperatures. Values for thermodynamic quantities for other iron solids at lower temperatures are often linked to experiments done at high temperature using wüstite.

There were the usual TDB problems of somewhat dated auxiliary data anchored in the 20-30 year old CODATA compendium, and lack of consistent TDB sets of certain types of auxiliary data (*e.g.*, high- T functions for common gases). However, two specific problem areas were noted. First, when data are obtained on “almost anhydrous” solids or poorly defined hydrates, how should entropy and enthalpy contributions be estimated to obtain values for stoichiometric compositions? Second, for highly-charged ions it is difficult to separate weak complexation, hydrolysis, and long-range ionic interactions (ionic-strength functions). This is especially true for calorimetrically measured enthalpies of reaction, which often have been carried out at a single ionic strength.

Also, it is becoming more difficult to search the literature, and strangely the problem is greater for some of the *recent* literature. Access to Chemical Abstracts has become more difficult, and overall, the way literature is reviewed and “published” is changing. Peer review has deteriorated, journals have proliferated and website material (and references) may be ephemeral. At the same time, some older journals are becoming more difficult to find, access to copies of early 20th century theses is becoming challenging (theses often contain primary data), and some grey-literature is disappearing (and microcards and microfiche are becoming hard to access).

FROM TDB TO A WORKABLE DB -DEVELOPMENT OF THE PSI/NAGRA TDB

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No abstract supplied

FROM TDB TO A WORKABLE DB – THE CASE OF JAEA-TDB

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Japan Atomic Energy Agency (JAEA) has developed the thermodynamic database (JAEA-TDB) for performance assessment (PA) of geological disposal of high-level radioactive waste (HLW) and TRU waste (a kind of intermediate-level radioactive waste). Twenty-five elements which are important for the performance assessment of geological disposal (shown in

Figure 1) were selected. The fundamental plan of TDB development was based on the guidelines established by the NEA. Most of selected data for Ni, Se, Zr, Th, those for of Tc, U, Np, Pu and Am in update version (including those for selected organic complexes), and the selected auxiliary data by the NEA were accepted and taken to JAEA-TDB as shown in Table 1. In this presentation, I will focus to answer three questions by Chairman about comprehensiveness of the TDB books by the NEA.

As mentioned previously, we took most of thermodynamic data selected by the NEA, after confirming the review of data selection. However, the selected data for some elements were insufficient to apply to performance assessment of geological disposal from reliable (often conservative) point of view. Also we found the difficulty of selection of thermodynamic data for some elements without sufficient and reliable experimental data, for example, Ac and Pa.

After finding the gaps between the NEA's TDB and TDB for PA, we additionally selected some thermodynamic data, for example, mixed carbonatohydroxo complexes of actinides(IV). Furthermore, we applied chemical analogues to selection of thermodynamic data for some systems, for example, Ni(II)–Co(II) and Sm(III)–Ac(III)–Pu(III)–Am(III) –Cm(III) systems, after confirming their applicability.

I would also like to show current status on applicability of JAEA-TDB to “real situations” which will be discussed in the present symposium.

Figure 1: Elements of interest for JAEA-TDB and those published as TDB books by the NEA

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn						

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

red : Elements of interest for PA in Japan

green : Elements published in NEA-TDB as of 2009

Table 1: Comprehensiveness of coverage of the selected thermodynamic data by the NEA for JAEA-TDB

Element	Acceptance of thermodynamic data by the NEA to JAEA-TDB
Zr, Th, Am	All selected $\log K^\circ$ values were accepted without any additions and modifications.
Ni	All selected $\log K^\circ$ values were accepted. A few $\log K^\circ$ values (<i>e.g.</i> for $\text{Ni}(\text{OH})_2(\text{aq})$) were additionally selected.
Se	All selected $\log K^\circ$ values were accepted. A few $\log K^\circ$ values (<i>e.g.</i> for $\text{FeSe}_2(\text{cr})$) were additionally selected with calculation from $\Delta_f G^\circ_m$.
Tc	Almost all selected $\log K^\circ$ values were accepted. A few latest $\log K^\circ$ values (<i>e.g.</i> for TcOOH^+) were reviewed and replaced.
U, Np, Pu	Almost all selected $\log K^\circ$ values were accepted. A few latest $\log K^\circ$ values (<i>e.g.</i> for $\text{NpO}_2(\text{am})$) were reviewed and replaced. Some $\log K^\circ$ values (<i>e.g.</i> for $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$) were additionally selected.

HIGH PH SYSTEMS

Steve Williams

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Cementitious backfills used in engineering barrier systems provide an important barrier to radionuclide migration in many geological disposal facility designs and concepts. They are typically employed to condition incoming groundwater to a high pH, and have an extensive buffering capability that maintains these conditions for an extended period of time. The aqueous concentrations of many radionuclides at high pH are lower than in groundwaters at near-neutral pH values due to the formation of solid phases of low solubility. These contribute part of the 'chemical containment' of radionuclides in cement-based engineered barrier systems. An understanding of high pH systems and their effects on the behaviour of radionuclides is an important input to the safety case. Two topics are considered here:

- the solubility of elements in high pH cement systems;
- how the leaching of calcium silicate hydrate (CSH) gels supports the understanding of the evolution of cement systems.

Radionuclide Behaviour

The long-term aqueous solubility of radionuclides in a cement-based system will be influenced by the evolution of porewater chemistry affecting aqueous speciation. However, the presences of high concentrations of hydroxyl ions play an important role in defining the aqueous conditions. The hydroxyl complexation of many elements and the formation of solid hydroxides explain the observed solubility behaviour of many important elements at high pH and in cement porewaters, including the behaviour of thorium(IV), uranium(IV), plutonium (IV), neptunium(IV) and americium(III). However, the behaviour of some elements at high pH either cannot be explained on this basis or there are inconsistent observations. For example:

- There are discrepancies between experimental data for technetium(IV) solubility at high pH > 11 although data at lower pH are generally similar (for example Warwick et al 2007). These may be a reflection of the redox-sensitive system and the high solubility of technetium(VII), uncertainty in the formation constant of the higher hydroxyl species or differences in the solid phases formed.
- Tin(IV) is highly soluble in alkaline sodium hydroxide solutions. In calcium hydroxide solutions the solubility is much lower. Experimental data show that the presence of calcium in solutions of its hydroxide or in cement leachates leads to a decrease in solubility (Lothenbach et al 2000) due to the formation of burtite ($\text{CaSn}(\text{OH})_6$) as a solid phase. Tin solubilities calculated on this basis give good agreement with experimental observations.
- There is currently poor knowledge of the solubility of niobium hydrolysis and the phases formed at high pH. The available thermodynamic data suggest very high solubility at high pH, however solubility data measured in cement systems indicate low solubility. A study by Talerico et al resolves this discrepancy by showing that niobium solubility is also influenced by the presence of calcium. Therefore it is important to take into account the formation of calcium niobate phases in cement systems. The study gives an empirical relationship for the concentration of niobium as a function of calcium concentration and pH in the absence of reliable thermodynamic data.

- The solubility of nickel phases in cement systems is not well represented by a model based on simple nickel hydroxides. Although a somewhat 'better' empirical fit to the measured concentrations can be achieved by reducing the value of the $\text{Ni}(\text{OH})_3^-$ (aq) formation constant from currently accepted values this does not provide a satisfactory explanation. Mixed Ni-Al layered double hydroxides have been found to form in cements (Vespa et al 2006) and such phases may account for the observed aqueous concentrations.

The long-term aqueous solubility of radionuclides may also be influenced by possible long-term mineralisation and formation of more stable radionuclide-bearing phases. This may lead to lower aqueous concentrations than determined for amorphous phases formed on laboratory timescales.

Evolution of cement systems

The evolution of cement-based backfills in the engineered barrier system of a disposal facility will be driven by a number of processes that may occur under post-closure conditions, for example the dissolution of cements in groundwater and reactions with groundwater solutes. Such processes, and the resulting evolution of the physical and chemical properties of a cement backfill, will depend on the prevailing conditions (e.g. temperature and pressure), the extent of groundwater flow into the near field, any creep or other mechanical deformation caused by stresses in the host rock, and various chemical processes.

The understanding of the pH evolution of cement pore waters in dilute unreactive groundwaters is based on extensive studies made by a number of workers on the leaching of CSH gels in deionised water (for example Chen et al 2004, Harris et al 2002, Walker et al 2007). One model, by Carey and Litchner (Carey and Litchner 2007) represents the continuously variable solid-solution composition by a discrete set of stoichiometric solids that cover the composition range and is combined with a kinetic formulation of the rates of reaction. They applied their model successfully to the degradation of CSH using end members of portlandite and silica. Such a model can be used to model the behaviour of cement systems with the thermodynamic data updated when appropriate to maintain consistency with the current values (Lothenbach et al 2008, Matschei et al 2007).

Conclusions

- Hydroxyl is an important species for aqueous radionuclide speciation and formation of solubility-limiting phases for many radionuclides at high pH but other but other species may need to be considered in cement systems.
- There may be uncertainty in formation constants of some hydroxyl species.
- Calcium has an important role to play in determining the solubility-limiting phases for some radionuclides in cement systems; more complex mixed phases may also be formed.
- Empirical models can be useful in the absence of reliable thermodynamic data.
- Modelling and understanding of CSH continues to develop and is important for understanding cement evolution.

- P. Warwick, S. Aldridge, N. Evans and S. Vines, The Solubility of technetium(IV) at high pH, *Radiochimica Acta* 95, 709, (2007)
- B. Lothenbach, M. Ochs and D Hager, Thermodynamic data for the solubility of tin(IV) in aqueous cementitious environments, *Radiochimica Acta* 88, 521, (2000)
- C. Talerico, M. Ochs and E. Giffaut, Solubility of niobium(V) under cementitious conditions; Importance of a-niobate, *Mat Res Soc. Symp Proc Vol 824*, 2004
- M. Vespa, R. Dähn, E. Gallucci, D. Grolimund, E. Wieland and A.M. Scheidegger, Microscale investigations of Ni uptake by cement using a combination of scanning electron microscopy and synchrotron-based techniques, *Environ Sci Technol* 40, 7702, (2006)
- J.J. Chen, J.J. Thomas, H.F.W Taylor and H.M Jennings. Solubility and Structure of Calcium Silicate Hydrate. *Cement and Concrete Research*, 34, 1499-1519 (2004),
- A.W. Harris, M.C. Manning, W.M. Tearle and C.J. Tweed. Testing of Models of the Dissolution of Cements – Leaching of Synthetic CSH Gels. *Cement and Concrete Research*, 32, 731-746 (2002),
- C.S.Walker, D. Savage, M. Tyrer and K.Vala Ragnarsdottir. Non-ideal Solid Solution Aqueous Solution Modeling of Synthetic Calcium Silicon Hydrate. *Cement and Concrete Research*, 37, 502-511 (2007)
- J.W. Carey and P.C. Lichtner. Calcium Silicate Hydrate (C-S-H) Solid Solution Model Applied to Cement Degradation Using the Continuum Reactive Transport Model. In: eds Mobasher and Skalny, *Transport Properties and Concrete Quality: Materials Science of Concrete*, special edition. ISBN: 978-0-470-09733-5 (2007)
- B. Lothenbach, T. Matschei, G. Möschner and F. Glasser. Thermodynamic Modelling of the Effect of Temperature on the Hydration and Porosity of Portland Cement. *Cement and Concrete Research*, 38, 1-18 (2008)
- T. Matschei, B. Lothenbach and F. Glasser. Thermodynamic Properties of Portland Cement Hydrates in the System CaO-Al₂O₃-SiO₂-CaSO₄-CaCO₃-H₂O. *Cement and Concrete Research*, 37(10), 1379-1410 (2007)

USING THERMODYNAMIC MODELS: SALINE SYSTEMS

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Thermodynamic models of saline systems are needed to support ongoing and future nuclear waste repository concepts in salt. These models are currently being applied to support the safety case for the Waste Isolation Pilot Plant (WIPP) which is an operating TRU waste repository in bedded salt in Southeastern New Mexico (USA). Continued model development is also needed to address potential contaminant subsurface issues (*e.g.*, deep US aquifers) and evaluate the utility of future salt-based nuclear waste repository concepts (*e.g.*, Gorleben in Germany).

The brine chemistry that typifies these sites are high in ionic strength ($I = \sim 5\text{-}6\text{ M}$) and cannot be modeled using the Specific Ion Interaction Theory (SIT) approach ($I < 3.5\text{ M}$). For this reason the Pitzer formalism (see *Modeling in Aquatic Chemistry*, OECD, ISBN 92-64-15569-4), which is a semi-empirical approach, is used to model the radionuclide speciation and brine chemistry for these applications. There are relatively few Pitzer data available and existing data sets are currently very project/program-specific. Given the likely rise in importance of these high ionic strength systems in nuclear waste management, there is a need for a more systematic approach to the development and application of speciation models using the Pitzer formalism.

The WIPP project is the only repository program that has an existing Pitzer-based model that has been approved by their regulator (the US Environmental Protection Agency –EPA). This repository was first licensed in 1998, was recertified in 2006, and is in the late stages of getting a second recertification. Actinide solubility is modeled using the Fracture Matrix Transport (FMT) Pitzer-based model that uses a relatively small, but highly conservative, analog/actinide data set. The lessons learned from the experience of this repository program with its EPA regulator are:

- A simple, conservative, and defensible actinide speciation approach has worked the best.
- The use of oxidation-state analogs that conservatively bracket oxidation state distribution is accepted by the regulator.
- NEA databases, as they are released or updated, are impactful because they are recognized by the regulator and scientific community as a key source of peer-reviewed data. The database used within the WIPP project must address and justify differences when they exist.
- The regulator has a key and important role in the database selection process and once a license is in place it is relatively difficult to make substantial changes in the database.

The culmination of the experience in the WIPP project points to the importance of maintaining and developing radionuclide databases through the NEA process. In the specific case of saline systems, there remains a need for a more robust and self-consistent Pitzer database to more realistically model the high ionic-strength brine and actinide chemistry to support the safety case.

PRINCIPLES AND LIMITATIONS OF THERMODYNAMIC MODELLING OF REDOX SENSITIVE SYSTEMS

Jordi Bruno

Amphos²¹

Electron transfer processes are at the very essence of life in planet Earth and redox disequilibria is fundamental for the persistence of our (already stressed) atmosphere composition (Stumm, 1996). Many natural water systems show indications that several redox states can coexist in apparent disequilibrium and that a meaningful redox potential cannot be established for open natural water systems (Lindberg, 1984).

This is basically because electron transfer processes have slow rates in the absence of catalyst and/or microorganisms and the characteristic reaction times of heterogeneous and homogeneous multielectron transfer processes is much larger than the average residence times of the components in most natural water systems (Bruno, 1997). There has been a large amount of dedicated research to understand the role of mineral surfaces as redox catalysts and more recently the role of bacteria on mediating electron transfer processes.

Under these premises, non perturbed groundwater systems could have the right conditions for local or global redox equilibrium to occur and the combination of waste packages (particularly UO₂ spent fuel) and EBS have a large Reducing Capacity which is prone to impose buffered redox states. Under these conditions it is meaningful although difficult to measure redox potentials in site characterization and it is advisable to use the Eh as a master variable to assess the evolution of anoxic repository systems. The use of Eh as a master variable requires that the thermodynamic data for redox sensitive elements is reliable enough to build the necessary quantitative model. Most of the NEA-TDB work has indeed provided a sound basis for this but some fundamental data are missing.

Further to this the necessary modelling tools have to be properly tuned to handle the notion of local/global equilibrium and to be able to work in calculation conditions which are mathematically demanding and therefore pose some calculation problems which may hamper the use of redox equilibria in geochemical modelling.

In his presentation, Bruno gave an overview of the current state of the redox state issues, in terms of site characterization and performance assessment related modelling in order to illustrate some of the pending challenges in terms of *in situ* redox measurements, thermodynamic data and radwaste related geochemical modelling.

W. Stumm and J.J. Morgan (1997), *Aquatic Chemistry*. John Wiley and Sons.

R.D. Lindberg and D.D. Runnells (1984), *Ground water redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modelling*, *Science*. 225, p. 925-927.

J. Bruno (1997), *Trace Element Modelling*, in *Modelling in Aquatic Chemistry*, ed. I. Grenthe and I. Puigdomènech. NEA (OCDE).

RADIONUCLIDE SOLUBILITY CONTROL IN SOLID SOLUTION – AQUEOUS SOLUTION SYSTEMS

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The migration of radionuclides in the geosphere is to a large extent controlled by sorption processes onto minerals and colloids. On a molecular level, sorption phenomena involve surface complexation, ion exchange as well as co/precipitation reactions. Co-precipitation leads to the formation of structurally incorporated radionuclides in a host structure. Such solid solutions are ubiquitous in natural systems – most minerals in nature are atomistic mixtures of elements rather than pure compounds. In many cases the formation of solid solutions leads to a thermodynamically more stable situation compared to the formation of pure compounds, due to a negative excess Gibbs energy of mixing. Deriving a thermodynamic model requires a molecular level concept including information such as the actual substitution mechanism, site occupancies and related ordering phenomena (Geiger, 2001. Ganguly 2001. Bruno, 2007).

In natural systems almost all minerals are solid solutions and pure compounds are rather an exception. However, radionuclide solubility related to solid solution formation is currently not considered in long term safety aspects for a nuclear waste repository system. One reason is related to the fact that only a limited number of rather simple solid solution systems have been studied to a sufficient level. Nevertheless, the thermodynamic concepts for solid solution formation under nuclear waste repository relevant conditions are very well developed. The importance of a molecular level mixing model should be emphasized. Furthermore, analytical tools (as well as computational approaches) to identify involved species, to characterize the mixing behaviour at molecular scales and to derive thermodynamic data are available (even to work on complex solid solutions).

However, in particular with respect to the conditions of interest here, two questions are always: (1) Do measured data of the solid solution and the aqueous solution represent equilibrium conditions or do they represent a metastable situation? The challenge is to derive thermodynamic data from experiments in aqueous solution at rel. low temperatures with potentially metastable states. (2) Can thermodynamic data on solid solutions be applied to radionuclide solubility control?

Considering the available experimental data it seems reasonable to state that Ra solubility control by binary $Ba_x Ra_{1-x} SO_4$ solid solution may be applied for the long term safety assessment.

C.A. Geiger (2001), Solid solutions in silicate and oxide systems. European Mineralogical Union, Eötvös University Press, Budapest.

J. Ganguly & S.K. Saxena (2001) Mixtures and mineral reactions. Springer, Berlin

J. Bruno, D. Bosbach, D. Kulik & A. Navrotsky (2007) Preparation of guidelines for the evaluation of thermodynamic data for solid solutions: A state-of-the-art report. OECD Nuclear Energy Agency, Issy-les-Moulineaux (France)

TAKING THERMODYNAMICS TO REAL SYSTEMS

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No abstract supplied

THEORETICAL AND EXPERIMENTAL BASIS OF THERMODYNAMIC SORPTION MODELS

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The TSM approach is based on similar thermodynamic concepts to those utilised in modelling aqueous chemistry. The distinguishing feature of the TSM is the presence of surface sites, which can interact with aqueous species to form surface complexes. The representation of sorption by surface reactions makes TSMs more chemically realistic than descriptive parameters, such as the distribution coefficient.

The basic building blocks of TSMs include chemical components which combine to form aqueous species and surface species. The set of chemical components includes one or more surface sites. Each of the species is defined relative to its components by chemical equations. Mass balance constraints are applied and the activities of all species involved in reactions are related by equilibrium constants. Activity corrections of surface species are defined by reference to electrostatic equations, with a number of alternatives being available, although there is no clear consensus on the most applicable.

Key components in TSMs include surface areas and site populations, surface site hydrolysis reactions, radionuclide surface reactions and electrical double layer parameters. The choice of representations for each of these components is usually constrained by theoretical relationships and/or experimental measurements. For example, the type of surface species can be supported by the results of synchrotron extended x-ray absorption fine structure (EXAFS) analysis or by ATR-FTIR spectroscopy. The surface sites of simple minerals such as clays and oxides are relatively well understood, and their chemical properties can be incorporated in TSMs (Figs 1 and 2). In other situations, such information is unavailable and generic surface sites are employed. The ideal case for a sound experimental data base to develop a TSM is demonstrated by a case study involving the adsorption of a monoprotic acid on goethite. This example includes solution speciation, acid-base properties of the solid, adsorption data of the acid on goethite, and titration data of the acid in presence of goethite.

It is important that the purpose of the model should be well defined at the outset, and the adequacy of the model should be assessed against the modelling objectives. There are specific requirements of TSMs having a proposed application in nuclear waste disposal, which will differ from an academic or fundamental sorption model. It is unlikely to be feasible, or necessary, to constrain a real-world TSM to the same degree as a model of a simple laboratory system. We present some criteria by which TSMs could be assessed, in terms of their ability to simulate experimental data, traceability, number of adjustable parameters, appropriate level of complexity, and internal consistency.

The Third Phase of the NEA sorption project has enabled a greater consensus between experts on how to develop TSMs, with conclusions reflected in the draft report. In addition, the discussions have led to a detailed examination of some important fundamental issues (for example, an investigation of the thermodynamically consistent handling of multi-dentate surface complexes). The conclusions of these studies will be reported in subsidiary publications in the open literature, which will be referenced by the final report.

Figure1: Different coordination of hydroxyl groups on the surface of goethite

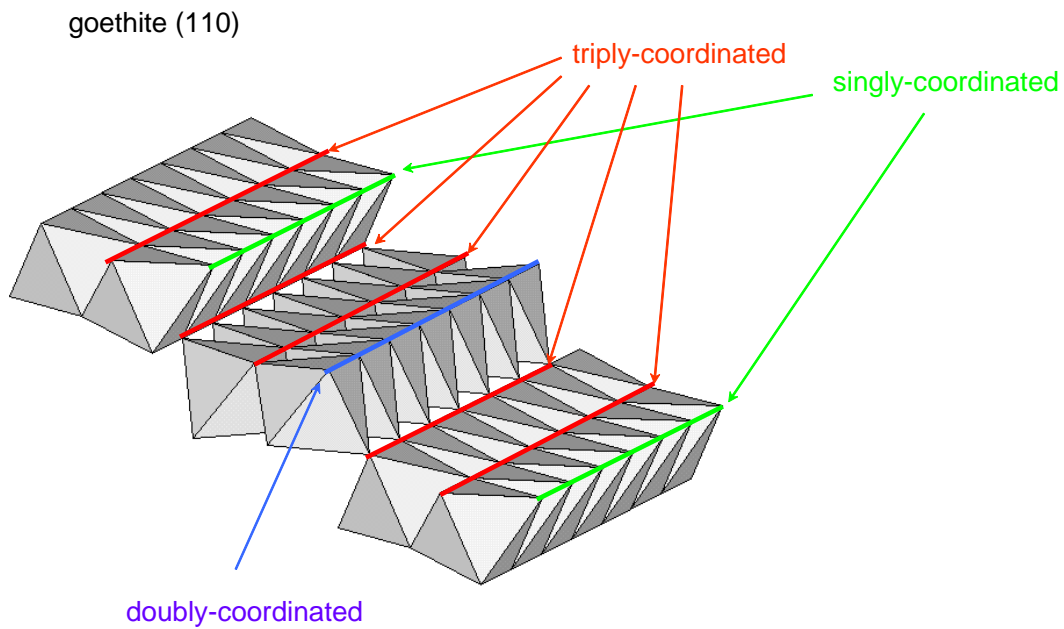
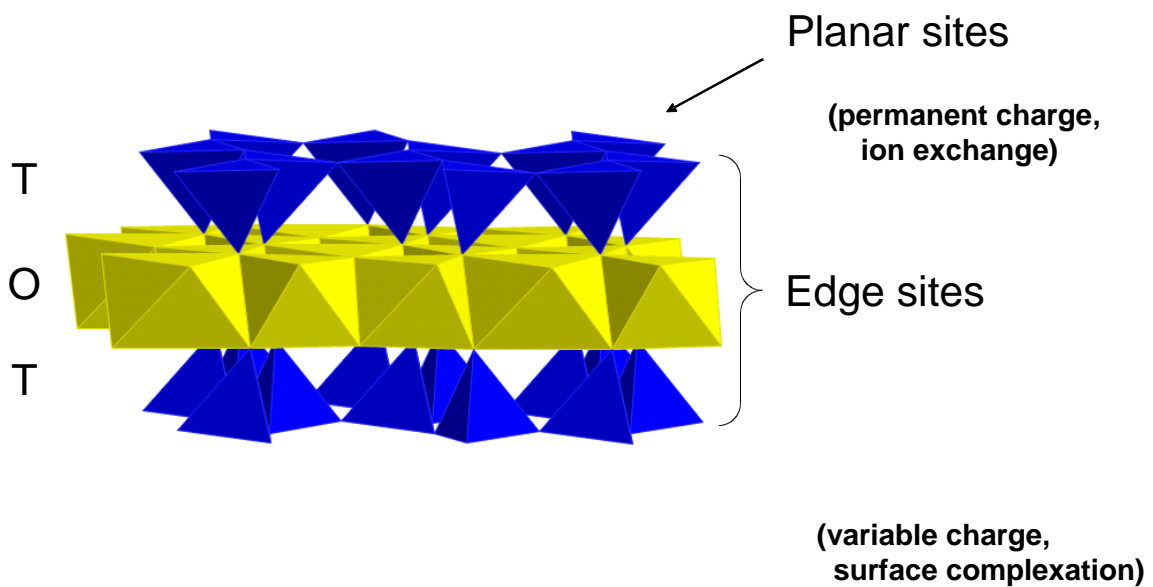


Figure 2: Surface sites on a clay mineral



APPLICATIONS OF THERMODYNAMIC SORPTION MODELS (TSMs) TO REAL SUBSTRATES

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The usefulness of TSMs in the context of radioactive waste disposal is tied to the ability to predict radionuclide sorption by 'real' materials of direct relevance to disposal scenarios. In comparison to single minerals, these materials have a greater degree of chemical complexity that originates from the presence of several solid phases in a given substrate. Additional complexity may arise from non-additivity of the sorption contributions of individual components and from physical effects related to the compacted nature of the substrates.

Real substrates often pose a challenge not only to sorption modelling but also to the determination of the various fundamentals underlying any TSM, such as difficulties in the identification/characterisation of solid phases and solution composition. While outside the scope of actual sorption modelling, the use of TSMs in the context of complex intact substrates also requires careful delineation of representative volume elements for sampling, model parameterisation and model application. Important aspects of chemical and physical complexity can be illustrated using examples from complex mineral assemblages and compacted clays:

The sorption-relevant solids in **compacted clays** typically are well defined components whose contribution to overall sorption can be modelled in an additive way. On the other hand, the porespace of clay rocks and especially of compacted bentonite is not directly accessible to experimental investigations. The solution composition underlying any TSM application therefore has to be modelled itself, *e.g.* by basic TSMs (including ion exchange and surface protolysis) in combination with model concepts of elementary pore characteristics. A fundamental issue related to the justification of TSM applications to compacted clays is the question whether the electrostatic effects in the narrow porespace allow the straightforward application of TSM parameters obtained in disperse systems. Several lines of support (direct sorption measurements on compacted material and indirect evidence from diffusion experiments) are suggesting that this is indeed feasible.

For far-field applications, the best approach may require the collection of field-relevant **sediments or rock samples**. An example modeling and transport prediction study of uranium(VI) migration at Naturita, CO (USA) is described. Sorption was studied in batch as a function of pH and U(VI) and dissolved carbonate concentrations in artificial groundwater solution. The major minerals in the sediments were quartz, feldspars, and calcite. Chemical extractions of quartz grains removed from the sediments were used to estimate the compositions of minerals in grain coatings. Various TSMs were compared in terms of modeling capability and data requirements. Predictions of component additivity models were variable, generally over- or under-predicting experimental data. The results suggested that uncertainties in the predictions are caused primarily by poor knowledge of: 1) the proportion and types of surface functional groups available for sorption in grain coatings, 2) the electric field at the interface, and 3) surface reactions of major ions in the aqueous phase, such as Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , H_4SiO_4 , and organic acids. In contrast, a semi-mechanistic surface complexation modeling approach can be used to describe the data

more precisely. This approach was useful as a tool to describe U(VI) in field-scale reactive transport simulations.

IMPACT OF MODEL CHOICES AND PARAMETER UNCERTAINTY ON K_D REPRESENTATION

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Thermodynamic sorption models (TSM) in the framework of performance assessment for nuclear waste repositories are rather complex models, fed by a large pool of data. Thus, a detailed understanding of magnitudes, reasons, effects and internal relationships of uncertainties is crucial. Here, answers are provided to the question “How do modeling choices (conceptual variability) and uncertainties in model parameters translate into K_D uncertainties?” The two most evident benefits from answering this question are:

- It becomes possible to identify key parameters (model features) to allocate further efforts to reduce uncertainties in an efficient way.
- Strategies emerge to investigate the effects of different TSMs on the computed K_D values: whether they are significant and how they depend on the TSM choice.

The talk covers two types of uncertainties (model uncertainty as well as parameter uncertainty), see Fig. 1 for the different origins of uncertainty. They span a very wide range: analytical errors, sampling errors, container wall adsorption, drifts of temperature, pH or EH. Whereas these uncertainties can be quantified to a certain degree, others such as inadequate use of analytical methods, undiscovered phase alterations and precipitation of secondary phases, or contaminations, may provide errors of unknown magnitude. Uncertain parameters can be grouped as follows:

a) TSM inherent parameters

- mineral specific values (specific surface area SSA, surface site densities SSD, protolysis constants of the binding sites pK, capacitance C, point of zero charge PZC)
- surface complex formation constants, log K
- formation constants (log K) for all reactions in aqueous solution

b) data characterizing the geochemical environment

- solid-liquid ratio / porosity (SLR)
- aqueous phase composition and concentrations (most important: complexing ligands and ions competing for surface binding sites)
- gas phase partial pressures
- pH, redox potential, E_H , temperature, T

Several representative test cases were elaborated within the NEA Sorption Project to investigate the impact of TSM parameter vs. geochemical uncertainties. They are explained and their parameterization is presented. This involves the following (geo)chemical systems:

- Np(V) sorption onto hematite (1-site, 2pK DDLM)
- Se(IV/VI) sorption onto goethite (1-site, 2pK DDLM)
- Co(II) sorption onto kaolinite (2-site, 2pK CCM)

The input parameters identified to be most sensitive are presented, together with an uncertainty analysis. The effect of the choice of the experimental data on the resulting parameters of a predefined

adsorption model and on the goodness of fit parameters was evaluated. Another important issue is the effect of parameter correlation. It is illustrated by another example, see Fig. 2 for results.

Finally, the various decisions creating model uncertainty and their consequences with regard to K_D computations are presented

Figure 1: Schematic representation of sources of uncertainty.

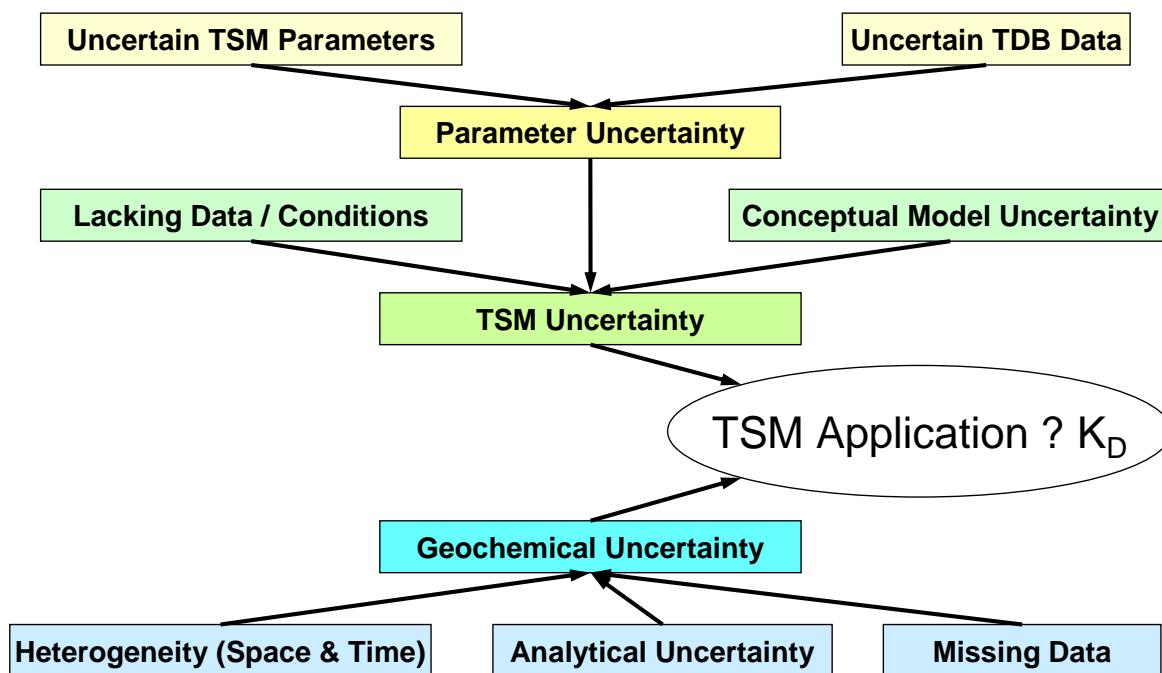
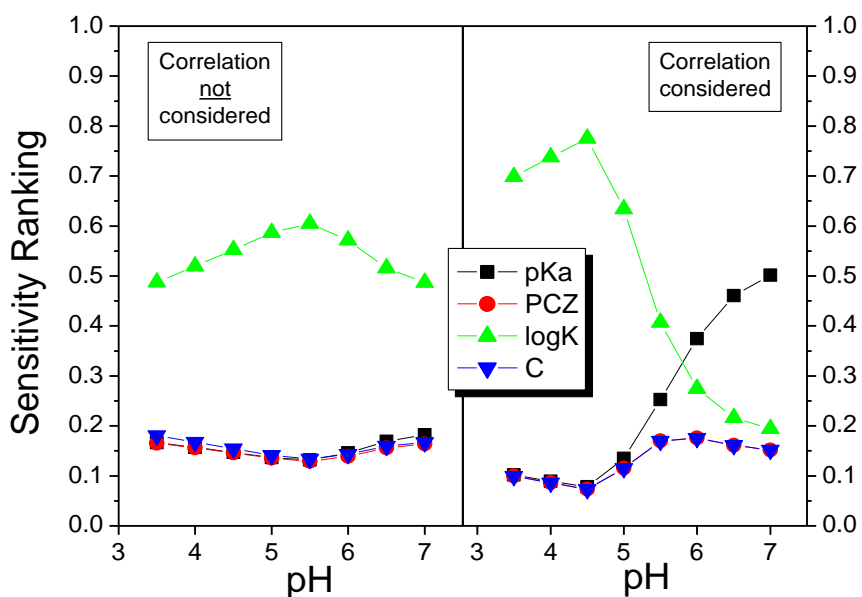


Figure 2: Normalized ranking of the sensitivity of input parameters as a function of pH, ignoring the internal parameter correlation (left part) and explicitly taking it into account (right part).



HOW THERMODYNAMICS UNDERPINS A SAFETY CASE

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The safe management of radioactive waste has been widely discussed, and agreements on how to treat and dispose of radioactive waste have been reached at an international level (IAEA, 2006). The aim of geological disposal is to isolate the waste from the biosphere. Since total isolation over extended timescales is not possible, radionuclides will eventually be released from the waste matrix and migrate through the engineered and natural barriers. The safety case is an overall evaluation of the long-term safety of a closed geological repository. The assessment of radionuclide mobility in the engineered and natural barriers is essential for the safety case.

Water is the main transport medium for the radionuclides. In backfills and host rocks of low permeabilities, diffusion may be the dominating transport mechanism. Slow dissolution of the waste matrix causes the concentration of many radionuclides to increase until their solubility limit is reached. The stable solid phase will precipitate thus limiting the quantity of the radionuclide which can migrate through the backfill. Solubility limitation is one of the retardation processes which may significantly contribute to the confinement of the radionuclides in the repository. Solubility limits are usually predicted from the chemical composition of the relevant aqueous solution by using a chemical thermodynamic database.

Another chemical retardation process is adsorption, which can take place by ion-exchange or surface complexation. Surface complexation of cations is a process analogous to hydrolysis in aqueous solution, while surface complexation of anions takes place by ligand exchange, *i.e.*, by the exchange of a surface hydroxyl group by the sorbing anion. Surface complexation is strongly dependent on pH. Adsorption is usually determined experimentally in batch experiments simulating “realistic” conditions, or by measuring sorption isotherms (sorption as a function of radionuclide concentration) or sorption edges (sorption as a function of pH). For the interpretation and evaluation of experimental sorption data it is essential to know the speciation of the radionuclide in the solution, which is – like solubility limits – calculated from the chemical composition of the aqueous solution by using a chemical thermodynamic database.

The chemical thermodynamic databases required to calculate maximum solubilities of radionuclides and to interpret sorption data need to include “complete” equilibrium data sets. Gaps in the thermodynamic databases may lead to erroneous predictions. The international NEA-TDB project (Mompeán, 2003) provides high-quality data sets which focus on the requirements of radioactive waste disposal and refer to a common reference state. These critically evaluated data sets are based on experimental data only; data of poor quality and predicted data are not taken into account. A drawback of this high-quality claim is that equilibrium constants of complexes which are poorly investigated, such as complexes with important naturally occurring ligands such as silicates and phosphates, are often missing in the NEA-TDB database. The same is true for ternary species such as hydroxo-carbonato complexes, which are often known or expected to exist, but whose stability constants are unknown. While the NEA-TDB has a great merit of providing high-quality data sets, specific applications will require careful examination of potential gaps in the data sets. In some cases, it may be advisable to predict missing data in order to fill such gaps. Such “in-house” complementation of the NEA-TDB should be undertaken with care and with special attention to the maintenance of internal consistency and to the compatibility with experimental observations. Several “national” or “in-house” databases are under development or exist already, *e.g.*, (Hummel, 2002).

Missing data and insufficient knowledge of the solubility-limiting processes increase the uncertainties and require pessimistic assumptions in the safety analysis. Using analogies may be acceptable in some cases, but care has to be taken. From a performance assessment perspective, pessimistic assumptions are usually not detrimental to safety owing to the robustness of the multibarrier approach. However, a certain understanding of the radionuclide chemical and migration processes is required for generating confidence in the use of laboratory data in the safety case. The understanding of these processes also helps to assess the evolution of the multibarrier systems with time (*e.g.* high pH-plume, carbonation, salt or fresh water ingress).

IAEA (2006), *Geological Disposal of Radioactive Waste*, IAEA Safety Standards, Safety requirements No. WS-R-4, International Atomic Energy Agency, Vienna

F. Mompeán (2003), H. Wanner. *Radiochim. Acta* **91**, 617.

W. Hummel, U. Berner, E. Curti, F. J. Pearson, T. Thönen (2002), *Nagra/PSI Chemical Thermodynamic Data Base 01/01*, Universal Publishers, New York (*Update completed, to be published.*)

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