Data Bank

OECD

The Use of Thermodynamic Databases in Performance Assessment

Workshop Proceedings
Barcelona, Spain
29-30 May 2001

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Hosted by
ENRESA

NUCLEAR ENERGY AGENCY
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

Pursuant to Article 1 of the Convention signed in Paris on 14th December 1960, and which came into force on 30th September 1961, the Organisation for Economic Co-operation and Development (OECD) shall promote policies designed:

- to achieve the highest sustainable economic growth and employment and a rising standard of living in Member countries, while maintaining financial stability, and thus to contribute to the development of the world economy;
- to contribute to sound economic expansion in Member as well as non-member countries in the process of economic development; and
- to contribute to the expansion of world trade on a multilateral, non-discriminatory basis in accordance with international obligations.

The original Member countries of the OECD are Austria, Belgium, Canada, Denmark, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, the Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, Turkey, the United Kingdom and the United States. The following countries became Members subsequently through accession at the dates indicated hereafter: Japan (28th April 1964), Finland (28th January 1969), Australia (7th June 1971), New Zealand (29th May 1973), Mexico (18th May 1994), the Czech Republic (21st December 1995), Hungary (7th May 1996), Poland (22nd November 1996), Korea (12th December 1996) and the Slovak Republic (14 December 2000). The Commission of the European Communities takes part in the work of the OECD (Article 13 of the OECD Convention).

NUCLEAR ENERGY AGENCY

The OECD Nuclear Energy Agency (NEA) was established on 1st February 1958 under the name of the OEEC European Nuclear Energy Agency. It received its present designation on 20th April 1972, when Japan became its first non-European full Member. NEA membership today consists of 28 OECD Member countries: Australia, Austria, Belgium, Canada, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Japan, Luxembourg, Mexico, the Netherlands, Norway, Portugal, Republic of Korea, Slovak Republic, Spain, Sweden, Switzerland, Turkey, the United Kingdom and the United States. The Commission of the European Communities also takes part in the work of the Agency.

The mission of the NEA is:

- to assist its Member countries in maintaining and further developing, through international co-operation, the scientific, technological and legal bases required for a safe, environmentally friendly and economical use of nuclear energy for peaceful purposes, as well as
- to provide authoritative assessments and to forge common understandings on key issues, as input to government decisions on nuclear energy policy and to broader OECD policy analyses in areas such as energy and sustainable development.

Specific areas of competence of the NEA include safety and regulation of nuclear activities, radioactive waste management, radiological protection, nuclear science, economic and technical analyses of the nuclear fuel cycle, nuclear law and liability, and public information. The NEA Data Bank provides nuclear data and computer program services for participating countries.

In these and related tasks, the NEA works in close collaboration with the International Atomic Energy Agency in Vienna, with which it has a Co-operation Agreement, as well as with other international organisations in the nuclear field.

FOREWORD

For the past ten years, the OECD Nuclear Energy Agency has been co-ordinating a multinational effort to produce a database of selected thermochemical values for elements of interest in the geological disposal of long-lived radioactive waste. This project is known as the NEA Thermochemical Database (TDB) Project and has produced high-quality, critically reviewed thermodynamic data for the inorganic species (and species with some selected organic ligands) of several elements including U, Np, Pu, Am, Tc, Se, Ni and Zr.

Both deterministic and probabilistic performance assessment (PA) exercises rely on the availability of such qualified thermodynamic data for many radionuclides under the varying physico-chemical conditions of radioactive waste repositories. Two of the major obstacles found in the PA process had been identified as the lack of experimental thermodynamic information for some chemical systems and the limited awareness in part of the scientific community of the precise thermodynamic database requirements for PA applications.

Hence, the objective of this workshop was to provide a professional forum in which PA experts (as users of thermodynamic databases) and scientists involved in the field of chemical thermodynamics could come together to further discuss the thermodynamic data requirements and applications for PA with a view to helping define future activities of the NEA TDB Project.

The workshop, held on 29-30 May 2001 at the *Universitat Politècnica de Catalunya* in Barcelona (Spain), was attended by approximately 50 participants from both OECD Member and non-member countries, with mixed representation from the fields of PA and chemical thermodynamics.

These proceedings contain the full papers delivered by invited speakers as well as summary records of the session discussions. Dr Jörg Hadermann, from Paul Scherrer Institute (Switzerland), kindly agreed to moderate the special panel session held at the end of the workshop. The recorded transcript of the discussion periods and panel session was prepared by the local organising committee (see Annex 2) and edited by the NEA Secretariat.

The opinions and conclusions expressed in these proceedings are those of the authors only and do not necessarily reflect the views of the organisations participating in the NEA TDB Phase II Project or the OECD Member countries concerned.

Acknowledgements

The organisation of the workshop and the preparation of the proceedings have benefited from the support from the following organisations, in the framework of the NEA TDB Phase II Project:

ANSTO, Australia	SKB, Sweden
NIRAS/ONDRAF, Belgium	SKI, Sweden
RAWRA, Czech Republic	HSK, Switzerland
POSIVA, Finland	NAGRA, Switzerland
ANDRA, France	PSI, Switzerland
IPSN, France	BNFL, United Kingdom
FZK, Germany	NIREX, United Kingdom
PNC, Japan	DoE, USA
ENRESA, Spain	

The NEA wishes to further thank ENRESA along with QuantiSci, S.L. and the Universitat Politècnica de Catalunya for their specific contributions and support to the local organisation of the workshop.

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EXECUTIVE SUMMARY

The "Workshop on the use of Thermodynamical Databases in Performance Assessment", hosted by ENRESA, was held in Barcelona, Spain on 29-30 May 2001 with 46 participants from 12 countries. The workshop emerged as a direct result of current activities in the framework of the OECD NEA Thermochemical Database Project (NEA TDB) which aims at providing basic chemical thermodynamic data for the modelling requirements for the safety assessment of radioactive waste disposal systems.

There were 16 oral presentations from invited speakers and a special panel session, all followed by general discussions also contained in these proceedings, which is divided into four plenary sessions:

- Session I: The TDB Project
- Session II: Building the Bridges: Data to Performance Assessment (PA)
- Session III: Performance Assessment
- Panel Session: TDB Input in Performance Assessment

Session I comprised presentations dealing with the origins, past and present organisation and status of the NEA TDB Project, the main scientific achievements during both Phase I and Phase II of the project and feedback from the use of Phase I thermodynamic compilations.

Session II was devoted to a thorough presentation of the scientific methodology employed in the critical review and database compilation exercises, such as NEA TDB. To this purpose, in a first sub-session (*Ionic Strength – Theory, Use, Cautions, Sources of Error*) the basic solution thermodynamic tools for the reduction of data to a common standard state were presented in detail. In a second sub-session (*Data Estimation*) methods available to estimate – when experimental data is incomplete or not available – thermodynamic magnitudes for various types of systems were presented, together with the programme of work and study cases contemplated in a major EU-funded research project on the chemical thermodynamics of actinides.

Session III was divided also in two sub-sessions dealing respectively with the *Applications and Limitations of Using Thermodynamic Data in PA*, where presentations focused on the problems that are posed when the actual physico-chemical conditions found in repositories need to be described from the limited existing databases, and *How does Performance Assessment Use the Data?*, where examples extracted from three particular PA exercises (using probabilistic and deterministic approaches) were presented.

The last session of the workshop took the form of a panel discussion during which the main aspects of the preceding sessions were summarised by the panel members and emphasis was placed on gathering the opinions of all the workshop participants on the topics that, from the current PA standpoint, should be contemplated in a subsequent phase of the NEA TDB Project.

An important characteristic common to discussions held throughout the workshop was the active participation in nearly all the debates of experts from the two communities: those closer to the experimental determination of thermochemical data and those closer to their application in PA. This joint debate is a significant progress in bringing together the two communities and therefore in fulfilling the objective of the workshop.

OPENING SESSION

WELCOME SPEECH

Antoni Marí
Vice-rector in Charge of Research
Universitat Politècnica de Catalunya

Professor Marí welcomed all the participants to the university with a brief speech in which he highlighted the role played by international collaborative projects in the life of academic and research establishments and wished everyone a successful and productive stay in Barcelona.

WELCOME ADDRESS ON BEHALF OF THE OECD/NEA

Claes Nordborg
Head, Nuclear Science Division
OECD Nuclear Energy Agency

Ladies and Gentlemen,

It is a great pleasure for me to welcome you, on behalf of the OECD Nuclear Energy Agency (NEA), to this workshop on “The Use of Thermodynamic Databases in Performance Assessment”. I am pleased to say that this is a welcome, not only from one division within NEA, which is often the case at NEA organised workshops, but from two of the five NEA divisions. The Thermochemical Data Base (TDB) Project is one of the first established cross-cutting activities within our agency and it has served as a model for other later projects, such as the NEA Sorption Project. The TDB project is well established within the NEA and has had, for many years, full support from all the committees and steering groups concerned.

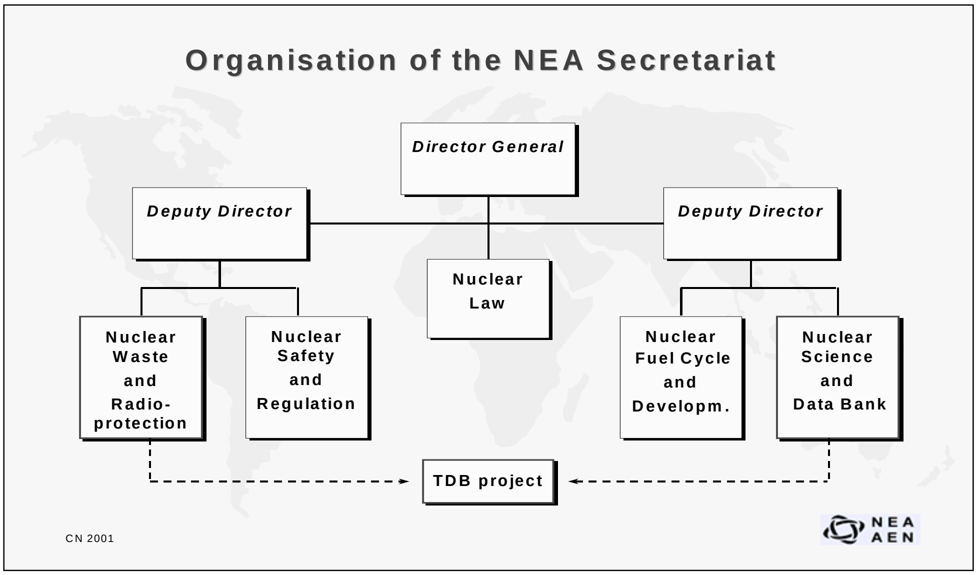
I am not going to describe the TDB Project in this short talk, as you will hear all about it later this morning. Instead I would like to give you a quick overview of how the project fits into the NEA structure and what we expect from the outcome of this meeting.

For those of you who are not familiar with the NEA organisation, I can show you here a very simplified chart of the different divisions (Figure 1). This chart shows that the TDB project does not really belong to any one of the divisions, but is a semi-autonomous project, which receives scientific guidance from the NEA Radioactive Waste Management section. The Data Bank acts as project co-ordinator and is responsible for the day-to-day work and the maintenance and update of the thermochemical database. The Data Bank has one staff member working full time for the TDB project. This person, Federico Mompean, is here today and he is one of the individuals who will be speaking about the TDB project later this morning.

The workshop today and tomorrow is of particular interest to us in the NEA for two main reasons. First of all, we are just now in a phase of the TDB Project where we need guidance for our future programme of work. In addition, we have always stated that the goal of the TDB Project is to provide internationally recognised thermodynamic data for the safety assessment of geological waste disposal sites. It is to ensure that this statement is really true and also, as mentioned, to receive some guidance about future work that this workshop is organised. The idea is thus to have users and producers of chemical thermodynamic data come together and discuss both data needs in performance assessment and possibilities to fulfil these needs.

Due to other commitments, I will unfortunately not be able to remain for the whole of the workshop. However, I will be extremely interested to learn, later this week, about the outcome of your discussions. I especially hope that the panel session at the end of the workshop will bring some interesting and constructive ideas for future work within the TDB project.

Figure 1. Simplified chart of NEA divisions



In closing my short talk, I would first of all like to thank our hosts ENRESA, for their excellent organisation and preparation of this meeting. I will take this opportunity to express our regret for the extra work we imposed on the hosts, by postponing the meeting about six months from its original schedule.

I would also like to thank the organising committee for all the work they devoted to the arrangement of this workshop and especially our local hosts, the Technical University of Catalonia and Jordi Bruno, who will ensure that you will have a good meeting and a very enjoyable stay here in Barcelona.

I wish you all a very interesting and productive workshop and I thank you for your attention.

WELCOME ADDRESS ON BEHALF OF THE MANAGEMENT BOARD OF THE TDB PROJECT

Mehdi Askarieh
Chairman of the OECD/NEA TDB Phase II Management Board
Nirex Ltd, Curie Avenue, Harwell, Oxfordshire, OX11 0RH, UK

Dear Colleagues,

On behalf of the organisations represented in the Management Board of the OECD/NEA Thermochemical Database Project Phase II (TDB-II), I would like to welcome you to this workshop.

The present phase of the NEA TDB Project was started in 1998 to continue the activities launched by the Radioactive Waste Management Committee of the NEA with two primary aims:

- to make available a comprehensive, internationally recognised and quality-assured thermodynamical database that will meet the specialised modelling requirements for safety assessments of radioactive waste disposal systems;
- to improve the exchange of information and communication on chemical thermodynamic data amongst the OECD/NEA Member countries.

For the next two days we are going to have the opportunity to contribute to achieving these two aims by addressing a specific topic: the use of the data contained in the thermochemical compilations, with particular attention to those selected in the NEA TDB critical reviews.

We shall have sessions in which the scientific framework for data selection will be presented and discussed. We shall move later on to specific examples of the use of this data in performance assessment and to the problems that can arise at this stage. The two communities that participate in this aspect of radioactive waste management (those working in the chemical laboratories and those responsible for the modelling of the repository concepts) will therefore have the opportunity to jointly discuss their research potential and specific needs. A final panel session has been contemplated for this purpose.

I would like to encourage your active participation in the workshop. It will constitute a very valuable feedback to those working on thermochemical databases and, more specifically, will be instrumental in orienting the future activities of the OECD/NEA TDB Project.

Many thanks for your attention and I wish you a successful workshop.

WELCOME ADDRESS ON BEHALF OF ENRESA

Julio Astudillo
Head of the R&D Department
ENRESA

Dear Colleagues,

It is a pleasure for ENRESA to welcome you to this TDB workshop of the NEA in which ENRESA, together with other Spanish organisations, has collaborated since its conception.

From the point of view of the radioactive waste management agencies, the work to be developed within the TDB project is of outstanding importance in order to be able to obtain not only a more realistic knowledge of the thermodynamic properties of the main radionuclides included in high-level wastes, but also and even more important, to dispose of reliable and contrasted data that can be applied, both in the research of the long-term behaviour of high-activity wastes and in performance assessment.

The OECD/NEA Data Bank has been making great efforts in this respect, and it is the ENRESA intention to collaborate in this field, in which the harmonisation and comparison of data must contribute with strength to the proposed analyses of each one of the user organisations.

We expect that the workshop will fulfil its established objectives and we also want to thank UPC-QUANTISCI for their efforts concerning the organisation of this workshop, joining scientific activities with the enjoyment of a great city like Barcelona.

Thank you very much and enjoy the workshop.

SESSION I

The TDB Project

Chair: M. Askarieh

OVERVIEW OF WORK AT THE OECD/NEA DATA BANK FOR THE TDB PROJECT

Federico Mompean
TDB Project Supervisor
OECD/NEA Data Bank

The NEA TDB Project aims at making available a comprehensive, internally consistent and quality-assured chemical thermodynamic database of selected chemical elements in order to meet the specialised modelling requirements for safety assessments of radioactive waste disposal systems. The project was initiated by the NEA in 1984 and reorganised in 1998. During the period 1984-1998 (TDB Project Phase I, TDB-I), reviews on the chemical thermodynamics for the following elements were completed: U [1], Am [2] and Tc [3]. A further review originating from TDB-I and dealing with data for Np and Pu appeared in print in May 2001 [4]. Although not strictly a part of TDB-I, a further collective publication of OECD/NEA [5] is a much-cited reference in the field of aquatic chemistry.

The second phase of the TDB Project (TDB Project Phase II, TDB-II) was started in 1998 following an agreement between the following Participating Organisations ("participants"):

- ANSTO (Australia);
- NIRAS/ONDRAF (Belgium);
- RAWRA (Czech Republic);
- POSIVA (Finland);
- ANDRA and IPSN (France);
- FZK (Germany);
- PNC (Japan);
- ENRESA (Spain);
- SKB and SKI (Sweden);
- HSK, NAGRA and PSI (Switzerland);
- BNFL and NIREX (UK);
- DOE (USA).

These funding organisations integrate the Management Board of the project. For technical matters, the Management Board is assisted by an Executive Group.

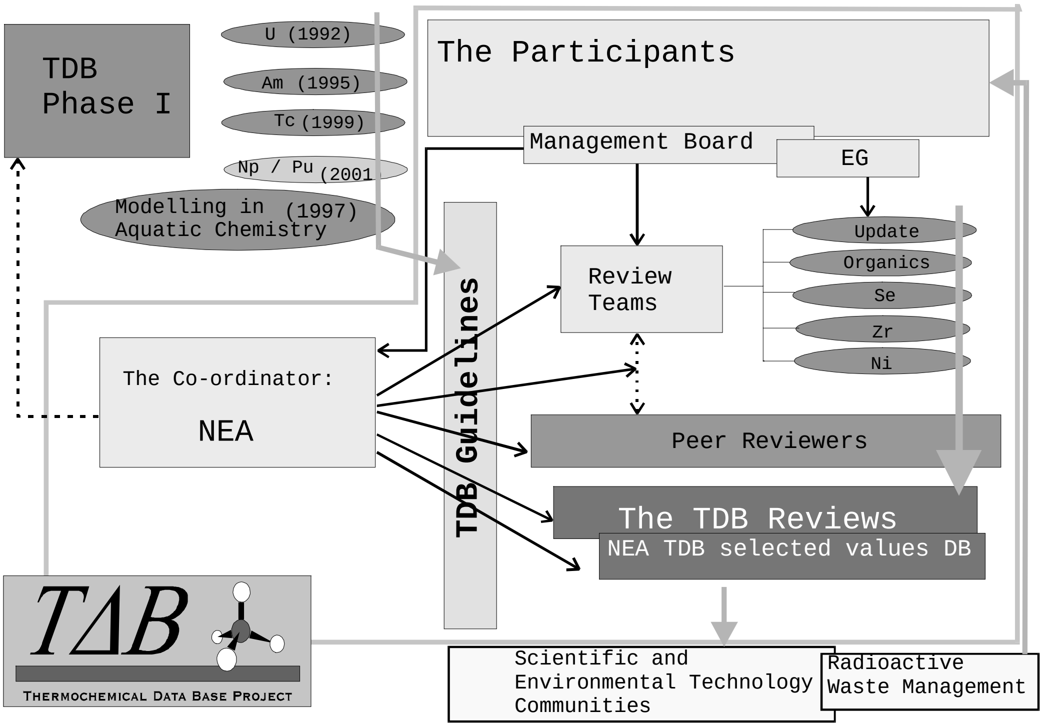
The NEA acts during this second phase as Project Co-ordinator, implementing the work programme according to the TDB Guidelines, which accrue the experience gained in the previous phase of the project and constitute one of the pillars of the quality assurance of the NEA TDB Database.

The TDB-II Agreement was initially concluded for a three-year period but, following its provisions, it was recently been renewed until the end of 2002 in order to accommodate changes in the time schedule of the Review Teams.

Figure 1 illustrates the relations between the different agents in the NEA TDB Project.

Figure 1. Organisation of the NEA TDB Project

The current phase of the project benefits from the past experience during TDB Phase I and is funded by the Participating Organisations. The NEA assumes the role of Co-ordinator, implementing the programme of work decided by the TDB Phase II Management Board.



The NEA TDB Phase II Review Teams

One of the responsibilities of the NEA, as Project Co-ordinator, is the nomination of the TDB-II Review Teams and day-to-day follow up of their work. For TDB-II, the following reviews were considered by the TDB Management Board as priority issues:

- update on the chemical thermodynamics of the inorganic species for the elements dealt with in Phase I (U, Am, Tc, Np, Pu);

- chemical thermodynamics of inorganic species of Ni;

- chemical thermodynamics of inorganic species of Se;
- chemical thermodynamics of inorganic species of Zr;
- chemical thermodynamics of species comprising all the above elements co-ordinated with selected organic ligands (EDTA, isosaccharinic acid, oxalate and citrate).

Accordingly, five Review Teams were constituted during 1999 and are integrated by 25 experts of international reputation in the field of chemical thermodynamics from both OECD and non-OECD countries.

The TDB-II Review Teams perform their work by critically reviewing the scientific literature and when necessary by re-evaluating the published data according to common standards. These standards and other procedures followed in the TDB Project are detailed in the TDB Guidelines, which are available for public consultation on the TDB Project web pages (http://www.nea.fr/html/dbtdb). The Guidelines also specify the rules for the assignment of the uncertainties of the thermodynamic data.

An essential characteristic of the data contained in the NEA TDB Reviews is the final stage of "peer review" of the manuscripts prepared by the Review Teams. This peer review is performed by independent experts from the scientific community, nominated by the NEA, who follow a detailed documented procedure to revise the Review Team work. The final publication of the reviews is conditioned to the satisfactory response to all comments and criticism raised by the peer reviewers.

Further roles of the NEA as TDB Phase II Project Co-ordinator

The NEA Data Bank makes a further effort to collect and preserve all information and data relevant to the project. One of its major assets is a compilation of nearly 10 000 scientific and technical documents extracted from the scientific literature in the field of chemical thermodynamics through the combined efforts of the TDB Reviewers and the NEA Data Bank staff.

A substantial effort is required to ensure the timely publication of the reviews in the public scientific literature. The NEA Data Bank co-ordinates to this purpose:

- the edition of the drafts prepared by the reviewers;
- the organisation of the peer review process;
- the compilation of the TDB bibliographical database;
- the maintenance and development of the selected values database and associated scientific software.

Status of the TDB Phase II Reviews

During 2000, the TDB Review Team on the update for U, Am, Np, Pu and Tc and the Review Team dealing with organic ligands have completed a major part of their work. The Review Team on dealing with the update has revised all the new literature which has appeared since the publication of the reviews for the corresponding elements during TDB Phase I. Both teams will therefore be ready to submit their manuscripts for peer review during 2001, with an estimated date of publication in 2002.

Literature review work has been the major task of the Review Teams on Ni, Se and Zr during 2000 and it is foreseen that 2001 will be devoted to the draft review preparation, aiming at publication late in 2002.

Acknowledgements

The present status of the NEA TDB Project Phase II has benefited from the work at the NEA of Erik Östhols and Stina Lundberg.

REFERENCES

[1] 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).

[2] R.J. Silva, G. Bidoglio, M.H. Rand, P.B. Robouch, H. Wanner, I. Puigdomènech, "Chemical Thermodynamics of Americium", Elsevier Science Publishers B.V., Amsterdam (1995).

[3] J.A. Rard, M.H. Rand, G. Anderegg, H. Wanner, "Chemical Thermodynamics of Technetium", Elsevier Science B.V., Amsterdam (1999).

[4] R.J. Lemire, J. Fuger, H. Nitsche, P. 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 B.V., Amsterdam (2001).

[5] 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).

THE TDB STORY

Hans Wanner
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CH-5232 Villigen-HSK, Switzerland

The initiator of the NEA TDB project was Anthony Muller. He came from Sandia and was employed at the NEA Division of Radiation Protection and Radioactive Waste Management from 1983 to 1986. He was aware that the radioactive waste management community needed a high-quality thermodynamic database that is focused on the particular needs of this community. At that time, some critically reviewed and widely used databases did exist: The Critical Stability Constants by Smith and Martell (1974-1977), the NBS Tables of Chemical Thermodynamic Properties (1982) and the IAEA project on Chemical Thermodynamics of the Actinides (10 volumes appeared between 1976 and 1992, four volumes were not published, among which the volume on the actinide oxides). However, none of them presents sufficiently comprehensive data sets for the needs of radioactive waste management. Anthony Muller was very talented in convincing people. He thus succeeded to persuade the Radioactive Waste Management Committee of the NEA of the need to start such an international effort. He defined ten key elements (U, Np, Pu, Am, Tc, Cs, Sr, Ra, I, Pb) and set up expert teams for each element. However, he greatly underestimated the effort needed for such a critical review, and he announced a timetable that promised the review reports of all ten elements within a total duration of two to three years. This unrealistic estimate put us and the TDB project into serious trouble in the late 1980s.

The writer of the present article was in charge of the TDB project from 1986 to 1992. He was employed at the NEA Data Bank, which is a scientific environment with similar projects in the nuclear data field. In order to build a quality assurance framework, the development of procedures for the treatment and selection of data was started, which resulted in the following guidelines:

- TDB-0 – The NEA Thermochemical Data Base Project (overview)
- TDB-1 – Guidelines for the Review Procedure and Data Selection
- TDB-2 – Guidelines for the Extrapolation to Zero Ionic Strength (SIT)
- TDB-3 – Guidelines for the Assignment of Uncertainties
- TDB-4 – Temperature Corrections to Thermodynamic Data and Enthalpy Calculations
- TDB-5 – Standards and Conventions for TDB Publications
- TDB-6 – Guidelines for the Independent Peer Review of TDB Reports

All these guidelines are available as PDF files on the Internet. These procedures uniformed the extrapolation to zero ionic strength (SIT), the rationale in assigning uncertainties, the weighting of the data in the SIT procedure, the treatment of inconsistent data, and it gave instructions on symbols and terminology, as well as on the correction from molarity to molality (used by SIT) and from the 1 atm to the 1 bar standard state.

In addition, some important decisions were taken in the early course of the project:

- All accepted data are based on experiments.
- All selected data refer to 25°C, 1 bar and $I = 0$.
- All selected data are provided with uncertainties (95% confidence level, including systematic errors).
- CODATA Key Values are used as auxiliary data.
- Further auxiliary data are selected according to the TDB procedures.
- Total transparency in the judgement of the literature and in the data selection is required.

The NEA arranged for agreements with various national organisations which guaranteed financial support of the reviewers, which is the standard way OECD projects work. However, the main reason for slow progress was the limited availability of the reviewers. In view of the considerably larger effort and slower progress than anticipated, it was decided to focus on the five elements U, Np, Pu, Am and Tc, and to start on new elements only when these five are close to completion.

In 1989, a first draft of the uranium review was disseminated in 200 copies. Some data have been revised or deleted between this draft and the final book published in 1992, and unfortunately several databases still contain some of the old data.

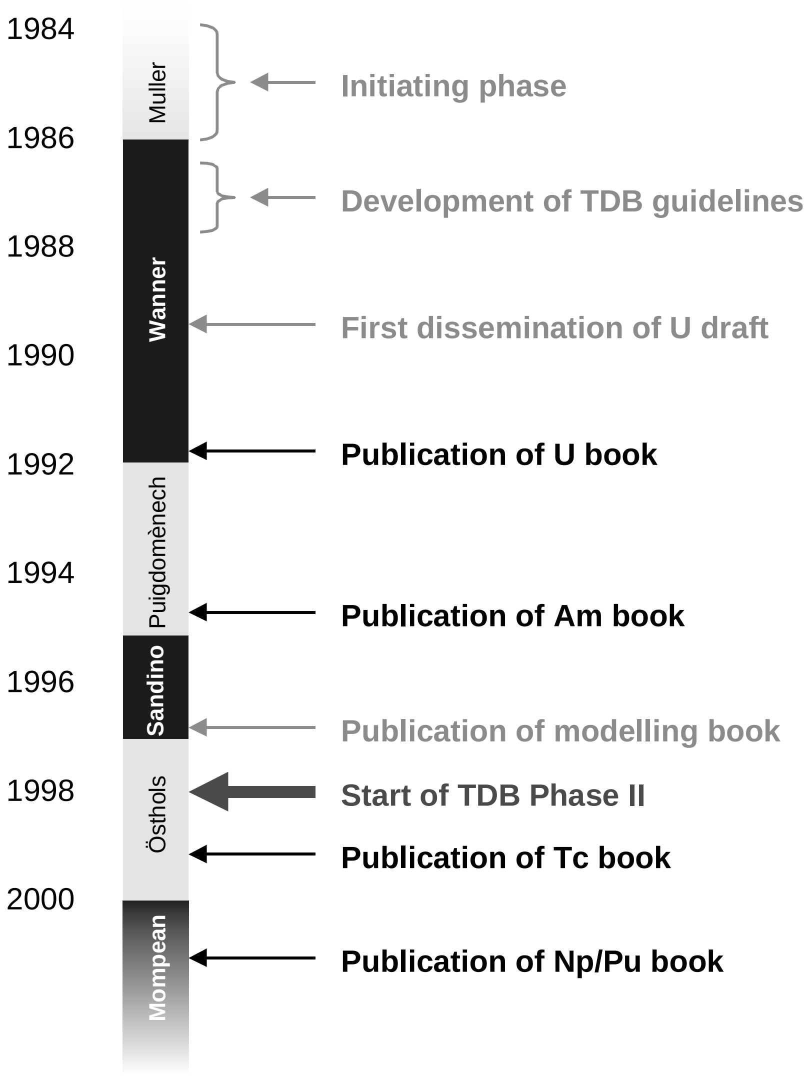
Non-permanent posts at the OECD are limited to five years, which means that new project co-ordinators for TDB have to be recruited every few years. Such a change of responsible personnel leads to a delay of about six months in the progress of the project.

Ignasi Puigdomènech was TDB co-ordinator from 1992 to 1995 and published the americium book. Amaia Sandino was responsible for the project between 1995 and 1997. In this period the book on *Modelling in Aquatic Chemistry* was completed and published. The preparation of this book was started with the publication of the uranium book in 1992, and its purpose is to give advice to the users of these data with regard to their application in performance assessment.

At this time, the success of the TDB project was undisputed, and since the last two publications were expected to appear within very little time, a meeting was held at the NEA in which a continuation of the project was discussed. It was decided that the NEA should have a budget that is sufficient to pay the reviewers, in order to increase the influence on the progress of the work. This fell into the era of Erik Östhols, who co-ordinated the TDB project from 1998 to 2000, and who succeeded in issuing the technetium book in 1999. Federico Mompean joined the NEA last year and managed the final rush of the publication of the Np/Pu book, which appeared very recently.

Figure 1 provides an overview of the history of Phase I of the NEA TDB Project and lists the major milestones.

Figure 1. Overview of the major milestones in Phase I of the NEA TDB Project



PHASE II OF THE NEA TDB PROJECT AND SOME LESSONS LEARNED FROM THE USE OF PHASE I DATA

Kastriot Spahiu
SKB, Sweden

Introduction

As the five initial reviews of the TDB Project come to their conclusion, the negotiations for an independently funded continuation of the TDB Project through two meetings of an *ad hoc* group were completed in late 1997. The participating organisations are ANSTO (Australia), NIRAS/ONDRAF (Belgium), RAWRA (Czech Republic), POSIVA (Finland), ANDRA and IPSN (France), FZK (Germany), JNC/PNC (Japan), ENRESA (Spain), SKB and SKI (Sweden), HSK, NAGRA and PSI (Switzerland), BNFL and NIREX (UK) and the DOE (USA). This project is referred to as the TDB Phase II Project, or simply TDB II. The following new reviews will be performed within this project:

- an update of the existing U/Am/Tc/Np/Pu reviews (one review team for all elements);
- the inorganic chemistry of Ni;
- the inorganic chemistry of Se;
- the complexation of selected simple organic ligands (ISA, EDTA, citrate and oxalate) with U, Am, Tc, Np, Pu, Ni, Se, Zr and some selected competing cations;
- the inorganic chemistry of Zr.

These review areas have been decided on taking into account the toxicity, mobility, radioactivity and half-lives of the commonly occurring nuclides in radioactive waste, as well as the particular areas of interest of the funding organisations.

To avoid the delays that have plagued Phase I, the organisation of the TDB Project has been restructured (see below), and the funding provided has been calculated to cover all necessary expenses for the project.

Organisation of the TDB II Project

The second phase of the TDB Project is organised as a semi-autonomous project under the guidance of a management board, representing the participating organisations or countries. The NEA acts as the project co-ordinator, obtaining assistance and advice concerning technical matters from an Executive Group within the Management Board. As in Phase I, Review Teams evaluate existing data and prepare interim and final reports. The Management Board is ultimately responsible for the project and defines and approves the annual programme of work and budget. The Executive Group, which consists of four persons of strong technical background, acts as a technical adviser to the Management Board. It also gives advice and assists the project co-ordinator. The main part of the work at the NEA is performed by the NEA Data Bank and covers the co-ordination of the review teams (meetings, etc.), editing of review report manuscripts and the update and maintenance of the TDB database. The Review Teams consist of four to seven experts.

Team experts must be highly qualified in the scientific area covered by the review, and have a wide range of direct experimental experience. This experience is crucial for the experts to be able to judge the quality and completeness of the scientific publications under review. The reviewers critically review the chemical thermodynamic data available for the element or ligand in question. The review is carried out according to specified procedures, to ensure consistency and quality control. These procedures are documented in the TDB Guidelines, available on the OECD/NEA TDB web site [1]. Based on their review, the reviewers recommend a set of data, and present these data along with their associated uncertainties. They also provide a detailed justification for the selection, including their primary data sources in the resulting report.

Currently, no sorption, diffusion or kinetic data are included in the project database, nor are data for polyelectrolytes or organic ligands other than the selected set treated by the review group for simple organic ligands.

The parameters included in the TDB database are not measured directly, but are obtained by interpreting experimental results and using a set of auxiliary data, *i.e.* data for chemical species and compounds which are not under direct investigation, but which nevertheless are necessary to evaluate the data of interest. These auxiliary data are also required to make experimental equilibrium data applicable to different sets of component (“master”) species.

In general, selected data are presented for a temperature of 298.15 K and a pressure of 1 bar. More details about the specific reference conditions for the parameters used in the NEA TDB Project reviews can be found in the TDB Guideline Report TDB-5 [2]

Timetable for the TDB II project

The TDB II Project was started on 1 April 1998 and formally ends when all review reports from the TDB II Review Teams are finished and ready to send to print.

The review procedure

The first step of the review procedure is the compilation of data published in the scientific literature for each key element. In principle, the literature search should cover everything relevant that has ever been published on the subject (for update reviews, the literature search will obviously start at the date where the previous review report stopped). For most reviews, however, some restrictions have to be made since the resources available are not sufficient to cover everything that could possibly be included. These restrictions are subject to the consent of the Executive Group and ultimately the Management Board. The restrictions are made primarily taking into account the needs of the nuclear waste site performance assessment community, insofar as possible. The restrictions made are documented in the respective review reports. As mentioned above, no sorption, diffusion or kinetic data are included. Usually, alloys are also excluded, as are many ternary and quaternary compounds of certain elements. Minerals are usually excluded because of the lack of well-defined stoichiometries; reliable thermodynamic data for minerals are, in any case, scarce (see *e.g.* [3], Appendix D).

In general, the OECD/NEA TDB reviews only take into account primary experimental data, not estimates or calculated parameters. However, if scientifically well-established procedures for making estimates of otherwise unavailable data (*i.e.* by analogies with similar elements) exist, such procedures may be employed. If no reliable experimental data exist and no data are available for similar elements that would allow estimates to be made, the TBD reviews do not attempt to fill the resulting gaps in the thermodynamic database. Areas that merit further experimental investigation are pointed out in the review reports.

When possible, experimental source data are re-evaluated by using chemical models which are found to be more accurate than those used by the original authors.

The final result is a selected set of data of formation and reaction for each key element considered by the review, as well as for the auxiliary data that were used for recalculations in the critical review. It is essential that a consistent auxiliary data set be used in conjunction with the data set of the key element. The selection procedure is described in detail in the TDB-1 Guideline [4].

These data and their uncertainties are stored in the TDB database. Since various publications in the scientific literature contain equilibrium constants or thermodynamic data of reaction rather than the thermodynamic data of formation of single species, the database can also store chemical reactions, as well as the corresponding reaction data with uncertainties in SI units. This also allows selected data to be stored for reactions where no formation data can be extracted, as well as giving users of the database the possibility to use the selected reaction data directly without having to recalculate these data from formation data. Such recalculations usually lead to uncertainties that are much larger than those assigned to the original experimental data.

Uncertainty estimates of equilibrium data

One of the principal objectives of the NEA TDB development effort is to provide an idea of the uncertainties associated with the data selected in this review. This makes the calculation of confidence limits for the derived quantities possible. In general, the uncertainties should define the range within which the corresponding data can be reproduced with a probability of 95% at any place and by any appropriate method. In many cases, statistical treatment is limited or impossible due to the availability of only one or a few data points. A particular problem has to be solved when significant discrepancies occur between different source data. The TDB-3 Guideline [5] contains a description of the statistical procedures that are used for the problems encountered.

Independent peer review

As in TDB Phase I, the reports are reviewed by an independent set of experts before final publication. Then as now, the purpose of this additional “peer review” is to obtain an independent view of the judgements and assessments made by the primary reviewers, to verify assumptions, results and conclusions, and to check whether the relevant literature has been exhaustively considered. The procedures for performing the peer reviews are described in detail in the TDB-6 Guideline [6]. This is a very important part of the quality assurance for the published reviews. The independent peer review is performed by personnel having technical expertise in the subject matter to be reviewed, to a degree at least equivalent to that needed for the original review. Since the authors of the reviews are specialists within the scientific area concerned, they are the persons best positioned to find suitable scientists to perform the peer reviews. Hence, the peer reviewers are suggested by the members of the Review Team, and submitted to the TDB Executive Group and Management Board for approval.

Some lessons learned from the use of Phase I data

To be useful in performance assessment work, a database must contain data for all the elements of interest in nuclear waste disposal and document why and how the data was selected. It should document the sources of experimental data used, treat all published data on the solids and aqueous species of the elements of interest, and finally be internally consistent.

The NEA TDB project [7] was started in response to the recognition of shortcomings in these existing national databases. At the time, it was clear that although a number of thermodynamic data compilations and reviews had already been published [8-11], none of them could be used reliably as a complete source data table to study the behaviour of radioelements in the environment. In particular, the documentation on how and why a particular datum was selected is often omitted, in favour of general guidelines or no information at all.

Grauer [12] discusses the consequences of this lack of documentation in the case of cadmium carbonate solubilities reported in these reviews and compilations. Cadmium is an important industrial contaminant and one of its potential solubility limiting solids in the environment is cadmium carbonate. Stipp, *et al.* [13], besides carefully measuring the solubility of $CdCO_3$(s), also reconstructed a diagram of the origin of the various solubility constants reported in literature for this compound. They showed that the current table values for this constant are mostly based on a heat of dilution determined in 1883 and differences in the assessment of this work and the use of different auxiliary constants resulted in the spread of values given for the solubility product.

In order to represent the main processes governing the release of the radionuclides from the waste form discussed above, and their migration to the biosphere, there is a need for a variety of data and geochemical models. The solubility and adsorption behaviour of the radionuclides depends strongly on their speciation.

The actinides are the main contributors to the radioactivity of HLW after a few hundred years (however, fission products contribute during the initial period to a much higher activity). The aqueous chemistry of the actinides is characterised by multiple oxidation states (from III to VI in the environment, but II and VII are also known). For plutonium under certain conditions all four oxidation states may coexist in water solutions. The chemical behaviour of the actinide elements in a particular redox state [*e.g.* Th(IV), U(IV), Np(IV), Pu(IV), Am(IV)] is quite similar. However their redox behaviour is quite different. The actinides are hard ions, *i.e.* form strong complexes with oxygen containing ligands (OH^-, CO_3^{2-}, PO_4^{3-}, SO_4^{2-}). Especially in their lower oxidation states they have strong hydrolysis and a tendency to polymerise, as well as very insoluble hydroxides. This, together with the ease of oxidation of, *e.g.* U(IV), makes it difficult to perform high-quality measurements and their evaluation, and require in most cases the use of tracer methods. Thus, a large number of studies concerning the solubility of amorphous and crystalline uranium (IV) oxide under reducing conditions do exist. However, the measured uranium solubilities differ by more than five orders of magnitude ([14] and therein).

As an example of the review work, the critical review of a study [15] of the phosphate complexation of Pu(III) through solubility measurements of $PuPO_4xH_2O$ is presented below [16]. Then an overview of the data and the need for future studies in the field of plutonium phosphate aqueous chemistry will be presented.

The composition of the solid in the work of Moskvin [15] has been verified only by chemical analysis, and no water content is reported. The solubility was measured at 20±1°C, an ionic medium

0.5 M $NaClO_4$, at the pH interval 0.3-7.2. The author explains the solubility data assuming the formation of the complex $PuPO_4$ with $\log_{10}\beta(PuPO_4) = 19.2$ and obtains $\log_{10}K_{s,0} = -24.4$ for the reaction:

$$PuPO_4 \cdot xH_2O(s) \rightleftharpoons Pu^{3+} + PO_4^{3-} + xH_2O$$

No phase verification before and after equilibration was performed, and no holding reductant or test of the oxidation state of plutonium in solution is reported. The solubility is measured only from under-saturation. The third dissociation constant of the phosphoric acid used by the authors is high, even compared to values used by the same author in other works. The formation of the complex $PuPO_4$ at the very low total phosphate concentrations resulting from the dissolution of the solid and low pH is not supported by studies in similar systems.

Recent studies on phosphate complexation of three valent lanthanides [17,18] and americium [3,19] have shown that the stability of similar $M(III)PO_4$ complexes has been overestimated by several orders of magnitude. The same is true in the present case, namely almost all Pu(III) in the ion exchange experiments discussed in the second part of this same work should be in the form of $PuPO_4$, while the author considers here only the formation of complexes with $H_2PO_4^-$ as ligand.

The formation of the complex is based on the levelling-out of the solubility curve for pH ≥ 4. This is probably due to some experimental shortcomings, especially if the pH shift (from Table 2 in [15]) during the attainment of equilibrium is considered. Among possible explanations for the acidification of the solution during the equilibration with the solid may be only solution reactions involving Pu^{3+} (and at these pH values the hydrolysis is negligible), or a phase transformation of the solid to some hydroxyphosphate. Since no details on the holding reductant or the filtration procedure are reported, it is also possible that Pu(III) is partially oxidised to Pu(IV) and the colloidal Pu(IV) is considered as soluble Pu(III). For these reasons the solubility data for pH > 4 were discarded. The resulting solubility product $\log_{10}K_{s,0}$(0.5 M $NaClO_4$, 20°C) = -21.5 ± 0.5 was recalculated at standard conditions with the interaction coefficient $\varepsilon_{(Pu^{3+},ClO_4^-)} \cong \varepsilon_{(Nd^{3+},ClO_4^-)} = 0.49$, obtaining $\log_{10}K_{s,0} = -24.57\pm0.8$, where the increased error should account for the different temperature and the approximate interaction coefficient.

The same holds for the five phosphate complexes of Pu(IV), $Pu(HPO_4)_n$, $n = 1\text{-}5$, which are present in most of the databases. It is shown [16] that the reported constants [20] are overestimated by several orders of magnitude and for this reason have been rejected.

This type of review work, including recalculation of primary data and discussion of experimental details in the original publication, is very time consuming and difficult to achieve in the various national database compilations, where all species of all radionuclides have to be reviewed within relatively limited time and resources.

On the other hand, this does not mean that Pu(III or IV) phosphate complexes do not exist, it simply means that further studies of plutonium-phosphate aqueous system are needed.

As mentioned above, special care is taken to estimate the *uncertainties* in each stored datum at the OECD/NEA database. There is, though, an apparent contradiction in the use of these data with various geochemical calculation codes: to my knowledge none of the codes can make use of these uncertainties. Thus, *e.g.* no code can use the uncertainties of all the possible complexes and of the solubility product when calculating the solubility of a radioelement in a given medium. This is not a simple task, but some more effort may be needed in this direction.

In general, the OECD/NEA TDB reviews only take into account primary experimental data, *not estimates* or calculated parameters. Thus, the fact that data for a certain species or solid is missing in the NEA database does not mean that it does not exist. In this case, if established procedures for making estimates of unavailable data (*i.e.* by analogies with similar elements) exist, they may be employed in performance assessment calculations. This is illustrated with the example of nickel solubilities in reducing sulphidic groundwaters [21]. The published solubility product constants for NiS(s) vary by many orders of magnitude. Furthermore nickel sulphide complexes are very poorly studied and their neglect may lead to a severe underestimation of nickel solubility, as judged from analogy with the carefully studied analogue ZnS(s). In this case, besides recommending new careful studies of the sulphide complexation of nickel and NiS(s) solubilities, a non-conservative estimation of nickel solubilities in performance assessment may be avoided by using the analogy with Zn.

In the mean time, for certain elements like, for example, Th, a literature collection and storage in a database is continuously maintained at the OECD/NEA. It is important to know that in this case the database has only a list of constants as published in the literature, without any critical review of the data. It may be used to save time searching literature, but the quality of the data should be judged from the original publication.

The various geochemical codes like EQ 3/6, PHREEQE, etc., in their various versions use databases not always of guarantied quality. Striving towards completeness, their databases sometimes contain published data which have been shown later in the literature to be erroneous. Thus species as $UO_2(H_2PO_4)$ or $Pu(IV)(CO_3)_x$, x = 1-5 are included in relatively recent versions of databases with constants having more than 35 orders of magnitude error. It is the task of the modeller to assure the highest possible quality of the database.

Even when using a high quality database, a modeller may find that important information is still missing. The databases contain data at standard state conditions and at a reference temperature, which means that they should be recalculated at the appropriate ionic medium and temperature.

Conclusion

The published TDB Project reviews have earned widespread recognition due to their high quality, and have also found many users in the general research community, in addition to the intended audience of specialists in safety assessment studies. As the project now enters a new phase, it will aim to continue producing high-quality, relevant review reports useful to scientists and safety assessment modellers alike.

REFERENCES

[1] NEA web site, URL http:// www.nea.fr/html/dbtdb/guidelines/guidelines.html.

[2] H. Wanner and E. Östhols, "TDB-5: Standards and Conventions for TDB Publications", OECD/NEA, version of 3 May 2000.

[3] R.J. Silva, G. Bidoglio, M.H. Rand, P.B. Robouch, H. Wanner, I. Puigdomenech, "Chemical Thermodynamics of Americium", Elsevier Science Publishers B.V., Amsterdam (1995).

[4] H. Wanner, "TDB: Guidelines for the Review Procedure and Data Selection", OECD/NEA, version of 6 January 2000.

[5] H. Wanner, "TDB-3: Guidelines for the Assignment of Uncertainties", OECD/NEA, version of 1 June 1999.

[6] H. Wanner, "TDB-6: Guidelines for the Independent Peer Review of TDB Reports", OECD/NEA, version of 1 June 1999.

[7] H. Wanner, "The NEA Thermochemical Database Project", in Scientific Basis for Nuclear Waste Management XIV, Mat. Res. Soc. Symp. Proc., Vol. 212**,** 815–822 (1991).

[8] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney, R.C. Nuttall, *J. Phys. Chem. Ref. Data*, 11, Supp. 2, 1-392 (1982).

[9] S.L. Philips, F.V. Hale, L.F. Silvester, M.D. Siegel, "Thermodynamic Tables for Nuclear Waste Isolation: Vol. 1, Aqueous Solutions Database", Report LBL-22860, NUREG/CR-4864, SAND87–0323, Lawrence Berkeley Lab., Berkeley, CA, USA (1988).

[10] "CODATA Recommended Key Values for Thermodynamics 1977", Committee on Data for Science and Technology (CODATA), Bulletin 28, International Council for Scientific Unions, Paris (1978).

[11] J.D. Cox, D.D. Wagman, V.A. Medvedev, "CODATA Key Values for Thermodynamics", Hemisphere Publ. Corp., New York (1989).

[12] R. Grauer, "Solubility Products of M(II) Carbonates", U. Berner, ed. and trans., PSI Bericht Nr. 99-04, January 1999.

[13] S.L.S. Stipp, G.A. Parks, D.K. Nordstrom, J.O. Leckie, "Solubility-product Constant and Thermodynamic Properties for Synthetic Octavite, $CdCO_3$(s), and Aqueous Association Constants for the Cd(II)-CO_2-H_2O System", *Geochim. Cosmochim. Acta*, 57, 2699 (1993).

[14] J. Fuger, "Problems in the Thermodynamics of the Actinides in Relation with the Back-end of the Nuclear Fuel Cycle", *J. Nucl. Mater*., 201, 3-14 (1993).

[15] A.I. Moskvin, "Investigation of the Complex Formation of Trivalent Plutonium, Americium and Curium in Phosphate Solutions", *Sov. Radiochem.*, 13, 688-693 (1972).

[16] R. Lemire, J. Fuger, H. Nitsche, P. Potter, M. Rand, J. Rydberg, K. Spahiu, J.C. Sullivan, W. Ullman, P. Vitorge, H. Wanner, "Chemical Thermodynamics of Neptunium and Plutonium, OECD/NEA, ed., Elsevier Publishers (2001).

[17] R.H. Byrne, J.H. Lee, L.S. Bingler, "Rare Earth Element Complexation by PO_4^{3-} Ions in Aqueous Solutions", *Geochim. Cosmochim. Acta*, 55, 2729-2735 (1991).

[18] R.H. Byrne, L.S. Bingler, Comment on "Cerium: A Chemical Tracer for Paleo-oceanic Redox Conditions" by Y.G. Liu, M.R.U. Miah, R.A. Schmitt, *Geochim. Cosmochim. Acta*, 53, 1475-1476 (1989).

[19] D. Rai, A.R. Felmy, R.W. Fulton, "Solubility and Ion Activity Product of $AmPO_4 \cdot x\ H_2O(am)$, *Radiochimica Acta*, 56**,** 7-14 (1992).

[20] R.G. Denotkina, A.I. Moskvin, V.B. Shevchenko, "The Composition and Dissociation Constant of Phosphate Complexes of Pu(IV) Determined by the Solubility Method, *Russ. J. Inorg. Chem.*, 5, 731-734 (1960).

[21] T. Thoenen, "Pitfalls in the Use of Solubility Limits for Radioactive Waste Disposal: The Case of Nickel in Sulfidic Groundwaters", *Nuclear Technology*, 126, 75-87 (1999).

DISCUSSION

J. Bruno remarked that it is not unusual to find data in some compilations for species for which there is no evidence of their existence.

I. Grenthe criticised the analysis of some systems, whose chemistry is dominated by binary species, in terms of species of higher order.

T. Fanghanel showed evidence contrary to the existence of the mixed hydroxicarbonate $CmOHCO_3(s)$ based on fluorescence studies, which can have important implications for its chemical analogue, Am. He also commented on the phase transformation occurring between the two Am carbonates: $Am_2(CO_3)_3(am)$ to $NaAm(CO_3)_2(s)$ when increasing the ionic strength over 0.1 M.

L. Wang commented that some of the irregularities mentioned previously in the databases associated with the inclusion of non-existing species had been corrected in the most recent releases, as in the case of the database accompanying the EQ3/6 code.

K. Spahiu raised some issues on the uncertainties on the solubilities as well as on the incorrect, but sometimes encountered, use of solubility product data from the compilations for each individual isotope of a given element when various isotopes are present.

SESSION II

Building the Bridges: Data to Performance Assessment

Chair: J. Bruno

Ionic Strength – Theory, Use, Cautions, Sources of Error

APPLICATION OF PITZER'S ION-INTERACTION APPROACH FOR THE CALCULATION OF EXCESS PROPERTIES OF TRACE RADIONUCLIDES IN ELECTROLYTE SOLUTIONS

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Introduction to excess properties in electrolyte solutions

Two basic problems are commonly encountered in aquatic chemistry:

- What is the stoichiometry (and the structure) of the species formed in the solution?
- What are the quantities of these species as a function of the system composition and other basic thermodynamic variables (such as temperature or pressure)?

To provide answers to these questions a first assumption is to consider that the system being studied is in equilibrium. Under this assumption, in this paper the focus of attention will be on the methods leading to answers for the second of the above-mentioned questions.

For a system in equilibrium at constant temperature and pressure, Gibbs free energy, *G*, should have a minimum value. Let us consider a system that can described by chemical equilibria such as the following:

$$\mathrm{M(aq) + L(aq) \rightleftharpoons M(aq)}$$
$$\mathrm{M(aq) + nH_2O(l) \rightleftharpoons M(OH)_n(aq) + nH^+(aq)}$$
$$\mathrm{MX{\cdot}nH_2O(s) \rightleftharpoons M(aq){+}X(aq){+}nH_2O(l)}$$

It is convenient to express the change in Gibbs energy upon reaction as a function of the chemical potential of the species involved in each case, μ_i, by using the stoichiometric coefficients ν_i as:

$$\Delta_r G_m = \sum \nu_i \mu_i$$

The chemical potentials are themselves expressed in the customary way as a sum of a standard-state contribution (standard chemical potential) plus a term which is a function of the activity of the corresponding species:

$$\mu_b = \mu_b^o + RT \ln a_b$$

Before proceeding any further in practice, it would be useful to define the standard state. For solution equilibria two standard states are considered:

- For the solids (s) or solvent (l), *i.e.* H_2O, involved in the equilibria, the standard state is chosen as that corresponding to the pure components:

$$\mu_b = \mu_b^o + RT \ln a_b ; x_b \to 1; a_b \to 1$$

- For the aqueous species (aq), the standard state is that corresponding to a hypothetical 1 molal solution holding the same interactions as an infinite dilution solution, where activity coefficients will become unity:

$$\mu_b = \mu_b^o + RT \ln a_b ; \gamma_b = \frac{a_b}{m_b} ; m \to 0; \gamma_b \to 1$$

By reference to these standard states, it is possible to rewrite the change in Gibbs energy for the relevant reaction as:

$$\Delta_r G_m = \sum \nu_i \mu_i = \sum \nu_i \mu_i^o + RT \sum \nu_i \ln a_i$$

Since in equilibrium $\Delta_r G_m = 0$, using $K^o = \Pi a_i$ the well-known equation relation between standard chemical potentials and the standard state equilibrium constant:

$$\sum \nu_i \mu_i^o = -RT \ln K^o$$

This equation shows that in order to determine the equilibrium composition of the system, knowledge is needed of:

- Standard chemical potentials, themselves functions of temperature and pressure: $\mu_b^o = f(T, p)$;

- Activity coefficients, $\gamma_b = f(m_1,\ldots,m_n,T,p)$ and water activities, $a_w = f(m_1,\ldots,m_n,T,p)$, in turn obtained from osmotic coefficients: $\phi = -1000 \ln a_w \big/ M_w \sum_i m_i$.

For most systems, the following additional simplifications can be safely introduced:

- neglecting the dependence on pressure for the activity coefficients and water activities (for pressure excursions below 500 bar): $\gamma_b, a_w \neq f(p)$;

- assuming constant temperature (that corresponding to the standard state);

- neglecting the dependences of activity coefficients on the molalities of trace species (*i.e.* those species for which $m_i \ll m_{tot}$): $\gamma_b \neq f(m_{tr})$;

These simplifications result in the following practical dependences of activity coefficients and water activities on the molalities of the different species present:

$$\gamma_b = f_1(m_1,\ldots,m_n)$$
$$a_w = f_2(m_1,\ldots,m_n)$$

This results in the expression for the excess Gibbs energy, G^{ex}, which is a function of the molalities of the present species:

$$G^{\mathrm{ex}} = f\left(m_1,\ldots,m_n\right) = \mathrm{RT}\Sigma n_i\left(1-\phi+\ln\gamma_i\right)$$

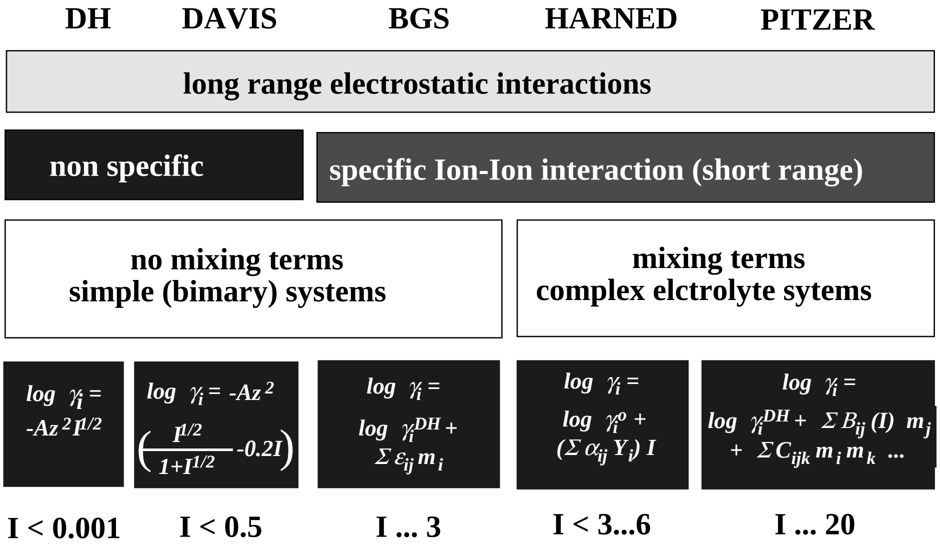
where the excess property is defined as the difference between the actual value of the magnitude and the value for an ideal system:

$$X^{ex} = X(\text{actual}) - X(\text{ideal})$$

Electrolyte thermodynamics

Lacking a suitable *ab initio* theory describing electrolyte solutions, recourse is often made to extensions of the limiting law established by Debye and Hückel. This limiting law provides a description based on coulombic forces, but neglects all direct effects that are expected at short range. Therefore Debye-Hückel law is appropriate only to work near the infinite dilution limit and constitutes only a crude approximation at slightly higher concentrations. Several extensions of the Debye-Hückel limiting law have been proposed bearing in mind the need to describe short-range interactions under varying degrees of specificity and resulting in different ranges of applicability. Figure 1 contains a summary of some of these approaches. The rest of this section is devoted to the illustration of the basic elements of the approach due to Pitzer.

Figure 1. Activity coefficient models



The paper by Dr. Spahiu in these proceedings focuses on the Brønsted-Guggenheim-Scatchard (BGS) specific ion-interaction model (SIT). Here we shall only mention that within this latter model, the activity coefficients are calculated using the expression:

$$\log_{10}\gamma_i = \log_{10}\gamma_i^{DH} + \sum \varepsilon_{ij} m_i$$

where the first term represents an “effective distance” Debye-Hückel contribution and the second represents an expansion reflecting other cation-anion interactions.

In Pitzer's approach, the excess Gibbs energy is expressed as the following expansion:

$$\frac{G^{ex}}{w_{\mathrm{w}}RT} = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk}$$

where $I = \frac{1}{2}\sum_i m_i Z_i^2$ is the ionic strength, w_{w} represents the number of kilograms of water, $f(I)$ is the Debye-Hückel limiting law, and the coefficients $\lambda_{ij}(I)$ and μ_{ijk} represent the binary and triple short range interactions between the *i*, *j* and *k* ionic species respectively. Correspondingly, the expression for the activity coefficients and the osmotic coefficient are derived from the excess Gibbs energy using:

$$\ln \gamma_i = \left[\frac{\partial\left(G^{ex}/w_{\mathrm{w}}RT\right)}{\partial m_i}\right]_{n_{\mathrm{w}}}$$

$$\phi - 1 = -\frac{\left(\partial G^{ex}/\partial w_{\mathrm{w}}\right)_{n_{\mathrm{i}}}}{RT\sum_i m_i}$$

resulting in (the following formula is written for the case of the cation M in an electrolyte MX, similar formulae can be derived for $\ln\gamma_{\mathrm{X}}$ and ϕ):

$$\ln \gamma_{\mathrm{M}} = Z_{\mathrm{M}}^2 F + \sum_{\mathrm{a}} m_{\mathrm{a}}\left(2B_{\mathrm{Ma}} + ZC_{\mathrm{Ma}}\right) + \sum_{\mathrm{c}} m_{\mathrm{c}}\left(2\Phi_{\mathrm{Mc}} + \sum_{\mathrm{a}} m_{\mathrm{a}}\psi_{\mathrm{Mca}}\right)$$
$$+ \sum_{\mathrm{a}} \sum_{<\mathrm{a}'} m_{\mathrm{a}} m_{\mathrm{a}'}\psi_{\mathrm{Maa}'} + Z_{\mathrm{M}} \sum_{\mathrm{c}} \sum_{\mathrm{a}} m_{\mathrm{c}} m_{\mathrm{a}} C_{\mathrm{ca}} + 2\sum_{\mathrm{n}} m_{\mathrm{n}}\lambda_{\mathrm{nM}}$$

where c stands for cations, a for anions, n for neutral species, Z_{M} for the charge of the cation M and $Z = \sum_i m_i |Z_i|$. *F* includes the Debye-Hückel slope term and other terms depending on the ionic strength. B_{Ma} and C_{Ma} can be written in terms of the $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} coefficients for each ion pair and the ionic strength, Φ_{Mc} as a function of the corresponding θ for cation pairs and the ionic strength so that the calculated activity coefficient accounts for the following interactions:

- cation-anion – $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} coefficients;
- ion-neutral species – λ;
- cation-cation or anion-anion – θ;
- cation-cation-anion or cation-anion-anion – ψ.

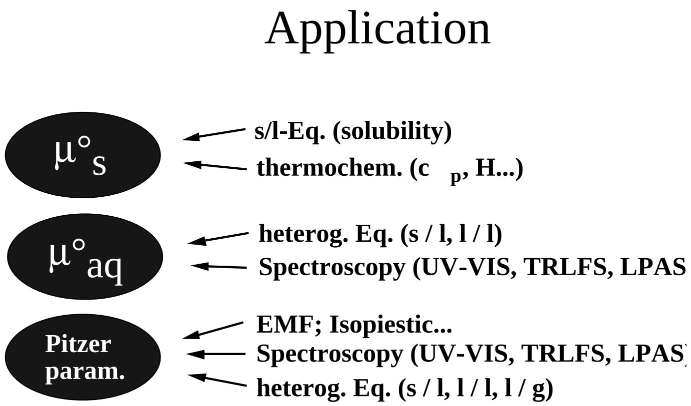
Applicability of the Pitzer approach

Within the framework presented above an accurate description of the thermodynamic properties of electrolyte systems of high complexity has been possible up to high values of the ionic strength ($I \approx 20$ m). An example of this extended range of applicability is the description of seawater based on the species: Na^+, K^+, Mg^{2+}, Ca^{2+}/Cl^-, SO_4^{2-} and the (HCO_3^-, CO_3^{2-}, CO_2) sub-system. Moreover, the approach is flexible enough to account for complex formation equilibria.

Figure 2 illustrates the three main types of data needed in order to apply the theoretical framework together with the experimental methods more adequate to obtain the desired information:

- data for the standard chemical potential of the solid species involved in the equilibria, which can be obtained from solubility measurements of from thermochemical measurements;
- data for the standard chemical potential of the aqueous species, obtained from heterogeneous solid-liquid or liquid-liquid equilibria conjugated with spectroscopic techniques such as UV-VIS, time-resolved laser fluorescence spectroscopy or laser photoacoustic detection spectrosocopy;
- Pitzer's theory parameters, obtained from heterogeneous equilibria by means of emf or isopiestic measurements and the full range of spectroscopic techniques mentioned above.

Figure 2. Appropriate experimental methods to obtain the needed data, $\mu^{o}_{s}, \mu^{o}_{aq}$ and Pitzer parameters



1. Chemical model (γ_i = const.)

2. Excess properties (β, K = f(composition)

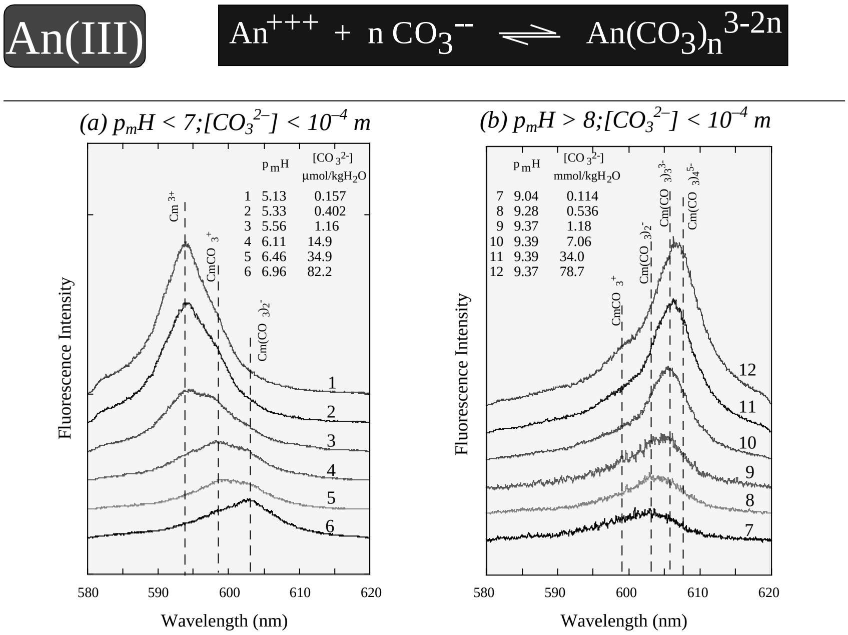
Figure 2 also illustrates the need to identify a chemical model under conditions where the activity coefficients are constant and then proceed to determine the excess properties represented by the model parameters.

Among the wealth of examples that can be extracted from the literature dealing with the application of Pitzer's approach, the An(III) carbonate system can be mentioned. For this system, complex formation can be depicted by the equilibria:

$$\mathrm{An}^{3+} + n\mathrm{CO}_3^{2-} \rightleftharpoons \mathrm{An}(\mathrm{CO}_3)_n^{3-2n}$$

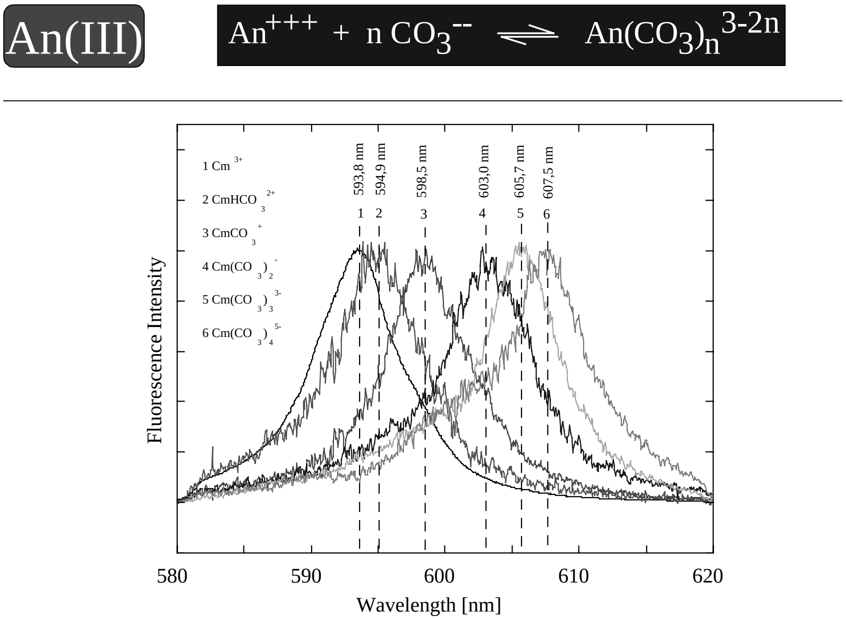
Selected fluorescence emission spectra measured over a wide range of carbonate concentrations and at constant NaCl molality (1 molal) are presented in Figure 3. Figure 3(a) contains spectra measured at low carbonate concentrations ($[\mathrm{CO}_3^{2-}] < 10^{-4}$ molal) and low pH (pH < 7) while in Figure 3(b) the results of batch experiments ($[\mathrm{CO}_3^{2-}] > 10^{-4}$ molal; pH > 8) are presented. As the carbonate concentration is increased, a shift of several nm in the maximum of the emission band towards higher wavelength is

Figure 3. Fluorescence spectra of $Cm(CO_3)_n^{3-2n}$ (*n* = 0-4) at different $[CO_3^{2-}]$ concentrations



observed. This shift is attributed to the formation of inner-sphere carbonate complexes of Cm(III). The single component emission spectra of the Cm^{3+} aqueous ion, Cm(III) bicarbonate and Cm(III) carbonate complexes derived by peak deconvolution are plotted in Figure 4 in the wavelength range 580-620 nm.

Figure 4. Single component fluorescence emission spectra of Cm^{3+} and Cm(III)carbonate complexes



Using the emission spectra of these individual species, all emission spectra measured at varying carbonate concentrations and constant ionic strength (1 m NaCl) are deconvoluted. In order to verify the postulated complex formation equilibria, $\log_{10}[\mathrm{Cm(CO_3)}_n^{3-2n}]/[\mathrm{Cm(CO_3)}_{n-1}^{5-2n}]$ is plotted as a function of $\log_{10}[\mathrm{CO_3^{2-}}]$ in Figure 5. Straight lines with a slope of one confirm the initially postulated Cm carbonate complexes.

Figure 5. Correlation of the experimentally ratio $\log_{10}[\mathrm{Cm(CO_3)}_n^{3-2n}]/[\mathrm{Cm(CO_3)}_{n-1}^{5-2n}]$ with the $\log_{10}[\mathrm{CO_3^{2-}}]$

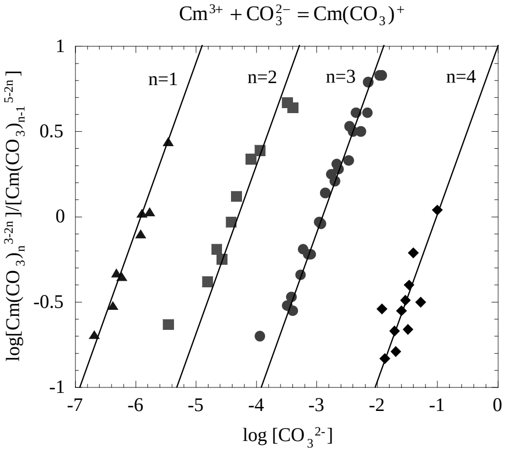
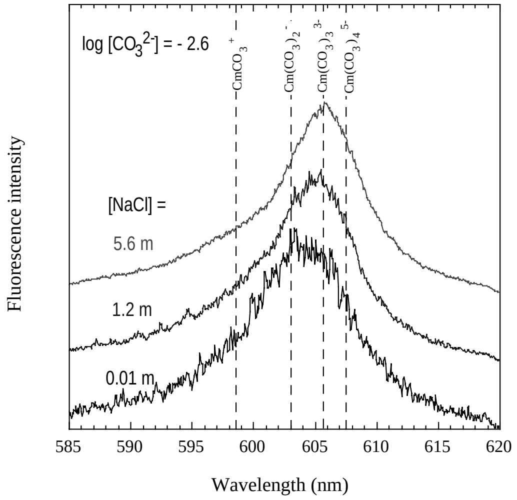


Figure 6 contains selected fluorescence emission spectra in a series of solutions at constant carbonate concentration and increasing NaCl molality. With increasing NaCl concentration, the spectrum is shifted toward higher wavelength, which indicates a change in the Cm(III) species distribution due to changes in the activity coefficients. The increase in m_{NaCl} leads to a stabilisation of the higher carbonate complexes with higher negative charge.

Figure 6. Fluorescence spectra of $\mathrm{Cm(CO_3)}_n^{3-2n}$ (n = 1-4) at different [NaCl] concentrations



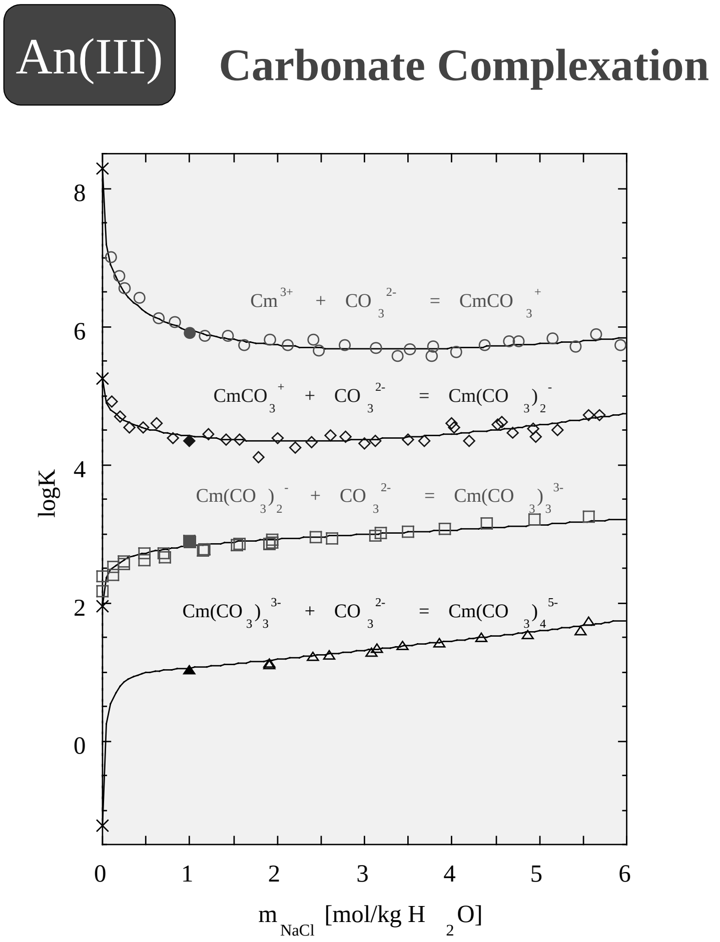
Emission spectra of Cm(III) at constant $\mathrm{CO_3^{2-}}$ concentration and various NaCl molalities

The stepwise carbonate complexation equilibria:

$$\mathrm{Cm(CO_3)}_{n-1}^{5-2n} + \mathrm{CO_3^{2-}} \rightleftharpoons \mathrm{Cm(CO_3)}_{n}^{3-2n} \qquad (n = 1-4)$$

measured spectroscopically as a function of the NaCl molality are plotted in Figure 7. These data are used to determine the ion-interaction parameters for all Cm carbonate complexes.

Figure 7. Complexation constants of $\mathrm{Cm(CO_3)}_n^{3-2n}$ (n = 1-4) obtained from the Pitzer approach



The carbonate complexation constants
as function of the NaCl molality.

The lines in Figure 7 represent the complexation constants calculated with the Pitzer approach. Taking into account available literature data on the carbonate complexation of trivalent actinides an overall model was derived, as illustrated in Figures 8 and 9, resulting in a fairly good agreement between model and experiment.

The present state of our knowledge on the thermodynamics of trivalent actinides (chemical potentials of aqueous and solid species and ion-interaction parameters of the aqueous species) is illustrated in Figure 10.

Figure 8. Overall model

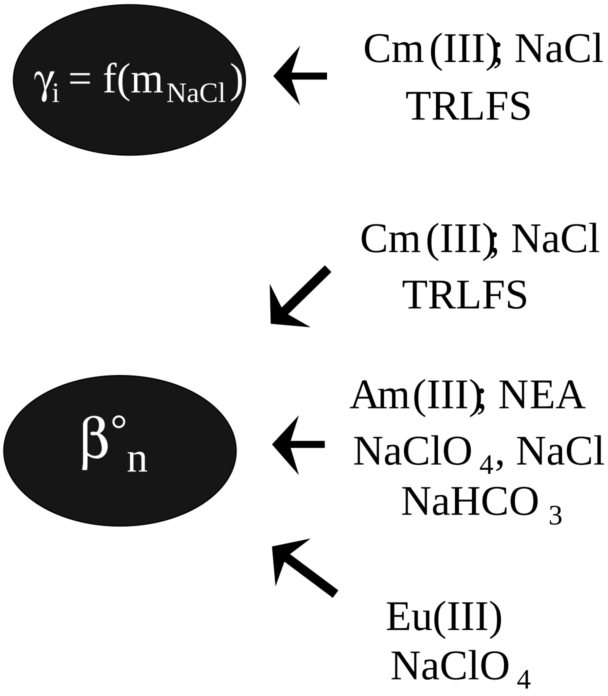
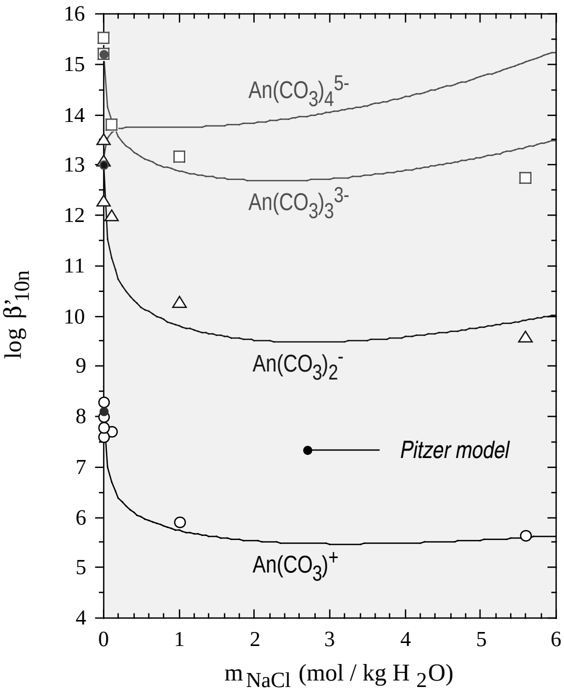
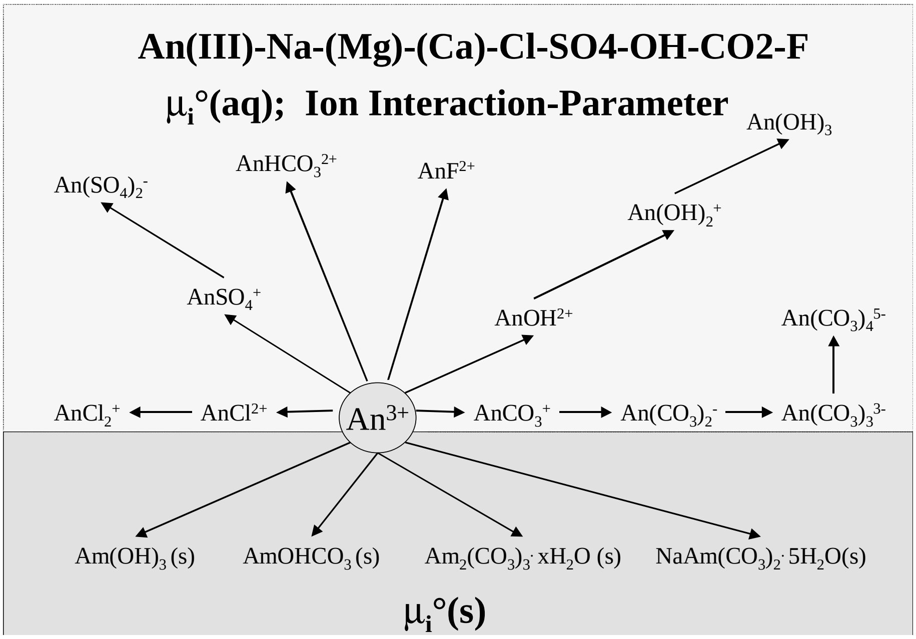


Figure 9. The formation constants of An(III) carbonate complexes



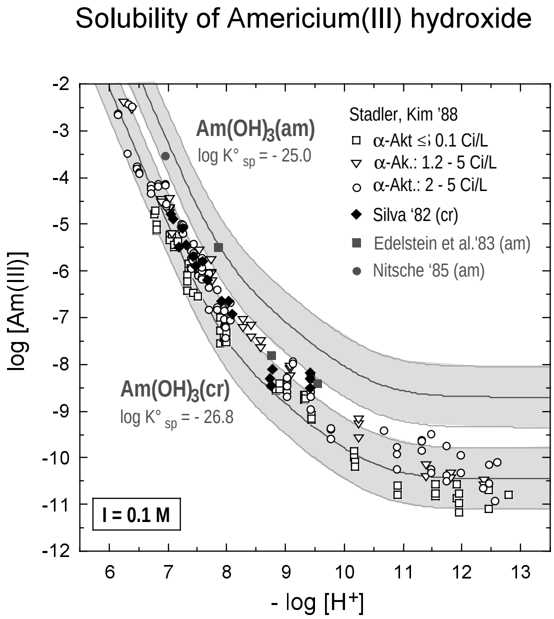
Formation constants of An(III)
carbonate complexes in 0-6 m NaCl, 25°C

Figure 10. Present state of our knowledge on the thermodynamics of trivalent actinides



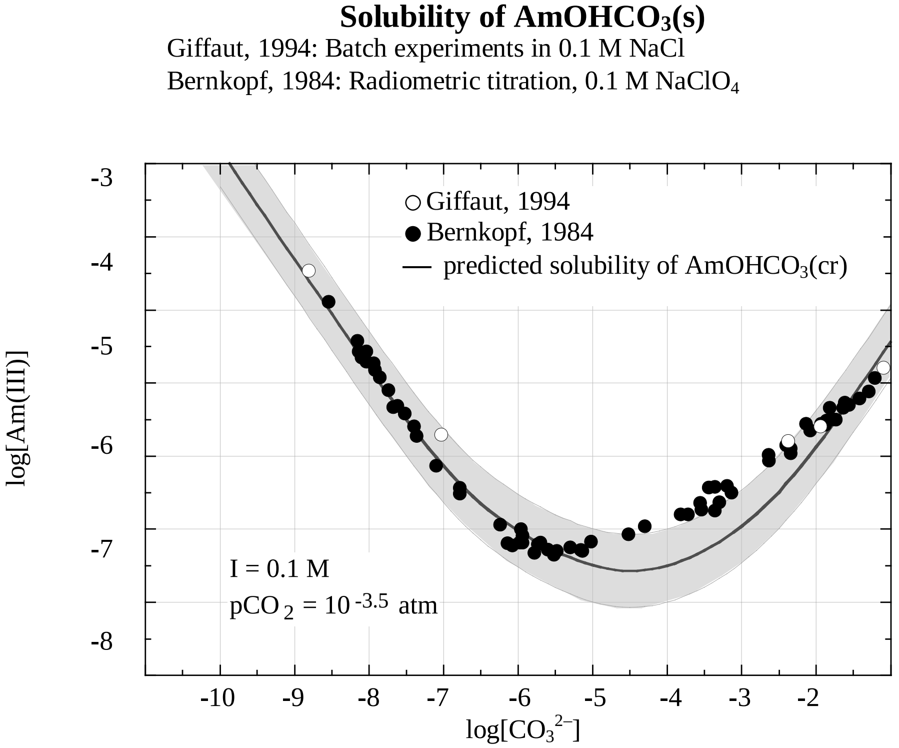
Figures 11, 12 and 13 show experimental and model calculations for the variation of the solubility of various trivalent actinides solids as a function of the acidity or the carbonate concentration for various types of well-characterised solids in different media. In all cases the model curves shown have been calculated by using the available Pitzer's approach parameters. Figure 13 illustrates further the applicability of the model in accounting for the solubility products of various Np(V) solid phases.

Figure 11. Solubility of Am(III) solids as a function of [H$^+$]



Comparison of experimental and calculated (continuous line)
solubilities at I = 0.1 M (NaClO$_4$/NaOH or NaCl/NaOH)

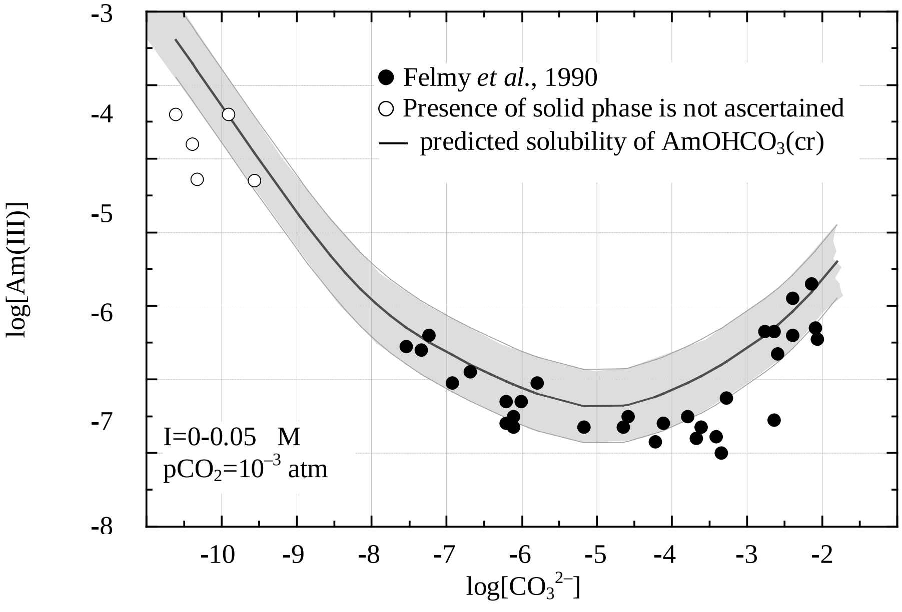
Figure 12. Solubility of $AmOHCO_3(s)$



Solubility of $AmOHCO_3(s)$

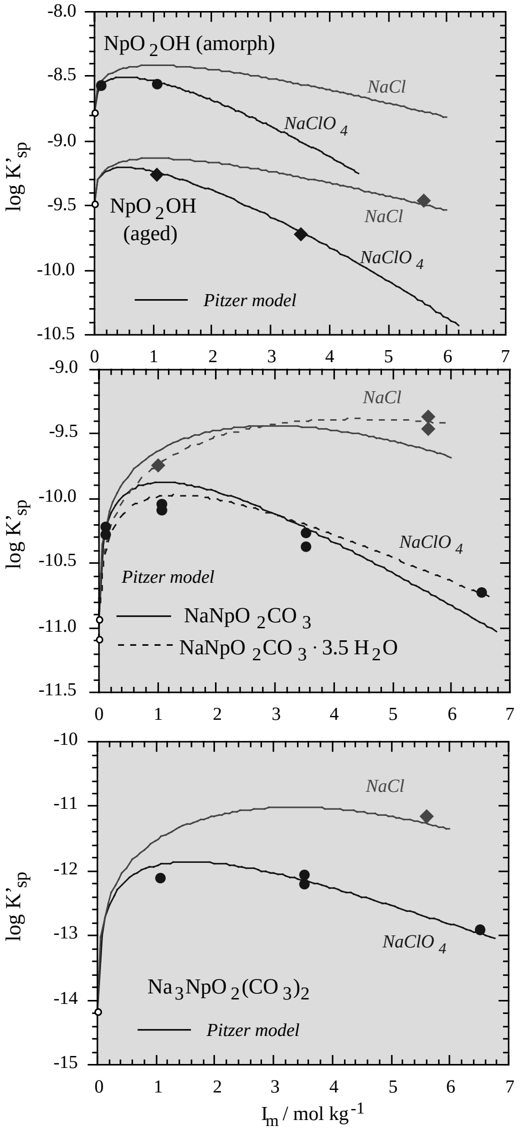
Giffaut, 1994: Batch experiments in 0.1 M NaCl

Bernkopf, 1984: Radiometric titration, 0.1 M $NaClO_4$



Felmy *et al.*, 1990: Batch exp. in $Na\text{-}HCO_3\text{-}CO_3$ solution

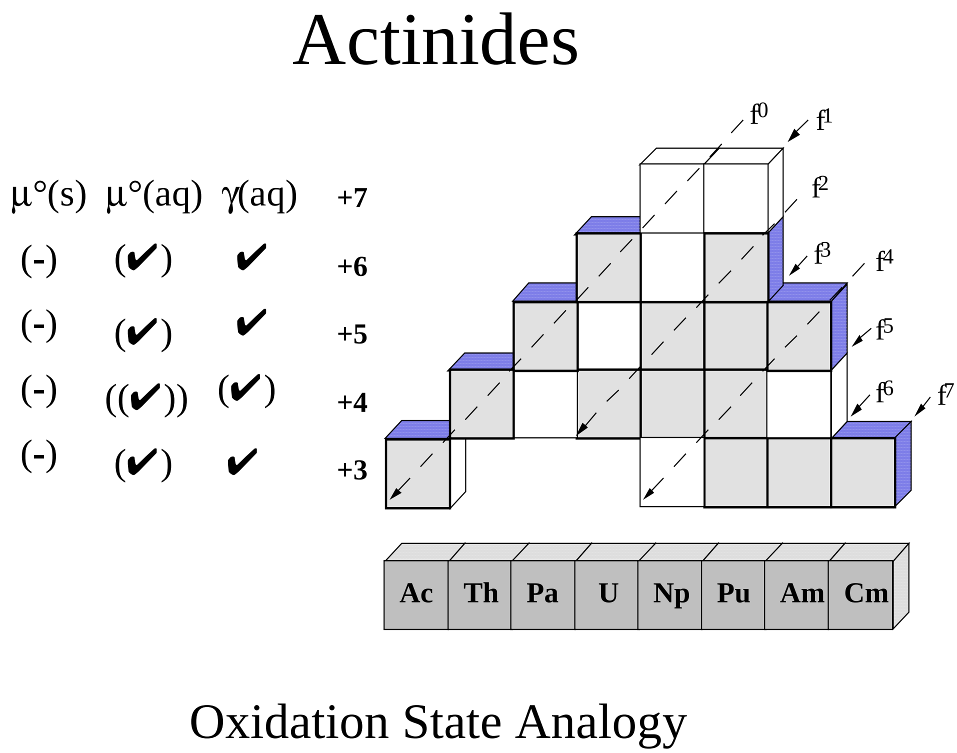
Figure 13. Experimental and predicted solubility products of Np(V) hydroxide and carbonate solid phases as a function of $NaClO_4$ and NaCl molality



The schematic representation in Figure 14 summarises the present situation with respect to the available experimental information for different oxidation states for the actinide series. In particular, the limited data existing for the tetravalent aqueous species and the problem of characterisation of the solid phases are highlighted.

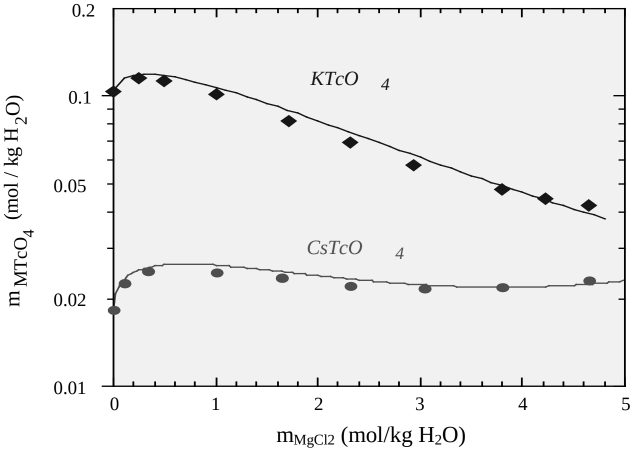
Outside the actinide series, an example for another element with waste management implications can be shown for Tc. Figure 15 shows the solubility data for $KTcO_4$ and $CsTcO_4$ solids in $MgCl_2$ media and the fit to Pitzer's approach equations. The corresponding parameters have been used to predict the solubility of $KTcO_4(s)$ in four concentrated multi-component solutions of different composition (shown in Figure 16 as I, II, III and IV). The predictions for these brines evaluated using Pitzer's approach can be compared to the experimental values in the table contained in Figure 17.

Figure 14. Available experimental data for different oxidation states for the actinide series



μ°(s)	μ°(aq)	γ(aq)	
			+7
(-)	(✔)	✔	+6
(-)	(✔)	✔	+5
(-)	((✔))	(✔)	+4
(-)	(✔)	✔	+3

Figure 15. Comparison between experimental and predicted solubility of $KTcO_4$ and $CsTcO_4$ in $MgCl_2$



Solubility of $KTcO_4$ and $CsTcO_4$ in 0-5 $MgCl_2$; experimental data and Pitzer model predictions denoted by continuous line

Figure 16. Model validation by comparing predicted and independent experimental solubility data of $KTcO_4$(s) in concentrated multi-component solutions of different composition

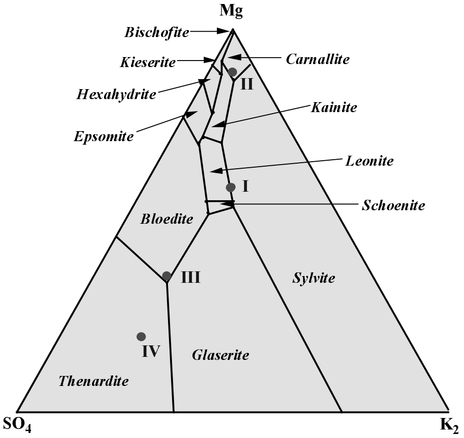


Figure 17. Experimental and calculated solubilities of $KTcO_4$ in high-saline brines

Brine	main components (molal)						I	$\log m_{TcO_4}$	
	Na	K	Mg	Ca	Cl	SO_4		(exp)	(pred.)
I	2.500	1.400	2.000	0	6.500	0.700	10.60	-2.24	-2.24
II	0.499	0.498	4.000	0	8.500	0.249	13.25	-2.26	-2.32
III	4.990	0.894	0.893	0	5.290	1.190	9.75	-1.94	-1.83
IV	6.040	0.037	0.019	0.023	6.040	0.059	6.26	-1.00	-0.94

Limitations of Pitzer's and SIT approaches

Table 1 summarises some of the acknowledged limitations and advantages of the two most currently used theoretical approaches for evaluation of excess properties in electrolyte solutions.

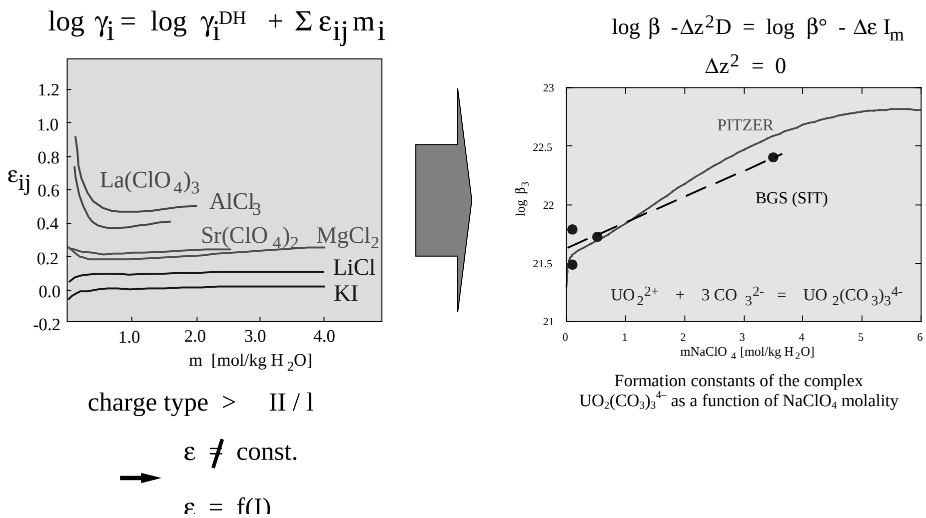
Table 1. Summary of acknowledged limitations and advantages of Pitzer's and SIT approaches

	Pitzer's	SIT
Range of ionic strength for recommended application	6-20	3-4
Systems	No restrictions on complexity of systems or charge of the species.	Restricted to simple systems. Systematic errors for ions with charge ≥ 2 since trenary interactions and ionic strength dependence of interaction parameters are neglected
Parametrisation	Relatively large quantities of precise experimental data are needed. Redundancy among parameters. Restricted experimental information. Difficult physical interpretation of parameters.	Few experimental data are sufficient to implement equations.

Some of the points contained in Table 1 are further illustrated in Figures 18, 19 and 20. Figure 21 highlights the limitations found in the application of Pitzer's approach to tetravalent actinides due to the current lack of experimental data on trace activity coefficients.

Figure 18. Limitations of BGS (SIT)

Neglecting the ionic strength dependence of ion interaction



Formation constants of the complex $UO_2(CO_3)_3^{4-}$ as a function of $NaClO_4$ molality

Figure 19. Limitation of BGS (SIT), neglecting ternary interactions. Example: Divalent anions, *e.g.* SO_4^{2-}, CO_3^{2-} in different media (NaCl, $NaClO_4$, $NaTcO_4$)

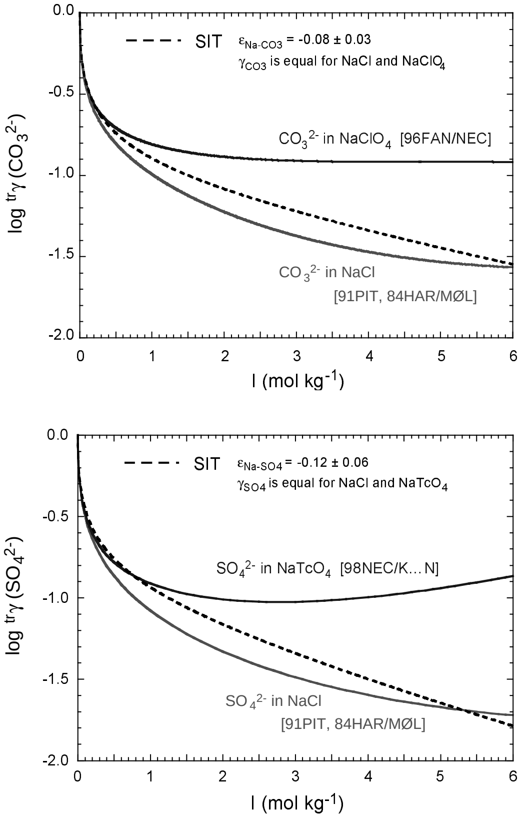


Figure 20. Limitation of BGS (SIT), neglecting ternary interactions. Example: H^+ in different media (NaCl, CsCl)

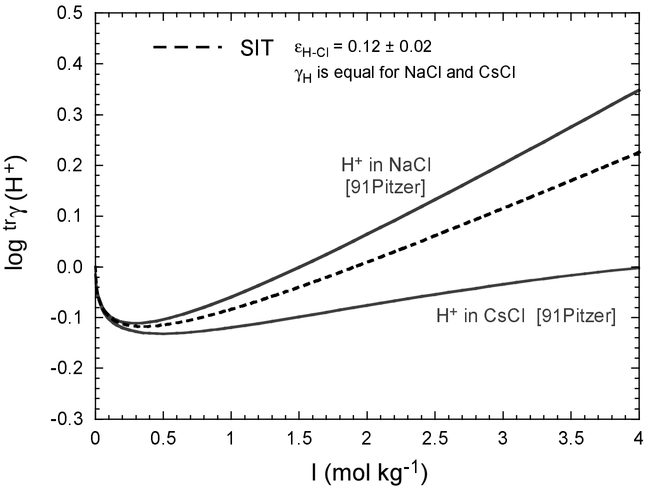
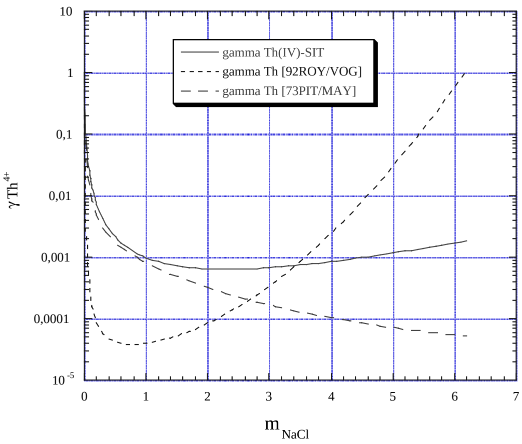


Figure 21. Tetravalent actinides

No exp. data on trace activity coefficients !

2 studies:

- Isopiestic ➜ osmotic coeff. in acidic $ThCl_4$ solutions [Robinson]
- EMF ➜ a_{HCl} in $ThCl_4$-HCl-H_2O [Roy et al.]



Situation is even worse for other tetravalent actinides and complexes !!!

THE USE OF SIT IN THE NEA TDB PROJECT – ADVANTAGES, DRAWBACKS AND COMPARISON WITH THE APPROACHES USED IN SOME GEOCHEMICAL CODES

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Introduction

The problem of the estimation of medium effects on equilibrium constants can be separated in two closely related parts:

- Extrapolation of the values obtained at relatively high ionic medium concentrations, but in general trace concentrations of the species of interest, to the standard state (often named extrapolation to zero ionic strength)

- Recalculation of the constants thus obtained to electrolyte mixtures of various ionic strengths, depending on the type of the system studied.

Chemical equilibria form the basis of many geochemical codes and the pertinent database contains thermodynamic constants for all the relevant equilibria, including complexation, solubility, redox reactions, etc. Thermodynamic models can not be better than the quality of the database used, thus its selection and validation is of crucial importance.

The compilation of the database is related to activity coefficient calculations, since, except in very special cases, it is impossible to study equilibria in standard state conditions, that is infinitely dilute aqueous solutions. In general the constants are determined at a certain ionic strength, depending on the choice of the experimentalist and related to the complexity of the system to be studied. These constants are conditional constants and are valid only for the conditions in which they have been determined.

Complexation, redox or solubility equilibria studies are based on the determination of the activity of the ligand, of the free metal ion or of the complexes formed for known total concentrations which vary within broad limits. Experimental techniques include, among others, ion selective electrodes, redox electrodes, radioactive tracers and spectrophotometric techniques of various types. The aim of the studies is the simultaneous determination of the species formed (chemical model) and their stability constants. Calculation methods are based on the comparison of the experimental data with the pertinent mathematical model, through graphical methods and/or computer programs.

Except for very simple cases, *e.g.* dissociation constants of weak acids, it is impossible to measure at very low ionic strengths, since the signal measured while making a change in the system may change due to the change in the chemical composition of the system studied and/or because of the change of the activity coefficients, that is the reciprocal influence of all the species present in the system.

An important achievement in chemical equilibrium analysis was the use of the ionic medium method, as of 1940. According to this method precise thermodynamic information for a given system can be obtained in the presence of an inert electrolyte of fairly high concentration (0.5-4 M), in order to ensure that activity factors remain reasonably constant during the measurements. This seems to be the only possibility to decouple the effect of changes in concentrations due to chemical reactions from the variation of the activity coefficients. This is particularly critical for ions of charge higher than 2 where strong hydrolysis and strong dependence of the activity coefficients on the ionic strength make very difficult the study of the equilibria in dilute media. Thus, there are otherwise excellent studies of reactions involving four valent actinide ions reaching concentrations of 1 mM, but realised in the presence of only 10 mM of an inert salt. The change of the concentration of the An(IV) ion is accompanied with changes in ionic strength in a region where activity coefficients depend very strongly on it (not to speak about changes in relative concentrations), rending the results almost useless.

Therefore most of the constants are determined in the presence of a relatively high concentration of an inert electrolyte. Consequently, we are then faced with the problem of converting these data to the standard state, which normally for solutes is the infinite dilute aqueous solution.

This simply means that a calculation of the activity coefficients of the species involved in the equilibrium studied, including metal complexes of various composition, should be carried out in the particular electrolyte mixture.

The same also applies to the second part of the problem, the recalculation of the database constants to the geochemical medium of interest. The range of applicability of geochemical models goes from very diluted groundwaters through seawater up to brines.

There are different ways of tackling this problem, all of them related to the state of the art of the theory of electrolyte solutions and to the required precision.

The specifics with complexation equilibria is that the activity coefficients of metal complexes (except for very strong ones *e.g.* $[Fe(CN)_6]$) can not be measured by, *e.g.* isopiestic measurements in pure solutions of the complex ion and a counter-ion, simply because it is impossible to prepare such solutions. They are measured indirectly through time-consuming measurements of the corresponding constant in 4-5 ionic strengths (at best) and with a precision quite often much lower than activity coefficient measurements of pure electrolytes (*e.g.* isopiestic measurements).

Actually, there is no feasible quantum statistical theory to solve the problem of activity coefficient calculation even for pure electrolytes at moderate and high ionic strengths. For the most part, empirical formulas (*e.g.* Davie’s for low ionic strengths) and semi-empirical approaches have been used. Of the latter, the most important are:

- ion association approaches;
- specific ion interaction approaches;
- ion hydration approaches.

In all these approaches equations of various degrees of complexity are available, and in general higher precision is reached by increasing the number of experimentally determined parameters to be introduced.

Ion association approaches consider ion pair formation, and take this into account in the calculation of a reduced ionic strength, then use different equations (from Davie's to Helgeson's) to calculate the activity coefficients of the species present in the system as functions of only ionic strength [1,2]. They have been and continue to be extensively used in geochemical codes. Their use at moderate or high ionic strengths, especially for "trace species", is not recommended following arguments presented, *e.g.* by Harvie, *et al.* [3].

Specific ion interaction approaches use a Debye-Hückel term for long-range electrostatic forces and a virial series in powers of molality for short-range forces [4], with coefficients specific for each pair of ions (included in short-range forces are all quantum-statistical interactions of ions with each other, with the solvent, triple interactions, etc.).

In the following only ion interaction approaches will be discussed. Some of their advantages concerning the specific problems of ionic strength effect on equilibrium constants are:

- The equations are easily extended to mixtures of electrolytes with the same parameters determined from activity coefficient measurements in pure electrolytes (or in simpler binary mixtures in the more elaborated versions as Pitzer's).
- A separation in conventional single ion activities is possible.
- The same equations are used for "trace components", as is often the case for metal ion complexes.

The most successful equations of the specific interaction (SI) approaches have been Pitzer's [5-8], used in a variety of geochemical systems up to very high ionic strengths, mainly for solubility equilibria [3,9-11]. The problem with their use in complexation equilibria is that the equations contain three parameters for pure electrolytes and for mixtures extra parameters are added. It seems almost impossible to obtain these parameters from indirect measurements of relatively low precision, as is the case with equilibrium constants. The main difficulty in the case of complex ions relays exactly in the main advantage of this approach for common electolytes: its high precision is due to a large Debye-Huckel term, which is compensated by pure electrolyte terms and mixing terms. In the case of metal ion species, the only data available are those obtained in electrolyte mixtures and it seems to be a not-so-simple task to split the two contributions.

The method used in the NEA reviews for estimating ionic strength effects is the simplest SI approach, mainly developed according to the ideas of Brønsted [12,13], Guggenheim [14] and Scatchard [15], which for consistency with previous literature [16,17], will be referred to as Specific Interaction Theory (SIT). The SIT method was established as the method of choice for the TDB Project during Phase I, and it will also be used in Phase II.

General representation of SIT and its use

According to SIT the activity factor γ_j of an ion of charge z_j in a solution of the overall ionic strength I ($I = 0.5\sum_i m_i z_i^2$) may be expressed as:

$$\log_{10}\gamma_\mathrm{j} = -z_\mathrm{j}^2\mathrm{D}(I) + \sum_\mathrm{k}(\mathrm{j,k},I)m_\mathrm{k} \qquad (1)$$

Here $\mathrm{D}(I)=\frac{0.5109\sqrt{I}}{1+1.5\sqrt{I}}$ (in aqueous solutions at 25°C, 1 atm) represents the Debye-Hückel term, accounting for long-range electrostatic interactions. The summation extends over all ions k present in the solution (single electrolyte or mixture) at the molality m_k. The $\varepsilon(j,k,I)$ terms, called interaction coefficients, account for various short-range forces between ions of opposite charge sign and are set equal to zero when the ions j and k are of the same charge sign. This means that short-range interactions between ions of the same charge sign are neglected, since they will be in general quite far apart from each other in moderately concentrated solutions, due to electrostatic repulsion. The factor 1.5 in the denominator of the Debye-Hückel term was suggested by Scatchard in order to minimise the concentration dependence of the interaction coefficients for 1:1, 2:1 and 1:2 electrolytes. Thus for $|z_i z_j| \leq 2$ the ionic strength dependence of the interaction coefficients is very small.

The main advantage of SIT, as compared to other specific interaction approaches, is its simplicity while applied in evaluating ionic strength effects on stability constants. It has all the advantages of the specific interaction approaches, being simpler at the cost of a lower accuracy, which still is often acceptable for most purposes. Also, certain trends on the magnitude of interaction coefficients make possible reasonable estimates when there is lack of data, *e.g.* for complexes of actinides.

Interaction coefficients can be calculated from data on activity coefficient measurements of solutions of pure electrolytes, tabulated, *e.g.* in Robinson and Stokes [18], in the manner described as follows.

By combining Eq. (1) with the expressions for the mean activity coefficient of the strong electrolyte $\mathrm{M}_{\nu+}^{z+}\mathrm{X}_{\nu-}^{z-}$:

$$(\nu_+ + \nu_-)\log_{10}\gamma_\pm = \nu_+ \log_{10}\gamma_{\mathrm{M}^{z+}} + \nu_- \log_{10}\gamma_{\mathrm{X}^{z-}} \tag{2}$$

and for the ionic strength of a solution of this electrolyte of molality *m*:

$$I = \frac{m}{2} z_+\nu_+(z_+ + z_-) = \frac{m}{2} z_-\nu_-(z_+ + z_-) = \frac{m}{2} z_+ z_-(\nu_+ + \nu_-) \tag{3}$$

the following expression is obtained:

$$\varepsilon(\mathrm{M}^{z+},\mathrm{X}^{z-},I) = \frac{(|z_+| + |z_-|)^2}{4I}\left(\log_{10}\gamma_\pm + |z_+ z_-|\mathrm{D}\right) \tag{4}$$

Since SIT has been used mainly for extrapolating stability constants of metal ion complexes to zero ionic strength, interaction coefficients for the main cations with $\mathrm{ClO_4^-}$, $\mathrm{NO_3^-}$, $\mathrm{Cl^-}$ and for the main anions with $\mathrm{H^+}$, $\mathrm{Na^+}$ and $\mathrm{Li^+}$, are available, including many interaction coefficients of metal ion complexes. The values of interaction coefficients not reported in their most complete list [19] have been calculated for all 1:1, 2:1 and 1:2 electrolytes for which activity coefficient measurements in pure solutions are available, including organic salts with anions of considerable size. Data on activity coefficients of the corresponding pure electrolytes have been calculated using Pitzer's equations and coefficients [6], since they reproduce measured values with acceptable accuracy for this purpose. The values reported in Table 1 correspond to the interaction coefficient of the anion and cation of the salt, calculated in the ionic strength interval 0.5-4 m, along with the standard deviation. For 1:2

interaction coefficients the ionic strength dependence is given explicitly in a third column in the form $\varepsilon(i,j,I) = \varepsilon_1(i,j) + \varepsilon_2(i,j)\log_{10}I$, following previous experience [16,17]. In this way a better fit between measured and calculated activity coefficients is achieved.

In the case of 2:2 electrolytes the expression $\varepsilon_1 \cdot I^{-\varepsilon_2}$ has been tested for the interaction coefficient, where I is the stoichiometric ionic strength (I = 4 m) and is decreased by multiplying it with the factor $I^{-\varepsilon_2}$ to account for its lower values because of complexation.

Thus the activity coefficient of a two-valent ion in a solution of the corresponding 2:2 electrolyte of molality m_2 is written:

$$\log_{10}\gamma_2 = -4D(I) + \left(\varepsilon_1 I^{-\varepsilon_2}\right)m_2 \qquad (5)$$

By applying this equation to data of Pitzer [20] on activity coefficient measurements of 2:2 electrolytes in the range of ionic strength specified in Table 3 (including measurements in very low concentrations), values of ε_1 and ε_2 have been determined for all the electrolytes. In any case, these values are recommended for use only after an extensive test in mixtures of electrolytes.

In conclusion, new interaction coefficients for almost 100 electrolytes are available, greatly increasing the existing database to be used in the calculations. Interaction coefficients for ions of importance in nuclear repositories, like caesium and strontium, are included in Table 1, while interaction coefficients for organic ions can be used as guess values for complex ions of comparable charge, size and polarisability.

Advantages, drawbacks and future development of SIT

The SIT method has several advantages that make it more suitable for the TDB project. It is simpler (fewer parameters are needed), less sensitive to errors and missing parameters can easily be estimated from values for ions of similar charge and size [19]. For an extensive discussion on different methods for the estimation of activity coefficients in electrolyte solutions, see Chapter IX of Ref. [19].

Some of the drawbacks of SIT are the absence of a complete database for all the common electrolytes and especially of parameters for 2:2 electrolytes, on which an attempt is made here to improve the situation. This would make possible the use of SIT in the modelling of geochemical systems, since carbonate, sulphate, Mg and Ca ions are all important components of such systems. Another drawback of SIT is the limited range of ionic strength validity. It is not valid for high ionic strengths and an improvement is also needed at low ionic strengths for highly-charged ions. Another necessary improvement is the inclusion of θij terms for mixtures.

In any case, while using the OECD/NEA database with geochemical modelling codes, special care should be taken when performing calculations in non-dilute media. The geochemical modelling codes use other methods for ionic medium corrections (*e.g.* PHREEQE normally uses an ion association approach, while EQ 3/6 an ion hydration one). Sometimes weak complexes are used to account for ionic strength effects by the various codes, while the NEA TDB data were extrapolated at zero ionic strength neglecting these complexes [22].

REFERENCES

[1] C.W. Davies, “Ion Association”, Butterworths, Washington (1962).

[2] H.C. Helgeson, “Thrmodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures”, *Am. J. Sci*., 267, 729-804 (1969).

[3] C.E. Harvie, N. Moller and J.H. Weare, “The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O System to High Ionic Strength at 25°C”, *Geochim. Cosmochim. Acta*, 48, 723-751 (1984).

[4] K.S. Pitzer, “Theory: Ion Interaction Approach”, in *Activity Coefficients in Electrolyte Solutions*, R.M. Pytkowitz, ed., Vol. 1, Boca Raton, FL, USA: CRC Press, 157-208 (1979).

[5] K.S. Pitzer, “Thermodynamics of Electrolytes: I. Theoretical Basis and General Equations”, *J. Phys. Chem*., 77, 268-277 (1973).

[6] K.S. Pitzer and G. Mayorga, “Thermodynamics of Electrolytes: II. Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent”, *J. Phys. Chem*., 77, 2300-2308 (1973).

[7] K.S. Pitzer and G. Mayorga, “Thermodynamics of Electrolytes: III. Activity and Osmotic Coefficients for 2:2 Electrolytes”, *J. Sol. Chem*., 3, 539-546 (1974).

[8] K.S. Pitzer and J.J. Kim, “Thermodynamics of Electrolytes: IV. Activity and Osmotic Coefficients for Mixed Electrolytes”, *J. Am. Chem. Soc*., 96, 5701-5707 (1974).

[9] C.E. Harvie and J.H. Weare, “The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-Cl-SO_4-H_2O System from Zero to High Concentration at 25°C”, *Geochim. Cosmochim. Acta*, 44, 981-997 (1980).

[10] C.E. Harvie, H.P. Eugster and J.H. Weare, “Mineral Equilibria in the Six-component Seawater System, Na-K-Mg-Ca-SO_4-Cl-H_2O at 25°C. II: Composition of the Saturated Solutions”, *Geochim. Cosmochim. Acta*, 46, 1603-1618 (1982).

[11] R.T. Pabalan and K.S. Pitzer, “Thermodynamics of Concentrated Electrolyte Mixtures and the Prediction of Mineral Solubilities to High Temperatures for Mixtures in the System Na-K-Mg-Cl-SO_4-OH-H_2O”, *Geochim. Cosmochim. Acta*, 51, 2429-2443 (1987).

[12] J.M. Brønsted, “Studies on Solubility: IV. The Principle of Specific Interaction of Ions”, *J. Am. Chem. Soc*., 44, 877-898 (1922).

[13] J.M. Brønsted, “Calculation of the Osmotic Activity Functions of Uni-univalent Salts”, *J. Am. Chem. Soc*., 44, 938-948 (1922).

[14] E.A. Guggenheim and J.C. Turgeon, “Specific Interaction of Ions”, trans. Faraday Soc., 51, 747 (1955).

[15] G. Scatchard, “Concentrated Solutions of Strong Electrolytes”, *Chem. Rew*., 19, 309-327 (1936).

[16] G. Biedermann, “On the Nature of Seawater”, E.D. Goldberg, ed., Dahlem Konferenzen, Berlin (1975).

[17] L. Ciavatta, “The Specific Interaction Theory in Evaluating Ionic Equilibria”, *Ann. Chim*. (Rome), 70, 551-567 (1980).

[18] R.A. Robinson and R.H. Stokes, “Electrolyte Solutions”, 2nd ed., London, Butterworths (1968).

[19] B. Allard, S. Banwart, J. Bruno, J. Ephraim, R. Grauer, I. Grenthe, J. Hadermann, W. Hummel, A. Jakob, T. Karapiperis, A. Plyasunov, I. Puigdomenech, J. Rard, S. Saxena, K. Spahiu, “Modelling in Aquatic Chemistry”, OECD/NEA, Paris (1997).

[21] K.S. Pitzer, “Thermodynamic Properties of Aqueous Solutions of Bivalent Sulphates”, *J. Chem. Soc*., Faraday Trans., II 68, 101-113 (1972).

[22] K. Spahiu, I. Puigdomenech, “On Weak Complex Formation: Re-interpretation of Literature Data on Np and Pu Nitrate Complexes”, *Radiochim. Acta*, 82, 413-419 (1998).

Table 1. Interaction coefficients for 1:1, 2:1 and 1:2 electrolytes

*(a) 1:1 electrolytes**

Inorganic comp. (MX)	**$\varepsilon(M^+,X^-)$**	**1:1 salts of carboxylic acids**	**$\varepsilon(M^+,X^-)$**
HBr	0.15±0.01	Cs Acetate	0.11±0.01
HI	0.18±0.01	Rb Acetate	0.10±0.01
CsF	0.06±0.01	Tl Acetate	-0.07±0.02
CsCl	-0.05±0.02	Na Propionate	0.11±0.01
CsBr	-0.04±0.02	Na HMalonate	-0.04±0.01
CsI	-0.06±0.02	Na HSuccinate	-0.03±0.01
$CsNO_3$	-0.16±0.03	Na HAdipate	-0.01±0.01
$CsNO_2$	-0.04±0.02	K HMalonate	-0.07±0.01
RbF	0.05±0.01	K HSuccinate	-0.05±0.01
RbCl	-0.025±0.01	K HAdipate	-0.01±0.01
RbBr	-0.03±0.01	**Tetralkylammonium halides**	**$\varepsilon(M^+,X^-)$**
RbI	-0.03±0.01	Me_4NF	0.18±0.01
$RbNO_3$	-0.14±0.03	Et_4NF	0.32±0.01
$RbNO_2$	-0.09±0.03	Pr_4NF	0.43±0.03
NaH_2AsO_4	-0.08±0.01	Bu_4NF	0.48±0.02
KH_2AsO_4	-0.12±0.02	Me_4NCl	-0.08±0.02
$NaBF_4$	-0.07±0.01	Et_4NCl	-0.07±0.04
$NaBO_2$	-0.09±0.03	Bu_4NCl	-0.04±0.02

* Additional interaction coefficients for more than 40 other organic electrolytes (*e.g.* sulphonic acids and salts) have been calculated for almost all data in Ref. [6] and are available on request.

Table 1. Interaction coefficients for 1:1, 2:1 and 1:2 electrolytes (*cont.*)

*(b) Inorganic 2:1 electrolytes and 1:2 electrolytes**

2:1 salts (M_2X)	**$\varepsilon(M^{2+},X^{-})$**	**2:1 salts(M_2X)**	**$\varepsilon(M^{2+}, X^{-})$**		
$Sr(ClO_4)_2$	0.23±0.005	SrI_2	0.25±0.01		
$Sr(NO_3)_2$	-0.06±0.01	BaI_2	0.23±0.01		
$SrCl_2$	0.13±0.01	CoI_2	0.33±0.01		
$FeCl_2$	0.14±0.01	ZnI_2	0.32±0.03		
$ZnCl_2$	0.04±0.03	**1:2 salts(MX_2)**	**$\varepsilon(M^{2+},X^{2-})$**	**ε_1**	**ε_2**
$MgBr_2$	0.26±0.01	$Na_2S_2O_3$	-0.12±0.03	-0.135	0.079
$CaBr_2$	0.18±0.01	Na_2HasO_4	-0.21±0.06	-0.117	-0.121
$SrBr_2$	0.18±0.01	K_2HasO_4	-0.02±0.01	0.018	-0.038
$BaBr_2$	0.13±0.01	Rb_2SO_4	-0.15±0.04	-0.176	0.119
$CoBr_2$	0.25±0.01	Cs_2SO_4	-0.13±0.04	-0.151	0.113
$ZnBr_2$	0.21±0.03	$(NH_4)_2SO_4$	-0.23±0.07	-0.279	0.232
MgI_2	0.32±0.01	cis[Co(en) $_2NH_3NO_2]Cl_2$	-0.29±0.08	-0.362	0.278
CaI_2	0.27±0.01	tr.[Co(en) $_2NH_3NO_2]Br_2$	-0.36±0.09	-0.436	0.333

* I = 3 m, ε values calculated in the ionic strength interval I = 0.6-4.2 m. For 1:2 electrolytes with standard deviations larger than 0.03, $\varepsilon(i,j,I) = \varepsilon_1 + \varepsilon_2 \log_{10}I$, with the values of ε_1 and ε_2 in the right hand column.

Table 2. Interaction coefficients for 2:2 electrolytes calculated as $\varepsilon(\mathbf{i}, \mathbf{j}, I) = \varepsilon_1 \cdot I^{-\varepsilon_2}$ from data of Pitzer [20], without considering complexation

Electrolyte ($M^{2+}X^{2-}$)	**$\varepsilon(M^{2+}X^{2-}, I) = \varepsilon_1 \cdot I^{-\varepsilon_2}$**		**Ionic strength interval, molal**
	ε_1	**ε_2**	
$MgSO_4$	-0.632	0.723	0.02-7.2
$NiSO_4$	-0.816	0.676	0.02-7.2
$CuSO_4$	-0.916	0.693	0.02-7.2
$ZnSO_4$	-0.745	0.663	0.02-7.2
$CdSO_4$	-0.919	0.690	0.02-7.2
$MnSO_4$	-0.491	0.405	0.02-5.6
UO_2SO_4	-0.669	0.428	0.02-5.6
$BeSO_4$	-0.4025	0.464	0.02-6.4
$CaSO_4$	-0.927	0.724	0.02-0.8
$CoSO_4$	-0.767	0.645	0.02-0.8

DISCUSSION

J. Bruno opened the discussion by highlighting the usefulness of Davies' approach during the Chemval I project.

I. Grenthe argued that at the beginning of the NEA TDB Project there were not enough data in the literature to compare different ionic strength approaches. Therefore the SIT was used in NEA TDB as an attempt to unify criteria. Moreover, the impossibility of determining the Pitzer coefficients for all the relevant systems supported the decision of using the SIT approach.

K. Spahiu pointed out that SIT is used for correcting data to different ionic strength but that one of the problems is to extrapolate the data to infinite dilution.

T. Fanghänel agreed with the use of SIT provided there was a clear statement of its limitations, such as those occurring at high ionic strength and its lack of description of ternary interactions. Moreover, he pointed out the existing gap between thermochemical cycle data and electrolyte data due to the correction to zero ionic strength. It is very difficult to adequately transfer ionic strength corrections to geochemical codes due to, among other reasons, the fact that they are collected in very different ways.

J. Bruno summarised the main points of the discussion so far, specifically: the use and limitations of each approach, the difficulty in transferring the corrections to geochemical codes and the lack of consistency in collecting thermochemical data.

B. Grambow raised the point of how temperature affects the activity coefficients.

I. Grenthe said that in the NEA book "Modelling in Aquatic Chemistry", some indications of how these corrections can be undertaken are given.

B. Grambow asked whether there is any preferred approach for extending data to higher temperatures.

T. Fanghänel answered that for the calculation of ε empirical approaches are the only ones available and that a large influence of temperature is expected due to the change in the solvent properties. In general, he said that there exists a lack of knowledge on the subject.

K. Spahiu pointed out that SKB is interested in temperatures up to 70ºC and that the temperature effects within that range might not be dramatic.

J. Bruno argued that despite SKB being interested only in temperatures below 70ºC, other studies need to extend the temperature range up to higher values. Furthermore he disagreed with the perception of T. Fanghänel that there is no knowledge on this issue, the problem being that the existing knowledge is limited.

I. Grenthe pointed out the possibility of developing an experimental programme to study systems at higher temperatures. Another possibility would be to develop the models based on our fundamental understanding, that is: to see what are the consequences of introducing a given effect in the data and in this way to identify the main points worth studying. Finally, he highlighted the fact that problems arise when theories are used outside their domain of applicability.

C. Tweed stated the need of experimental data to validate the models. She noted that when we agree we usually think we are right, which is not mandatory. An agreement does not imply a correct assumption. Therefore, experiments must validate our agreements.

I. Grenthe said that the logical sequence for the modelling is: based on data build up the theory that allows developing an estimation procedure, which can then be validated with data. That is, carry out an iterative procedure. The important point being: What data must be considered?

T. Fanghänel said that it is difficult to find funds for developing an experimental programme at high temperatures. On the other hand, he said that there is a need for key experimental data because not only does the electrolyte chemistry change at higher temperature, but all chemistry is indeed affected. He further elaborated that, by using spectroscopic techniques, it is possible to validate data on, for example, the complexation of Cm.

I. Grenthe said that to obtain adequate data it is necessary to use specific experimental techniques, which in some circles may be considered to be “old-fashioned science”. Thus, the current difficulties experienced in obtaining financial support.

U. Berner raised the following question to the speakers: How chemically consistent is our system if we do not have a complete database for activity coefficients? And how can we estimate these parameters?

T. Fanghänel answered that correlations can be used for these purposes.

I. Grenthe said that it is feasible to ensure that two different models (such as SIT and Pitzer) converge at reasonably low ionic strength, a procedure that can be used to verify the consistency of the approach.

T. Fanghänel stated that problems exist for the highly charged species. In such cases, we can obtain up to 10 or 15 orders of magnitude of difference by using different approaches. He highlighted the need to find a solution for the problem of highly charged ions.

K. Spahiu commented on the experimental difficulty of isolating complexes, thus making the determination of interaction coefficients difficult.

Data Estimation

THERMODYNAMICS, DATA ESTIMATION AND PERFORMANCE ASSESSMENT

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Introduction

Performance assessment provides a narrative of a system and its development. One may use a literary metaphor; the procedure is like writing a novel where the "chapters" are the various sub-systems and where both the "plot" and the "grammar" are based on scientific and other information, some hard facts and other more or less reliable guesses. I will begin with some general remarks on models, which may provide a useful starting point for what follows.

- Models never provide complete descriptions of real systems; they are used to highlight certain aspects of them and to answer "what-if" questions.
- Modelling is an iterative process that provides guidance as to what are important phenomena and what is less relevant for the description of the system and its function.
- It is necessary to distinguish between model uncertainties and parameter uncertainties.
- It is often better to estimate a quantity for which no data are available than to exclude the particular process where it is needed. Thermodynamics provide not only numerical values for different chemical processes, but more important a theory framework that can be used for the estimation of data.

I will not discuss activity coefficient corrections of thermodynamic data, an important area that has already been addressed by Professor Fanghänel.

In the following overview I will be using examples of estimations of different kinds to illustrate what can be accomplished using thermodynamics in combination with chemical theories. Let us begin with the thermodynamics of solid phases and their solubility; I do not need to emphasise their importance in performance assessment. Let us take thermodynamic data for crystalline uranium dioxide as the first example. Table 1 shows thermodynamic data of two types, data obtained using calorimetry and data obtained using equilibrium measurements, solubility measurements in this case.

What happens if the two experimental methods do not provide concordant results? Which value should then be used? In general the one that is more precise, often the one based on calorimetry. This answer should be qualified – provided that the thermodynamic state of the system is the same in both experiments. In many cases this is not the case, as solubility data of oxide phases are hampered by ill-defined surface phases which determine the solubility, while the calorimetric data refer to bulk

Table 1. Thermodynamic data obtained using calorimetry and solubility measurements

Calorimetry

U(s, 298.15 K, 0.1 MPa) + O_2(g, f = 1, 298.15 K, 0.1 MPa) → UO_2(s, 298.15 K, 0.1 MPa) (1)

Using combustion calorimetry we measure $\Delta_\mathrm{r} H^\circ_\mathrm{m}(1) = \Delta_\mathrm{f} H^\circ_\mathrm{m}(\mathrm{UO_2(s)})$; Using calorimetry we can also measure the entropy of the reactants and products and therefore also $\Delta_\mathrm{r} S^\circ_\mathrm{m}(1)$. Using the relationship $\Delta_\mathrm{r} G^\circ_\mathrm{m}(1) = \Delta_\mathrm{r} H^\circ_\mathrm{m}(1) - T\Delta_\mathrm{r} S^\circ_\mathrm{m}(1)$ we can then calculate the Gibbs energy of formation of UO_2(s).

Solubility measurements

We measure the equilibrium concentration of U^{4+} is acid solutions according to:

$$\mathrm{UO_2(s)} + 4\mathrm{H^+} \rightleftharpoons \mathrm{U^{4+}} + 2\mathrm{H_2O} \qquad (2)$$

for which $\log_{10} {}^*K_\mathrm{s} = -\Delta_\mathrm{r} G^\circ_\mathrm{m}(2)/2.303\ \mathrm{R}T$ $\log_{10} {}^*K_s = -\ \Delta_\mathrm{r} G^\circ_\mathrm{m}/2.303\ \mathrm{R}T$.

$$\Delta_\mathrm{r} G^\circ_\mathrm{m} = \Delta_\mathrm{f} G^\circ_\mathrm{m}(\mathrm{U^{4+}}) + 2\ \Delta_\mathrm{f} G^\circ_\mathrm{m}(\mathrm{H_2O}) - \Delta_\mathrm{f} G^\circ_\mathrm{m}(\mathrm{UO_2(s)}) - 4\ \Delta_\mathrm{f} G^\circ_\mathrm{m}(\mathrm{H^+}) \qquad (3)$$

The Gibbs energy of formation, $\Delta_\mathrm{f} G^\circ_\mathrm{m}$, is a quantity that is tabulated in thermodynamic databases, *cf.* NEA [1]. It is obvious that the Gibbs energy of formation of UO_2(s) can be calculated from $\Delta_\mathrm{r} G^\circ_\mathrm{m}$ from solubility data, provided we know the remaining Gibbs energy of formation in Eq. (3). There is nothing strange about this, it is a consequence of the experimental fact that the thermodynamic quantities are *state functions*.

properties. In performance assessment the surface phases are in general more important than bulk phases. Notice that the discrepancy between solubility measurements and calorimetric data is often a problem of system definition and not due to experimental uncertainty. I do not think it correct to use thermodynamic data for bulk phases and claim that they are “conservative”. Be careful when using thermodynamic data for solid phases and look into the conditions under which these data have been measured.

Note that one can calculate the Gibbs energy of reaction for any hypothetical reaction provided the Gibbs energy of formation of reactants and products is known; this is not an estimation, it is precise information based on theory.

It is difficult, expensive and time consuming to determine thermodynamic data for solid phases and there are very few laboratories left with the competence to perform work of this kind. Methods for the estimation of thermodynamic quantities of solid phases are therefore important; Professor Ewing will describe such methods later this afternoon.

Before proceeding, I want to make a comment on the uncertainty estimates used in the NEA thermodynamic database [1]. The uncertainty is based on expert judgement in combination with the estimated precision of the experimental data given by the authors of the various papers. However, the quality of the latter information varies greatly between the different authors.

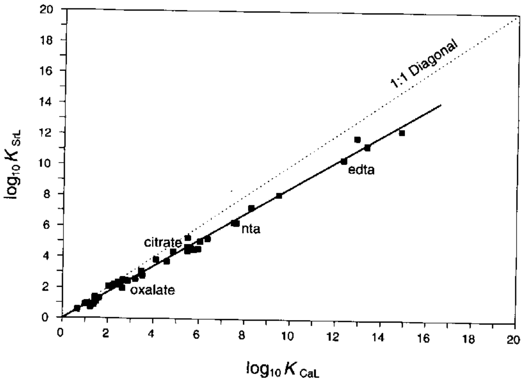
The thermodynamic data in a database are more than a compilation, they are the experimental basis for an important class of chemical theories which may be used for estimating unknown data. When evaluating thermodynamic data from the literature (as done in the NEA reviews), these theories provide an important additional check on the consistency of the thermodynamic data. Estimations must always be based on theory, and the characteristics of these theories differ widely, as exemplified in the following. Let us begin with the heuristic ones, as they all have their origin in concepts of chemical bonding and chemical structure (see Table 2)

Table 2. Heuristic models

Chemical bonding is directional and can be seen as the result of a balance between attractive and repulsive forces; these depend on the size and chemical character of the atoms linked. These factors will determine the geometry and the stoichiometry (the chemical composition) of the compounds we are studying, the co-ordination number of the metal ion is a reflexion of these characteristics. Stoichiometry is one of the most important quantities when making estimations of chemical properties, *e.g.* for the modelling of the chemical speciation in a complex ground- or surface-water system. It is often straightforward to suggest a reliable stoichiometry for species in solution; however, multi-component systems may pose problems. These can in many cases be overcome by estimates of the strength of the chemical bonding, in our case between a metal ion and a ligand. These estimates are qualitative and based on two simplified concepts of chemical bonding, the electrostatic vs. the covalent model. This will tell us that fluoride complexes are much stronger than chloride complexes for actinides, in the same way actinide-oxygen and nitrogen bonds are much stronger than the corresponding sulphur and phosphorous bonds. This fact will immediately indicate the metal-ligand interactions that will decide the speciation in solution.

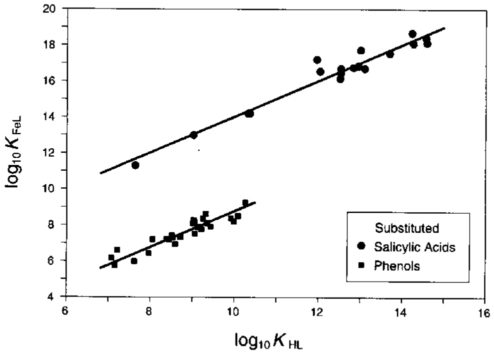
We can go one step further and use the heuristic models in correlations of various types; these will provide semi-quantitative estimates of equilibrium constants with an uncertainty that is often less than one order of magnitude. The correlation must always have a scientific basis, and this will to a large extent decide how successful it is for estimations. The rationale behind many correlations goes back to concepts of the chemical bonding.

If the chemical bonding between a group of metal ions, M_i, and two different ligands, X and Y, are similar we may expect a correlation between them, *e.g.* a linear relationship between log M_iX and log M_iY. This relationship may be used to estimate log M_IX for a particular metal, I, if the corresponding value for log M_IY is known. In the same way we can make a linear free energy plot for a set of ligands and two different metal ions. An example of the latter is shown below.



These correlations can only be used if there is evidence for similar type of bonding in the different systems, *e.g.* mainly ionic. In addition one must have structural information that the steric constraints in the complexes do not vary much.

Another example is the correlation between $\log_{10}MX$ and $\log_{10}HX$, where X is the anion of different weak organic acids HX. The underlying chemical principle here is the similarity in bonding between the proton and different metal ions. In the example the acid strength is varied through the use of substituents in the part of the ligand that does not participate in the bonding to the metal ion. This type of correlation is often quite good. Wolfgang Hummel may elaborate this theme in his presentation.



Another example of correlation is obtained by comparing the stepwise equilibrium constants in a given system. Here the metal ligand bond characteristics are presumably the same, and the step-wise constants will then depend on statistical factors and geometric constraints. More details are given in Chapter III, of “Modelling in Aquatic Chemistry” [2].

There are other models used to predict unknown equilibrium constants that superficially are more elaborate than the ones described so far, however they share the same characteristic features, *i.e.* a simplified model of chemical bonding and a “calibration” that is very similar to the correlation procedure described above. Neck and Kim [3] have suggested a simple and accurate model for the estimation of equilibrium constants for actinides based on the known value of one equilibrium constant and an electrostatic model to describe ligand-ligand repulsions:

$$\log_{10}\beta_n = n\log_{10}\beta_1 - {}^{rep}E_L(ML_n)/RT\ln 10 \qquad (4)$$

where ${}^{rep}E_L = N_A(1/2)(z_L z_{L'} e^2/(d_{L-L'} . \varepsilon_{L-L'})$.

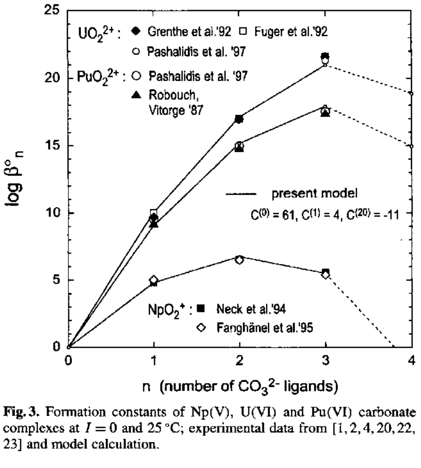


Fig. 3. Formation constants of Np(V), U(VI) and Pu(VI) carbonate complexes at $I = 0$ and 25 °C; experimental data from [1, 2, 4, 20, 22, 23] and model calculation.

$\varepsilon_{L\text{-}L'}$ is a parameter describing the electrostatic shielding between the negative charges of the ligands L and L′. This “dielectric constant” depends on the geometry and it is a “fitting” parameter that has to be determined from experimental equilibrium constants. The figure shows a comparison between model predictions and experimental data. Note that the relationship is only used to describe the variation of $\log_{10}\beta_n$ for a given metal-ion, the charge of which is a constant and therefore not included explicitly. This method seems useful when estimating the step-wise equilibrium constants for a given metal-ligand system, if experimental data cannot be obtained over the entire concentration range where the complexes exist in measurable amounts.

An appealing feature of this model is that it does not contain many adjustable parameters.

Brown and Sylva [4] have proposed a much more elaborate model which relies on simplified concepts of chemical bonding and parameters that have to be estimated from experimental data. The electron structure of the metal-ion and ligand are taken into account by introducing empirical parameters ε_M and ε_L. Their correlation equations have the following principle form:

$$\log_{10}\beta_1 = \mathrm{Int}_1 + \mathrm{Slp}_1\left[g_1\left(Z_M/r_M^2 + g_2\right)\right] \tag{5}$$

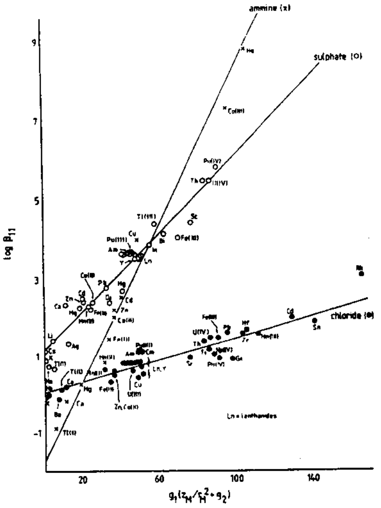
where Int_1 and Slp_1 are the intercept and slope, respectively, of the regression line.

$$g_1 = \left(1 + D + \varepsilon_L^2 S\right)\left(Z_M + 2\right) \tag{6}$$

and:

$$g_2 = g(n)\left(Z_M - 1\right) - 0.05d\left[(\gamma-1)\left(\varepsilon_L^4 - 3\right) - 1\right]\left[n - (3+2\gamma)\right]^2\left[1 - \gamma Z_M\right]\left(1 - S\right) \tag{7}$$

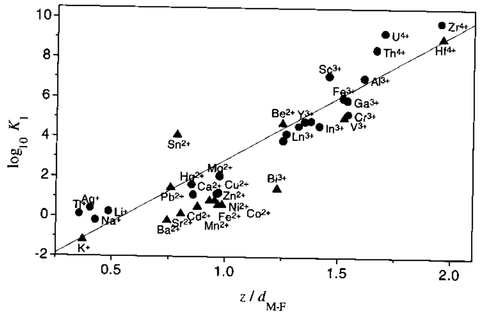
S has the value zero or unity depending on the absence or presence of s-electrons in the valence shell; D = 1 when d-electrons are present, and is otherwise zero. The principal quantum number is n; g(n) is a Slater function and γ is a new ligand-dependent parameter. A disadvantage of the model is that there are a larger number of fitting parameters, but also a “shaky” theoretical foundation. An example of the type of correlation obtained is given in the following figure:



Experimental log β_{11} values plotted against the function $g_1(z_M/r_M^2 + g_2)$ for the sulphate, ammine, and chloride ions

The last two models are based on an electrostatic model of the chemical bond. Other types of correlations are based on the same assumption, as indicated by the following example:

Figure III.21: The dependence of $\log_{10} K_1$ for the formation of metal fluoride complexes, MF^{n+}, with the ratio of the charge to the M-F distance. Ionic radii are from [69SHA/PRE], and stability constants are from [76SMI/MAR, 82MAR/SMI, 89SMI/MAR] (circles: data at $I = 0$, triangles: data at $I > 0$).



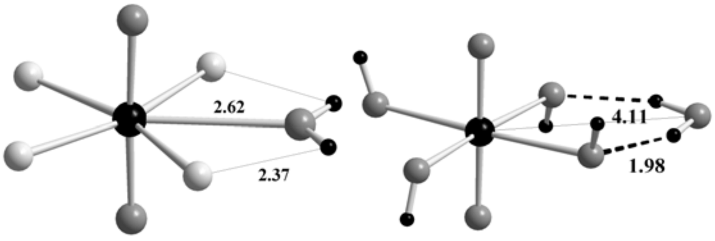
What is the theoretical justification of the electrostatic assumption? The answer can only be given if we compare the simple model approaches with one that has a firm theoretical foundation. This is where quantum chemistry and *ab initio* models enter the stage (see Table 3).

Table 3. ***Ab initio*** **model**

These models use "first principles", they start from the known electronic structure of a certain reactants and products. These are approximated by a set of wave functions and the total energy of the system is determined. These data provide detailed information of the geometry of the different species as well as thermodynamic quantities such as equilibrium constants. The parameter-fitting is not related to the specific species/reactions studied but is related to the properties of the inner electron shells and the directional characteristics of the valence orbitals. These properties are general, not element specific. We are NOT dealing with a parameter-fitting of the type used in the first set of examples of estimation methods. This is an area where there is much current activity, and it is an area that should be followed closely by this community.

It turns out that electrostatic interactions are the dominating influence of chemical bonding in many actinide complexes and also for the interactions between complexes and the surrounding solvent. Hence, the *ab initio* models provide a qualitative validation of the electrostatic correlations described above.

I will conclude the remark on *ab initio* methods by the following figure that shows the results of some of our own recent studies. The structure of the complexes $UO_2F_4(H_2O)^{2-}$ and $UO_2(OH)_4^{2-} \cdot (H_2O)$ are shown in this figure; the water is not co-ordinated to uranium in the second complex.



The quantum chemical methods provide, in this case, not only a quantitative structure description that can be compared with experiments, but also information on the energy of reaction and on mechanisms of chemical transformations.

A paper on data estimation for aqueous species would be incomplete without a discussion of the effect of temperature on equilibrium constants and thereby on chemical speciation. The problem is straightforward if there is experimental data on the enthalpy of reaction, $-\Delta_r H_m^o$, or if this quantity can be estimated. The methodology has been described in detail in Chapter X of "Modelling in Aquatic Chemistry" and I will just make a short summary. An example of the use of an electrostatic model to describe the temperature dependence of equilibrium constants is given by Plyasunov and Grenthe. An outline of the method originally from Ryzhenko, Bryzgalin and Rafal'skiy is given below.

The standard Gibbs energy of reaction, $\Delta_r G_m^o$, is assumed to be a sum of two terms, one describing non-electrostatic and the other electrostatic contributions, where the latter is independent of *T* and *P*.

$$\Delta_r G_m^o(T,P) = \Delta_r G_{m_{\text{nonel}}}^o + \Delta_r G_{m_{\text{el}}}^o(T,P) \tag{8}$$

where $\Delta_r G_{m_{\text{el}}}^o(T,P)$ is described by assuming a coulomb model:

$$\Delta_r G_{m_{\text{el}}}^o(T,P) = -\left|Z_c Z_a\right|_{\text{ef}} \cdot e^2 N_A / a \cdot D(T,P) \tag{9}$$

where $\left|Z_c Z_a\right|_{\text{ef}}$ describes the effective charges of cation and anion, a the distance between them and D(*T*,*P*) the relative permitivity of the medium (the dielectric constant). The "effective" charge is a sum of three terms:

$$\left|Z_c Z_a\right|_{\text{ef}} = L\left|Z_c Z_a\right| - QZ_a^2 + \alpha Z_c^2 L/2a^3 - (\alpha Z_c)^2 Q/2a^3/2a^6 \tag{10}$$

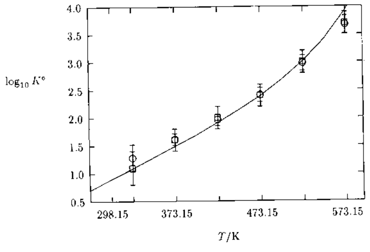
where L is the total number of ligands in the mononuclear complex, Q is a stereochemical factor that depends on L, Q = $(3L^2 - 5L + 2)/8$; α is the polarisability of the ligand.

Using standard thermodynamics one can then deduce:

$$\begin{aligned}\log_{10} K^o(T,P) &= (298.15/T) \cdot \log_{10} K^o(298.15,1) + \log_{10} K^o(T,P) \\ &= (298.15/T) \cdot \log_{10} K^o(298.15,1) + \frac{\left|Z_a Z_c\right|_{ef} e^2 N}{a(T,P) RT \ln 10}\left(\frac{1}{D(T,P)} - \frac{1}{298.15}\right)\end{aligned} \tag{11}$$

The results of this model are described in the following figure; for more details the reader is referred to Ref. [2].

Figure X.14: Comparison of experimental equilibrium constants (squares: [88PAL/DRI circles: [93PAL/HYD]) for reaction: $Fe^{2+} + CH_3COO^- \rightleftharpoons FeCH_3COO^+$ with those c tained on the basis of the Ryzhenko-Bryzgalin model.



This method can also be used to estimate $\Delta_{\rm r}S^{\rm o}_{\rm m}$ and $\Delta_{\rm r}C^{\rm o}_{p,\rm m}$, for which experimental data rarely are available. The problem with estimates that cover a large temperature range is that $\Delta_{\rm r}H^{\rm o}_{\rm m}$ is not constant. This problem can be circumvented by using "isocoulombic", or "isoelectric" reactions. An example of the first type is the reaction:

$$\mathrm{M(OH)^{+} + HCO_3^{-} \rightleftharpoons MCO_3^{+} + OH^{-}} \qquad (12)$$

and of the second type:

$$\mathrm{UO_2^{2+} + CO_2(aq) + H_2O \rightleftharpoons UO_2CO_3(aq) + 2H^{+}} \qquad (13)$$

For both of these types of reaction the electrostatic contributions discussed above cancel, resulting in an enthalpy of reaction, $\Delta_{\rm r}H^{\rm o}_{\rm m}$, that is very near constant. The reaction:

$$\mathrm{UO_2^{2+} + CO_3^{2-} \rightleftharpoons UO_2CO_3(aq)} \qquad (14)$$

is obviously not an isocoulombic/isoelectric reaction, but it can be transformed to one if we combine it with:

$$\mathrm{CO_2(aq) + H_2O \rightleftharpoons CO_3^{2-} + 2H^{+}} \qquad (15)$$

for which accurate enthalpy data are available over a large temperature range. The following two figures show the variation of $\log_{10}K$ for an isocoulombic and an "ordinary" reaction.

Figure X.3: Equilibrium constants from [76NIK] for Reaction (X.26), $\mathrm{H_2O(l) + UO_2^{2+} \rightleftharpoons H^{+} + UO_2OH^{+}}$ (◇), compared with results from the "constant $\Delta_{\rm r}H^{\circ}_{\rm m}$" equation, Eq. (X.18), using $\log_{10} K^{\circ}(T_0) = -(5.157 \pm 0.005)$ and $\Delta_{\rm r}H^{\circ}_{\rm m} = (+50.4 \pm 0.1)$ kJ · mol^{-1} (solid line).

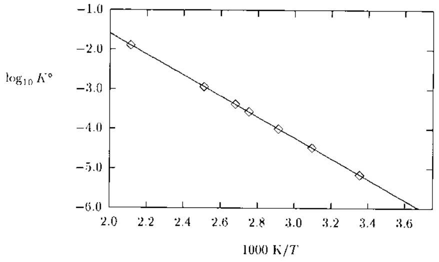
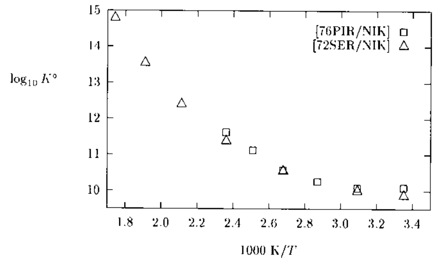


Figure X.4: Equilibrium constants from [72SER/NIK, 76PIR/NIK] for Reaction (X.27): $\mathrm{CO_3^{2-} + UO_2^{2+} \rightleftharpoons UO_2CO_3(aq)}$.



Conclusions

There is a wealth of implicit chemical information in the NEA (and other) thermodynamic databases that should be used both when planning laboratory experiments and when writing the performance assessment novels.

REFERENCES

[1] OECD/NEA, "Chemical Thermodynamics of Uranium, Americium".

[2] "Modelling in Aquatic Chemistry", I. Grenthe and I. Puigdomenech, eds., OECD/NEA, Paris (1997).

[3] V. Neck and J.I. Kim, *Radiochim. Acta*, 88, 815 (2000).

[4] P.L. Brown and R.N. Sylva, *J. Chem. Res*., Synop (1987), (1) 4-5; *J. Chem. Soc*., Dalton Trans., 4, 723 (1985).

[5] V. Vallet, *et al*., "Solvent Effects on Uranium(VI) Fluoride and Hydroxide Complexes Studied by EXAFS and Quantum Chemistry", to be published in *Inorganic Chemistry*.

CAN WE ESTIMATE WHICH ORGANIC COMPLEXES ARE IMPORTANT IN PA?

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Abstract

Can we estimate which organic complexes are important in performance assessments (PA) of repositories for radioactive waste? The answer is “yes”, but with a varying degree of uncertainty depending on the information available. This very general and somewhat trivial statement is illustrated by three worked examples. The examples focus on the behaviour of U(VI) in aqueous solution. They illustrate three cases in the sequence of decreasing amount of information available:

1) The complexing organic ligand is identified.

2) Some natural organics (humics) are present.

3) Some organic carbon is found in aqueous solution.

The modelling approach is the so-called “back door approach” (inverse modelling), beginning with the question, “What properties must an organic ligand have in order to significantly influence the speciation, and hence the solubility and sorption, of a given radionuclide?”

Introduction

Radionuclides dissolved in pore waters of underground repositories in general do not occur as free metal ions but as metal-ligand complexes. The complexing ligands can be inorganic anions like hydroxide, chloride or carbonate. However, depending on the situation, the speciation of radionuclides can be totally dominated by organic complexes. Geochemical models ignoring these organic ligands may produce grossly erroneous results concerning radionuclide speciation. As the aqueous speciation of metal ions is directly related to solubility and sorption of the radionuclides, in consequence these phenomena may also be misjudged by orders of magnitude. Hence, any assessment of the behaviour of radionuclides escaping from an underground repository critically depends on a sound treatment of the influence of organic complexation on radionuclide speciation.

Can we estimate which organic complexes are important in performance assessments (PA) of repositories for radioactive waste? The answer is "yes", but with a varying degree of uncertainty depending on the information available. In the following I discuss this very general and somewhat trivial statement by elaborating on three worked examples. The examples focus on the behaviour of U(VI) in aqueous solution. They illustrate three cases in the sequence of decreasing amount of information available:

1) The complexing organic ligand is identified.

2) Some natural organics (humics) are present.

3) Some organic carbon is found in aqueous solution.

In all these cases performance assessors would like to have clear statements as to if and how they should consider the organics in their model calculations.

In the past, it was attempted to get a handle on this problem by including complexation data of all kinds of organic ligands into geochemical speciation models. However, this effort proved to be futile as the number of potentially complexing organic ligands is large, and information concerning the concentration of these organic ligands in pore waters is sparse and varies by orders of magnitude. In addition, conventional geochemical models cannot be used to calculate the effects of natural organic ligands (humic substances). We started to solve these problems through a new modelling approach, the so-called "back door approach" [1], beginning with the question, "What properties must an organic ligand have in order to significantly influence the speciation, and hence the solubility and sorption, of a given radionuclide?" First, simple organic ligands were treated in this manner [2], and later the back door approach was extended to cope with humic and fulvic acids [3,4].

Case 1: The complexing organic ligand is identified

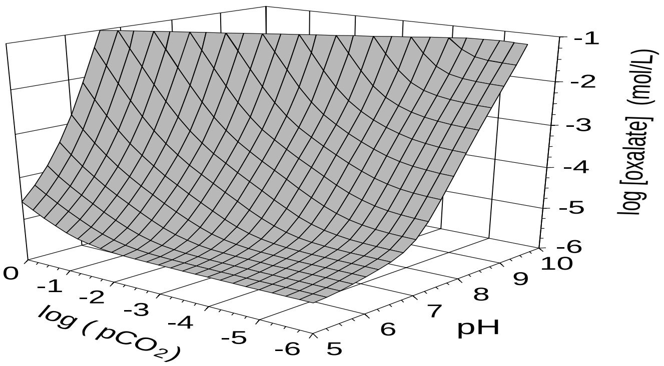
In some cases the complexing organic ligands have been identified. Some organics are widely used for decontamination processes, like ethylenediaminetetraacetate (EDTA) and citrate, and are part of the radioactive waste. Others form through radiolytic degradation of organic waste. For example, radiolytic degradation experiments with acidic ion-exchange resins revealed oxalate and a ligand X, characterised only by some measured stability constants, to be the most strongly complexing ligands of the degradation products [5]. In the case of anion exchange resins ammonia and methylamines are formed [6].

In our example we illustrate the influence of oxalate complexes on the aqueous speciation of U(VI). For the thermodynamic constants used in our "back door" calculations and for a detailed discussion of estimation procedures for ternary complexes in the systems U(VI)-oxalate-hydroxide and U(VI)-oxalate-carbonate see the worked example in Chapter 3 of *Modelling in Aquatic Chemistry* [2]. Further discussions of thermodynamic data and a detailed case study of the system Ni oxalate can be found in Ref. [7].

Figure 1 shows the oxalate concentrations as a function of pH and CO_2 partial pressure at which 90% of the total dissolved U(VI) is bound to oxalate. At low pH and low CO_2 partial pressure a few micromole per litre of dissolved oxalate are sufficient for this effect. With increasing pH U(VI) hydrolysis competes with oxalate complexation and thus more oxalate is needed to maintain 90% complexation. With increasing CO_2 partial pressure and increasing pH, the strong competition of U(VI) carbonate complexation rapidly increases the concentration of oxalate needed for 90% U(VI) oxalate complexation.

Figure 1. "Floating towel" representation of the conditions at which 90% of total dissolved U(VI) is bound to oxalate

Note that the somewhat arbitrary level of 90% complexation has been chosen in all examples as this number corresponds, in simple geochemical models, to one order of magnitude increase in radionuclide solubility or one order of magnitude reduction of radionuclide sorption



The surface of Figure 1 provides a quick overview of the general features of the U(VI) oxalate system. However, a two-dimensional contour plot of this surface is better suited for quantitative examination (Figure 2). I addition, pH and CO_2 partial pressure values of almost 1 000 Swiss groundwater analyses are plotted in Figure 2. It can be seen from the figure that most groundwater data are found in the range 0.0001 M < [oxalate] < 0.01 M.

The next question is whether such concentrations of dissolved oxalate are feasible in groundwater systems. Ca oxalate minerals are known and their solubility products are well-established [7]. Hence, precipitation of Ca oxalate solids will limit the concentration of dissolved oxalate in natural systems. In order to obtain a reasonable number of dissolved Ca we again inspect the database of Swiss groundwater analyses (Figure 3). This figure reveals that in most waters the dissolved Ca concentration ranges between 0.001 M and 0.01 M. Only in a few cases does the Ca concentration drop as low as 0.0001 M. This number has been designated the Ca concentration in subsequent "back door" calculations. In such a way the threshold of the effect of Ca oxalate precipitation on the U(VI) oxalate system can be estimated (Figure 4).

Figure 2. Two-dimensional representation of the “floating towel” in Figure 1 showing contour lines of oxalate concentrations at which 90% of total dissolved U(VI) is bound to oxalate

Triangles represent pH and CO_2 partial pressure data of Swiss groundwater analyses

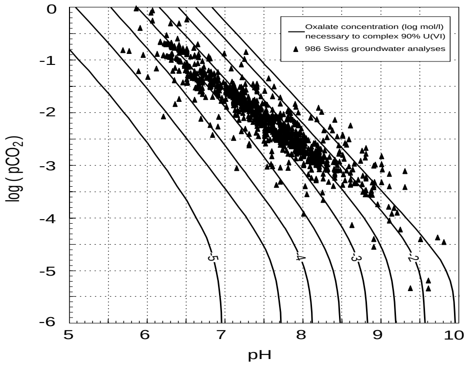


Figure 3. Concentration of total dissolved calcium in Swiss groundwaters as a function of pH

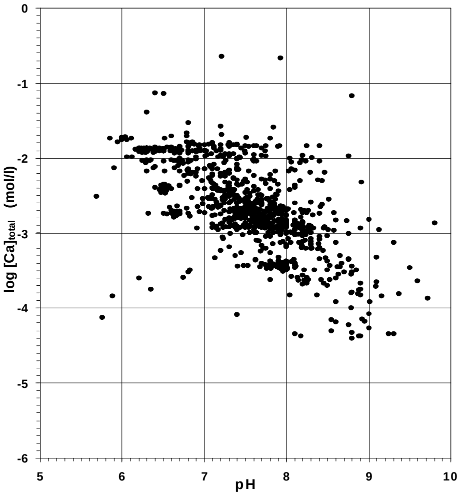
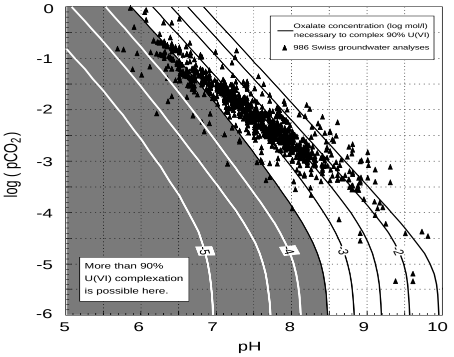


Figure 4. Contour lines of oxalate concentrations at which 90% of total dissolved U(VI) is bound to oxalate

Triangles represent pH and CO_2 partial pressure data of Swiss groundwater analyses. The grey area represents the range of feasible concentrations of dissolved oxalate assuming 0.0001 M dissolved Ca and precipitation of Ca oxalate solids.



As can bee seen in Figure 4, the concentration of dissolved oxalate is limited to less than 0.0003 M (grey area in Figure 4). Most groundwater data are located at higher concentrations of oxalate (white area of Figure 4) and in all these cases oxalate will not influence the U(IV) speciation. A few groundwater data are located in the grey area. What about these cases? The maximum oxalate concentration of 0.0003 M can only be reached if the concentration of dissolved Ca is as low as 0.0001 M. Figure 3 reveals that the Ca concentrations increase with decreasing pH, and at $pH < 7$ values above 0.001 M are generally found. As a consequence, the feasible concentrations of dissolved oxalate decrease in these cases due to increasing Ca oxalate precipitation. Comparing Figures 3 and 4 (and ignoring the few erratic Ca data in Figure 3 at $pH < 7$) we conclude that oxalate will not have any influence on the U(VI) speciation in groundwater systems. Hence, the influence of oxalate on U(VI) speciation is expected to be insignificant for performance assessments of Swiss repositories for radioactive waste.

Case 2: Some natural organics (humics) are present

Humic substances are ubiquitous constituents of natural waters. However, unlike the simple organic ligands discussed in the previous section, no chemical labelled "humic substances" exists, and there are no simple methods of analysis for humic substances. The fractionation of humic substances into humic and fulvic acids is only defined operationally. The number of compounds that constitute these fractions may be 10, 100, 1 000 or more compounds, and their molecular structure remains an interesting unresolved question. The modelling of metal-humate interactions has been a field of active research for more than three decades. A plethora of articles has been published in this time span discussing a multitude of humic binding models. For a detailed review of these binding models see Ref. [3]. However, despite all of this effort there is still no consensus on how to treat metal-humate interactions in a consistent way, and it is easy to predict that more work will be done on this topic in the future.

A synopsis of large sets of reliable experimental data for Ca, Co, Ni, Eu, Am, Cm, Np(V) and U(VI), originating from research done in our lab [8] and collected from the literature, reveals a consistent picture of the influence of metal concentration, pH and ionic strength on metal humic interactions [4,9]. The pH dependence of Eu, Am, Cm and U(VI) humate complexation at trace metal concentration is shown in Figure 5. Note that there is no statistically significant difference in the pH behaviour of U(VI) and the trivalent cations Eu, Am and Cm.

However, this consistent behaviour cannot be interpreted with high numerical accuracy by simple binding models, as the need for more adjustable parameters increases proportional to the width of the experimental parameter range to be fitted. This experience triggered the proposal of a pragmatic approach for performance assessment purposes. The "conservative roof" approach [4] does not aim to accurately model all experimental data (*e.g.* dashed line in Figure 5) but rather allows to estimate the maximum effects on metal complexation to be expected from humic substances (solid line in Figure 5).

The "conservative roof" model [4] now allows the same type of "back door" calculations for humic substances (Figure 6) as shown for the case of simple organic ligands like oxalate (Figure 1). The only difference is that the concentration of humics needed to complex 90% of the dissolved U(VI) is calculated in g/l instead of mol/l in order to circumvent the ambiguities concerning the molar mass of the ill-defined system "humic substance".

The concentration of humics needed to complex 90% of U(VI) and 90% of Eu is the same at low pH (Figure 6). This is a consequence of the similar complexation behaviour of U(VI) and Eu (Figure 5). With increasing pH the complexation strength in both cases increases and thus, the concentration of

Figure 5. The pH dependence of Eu, Am, Cm and U(VI) humate complexation at trace metal concentration

The dashed line represents a linear regression of the Eu, Cm and Am data and the solid line the trace of the "conservative roof" model [4]

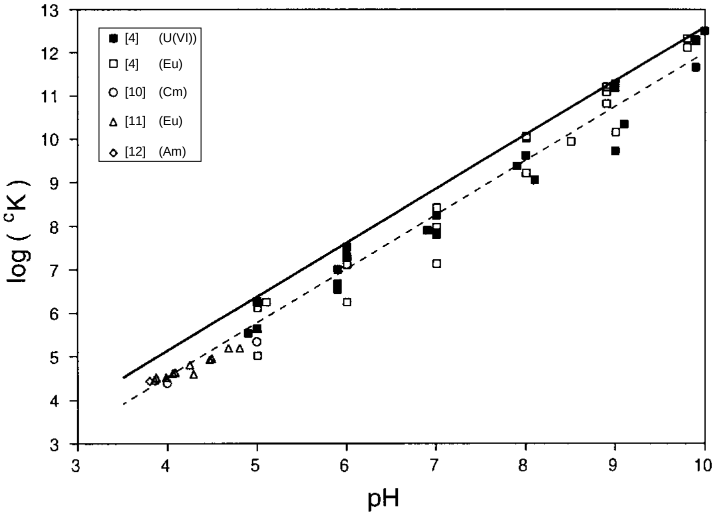
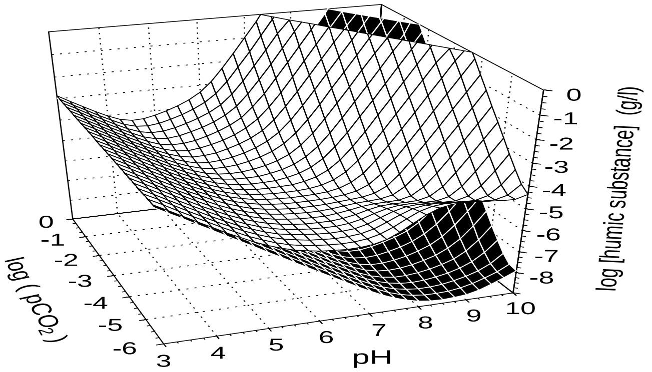


Figure 6. "Floating towel" representation of the conditions at which 90% of the total concentration of U(VI) is bound to humic substance (in g/l and for 0.1 M ionic strength, white surface). For comparison, the corresponding Eu "floating towel" is shown as black surface.

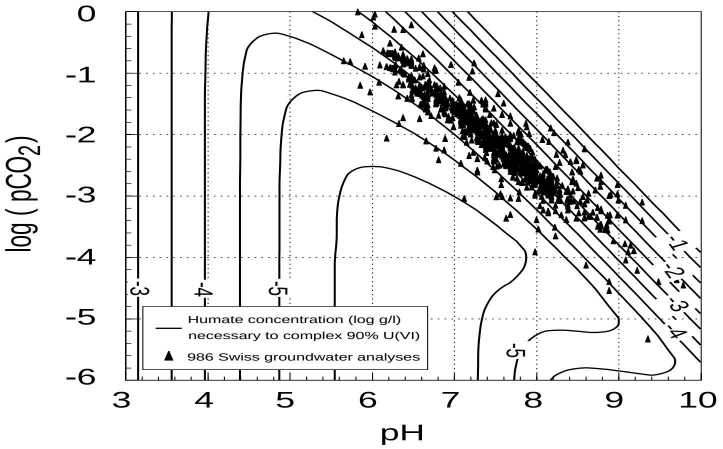


humics needed to maintain the 90% complexation level decreases. However, as soon as hydrolysis and carbonate complexation start to compete with metal-humate interactions the surfaces of U(VI) and Eu diverge rapidly. The much stronger U(VI) hydrolysis and U(VI) carbonate complexation induce a steep raise of the "floating towel" of U(VI) in the neutral and alkaline region of the parameter space (white surface in Figure 6).

These differences in inorganic competition between Eu and U(VI) cause large differences concerning the impact of humate complexation on Eu and U(VI) speciation in the region of natural groundwaters. Whereas 10^{-7} g/l (0.1 ppb) of dissolved humic substances is enough to dominate the Eu speciation (see [4] for a detailed discussion), humic concentrations of 0.1 to 1 mg/l (0.1 to 1 ppm) are needed to complex 90% of the dissolved U(VI) (Figure 7). Concentrations of dissolved humic substances in the range of 0.1 to 1 ppm can be reached in streams, rivers and lakes. Tea-coloured waters such as

Figure 7. Two-dimensional representation of the "floating towel" in Figure 6 showing contour lines at which 90% of total dissolved U(VI) is bound to humic substance (in g/l and for 0.1 M ionic strength)

Triangles represent pH and CO_2 partial pressure data of Swiss groundwater analyses



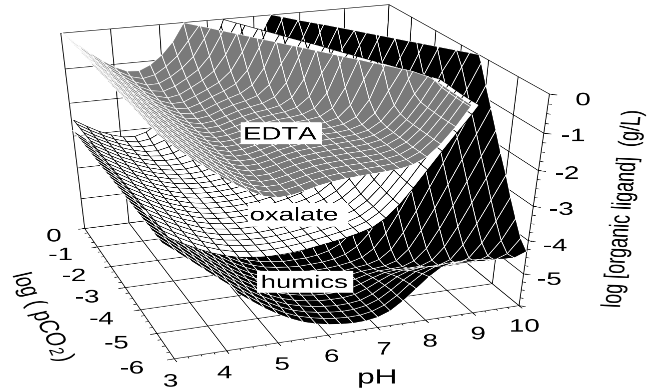
marshes, bogs and swamps vary from 10 to 30 ppm humic substances. There are indications that for Swiss groundwaters the humic concentration in general does not exceed the ppm range and in most cases it might be closer to ppb than ppm. Hence, the influence of humic substances on U(VI) speciation might be insignificant in all cases relevant for performance assessments of Swiss repositories for radioactive waste.

Case 3: Some organic carbon is found in aqueous solution

In most cases the information available for the geochemical modeller about organic ligands is restricted to some concentration measurements (or even vague guesses) of dissolved organic carbon. Nevertheless, performance assessors would like to have a clear statement as to if and how they should consider organics in such cases. The only feasible approach is now to push the "back door approach" to its full extent and ask the question, "What properties must an organic ligand have in order to significantly influence the speciation of a given radionuclide?" In practice, this question can be answered by the following sequence of actions. We first select a small number of organic ligands representing a wide range of complexation strength (due to different functional groups and molecular structures), perform a series of back door calculations for all these ligands, visualise all the results concomitantly using suitable computer graphics and draw some general conclusions by inspecting and interpreting the resulting figures.

In the following example I selected the minimum number of three ligands for clarity and brevity. In addition to the already-discussed ligands oxalate, representing simple organic acids, and humics, representing ill-defined natural organics, EDTA is added in this example. EDTA is widely used for decontamination processes and represents the class of strongly complexing synthetic ligands, forming chelate complexes with all metal cations. Figure 8 shows the results of back door calculations for U(VI) complexation with oxalate, EDTA and humic substances as a function of pH and CO_2 partial pressure. Note that all calculations have been carried out in g/l rather than mol/l for direct comparison of humics with the other organic ligands. As can be seen in Figure 8, the general features are the same for all organic ligands. At pH < 5 the protonation of the organic acid causes an increase of the total amount of ligand needed to maintain the 90% complexation level. Likewise, at high pH the increasing

Figure 8. “Floating towel” representation of the conditions at which 90% of the total concentration of U(VI) is bound to ethylenediaminetetraacetate (EDTA), oxalate or humic substances (in g/l and for 0.1 M ionic strength)

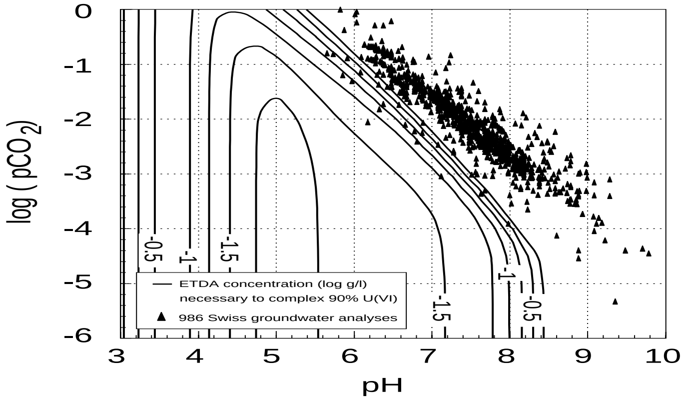


competition due to the formation of U(VI)-hydroxide complexes causes an increase in the ligand concentration needed for 90% U(VI) complexation. The strongest effect is seen at high pH and high CO_2 partial pressure because of the increasing competition of U(VI)-carbonate complexes. The plateau of the EDTA surface around neutral pH is caused by the competition of Ca-EDTA complexes. The level of this plateau is directly related to the calcium concentration assumed in the calculations. In Figure 8 the Ca concentration was fixed to 0.0001 M. In most natural waters the Ca concentration is higher than that value (see Figure 3) and thus the EDTA surface shown in Figure 8 represents the worst-case scenario with respect to the influence of EDTA on U(VI) speciation.

As can be seen in Figure 8, 0.01 mg/l of humic substance is sufficient in neutral and slightly acidic surface waters to dominate the U(VI) speciation, but we need at least 1 mg/l organic acid to achieve the same level of complexation with oxalate. In the case of EDTA, even higher concentrations (0.1 g/l) are needed to have 90% of U(VI) complexed by EDTA. In the case of Swiss groundwaters, several grams per litre EDTA would be needed to complex 90% of the dissolved U(VI) (Figure 9).

Figure 9. Two-dimensional representation of the EDTA “floating towel” in Figure 8 showing contour lines at which 90% of total dissolved U(VI) is bound to EDTA (in g/l and for 0.1 M ionic strength)

Triangles represent pH and CO_2 partial pressure data of Swiss groundwater analyses



This sequence is unexpected at the first glance. For most trace metals (*e.g.* transition metals and rare earth metals) the sequence is EDTA < humic substance < oxalate, *i.e.* EDTA has the strongest influence on trace metal concentration. In the case of U(VI), the opposite behaviour is found with EDTA causing the weakest influence on U(VI) speciation. Or, the other way round, we need very high EDTA concentrations for dominating the U(VI) speciation. What is the explanation for this erratic behaviour of EDTA? The reason is found in the molecular structure of the U(VI)-EDTA complex. In general, EDTA binds a metal ion with six functional groups (four carboxylate groups and two amine groups) which causes a strong chelate effect. Dissolved U(VI) has the structure of a linear O=U=O oxo-cation, and EDTA can bind this molecule with a maximum of only four functional groups instead of the usual six bonds. The result is a rather weak complex compared with other trace metals. In addition, the strong competition of Ca-EDTA complexes (where EDTA can bind Ca with all six functional groups) further decreases the influence of EDTA on U(VI) speciation.

The general conclusion from this rather limited example is that the influence of simple organic ligands, containing only carboxylate and amine groups, on U(VI) speciation might be insignificant in all cases relevant for performance assessments of Swiss repositories for radioactive waste. The same statement is also valid for Np(VI) and Pu(VI). However, this conclusion cannot be extended to other redox states of the actinides like Np(V), U(IV) or Pu(III). Furthermore, even if these organic ligands are not expected to dominate the speciation of hexavalent actinides they may reduce dissolved actinide cations to lower redox states, and thus change speciation, solubility and sorption of the actinides.

Acknowledgement

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REFERENCES

[1] W. Hummel, “A New Method to Estimate the Influence of Organics on the Solubility and Speciation of Radionuclides (“The Backdoor Approach”)”, *Radiochimica Acta*, 58/59, 453-460 (1992).

[2] I. Grenthe, W. Hummel, I. Puigdomènech, “Chemical Background for the Modelling of Reactions in Aqueous Systems”, in *Modelling in Aquatic Chemistry*, I. Grenthe, I. Puigdomènech, eds., OECD Nuclear Energy Agency, Paris, ISBN 92-64-15569-4, pp. 69-129 (1997).

[3] W. Hummel, “Binding Models for Humic Substances”, in *Modelling in Aquatic Chemistry*, I. Grenthe, I. Puigdomènech, eds., OECD Nuclear Energy Agency, Paris, ISBN 92-64-15569-4, pp. 153-206 (1997).

[4] W. Hummel, M.A. Glaus, L.R. Van Loon, “Trace Metal-humate Interaction. II. The “Conservative Roof” Model and its Application”, *Applied Geochemistry*, 15, 975-1001 (2000).

[5] L.R. Van Loon, W. Hummel, "Radiolytic and Chemical Degradation of Strong Acidic Ion-exchange Resins: Study of the Ligands Formed", *Nuclear Technology*, 128, 359-371 (1999).

[6] L.R. Van Loon, W. Hummel, "The Degradation of Strong Basic Anion Exchange Resins and Mixed-bed Ion-exchange Resins: Effect of Degradation Products on Radionuclide Speciation", *Nuclear Technology*, 128, 388-401 (1999).

[7] W. Hummel, L.R. Van Loon, "The Effect of Degradation Products of Strong Acidic Cation Exchange Resins on Radionuclide Speciation: A Case Study with Ni^{2+}", *Nuclear Technology*, 128, 372-387 (1999).

[8] M.A. Glaus, W. Hummel, L.R. Van Loon, "Trace Metal-humate Interaction. I. Experimental Determination of Conditional Stability Constants", *Applied Geochemistry*, 15, 953-973 (2000).

[9] W. Hummel, M.A. Glaus, L.R. Van Loon, "Complexation of Radionuclides with Humic Substances: The Metal Concentration Effect", *Radiochimica Acta*, 84, 111-114 (1999).

[10] C. Moulin, P. Decambox, P. Mauchien, V. Moulin, M. Theyssier, "On the Use of Laser-induced Time-resolved Spectrofluorometry for Interaction Studies Between Organic Matter and Actinides: Application to Curium", *Radiochimica Acta*, 52/53, 119-125 (1991).

[11] J.H. Ephraim, J.A. Marinsky, S.J. Cramer, "Complex-forming Properties of Natural Organic Acids: Fulvic Acid Complexes with Cobalt, Zinc and Europium", *Talanta*, 36, 437-441 (1989).

[12] R.A. Torres, G.R. Choppin, "Europium(III) and Americium(III) Stability Constants with Humic Acid", *Radiochimica Acta*, 35, 143-148 (1984).

AN EMPIRICAL METHOD FOR CALCULATING THERMODYNAMIC PARAMETERS FOR U(VI) PHASES, APPLICATIONS TO PERFORMANCE ASSESSMENT CALCULATIONS

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Abstract

Uranyl minerals form by oxidation and alteration of uraninite, UO_{2+x}, and the UO_2 in used nuclear fuels. The thermodynamic database for these phases is extremely limited. However, the Gibbs free energies and enthalpies for uranyl phases may be estimated based on a method that sums polyhedral contributions. The molar contributions of the structural components to $\Delta_f G_m^o$ and $\Delta_f H_m^o$ are derived by multiple regression using the thermodynamic data of phases for which the crystal structures are known. In comparison with experimentally determined values, the average residuals associated with the predicted $\Delta_f G_m^o$ and $\Delta_f H_m^o$ for the uranyl phases used in the model are 0.08 and 0.10%, respectively. There is also good agreement between the predicted mineral stability relations and field occurrences, thus providing confidence in this method for the estimation of $\Delta_f G_m^o$ and $\Delta_f H_m^o$ of the U(VI) phases. This approach provides a means of generating estimated thermodynamic data for performance assessment calculations and a basis for making bounding calculations of phase stabilities and solubilities.

Introduction

UO_2 under oxidising conditions is not stable and rapidly forms a wide variety of uranyl oxyhydroxides, silicates, phosphates, carbonates and vanadates depending on groundwater composition. A critical issue is the fate of the radionuclides released during the alteration and matrix corrosion of the UO_2. Some of the radionuclides are incorporated into the secondary uranyl phases [1-3] and, in fact, these phases may become the primary source term for the near-field release of radionuclides. Thus, the paragenesis, structure and stability of these phases are of critical importance in evaluating the long-term behaviour of spent nuclear fuel in a repository under oxidising conditions.

Unfortunately, the thermodynamic database for these uranyl phases is limited and in some cases contradictory [4]. There is an immediate need to be able to estimate thermodynamic parameters and solubility constants. This paper represents an effort to estimate by regression analysis the standard Gibbs free energies ($\Delta_f G_m^o$) and enthalpies ($\Delta_f H_m^o$) of formation of U(VI) phases based on their structural components. Although present experimental data are limited and the different types of uranyl polyhedra were not treated separately in this analysis, this approach allows one to utilise all data presently available and will allow for the immediate refinement of estimated thermodynamic values as new experimental data become available. We also identify phases for which future structural analysis and additional thermodynamic data will provide the greatest impact on the development of the required database. Additionally, the estimated values may be used when suitable samples are not available for experimental determinations (*i.e.* uranyl phases often occur as fine-grained mixtures of variable composition). We present a method that is similar to that developed by Chermak and Rimstidt [5] for estimating the $\Delta_f G_m^o$ and $\Delta_f H_m^o$ of silicate minerals.

A detailed summary of previous work is given by Chen, *et al.* [6]. The structural analysis of the U(VI) minerals is based on the work by Burns, *et al.* [7-8]. The approach proposed in this paper offers the following advantages over previous estimation techniques:

- The structural component-summation technique provides smaller uncertainty relative to the oxide-summation technique if the co-ordinations of the cations are considered.
- The $\Delta_f G_m^o$ and $\Delta_f H_m^o$ may be estimated even though data for representative phases in similar structural classes are not available because each type of cation polyhedron is considered to possess a set of well-defined properties.
- Small errors in individual data of the reference phases can be reduced through the averaging provided by multiple regression if the database is large enough.

Fictive structural component

A fictive structural component is a cation co-ordination polyhedron with a similar structural function, and it may be expressed in the form of an oxide or hydroxide. Because the cations in crystal structures are commonly co-ordinated directly to oxygen atoms, and the hydrogen ions sharing oxygen with other cations are considered to be part of the structural water, all structural components are expressed as cation oxides in this study. In U(VI) phases, the basic fictive structural components are uranyl polyhedra with different co-ordination numbers [8]. The $Ur\phi_n$ polyhedron polymerises with other $Ur\phi_n$ or other cation co-ordination polyhedra to form clusters, chains, sheets and even framework structures [7]. The structural units (clusters, chains and sheets) are connected by hydrogen bonds and low-valence cations that are commonly co-ordinated by 8 to 12 anions and are denoted by the subscript (I). In framework structures, the similar structural components are co-ordination polyhedra of those cations located in the voids of other structure types with co-ordination numbers of 8-12. The structural function of hydrogen ions that are part of the structural water is similar to that of low-valance cations in sharing oxygen with cations in the structure units, compensating charge in the structure and connecting the structural units. Thus, the structural water ($H_2O_{(S)}$) is regarded as an individual structural component and is different from the water of hydration ($H_2O_{(H)}$). On the other hand, the co-ordination polyhedra of cations other than UO_2^{2+} may also form individual co-ordination polyhedra within the structural units. These cations are different from those located in inter-structural unit sites. Their co-ordination numbers are no more than 6 and are indicated by the Roman numeral in the subscript of the relevant structural components. Constituent fictive structural components of example U(VI) phases are listed in Table 1 (a more comprehensive list is provided by Chen, *et al.* [6]), including some of the uranyl phases that may be important during the alteration of spent UO_2 fuel.

Table 1. Example constituent structural components for selected U(VI) phases

Mineral	Formula	Constituent structural components
Schoepite	$[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$	$6H_2O_{(S)} + 8Ur\phi_5 + 12H_2O_{(H)}$
Becquerelite	$Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_8$	$CaO_{(I)} + 3H_2O_{(S)} + 6Ur\phi_5 + 8H_2O_{(H)}$
Protasite	$Ba[(UO_2)_3O_3(OH)_2](H_2O)_3$	$BaO_{(I)} + H_2O_{(S)} + 3Ur\phi_5 + 3H_2O_{(H)}$
Curite	$Pb_3[(UO_2)_8O_8(OH)_6](H_2O)_3$	$3PbO_{(I)} + 3H_2O_{(S)} + 6Ur\phi_5 + 2Ur\phi_4 + 3H_2O_{(H)}$
α-uranophane	$Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$	$CaO_{(I)} + H_2O_{(S)} + 2Ur\phi_5 + 2SiO_{2(IV)} + 5H_2O_{(H)}$
Boltwoodite	$(K,Na)[(UO_2)(SiO_3OH)](H_2O)_{1.5}$	$0.5(K,Na)_2O_{(I)} + 0.5H_2O_{(S)} + Ur\phi_5 + SiO_{2(IV)} + 1.5H_2O_{(H)}$
Sklodowskite	$Mg[(UO_2)(SiO_3OH)]_2(H_2O)_6$	$MgO_{(I)} + H_2O_{(S)} + 2Ur\phi_5 + 2SiO_{2(IV)} + 6H_2O_{(H)}$
β-uranophane	$Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$	$CaO_{(I)} + H_2O_{(S)} + 2Ur\phi_5 + 2SiO_{2(IV)} + 5H_2O_{(H)}$
Soddyite	$[(UO_2)_2(SiO_4)](H_2O)_2$	$2Ur\phi_5 + SiO_{2(IV)} + 2H_2O_{(S)}$

Database

Grenthe, *et al.* [4] have completed a comprehensive review of the literature of thermodynamic data for uranium and have developed a database of uranium species, including some U(VI) minerals, for use in safety assessments of radioactive waste repositories. This database has been widely adopted among chemists and geochemists, and when available, the $\Delta_f G_m^o$ and $\Delta_f H_m^o$ data used in the regression analysis of this study for deriving the contributions of fictive structural components have been adopted from Grenthe, *et al.* [4]. We note that:

- The thermodynamic properties of fictive cation oxides in structures are quite different from those of pure oxides, as has been demonstrated for silicate minerals [5].
- α-UO_3 contains distorted polyhedra and studied samples may not have had the exact stoichiometry of $UO_{3.00}$.
- β-UO_3 and γ-UO_3 do not contain the uranyl ion, with the U^{6+} cation being co-ordinated in some other way, and the polyhedra are highly irregular.

Thus the $\Delta_f G_m^o$ and $\Delta_f H_m^o$ of the simple oxides for U(VI) were not included in the model data. Because the thermodynamic properties of a fictive component calculated in this way are average contributions of the component to the relevant properties of uranyl solid phases, thermodynamic data of phases with irregular structures (*e.g.* containing highly distorted polyhedra, involving U^{6+} cations not combined with oxygen anions to form uranyl cations) were not included in the model database. Only data for those phases for which the crystal structures are known were used in this study. In the limited amount of $\Delta_f G_m^o$ and $\Delta_f H_m^o$ data for uranium (VI) compounds given by Grenthe, *et al.* [4], notably absent are data for uranyl silicates. In recent years, new solubility data have been published for some uranyl phases, and the use of these data in this analysis are discussed in detail in Chen, *et al.* [6].

Although each type of cation polyhedron is considered to possess a set of well-defined properties, the linkage topology of the polyhedra can also account for a few per cent of the variation of thermodynamic properties for a particular type of cation polyhedron from structure to structure. Notably, the anion topology for the sheets of phases $M_XU_2O_7$ (M = K, Rb, Ca and Sr; X = 1 or 2) contain only hexagons, and each hexagon is populated with a uranyl cation to form a hexa-bipyramid with each edge of the hexagon in the plane of the sheet being shared with neighbouring polyhedra [7]. The linkage between the cation polyhedra within sheets of this type of structure is much stronger than that found in other sheet structures of U(VI) phases. In the course of the present analysis, we have found that the $\Delta_f G_m^o$(298) and $\Delta_f H_m^o$(298) values for phases with this structure type are always more negative than predicted. Because few phases possess this kind of structure, we suggest that thermodynamic properties of these phases neither be used in the reference database nor predicted using the present empirical method. Because the structures of most uranyl phases are based upon infinite sheets of polyhedra [7] and the prediction will be improved if the estimation is made within the phases that are structurally more analogous, uranyl phases containing isolated uranyl polyhedra were also not included in the model. Chen, *et al.* [6] provide a list (see their Table 2) of the thermodynamic data used to calculate g_i and h_i values in this study.

Calculation methods

Regression analysis was used to determine the molar contributions of structural components (g_i and h_i) to $\Delta_f G_m^o$ and $\Delta_f H_m^o$ of uranium (VI) phases for the following models: $\Delta_f G_m^o = \Sigma n_i g_i$ and $\Delta_f H_m^o = \Sigma n_i h_I$, where n_i is the number of moles of component i. The g_i or h_i of the components that occur in at least two phases for which the relevant thermodynamic data ($\Delta_f G_m^o$ or $\Delta_f H_m^o$) and structural information are available were included in the predictor variables of the regression analysis. The details of the technique are given in Chen, *et al.* [6]. We note that no significant differences exist among the calculated g_i or h_i values for different uranyl polyhedron types ($Ur\phi_4$, $Ur\phi_5$ and $Ur\phi_6$), and the result is rather sensitive to the change of the data used in the model. Because those phases that contain highly distorted or unusual polyhedra are excluded from the model, the number of the equatorial $<U^{6+}$--$O>$ bonds and their bond strengths generally depend on co-ordination number. Thus, differences are to be expected among the g_i or h_i values of different types of uranyl co-ordination polyhedron. We suspect significant differences will be demonstrated when the model database is enlarged. The sensitivity of the regression result to the variation of the data used in the model depends on the ratio of the number of data and predictive variables. Enlarging the database or reducing the number of variables will make the result less sensitive to the change of the data used in the regression, as is demonstrated by taking the three types of uranyl co-ordination polyhedra as a single component in order to reduce the number of predictive variables. Thus, when the database is small, this treatment makes the result more reliable. For the present calculations the different uranyl polyhedra are considered as a single component, as long as no significant differences occur among the calculated g_i and h_i values for the different uranyl polyhedron types. The different uranyl polyhedra can be considered separately as soon as additional data are available. In order to avoid under- or over-weighting of the contribution of a particular phase, the number of uranium (VI) polyhedra (the sum of $Ur\phi_4$, $Ur\phi_5$ and $Ur\phi_6$) for an individual mineral in the regression model was normalised to 1.0.

Based on the regression results, the molar contribution of other selected structural components to $\Delta_f G_m^o(298)$ or $\Delta_f H_m^o(298)$ of uranyl phases was calculated for each mineral for each component, because each of these structural components were contained in only one phase for which the crystal structure and $\Delta_f G_m^o(298)$ and $\Delta_f H_m^o(298)$ have been experimentally determined. All the thermodynamic data used to calculate the g_i and h_i values are given in Chen, *et al.* [6].

Results

The g_i and h_i values derived from the regression model are listed in Chen, *et al.* [6]. The average differences between the predicted and the measured values for the phases used in the regression analysis are 0.095% for $\Delta_f G_m^o(298)$ and 0.09% for $\Delta_f H_m^o(298)$, and these differences are normally distributed when the number of uranyl cations in the formula is normalised to 1.0. The average reported associated errors (2σ) of experimentally determined data for silicate minerals are 0.16% for $\Delta_f G_m^o$ and 0.13% for $\Delta_f H_m^o$ [5], and those for U(VI) minerals are slightly higher. Thus, the associated errors for the predicted $\Delta_f G_m^o(298)$ and $\Delta_f H_m^o(298)$ values are generally below those of the experimentally determined values within the model database. This is the statistical result of averaging the error over the entire data set.

As a blind test, Table 2 lists the measured and predicted $\Delta_f G_m^o(298)$ values for uranyl phases that were not used in the in the development of the database for the model. The measured $\Delta_f G_m^o(298)$ values for the uranyl phosphates were selected by Grenthe, *et al.* [4] in the uranium thermodynamic database, but their crystal structures remain unknown. The difference between the measured and predicted values for anhydrous uranyl phosphate, $(UO_2)_3(PO_4)_2$, is 0.32% and may mainly result from the uncertainty of g_i for $PO_{4(IV)}$ which was calculated using the $\Delta_f G_m^o(298)$ value of $UO_2HPO_4{\cdot}4H_2O$ by the error propagation method. From the difference between the measured $\Delta_f G_m^o(298)$ values of $(UO_2)_3(PO_4)_2{\cdot}6H_2O$ and $(UO_2)_3(PO_4)_2{\cdot}4H_2O$, we obtain the molar contribution of molecular water ($H_2O_{(H)}$) to the $\Delta_f G_m^o$ of uranyl phosphates to be -239.5 kJ/mol, which agrees with that obtained by the multiple-regression analysis. However, the difference between the measured $\Delta_f G_m^o(298)$ values of $(UO_2)_3(PO_4)_2{\cdot}4H_2O$ and $(UO_2)_3(PO_4)_2$ is –1 023 kJ/mol, indicating that the molar contribution of molecular water to the $\Delta_f G_m^o(298)$ of uranyl phosphates is -255.75 kJ/mol. This discrepancy accounts for the large residual of the predicted $\Delta_f G_m^o(298)$ values for $(UO_2)_3(PO_4)_2{\cdot}4H_2O$ and $(UO_2)_3(PO_4)_2{\cdot}6H_2O$, and experimental studies are needed to explain this discrepancy. Probable sources of this discrepancy include:

- The structure of $(UO_2)_3(PO_4)_2{\cdot}4H_2O$ and $(UO_2)_3(PO_4)_2{\cdot}6H_2O$ are similar to each other and quite different from that of $(UO_2)_3(PO_4)_2$.
- The number of molecular waters in the samples may not be identical to their nominal stoichiometries.
- The $\Delta_f G_m^o(298)$ value of $(UO_2)_3(PO_4)_2{\cdot}4H_2O$ is in error (the "measured" $\Delta_f G_m^o(298)$ value of $(UO_2)_3(PO_4)_2{\cdot}6H_2O$ was estimated based on that of $(UO_2)_3(PO_4)_2{\cdot}4H_2O$).

Table 3 lists the measured and predicted $\Delta_f H_m^o(298)$ values for selected uranyl phases that were not used in the development of the database for the model. Similar to the case for $\Delta_f G_m^o(298)$, the predicted $\Delta_f H_m^o(298)$ value of $(UO_2)HPO_4{\cdot}4H_2O$ is also much more positive than that measured, and

Table 2. Measured and predicted $\Delta_f G^o_m$ values for the uranyl phases not used in the model and their related residuals

Phases	Measured (kJ·mol^{-1})	Predicted (kJ·mol^{-1})	Residuals (kJ·mol^{-1})	% residuals
$(UO_2)_3(PO_4)_2$	-5 116.0 ± 5.5	-5 132.2	16.2	0.32
$(UO_2)_3(PO_4)_2 \cdot 4H_2O$	-6 139.0 ± 6.4	-6 093.4	-45.6	0.74
$(UO_2)_3(PO_4)_2 \cdot 6H_2O$	-6 618.0 ± 7.0	-6 574.0	-44	0.66
$Ca_2(UO_2)(CO_3)_3 \cdot 11H_2O$	-6 418.8 ± 12	-6 452.2	33.4	0.52
$CaMg(UO_2)(CO_3)_3 \cdot 12H_2O$	-6 561.4 ± 8	-6 556.4	-5.0	0.07
$Mg_2(UO_2)(CO_3)_3 \cdot 18H_2O$	-7 881.1 ± 8	-7 862.9	-18.2	0.23
$Na_2Ca(UO_2)(CO_3)_3 \cdot 6H_2O$	-5 207.1 ± 24	-5 215.7	8.64	0.17

Note: The measured values for the uranyl phosphates are from Grenthe, *et al.* [4] and the measured values for the liebigite group minerals were calculated based on the solubility data reported by Alwan and Williams [9].

Table 3. Measured and predicted $\Delta_f H^o_m$ values for uranyl phases not used in the model and their associated residuals

Phases	Measured (kJ·mol^{-1})	Predicted (kJ·mol^{-1})	Residuals (kJ·mol^{-1})	% residuals
$(UO_2)_3(PO_4)_2$	-5 491.3 ± 3.5*	-5 512.3	21.0	0.38
$(UO_2)_3(PO_4)_2 \cdot 4H_2O$	-6 739.1 ± 9.1*	-6 690.9	-48.2	0.72
$Ca_2(UO_2)(CO_3)_3 \cdot 11H_2O$	-7 301.6 ± 24	-7 306.3	4.7	0.06
$CaMg(UO_2)(CO_3)_3 \cdot 12H_2O$	-7 504.4 ± 20	-7 495.3	-9.1	0.12
$Mg_2(UO_2)(CO_3)_3 \cdot 18H_2O$	-9 164.2 ± 20	-9 165.7	1.5	0.02
$Na_2Ca(UO_2)(CO_3)_3 \cdot 6H_2O$	-5 893.0 ± 36	-5 826.3	-53.1	1.13
$Li_2U_2O_7$	-3 213.6 ± 5.3*	-3 024.7	-8.9	0.28

* From Grenthe, *et al.* [4]; the measured $\Delta_f H^o_m$ data for the liebigite group uranyl carbonates were calculated based on the dissolution enthalpy data reported by Alwan and Williams [9].

similar explanations are applicable. The $\Delta_f H^o_m$(298) values for the four liebigite group minerals were also recalculated using the respective dissolution enthalpy of these minerals reported by Alwan and Williams [9] and using the $\Delta_f H^o_m$(298) values for the relevant aqueous species provided by Grenthe, *et al.* [4]. There are two Ca-bearing phases ($CaUO_4$ and Ca_3UO_6) for which the measured $\Delta_f H^o_m$(298) values were available. As was indicated previously, the linkage between the cation polyhedra within the sheets in the structure of $CaUO_4$ is much stronger than that in the structures of the uranyl phases used in the model. Thus, the $\Delta_f G^o_m$(298) and $\Delta_f H^o_m$(298) values for $CaUO_4$ are more negative than those predicted (Table 3). However, Ca_3UO_6 is based on a structure containing isolated $U\phi_4$ polyhedra, and the linkage between the cation polyhedra is much weaker than that in the phases based on sheet structures. Thus, the $\Delta_f G^o_m$(298) and $\Delta_f H^o_m$(298) values for Ca_3UO_6 should be more positive than those predicted. The h_i values of $CaO_{(I)}$ calculated based on the $\Delta_f H^o_m$(298) values of $CaUO_4$ and Ca_3UO_6 are -764.6 kJ/mol and -689.2 kJ/mol, respectively. Therefore, these two values were averaged to obtain a rough estimation of the h_i of $Ca_{(I)}$ (726.9 kJ/mol) which was used to calculate the predicted $\Delta_f H^o_m$(298) values of the liebigite group minerals. For liebigite, swartzite and bayleyite, the predicted $\Delta_f H^o_m$(298) values are in good agreement with those measured. Structural information and the calculations made in this study indicate that the prediction of the $\Delta_f G^o_m$(298) and $\Delta_f H^o_m$(298) for liegibite group minerals is rather reliable. Thus, the large difference between the predicted and measured $\Delta_f H_m^o(298)$ values of andersonite suggests that the measured value may be in error, which is also indicated by the very large uncertainty of the measured value. The structure of $Li_2U_2O_7$ remains unknown, but the predicted $\Delta_f H_m^o(298)$ value is in fair agreement with the measured value. Adding liebigite, swartzite, bayleyite, UO_2CO_3, $MgUO_4$, $UO_2HPO_4{\cdot}H_2O$, $(UO_2)_3(PO_4)_2$ and $Li_2U_2O_7$ to the model, the regression analysis of the $\Delta_f H_m^o(298)$ values resulted in an average residual of 0.10% and a set of revised h_i values [6]. The analysis described above demonstrates that this technique provides reliable predictions of the $\Delta_f G_m^o(298)$ and $\Delta_f H_m^o(298)$ for most uranyl phases, and the prediction can be improved immediately as accurately determined new data become available.

Finally, we have identified some phases for which the $\Delta_f G_m^o(298)$ and $\Delta_f H_m^o(298)$ could not be predicted reliably using the model presented here, but the deviation can be explained based on structural information (available examples are listed in Table 4). These phases fall into three structure types according to the structural classification of uranyl phases by Burns, *et al.* [7]. The first type is based on sheet structure and includes the phases $M_xU_2O_7$ (M = K, Rb, Ca, Sr; x = 1 or 2). The anion topology of the sheets contain only hexagons, each populated with a uranyl cation to form a hexa-bipyramid with all the edges of the hexagon in the plane of the sheet being shared with neighbouring hexagon. The strong linkage between the cation polyhedra within the sheets makes the measured $\Delta_f G_m^o(298)$ and $\Delta_f H_m^o(298)$ values for the phases of this class more negative than those predicted (see Chen, *et al.* [6]). The second type is based on a chain structure in which the chains contain only uranyl polyhedra and are formed by sharing single corners between $Ur\phi_4$ polyhedra. The linkage between the cation polyhedra in this type of structure is usually much weaker than that in most uranyl phases. Phases belonging to this class are Na_4UO_5, Li_4UO_5, Ca_2UO_5, and Sr_2UO_5. The third class includes those phases consisting of isolated cation polyhedra (*e.g.* Sr_3UO_6 and Ca_3UO_6). The weak connection between cation polyhedra in the second and third structure types makes the measured $\Delta_f G_m^o(298)$ and $\Delta_f H_m^o(298)$ values for these phases more positive than those predicted. The $\Delta_f H_m^o(298)$ values for α-$SrUO_4$, β-$SrUO_4$, Sr_2UO_5 and Sr_3UO_6 are -1 989.0 kJ·mol^{-1}, -1 990.8 kJ·mol^{-1}, -2 635.6 kJ·mol^{-1} and –3 263.4 kJ·mol^{-1}, respectively [4].

Table 4. Phases for which the model predictions were unreliable based on their structural description

Phases	$\Delta_f G_m^o(298)$ (kJ·mol^{-1})		$\Delta_f H_m^o(298)$ (kJ·mol^{-1})	
	Measured	**Predicted**	**Measured**	**Predicted**
$CaUO_4$	-1 888.7	-1 876.8	-2 002.3	-1 960.3
$K_2U_2O_7$			-3 250.5	-3 154.5
$Rb_2U_2O_7$			-3 232.0	-3 156.5
$Cs_2U_2O_7$			-3 220.0	-3 161.8
Li_4UO_5			-2 639.4	-2 709.3
Na_4UO_5			-2 456.6	-2 706.4
Ca_3UO_6			-3 305.4	-3 413.5

Note: The measured values are from Grenthe, *et al.* [4].

The h_i values for $SrO_{(I)}$ calculated using these $\Delta_f H_m^o$ values are -755.85 kJ·mol^{-1}, -757.05 kJ·mol^{-1}, -700.93 kJ·mol^{-1} and -676.55 kJ·mol^{-1}, respectively. These results agree with the structural interpretation that the connection between the cation polyhedra in α-$SrUO_4$ and β-$SrUO_4$ is much stronger than that in Sr_2UO_5 and Sr_3UO_6, as described above. Therefore, the h_i value for $SrO_{(I)}$ should be between -700.93 kJ·mol^{-1} and -755.85 kJ·mol^{-1}.

Application to spent nuclear fuel

Uranyl phases are the solubility-limiting phases of uranium during the oxidative corrosion of spent nuclear fuel. Both the solution concentration of uranium and the secondary phase immobilisation of actinides and fission products depend largely on the structure and stabilities of the secondary phases formed. Thus, a defensible predictive model for assessing the corrosion of spent fuel must be based on a critical examination of the phases that will be important during the process. Natural analogue studies suggest that the long-term paragenesis during the oxidative corrosion of UO_2 fuel can be summarised as [1] an initial decomposition of UO_2 to uranyl oxide hydrates followed by the formation of more stable uranyl silicates or, in phosphorous-rich groundwaters, the formation of uranyl phosphates. Because phosphorus is not expected to be present in significant amounts in spent nuclear fuel or in the groundwater of the proposed high-level waste repository at Yucca Mountain, uranyl silicates will most probably be the solubility-limiting phases of uranium in the near field. Among the uranyl silicates in the UO_3-CaO-SiO_2-H_2O system, haiweeite has been suggested to be important during the oxidative corrosion of spent fuel by chemical simulation and experimental studies. Our prediction also indicates that haiweeite would be more stable in groundwaters from crystalline rocks. However, field observations indicate that uranophane is the most common uranyl silicate, and haiweeite is rare in nature. Because both the detailed structural information and thermodynamic data for haiweeite are unavailable, relevant experimental studies are strongly recommended, and experiments combined with studies of natural occurrences are necessary in order to provide an explanation for this discrepancy and to determine whether the precipitation of haiweeite should be suppressed in geochemical models of the oxidative alteration of spent fuel. Becquerelite is potentially an important secondary mineral during the corrosion of spent fuel in repositories, but significant discrepancies exist in the solubility experiments and no calorimetric thermodynamic datum is available for becquerelite. Uranyl phosphates are the most numerous and most commonly found in nature [1], and no thermodynamic data is available for the most abundant and structurally well-known phosphates, such as (meta)autunite, torbernite and phosphuranylite.

In order to achieve an immediate further improvement in the estimation of thermodynamic properties of uranyl phases and make successful predictions of the dominant uranyl phases formed during oxidative corrosion of spent fuel in underground repositories, we suggest that future experimental studies include:

- the determination of thermodynamic properties for uranyl oxide hydrates of potassium and calcium, and for uranyl silicates (*e.g.* sklodowskite and haiweeite), as well as the naturally abundant uranyl phosphates;

- structure refinements of $(UO_2)_3(PO_4)_2(H_2O)_n$ (n = 0, 4, 6), $(UO_2)_2P_2O_7$ and uranyl silicates, such as haiweeite and swamboite.

Finally, calorimetric and phase-equilibrium determinations must be based on materials for which structure refinements and accurate chemical analyses exist. The proper characterisation of experimental materials remains a major challenge in studies of these complex uranyl phase assemblages.

Because the molar contributions (g_i and h_i) obtained by the regression technique are average contributions of a polyhedron in selected U(VI) phase structures, the reliability of predicted values depends on the model database. Thus, the thermodynamic data for U(VI) phases with highly irregular structures should not be included in the model database or be predicted by these empirical methods. The predicted thermodynamic parameters are improved if the estimation is made within a group of phases which are structurally analogous.

Although this method provides a means of calculating thermodynamic parameters for U(VI) phases of known structures with a calculated error comparable to that obtained from direct experimental determinations, we want to emphasise the need for critical experimental data. The results of the statistical analysis of the presently available data should not be used as a justification for not completing the necessary experimental studies. The value of the statistical technique that we have described depends directly on the quality and quantity of experimental data that are available.

Finally, the use of thermodynamic parameters in a performance assessment requires careful attention to the effect of error on parametric and conceptual uncertainties in the performance assessment. In a recent example, Ewing, *et al.* [10] have shown that even small variations in the thermodynamic parameters (say less than 1% in the estimated value for the Gibbs free energy) can cause substantial changes in activity-activity diagrams that may be the basis for conceptual models in the performance assessment. This suggests that bounding calculations of phase stability and solubility may be the most prudent approach in using thermodynamic parameters in performance assessment calculations.

Acknowledgements

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REFERENCES

[1] R.J. Finch and R.C. Ewing, “The Corrosion of Uraninite under Oxidizing Conditions”, *Journal of Nuclear Materials*, 190, 133-156 (1992).

[2] P.C. Burns, R.C. Ewing and F.C. Hawthorne, “Incorporation Mechanisms of Actinide Elements into the Structure of U^{6+} Phases Formed during the Oxidation of Spent Nuclear Fuel”, *Journal of Nuclear Materials*, 245, 1-9 (1997).

[3] P.C. Burns, R.J. Finch, F.C. Hawthorne, M.L. Miller and R.C. Ewing, “The Crystal Structure of Ianthinite, $[U_2^{4+}(UO_2)_4O_6(OH)_4(H_2O)](H_2O)_5$: A Possible Phase for Pu^{4+} Incorporation during the Oxidation of Spent Nuclear Fuel”, *Journal of Nuclear Materials*, 249, 199-206 (1997).

[4] I. Grenthe, J. Fuger, R.J.M. Konings, R.J. Lemire, A.B. Muller, C. Nguyen-Trung and H. Wanner, “Chemical Thermodynamics of Uranium”, Elsevier, Amsterdam (1992).

[5] J.A. Chermak and J.D. Rimstidt, “Estimating the Thermodynamic Properties ($\Delta_f G_m^o$ and $\Delta_f H_m^o$) of Silicate Minerals at 298 K from the Sum of Polyhedral Contributions”, *American Mineralogist*, 74, 1023-1031 (1989).

[6] F. Chen, R.C. Ewing and S.B. Clark, “The Gibbs Free Energies and Enthalpies of Formation of U^{6+} Phases: An Empirical Method of Prediction”, *American Mineralogist*, 84, 650-664 (1999).

[7] P.C. Burns, M.L. Miller and R.C. Ewing, “U^{6+} Minerals and Inorganic Phases: A Comparison and Hierarchy of Crystal Structures”, *Canadian Mineralogist*, 34, 845-880 (1996).

[8] P.C. Burns, R.C. Ewing and F.C. Hawthorne, “The Crystal Chemistry of Hexavalent Uranium: Polyhedral Geometries, Bond-valence Parameters and Polymerization of Polyhedral”, *Canadian Mineralogist*, 35, 1551-1570 (1997).

[9] A.K. Alwan and P.A. Williams, “The Aqueous Chemistry of Uranyl Minerals. Part 2. Minerals of Liebigite Group”, *Mineralogical Magazine*, 43, 665-667 (1980).

[10] R.C. Ewing, M.S. Tierney, L.F. Konikow and R.P. Rechard, “Performance Assessments of Nuclear Waste Repositories: A Dialogue on their Value and Limitations”, *Risk Analysis*, 19 (5), 933-958 (1999).

THE AQUEOUS CHEMISTRY AND THERMODYNAMIC OF ACTINIDES AND FISSION PRODUCTS (ACTAF) PROJECT

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This paper was presented orally, but was unfortunately not available at the time of publication.

DISCUSSION

The discussion began with several specific comments from the speakers.

J. Bruno commented on the relevance of R. Ewing’s presentation from the viewpoint of retrievable repository concepts.

P. Hernán commented that the ACTAF project presented by T. Fanghänel was very ambitious in terms of technical objectives.

T. Fanghänel answered that the project was operating as expected and he was optimistic as concerns the planned objectives.

J. Bruno highlighted the relevance of this type of work for the source term.

The Chairman opened the general discussion.

J. Bruno said that it is necessary to use the full power of the theoretical/semi-empirical models to fill the gaps existing in the databases and that it is very important to assess how much data is needed. One of the issues is how to introduce solid-solution models and their corresponding activity coefficients in the most common databases.

I. Grenthe said that chemical knowledge should be used to help to develop theory and estimation approaches.

J. Bruno remarked on the use of approaches that help to build up a thermodynamical framework to study oxidative alteration.

R. Ewing did not see an immediate need for the development of solid-solution models.

T. Fanghänel pointed out that it is necessary to understand the processes but that it is very dangerous to use ideal solid-solution models because in most cases they are not conservative.

R. Ewing said that solid solution models have not been used in performance assessment.

J. Bruno replied that this type of models was included in SKB’s SR97 and it is being incorporated in Enresa2000 as well.

K. Spahiu insisted on the fact that solid-solution models are not conservative.

J. Bruno said that being conservative does not ensure accuracy, and that perhaps we have been wrong to look for this quality when it is not always the correct scientific manner in which to proceed.

M. Askarieh mentioned that it has been repeatedly stated that solubility is controlled by surface phases, not by the bulk solid. Therefore he asked for an explanation concerning the concept of transitory solubility.

I. Grenthe answered that it will be difficult to quantitatively model these systems and that from his point of view the important issue is to know how a system will evolve.

J. Alonso asked what are the gaps existing when trying to simplify the models for performance assessment.

T. Fanghänel answered that an example of the complexity encountered in transferring models to performance assessments is the surface phenomena just mentioned: finding the relation between surface complexation models and $K_{D.}$ One cannot transfer surface complexation models directly to performance assessment, but it is possible to support K_D values with surface complexation models.

P. Wersin mentioned that the use of ideal mixing models for solid solutions may lead to underestimating the solubility of radionuclides.

R. Ewing commented that performance assessment is more than chemistry, and posed the question of how far we are from the actual solution when we use input data that has been estimated or modelled but not experimentally determined.

J. Bruno answered that, in our field, modellers and scientists are or must be the same.

C. Tweed commented that estimated data are model (and thus modeller) dependent and that it is necessary to give the proper value to each source of estimated data.

M. Askarieh returned to the subject of ACTAF, and asked whether a thermodynamic database would be set up.

T. Fanghänel answered that it is not the aim of ACTAF to set up a database. The project aims at filling the current gaps in the existing data by experimentation and eventually incorporating the new information to databases such as NEA TDB.

I. Grenthe said that the maintenance of the NEA TDB is assured by the Agency and asked about the European TDB. He went on to comment on the fact that a sorption model based on K_D values can be useful when describing transport, but has important drawbacks when there are changes in the water/ solid compositions. Therefore, it is important to provide ranges of values, not only a central value, for this parameter.

B. Glassley asked about the sources of uncertainty. He commented on the development of a tool to deal with uncertainties. Specifically, he asked whether it is planned to study precipitation kinetics within the ACTAF project and whether it is possible to obtain kinetic information from the Th study presented by T. Fanghänel.

T. Fanghänel answered that it is not planned to perform any measure on kinetics of precipitation within ACTAF and that no information on kinetics can be obtained from the experimental data shown.

D. Kulik expressed his interest in the work presented by R. Ewing and asked about the possibility of estimating K_p values from that methodology.

R. Ewing answered that this is not a small step, that it is very difficult and that the estimation of enthalpy is still very complicated. It is theoretically feasible but not practical.

D. Kulik commented on the necessity of integrating mechanistic models with performance assessment.

P. Sellin was in agreement with I. Grenthe concerning the fact that the story sometimes is more important than the models themselves. He said that scientific modellers can assess experimental data and it would be desirable to have three different thermodynamic databases: 1) a reliable database, 2) an estimated database and 3) a compilation of “bad data”. He also said that for performance assessment users, an estimated database complementing the reliable database would be very useful.

K. Spahiu commented on the fact that the estimation of the data is not work contemplated by the NEA TDB. This field is left to other initiatives that estimate data and conduct modelling.

J. Bruno said that, still, there is a need for additional scientific production of data to feed and validate the models.

SESSION 3

Performance Assessment

Applications and Limitations of Using Thermodynamic Data in PA

Chair: H. Wanner

LIMITATIONS IN THE USE OF NEA TDB COMPILATIONS

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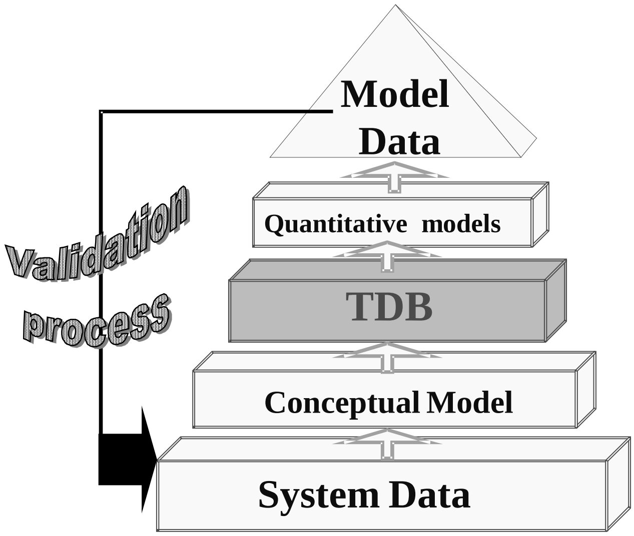
Introduction

The main reason for using thermodynamic data in performance assessment (PA) is that the chemical data requirements for both deterministic and probabilistic PA exercises critically rely on the availability of thermodynamic data. This statement is not questionable.

Thermodynamic data is one of the building blocks of thermodynamic modelling. Among these blocks (Figure 1) we have the system data, that is the data provided by site characterisation, waste-matrix characterisation, etc.; from there a conceptual model is developed requiring the use of thermodynamic data to transfer this model to a quantitative model to generate the model data. A very important issue is the feedback cycle throughout the entire system so that the model data is tested against the system data and therefore the conceptual model can be refined, etc., which is called the validation process.

Figure 1. Building blocks of thermodynamic modelling



Geochemical modelling is not simply science, it is also possessed of a certain artistic element which is very difficult to transfer to geochemical codes. The art of geochemical modelling is the manner in which the conceptual and quantitative model is adapted to the system data available. This endeavour does not lie within the mandate of the NEA.

How is TDB used in PA?

TDB are used in two ways:

1) to define source term concentrations by using solubility calculations to that end;

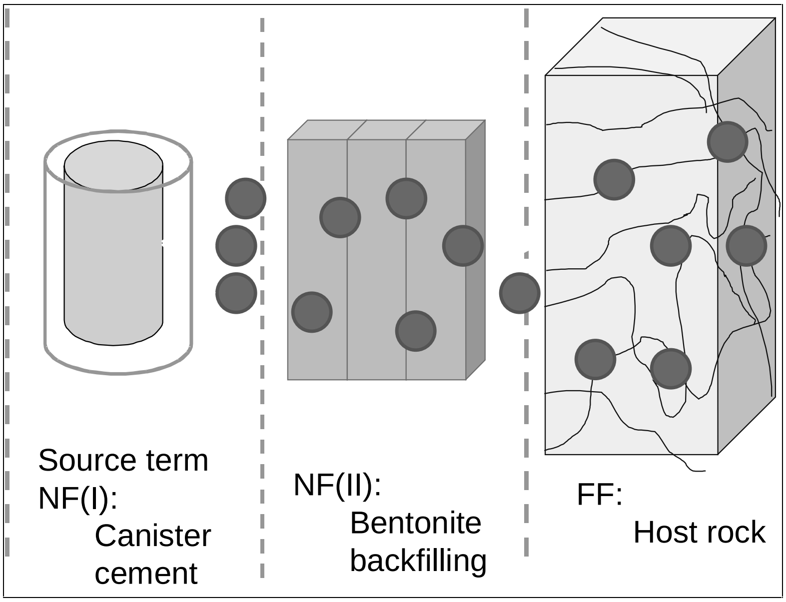
2) to calculate retardation in several aspects, the most famous example being the Kd approach in which a calculated chemical speciation of a radionuclide is used to reflect on the magnitude of the Kd; fortunately this has developed a little bit further.

TDBs are built from experimental work: titration, spectrophotometry, solid phase characterisation, etc. The experimentalists put all this information together as thermodynamic data and the NEA selects and compiles these data. For practitioners of thermodynamic modelling, taking into consideration the building blocks, solubilities are calculated using the TDBs. These solubilities should be compared with information from "dirty systems": waste matrix, dissolution experiments, etc., and from natural-system studies. Finally, stochastic or probabilistic source term concentrations can be calculated.

By examining the different elements of a repository system (Figure 2), considering geological disposal the way to go, some of the key processes for which the use of thermodynamic data would be helpful can be defined:

- the source term including the matrix and the canister;
- the near field including bentonite and backfilling;
- the far field that limits the retardation of the radionuclides.

Figure 2. HLNW repository scheme



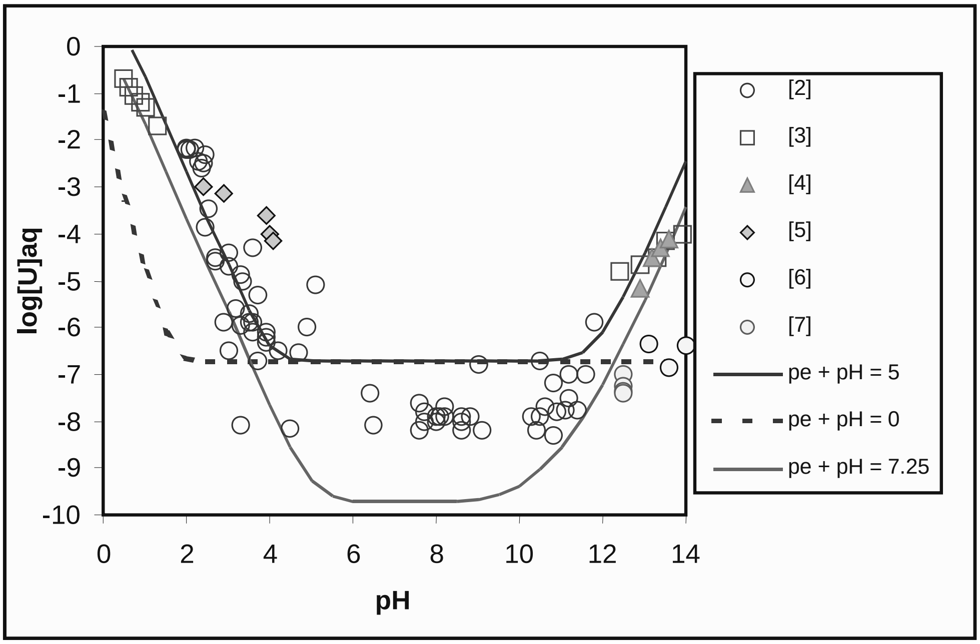
The warnings when using TDB compilations are illustrated in several examples.

NF(I)

Source term

Figure 3 shows a compilation of solubility data of uranium dioxide under different pH and redox conditions. The two boundaries are solubilities calculated by using two solubility constants. One was selected by the NEA TDB, and corresponds to a crystalline phase; the other was calculated from UO_2, taking into consideration that its surface is less ordered than the monocrystalline UO_2. If the value selected by the TDB compilation is considered, the U concentration obtained from experimental data will be underestimated, while if the less structured UO_2 is considered, an upper limit value is obtained that is more realistic within a certain degree of conservatism. The message here is that the values selected in the NEA TDB should be contrasted with experimental information; failing that, there is a risk of underestimation.

Figure 3. Solubility of UO_2; light grey line $\log_{10} K^{\circ}_{s,0}$ = -4.85 (NEA selection), dark grey lines $\log_{10} K^{\circ}_{s,0}$ = -1.6 (SKBU) (adapted from Casas, *et al.* [1])



Canister

Another example (Table 1) shows the relevance of the selection of auxiliary data. The table shows a summary of the redox potentials found in the literature for the reaction:

$$\mathrm{Fe}^0 \rightleftharpoons \mathrm{Fe}^{2+} + 2\mathrm{e}^- \tag{1}$$

Amazingly, given that this is very basic data, this redox potential is not well established. When it comes to the study of the stability of a given corrosion product, an enormous uncertainty can exist, up to 6 orders of magnitude. This is unacceptable for such an important parameter. No NEA group has been established to study this issue, but an important effort should be devoted to clarify such an important subject and to establish a value for this redox equilibrium.

Table 1. Summary of the redox potentials found in the literature for the reaction in Eq. 1

E^o (V)	Method	Comments	Original source
0.441	Potentiometry	Fe electrode: H_2 reduction. of oxide	Hampton, 1926 [8]
0.440	Potentiometry	Fe electrode: H_2 reduction. of oxide	Randall & Frandsen, 1932 [9]
0.409	Potentiometry	Fe electrode: iron carbonyl decomposed	Patrick & Thompson, 1952 [10]
0.443	Potentiometry	Fe electrode: H_2 reduction of oxide (O_2 present)	Patrick & Thompson, 1952 [10]
0.477	Potentiometry	Fe electrode: H_2 reduction of oxide (no O_2 present)	Patrick & Thompson, 1952 [10]
0.467	Amperometry	Fe electrode: H_2 reduction of oxide (no O_2 present)	Hurlen, 1960 [11]
0.473	Calorimetry	$FeSO_4 \cdot 7H_2O$ measurement of $\Delta_{sol}H_m^o$	Larson, *et al.*, 1968 [12]
0.415	Potentiometry	Fe electrode degassed	Johnson & Bauman, 1978 [13]
0.435	Potentiometry	Fe electrode not degassed	Johnson & Bauman, 1978 [13]
0.460	Solubility meas.	Solubility of Fe_3O_4	Tremaine & LeBlanc, 1980 [14]

NF(II)

Another area that Urs Berner will surely treat later on deals with the non-stoichiometry of some of the phases in the cementitious near-field. This deserves a certain degree of attention because there no realistic concept currently exists as to how to deal with cement.

Bentonite is a clear case in which the accessory is as important as the fundamental material. To clarify, in bentonite, most of the main processes controlling master variables, such as pH and Eh are related to the accessory minerals, mainly pyrite, calcite, quartz and gypsum. Of course ionic exchange plays its role, but the accessory minerals are very important.

Far field

Yesterday there was some discussion as to how solid solutions (SS) mixed solids are approached. During 1983, when I came across P. Schindler in Switzerland I tried to see how far simplified models could go toward explaining the incorporation of trace metals in major solids. Although there is an awareness of its limitations, it can be said that this is an area which has not yet been explored to the fullest extent. The fundamentals of the approaches can be seen in Figure 4.

In Figure 5 some of the first experimental results that were done in this area can be seen. Some of the results from Bruno, *et al.* [15] on the application of the co-precipitation approach to the system U(VI)-$Fe(OH)_3(s)$ are shown in Figure 5(a). At that time it was widely thought impossible. Later on it was demonstrated that this is not only possible but certain. Sorption data can also be defined using the same approach [Figure 5(b)], therefore allowing quantitative exchangeability although employing different conceptual phenomenon.

Figure 4. Basis of the simple models used to deal with mixed solids

Trace Metals – Major Components (1)

SI(M) >0: Co-precipitation approach

- ✓ Based on the thermodynamics of ideal solid solutions [15,16,17]
- ✓ Co-precipitation of a trace element T with a major metal (i.e. Ca) forming a mixed solid phase $T_xCa_{(1-x)}CO_3(s)$

$$TCO_3(s) \Leftrightarrow T^{2+} + CO_3^{2-} \qquad K_s = a_{T^{2+}} \cdot a_{CO_3^{2-}} / a_{TCO_3(s)}$$

$a_{TCO_3(s)}$=activity of the solid phase $\equiv \chi$, when $\chi \leq 0.05$

$$\mathbf{K^*_{so}} = K_{so} \cdot \chi_{TCO_3(s)} = [T^{2+}]\gamma_T \cdot [CO_3^{2-}]\,\gamma_{CO_3}$$

Trace Metals – Major Components (2)

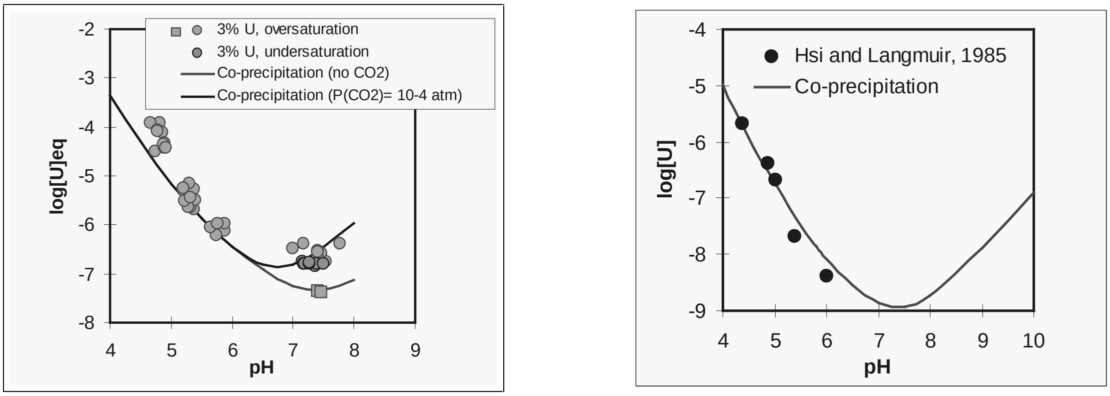
SI(M) <0: Co-dissolution approach

- ✓ Based on the stoichiometric saturation concept [18] Non-equilibrium systems.
- ✓ Ideally mixed solid (i.e. $T_xCa_{(1-x)}CO_3(s)$) dissolves in a congruent fashion

$$T_xCa_{(1-x)}CO_3(s) \Rightarrow xT^{2+} + (1-x)Ca^{2+} + CO_3^{2-}$$

$$\boxed{[T^{2+}] = x / (1-x) \cdot [Ca^{2+}]}$$

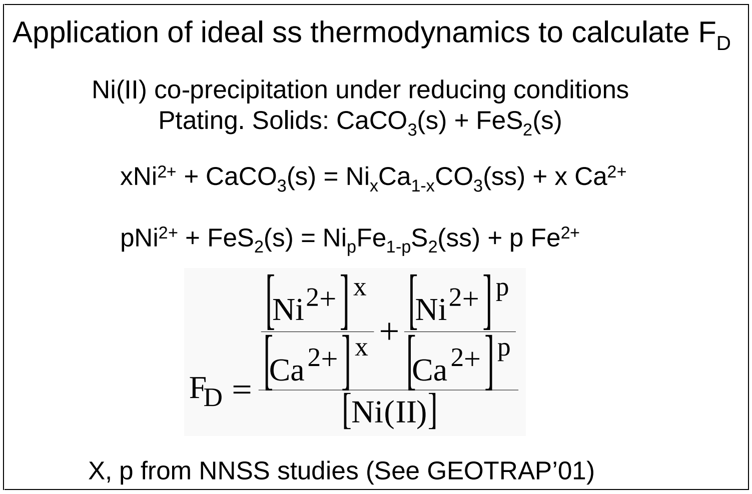
Figure 5. Application of the co-precipitation approach



(a) U(VI)-Fe(OH)$_3$ co-precipitation data from Bruno, et al. [15] *(b) U(VI)-Fe(OH)$_3$ sorption data from His and Langmuir* [19]

Three weeks ago, during the GEOTRAP workshop, an idea for the approach to large Kd parameters was developed. These large Kd include not only sorption but also other factors. A distribution factor that has to do with the partition of trace elements for different solid phases was defined. This was investigated for the incorporation of Ni in carbonates and iron sulphides at redox fronts (see Figure 6).

Figure 6. Application of ideal solid solution thermodynamics to calculate distribution factor for nickel at the redox front defined by calcite/iron sulphide



Application of ideal ss thermodynamics to calculate F_D

Ni(II) co-precipitation under reducing conditions
Ptating. Solids: $CaCO_3(s) + FeS_2(s)$

$$xNi^{2+} + CaCO_3(s) = Ni_xCa_{1-x}CO_3(ss) + x\ Ca^{2+}$$

$$pNi^{2+} + FeS_2(s) = Ni_pFe_{1-p}S_2(ss) + p\ Fe^{2+}$$

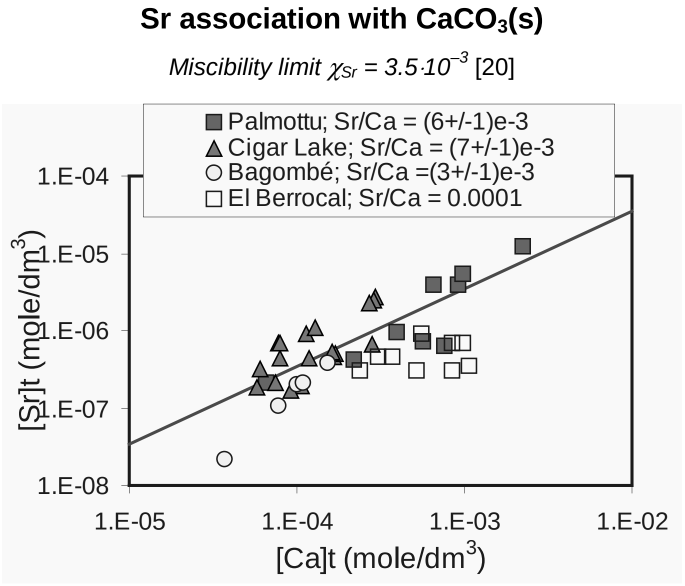
$$F_D = \frac{\dfrac{[Ni^{2+}]^x}{[Ca^{2+}]^x} + \dfrac{[Ni^{2+}]^p}{[Ca^{2+}]^p}}{[Ni(II)]}$$

X, p from NNSS studies (See GEOTRAP'01)

Relevance of natural systems data

Logically, the next area to be addressed is natural systems data. The "universal" relation between measured Sr and Ca concentrations in groundwaters can be seen in Figure 7. By "universal" is meant natural analogue data. The solid line describes the miscibility limit for the incorporation of Sr into calcite given by Tesoriero and Pankow [20]. By and large, most of the data are around this value, which is amazing, because the question is always: how can the molar fraction to be used in the solid phase be found? By exploring the situation in different natural systems perhaps the solution will be discovered.

Figure 7. Association of Sr with calcite in natural systems (adapted from Bruno, *et al.* [21])



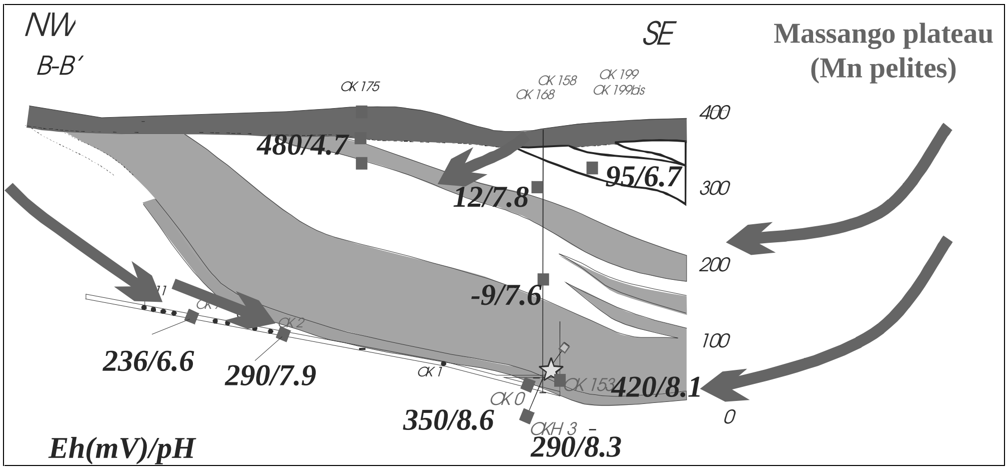
Sr association with $CaCO_3(s)$

Miscibility limit $\chi_{Sr} = 3.5{\cdot}10^{-3}$ [20]

Natural-systems data: The Oklo example

Figure 8 shows another example: Oklo. This is a very good example in which many components of a repository can be found. The star indicates the location of a uranium deposit which has been functioning as a natural reactor. On the right there is a plateau of manganiferous pelites. The arrows indicate the flow circulation, which is the first thing that must be known in order to understand the system. Here, there is a flow circulation through the Mn pelites, a surface infiltration and a circulation through the preferential path created by the existence of the gallery of the mine.

Figure 8. Okélobondo (Oklo) zone in Oklo showing the main flow pathways and the values of Eh and pH of the groundwater sampled at each bore hole



The redox potentials measured around the reactor are very oxidising, which is extraordinary. They are oxidising because they are influenced by the manganese control [see Figure 9(a)]. The rest of the measurements can be explained by the iron(II)/iron(III) system. This is an example of applying thermodynamic modelling to natural systems.

Now a comparison between measured and calculated uranium concentrations will be attempted. It could be expected that the U close to the reactor would be controlled by UO_2, but due to the oxidising character of these waters what results is U(VI), either in the form of U(VI) silicates or associated to $Fe(OH)_3$(s). The match is not perfect but it is the correct trend.

Examining the west gallery waters, it can be seen that they are oxidising given the effect of the open gallery. The best correspondence between measurements and calculations is given in this case by Na-zippeite. This solid is not a phase that you will find in the NEA selection, as the data is not good enough to be included in the compilation. The modeller, however, should consult the literature and search for the best value. Finally, the surface waters are controlled by U(VI)-$Fe(OH)_3$ co-precipitation; this is observed everywhere. Here is a clear example of how thermodynamic modelling can be applied to a dirty system.

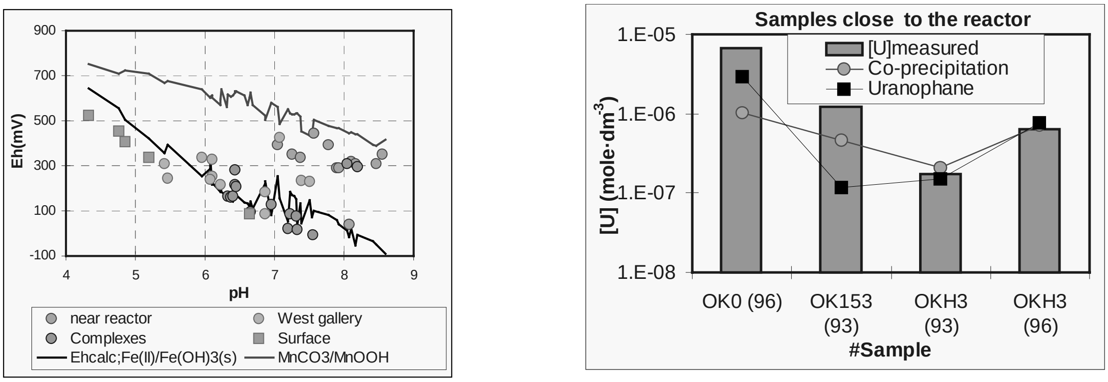
Dealing with uncertainty

This example is aimed at illustrating the implications of the uncertainty in a given value on the other values of the system. The case study is the uncertainty associated with the solubility constant of schoepite. This phase is of the utmost importance in PA given that it controls the solubility of U under

Figure 9

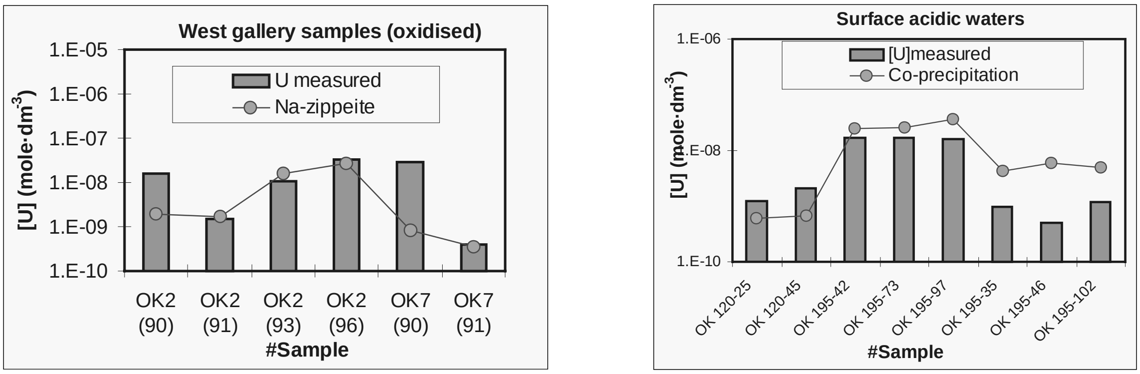
(a) Eh/pH values of the Oklo samples compared with the redox control exerted by the manganese and the iron systems

(b) Comparison between the uranium concentrations measured in the samples close to the reactor and the calculated by assuming equilibrium with uranophane and by assuming co-precipitation of U(VI) with $Fe(OH)_3(am)$



(c) Comparison between the uranium concentrations measured in the samples of the west gallery and those calculated by assuming equilibrium with Na-zippeite

(d) Comparison between the uranium concentrations measured in the surface samples and those calculated by assuming the co-precipitation of U(VI) with $Fe(OH)_3(am)$



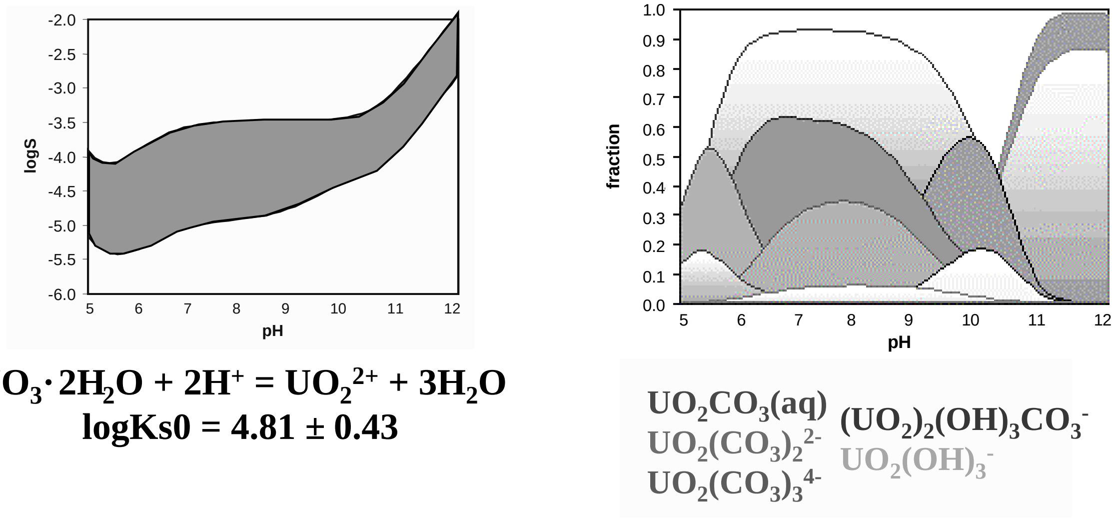
oxidising conditions; it is, for example, considered in Yucca Mountain. In Figure 10 the uncertainty associated to the solubility of schoepite is shown as the range of concentrations of uranium calculated. The manner in which this uncertainty is transferred to the aqueous speciation scheme of uranium can be seen in Figure 10(b). For example, the species $UO_2(CO_3)_2^{2-}$ almost disappears from the speciation plot when assuming the lowest value in the range of solubility of schoepite, while when assuming the upper value it accounts for the 30% of the aqueous uranium.

This means that the uncertainty not only affects the solubility, but also the speciation and, therefore, the sorption behaviour.

The plutonium case

This example deals with the application of thermodynamic data found in the NEA books. In the figure the available data on the solubility of $Pu(OH)_4(s)$ is shown. If only the data included in the NEA TDB book for Pu were used to calculate the solubility of this solid, the lines shown in the plot of

Figure 10



(a) Range of concentrations of U in equilibrium with schoepite as a function of pH. Upper solid line stands for the central value plus the uncertainty. Lower solid line stands for the central value minus the uncertainty.

(b) Aqueous U speciation scheme depending on the value of the solubility constant used for schoepite. Dark curves indicate the speciation scheme obtained when assuming the upper value for the schoepite solubility constant and light curves indicate the scheme when using the lower value.

$$UO_3 \cdot 2H_2O + 2H^+ = UO_2^{2+} + 3H_2O$$

$$\log Ks0 = 4.81 \pm 0.43$$

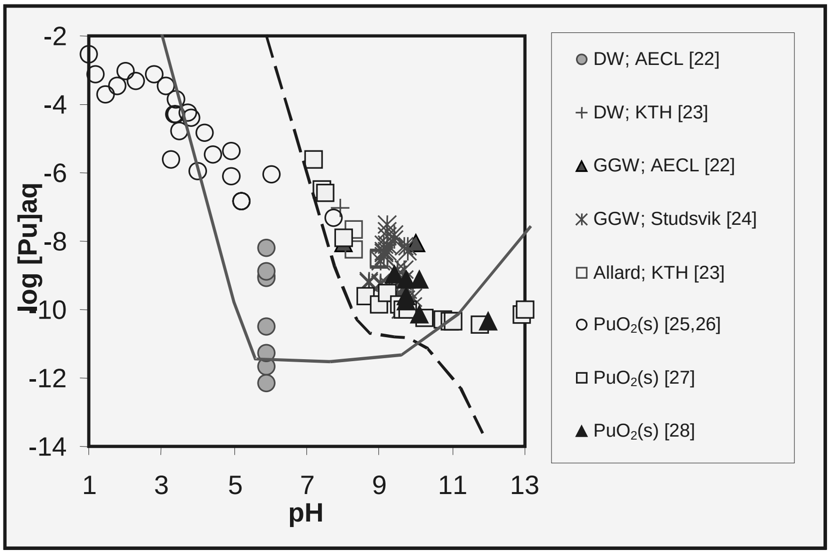
Figure 11(a) would be obtained, depending on whether carbonate exists in the system. What can immediately be appreciated from these results is that the data is unexplainable. Further, it is interesting to note that, if carbonate were assumed in the system, the solubility of Pu at alkaline pH goes down because in the NEA work no selection for the stability constant of $Pu(OH)_4(aq)$ is given; therefore the calculations could have been conducted without considering this species which is in turn the one that is actually providing the solubility in this pH region.

If a certain stability is considered for the neutral hydroxide species [see lines in Figure 11(b)], a reasonable description of the system with or without carbonate in the medium can be obtained.

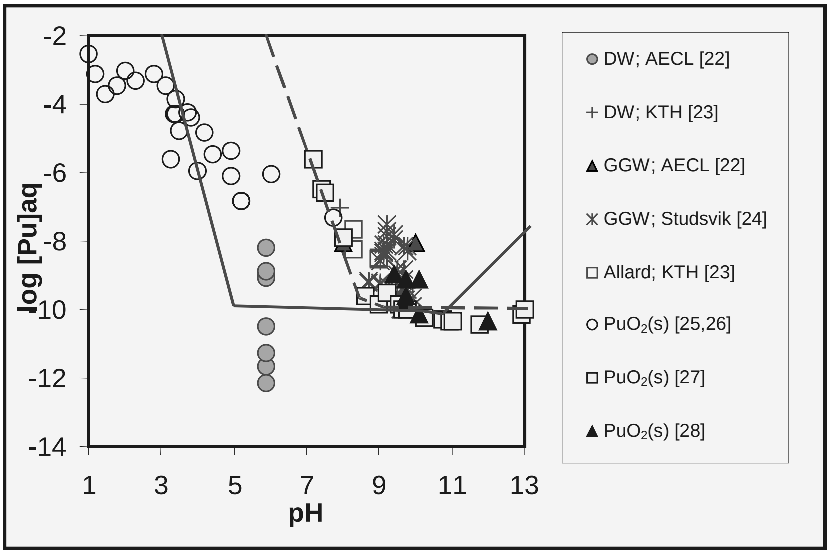
Therefore, one of the main conclusions that should be retained from the work presented here is that the NEA TDB, while a very important work, should not be solely relied upon. Data estimation and a full understanding of the problem in question are required in order to identify the data lacking in the description of the system.

Figure 11. Description of the measurements available in the literature on the solubility of $Pu(OH)_4(s)$

(a) Comparison of the data with the solubility calculated by using only thermodynamic data included in the NEA TDB book (solid and dashed line differ in the carbonate content and the redox potential)



(b) Comparison of the data with the solubility curves calculated by using additional species of Pu selected from published data that have not been selected by the NEA TDB team due to the poor quality of the data (as in the previous case solid and dashed lines differ in the carbonate content and the redox potential)



REFERENCES

[1] I. Casas, J. de Pablo, J. Giménez, M.E. Torrero, J. Bruno, E. Cera, R.J. Finch and R.C. Ewing, "The Role of pe, pH and Carbonate on the Solubility of UO_2 and Uraninite Under Nominally Reducing Conditions", *Geochim. Cosmochim. Acta*, Vol. 62 (13), 2223-2231 (1998).

[2] D. Rai, A.R. Felmy, J.L. Ryan, "Uranium(IV) Hydrolysis Constants and Solubility Product of $UO_2{\cdot}xH_2O$(am)", *Inorg. Chem.*, 29, 260-264 (1990).

[3] K.H. Gayer, H. Leider, "The Solubility of Uranium(IV) Hydroxide in Solutions of Sodium Hydroxide and Perchloric Acid at 25°C", *Can. J. Chem.*, 35, 5-7 (1957).

[4] Galkin and Stepanova (1961).

[5] N.M. Nikolaeva, A.V. Pirozhkov, "The Solubility Product of U(IV) Hydroxide at the Elevated Temperatures", *Izv. Sib. Otd. Akad. Nauk SSSR*, 5, 82-88 (1978), in Russian.

[6] J.L. Ryan, D. Rai, "The Solubility of Uranium(IV) Hydrous Oxide in Sodium Hydroxide Solutions Under Reducing Conditions", *Polyhedron*, 2, 947-952 (1983).

[7] P.R. Tremaine, J.D. Chen, G.J. Wallace, W.A. Boivin, "Solubility of Uranium(IV) Oxide in Alkaline Aqueous Solutions to 300°C", *J. Solution Chem.*, 10, 221-230 (1981).

[8] W.H. Hampton, *Jour. Phys. Chem.*, 30, 980 (1926).

[9] M. Randall and M. Frandsen, *Jour. Amer. Chem. Soc.*, 54, 47 (1932).

[10] W.A. Patrick and W.E. Thompson, *Jour. Amer. Chem. Soc.*, 75, 1184 (1953).

[11] T. Hurlen, *Acta Chem. Scand.*, 14, 1533 (1960).

[12] J.W. Larson, P. Cerutti, H.K. Garber and L.G. Hepler, *Jour. Phys. Chem.*, 72, 2902 (1968).

[13] G.K. Johnson and J.E. Bauman, *Inorg. Chem.*, 17, 2774 (1978).

[14] P.R. Tremaine and J.C. LeBlanc, *Jour. Sol. Chem.*, 9, 415 (1980).

[15] J. Bruno, J. de Pablo, L. Duro and E. Figuerola, "Experimental Study and Modelling of the U(VI)-$Fe(OH)_3$ Surface Precipitation/Co-precipitation Equilibria", *Geochim. Cosmochim. Acta*, Vol. 59 (20), 4113-4123 (1995).

[16] W. Stumm and J.J. Morgan, "Aquatic Chemistry", John Wiley and Sons (1981).

[17] J. Bruno, L. Duro, J. de Pablo, I. Casas, C. Ayora, J. Delgado, M.J. Gimeno, J. Peña, C. Linklater, L. Pérez del Villar and P. Gómez, "Estimation of the Concentrations of Trace Metals in Natural Systems. The Application of Co-dissolution and Co-precipitation Approaches to El Berrocal (Spain) and Poços de Caldas (Brazil)", *Chem. Geol*., Vol.151, 277-291 (1998).

[18] Thorstenson and Plummer (1977).

[19] D.C. Hsi and D. Langmuir, "Adsorption of Uranyl onto Ferric Oxyhydroxides: Application of the Surface Complexation Site-binding Model", *Geochim. Cosmochim. Acta*, Vol. 49, 1931-1941 (1985).

[20] A.J. Tesoriero and J.F. Pankow, "Solid Solution Partitioning of Sr^{2+}, Ba^{2+} and Cd^{2+} to Calcite", *Geochim. Cosmochim. Acta*, Vol. 60, 1053-1064 (1996).

[21] J. Bruno, L. Duro and M. Grivé, "The Applicability and Limitations of Thermodynamic Geochemical Models to Simulate Trace Element Behaviour in Natural Waters. Lessons Learned from Natural Analogue Studies", to be published in *Chem. Geol*. (2001).

[22] J.C. Tait, S. Stroes-Gascoyne, W.H. Hocking, A.M. Duclos, R.J. Porth and D.L. Wilkin, "Dissolution Behaviour of Used CANDU Fuel Under Disposal Conditions", Mater. Res. Soc. Symp. Proceed., 212, 189-196 (1991).

[23] J. Bruno, E. Cera, E-B. Eklund, T.E. Eriksen, M. Grivé and K. Spahiu, "Experimental Determination and Chemical Modelling of Radiolytic Processes at the Spent Fuel/Water Interface", *Radiochim. Acta*, 88, 513-519 (2000).

[24] R. Forsyth and U-B. Eklund, "Spent Nuclear Fuel Corrosion: The Application of ICP-MS to Direct Actinides Analysis", SKB Technical Report 95-04 (1995).

[25] D. Rai and J.L. Ryan, "Crystallinity and Solubility of Pu(IV) Oxide and Hydrous Oxide in Aged Aqueous Suspensions", *Radiochim. Acta*, 31, 45-50 (1982).

[26] D. Rai, "Solubility Product of Pu(IV) Hydrous Oxide and Equilibrium Constants of Pu(IV)/Pu(V), Pu(IV)/Pu(VI) and Pu(V)/Pu(VI) Couples", *Radiochim. Acta*, 35, 97-106 (1984).

[27] F.T. Ewart, R.M. Howse, H.P. Thomason, S.J. Williams and J.E. Cross, "The Solubility of Actinides in the Near Field", *Mater. Res. Soc. Symp*., Vol. 50, 701-708 (1985).

[28] T. Yamaguchi, Y. Sakamoto and T. Ohnuki, "Effect of the Complexation on Solubility of Pu(IV) in Aqueous Carbonate System", *Radiochim. Acta*, 66/67, 9-14 (1994).

MINIMISING UNCERTAINTY INDUCED BY TEMPERATURE EXTRAPOLATIONS OF THERMODYNAMIC DATA: A PRAGMATIC VIEW ON THE INTEGRATION OF THERMODYNAMIC DATABASES INTO GEOCHEMICAL COMPUTER CODES

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Abstract

Incorporation of temperature corrections is gaining priority regarding geochemical modelling computer codes with built-in thermodynamic databases related to performance assessment in nuclear waste management. As no experimental data at elevated temperatures are available *e.g.* for many actinide and lanthanide species, the simplest one-term extrapolations of equilibrium constants are usually assumed in practice. Such extrapolations, if set inappropriately, may accumulate large additional uncertainty at temperatures above 100°C. Such errors can be avoided because one-, two- and three-term extrapolations have great predictive potential for isoelectric/isocoulombic reactions which has to be explored and extensively used in geochemical modelling by LMA and/or GEM algorithms. This can be done efficiently and consistently via implementing a built-in "hybrid" database combining "kernel" thermochemical/EoS data for substances with the "extension" reaction-defined data for other species.

Introduction

Temperature correction of thermodynamic data is essential in geochemical thermodynamics, especially for studies of hydrothermal systems. In the past, this aspect has been rather uncommon in aquatic chemical modelling related to performance assessment in nuclear waste management. Recently, it has been recognised that within 1 000 years after closure of a HLW repository, temperature may increase up to 70-90°C or even higher [1]. Hence, incorporation of consistent data and methods for temperature corrections into computer codes and built-in thermodynamic databases is gaining priority. This question seems to be related more to pragmatic implementation issues than to scientific problems.

A plethora of existing techniques for temperature corrections of reaction equilibrium constants (mainly for aqueous species), as well as for estimation of entropies and heat capacities, has recently been reviewed by the NEA TDB Project experts [2]. Their comprehensive review encompasses the "state of the art" in science and recommends to test and compare several methods of extrapolation to higher temperatures to assess magnitude of the accumulated errors adding to the inherent uncertainty of $\log_{10}K^{o}(298)$ or $\Delta_{r}G_{m}^{o}(298)$ values. The experts emphasise the importance of estimation of standard molar entropies and heat capacities, and recommend the isocoulombic/isoelectric reactions approach [2], which has also recently been shown useful for temperature extrapolations of surface complexation [3].

However, a large gap still seems to exist between the advanced approaches proposed by experts in thermodynamic data evaluation for separately taken substances or reactions, and the level of their practical application in computer-aided equilibrium geochemical modelling. Even the advanced LMA speciation codes (PHREEQC [4], MINTEQA [5]) provide temperature corrections using the integrated Van't Hoff extrapolation ($\log_{10}K(298)$ and $\Delta_{r}H_{m}^{o}(298)$ at zero $\Delta_{r}C_{p,m}^{o}$) for the formation reactions of product species (aqueous complexes, minerals and gases). Other – much more reliable – extrapolation techniques [2] are still waiting to be incorporated into computer modelling codes. Database formats of some LMA codes also allow polynomial $\log_{10}K = f(T)$ expressions (PHREEQC) or sets of discrete $\log_{10}K(T)$ values for interpolation (SOLMINEQ [6]), but provide no tools for refitting.

When no data other than $\log_{10}K^{o}(298)$ are available for some aqueous, surface species or minerals, which happens fairly often in actual modelling applications, a common practice is to take $\log_{10}K(T) = \log_{10}K^{o}(298) = \text{const}$ (one-term extrapolation at $\Delta_{r}H_{m}^{o}(298) = 0$). A wiser setting is $\Delta_{r}H_{m}^{o}(298) = \Delta_{r}G_{m}^{o}(298) = -RT\ln K^{o}(298) = \text{const}$ (one-term extrapolation at $\Delta_{r}S_{m}^{o}(298) = 0$). One can also assume $\Delta_{r}G_{m}^{o}(T) = \Delta_{r}G_{m}^{o}(298) = \text{const}$ in absence of other parameter values in case the GEM equilibria calculation is used. Whether we like it or not, the above assumptions, in fact, define the three simplest temperature extrapolations with associated uncertainties, sometimes fortuitously good, but more often inadequate up to producing completely wrong temperature trends. As demonstrated below, the danger of introducing large errors by the one-term extrapolations depends on the species relevance and on how the reactions are written.

The objective of this contribution is to discuss in a pragmatic sense, how the introduction of serious errors of temperature extrapolations can be avoided in building thermodynamic data sets into computer codes for equilibrium geochemical modelling. In case of performance assessment (supported by NAGRA-PSI database [7,8] and PMATCH code [9]), extension of the model applicability is desirable over 0-90°C; applications to hydrothermal systems refer to a wider interval up to 350°C, usually at saturated vapour pressure P_{SAT}. Even though for many actinide aqueous complexes and minerals direct fitting of the HKF EoS or $C_{p,m}(T) = f(T)$ coefficients is not possible, the temperature correction methods and arrangement of the database must avoid accumulation of errors in $\log_{10}K(T)$ or $g^{o}(T)$ at 90-150°C considerably greater than the inherent uncertainties of the respective $\log_{10}K(298)$ or $\Delta_{r}G_{m}^{o}(298)$ values.

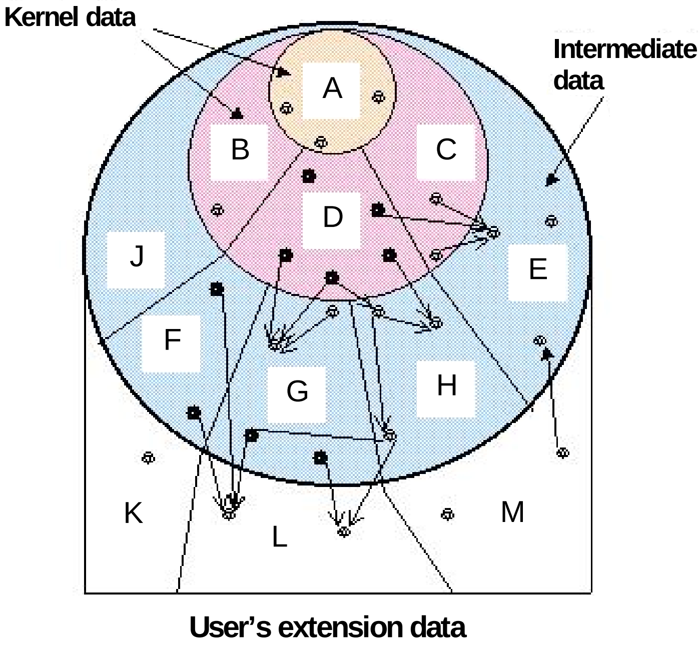
Representation of temperature corrections in geochemical modelling codes

It is known that many formation reactions used in LMA code databases (except maybe isoelectric hydrolysis or gas dissolution reactions) have large entropy and heat capacity effects, and even two-term (Van't Hoff) extrapolation may accumulate significant errors beyond 50-70°C. In such cases, the $\log_{10}K = f(T)$ polynomial coefficients can be provided. There are also codes which use the SUPCRT92 program and database [10,11] to obtain molar Gibbs energies $g_m(T,P)$ for aqueous ions, complexes, gases and minerals (*e.g.* Selektor [12]) to use them directly in GEM equilibria calculations, or further on to convert them into $\log_{10}K(T)$ values for LMA product species (*e.g.* LLNL database for EQ3/6 code [13]). The SUPCRT92 code itself gives priority to thermochemical and revised HKF EoS (Helgeson-Kirkham-Flowers Equation of State) data over the reaction $\log_{10}K_s$: at T,P of interest, the $g_m(T,P)$ of all involved species are calculated first, then $\log_{10}K(T,P)$ values can be found by algebraic summation [10].

Thus, combining directly thermochemical, EoS and reaction-defined data formats seems to be a preferential approach for future integration of thermodynamic databases into geochemical modelling codes. In this way, a common thermodynamic data basis can be constructed for alternative application of LMA or GEM algorithms even within a single software product. Such a structure can also ensure the transparent and consistent extension of the thermodynamic data set with the relevant new species by constructing isoelectric or exchange-type reactions referring to species and/or to model reactions, already provided in the database. Much work on compilation of consistent thermochemical data has already been performed, including that in the NEA TDB Project [14,15]. A prime time comes to make possible a full use of information through software implementation.

Figure 1. Schematic structure of a "hybrid" database

Open circles depict substances provided with standard-state thermochemical and $C_p = f(T)$ data, dark circles stand for the components characterised with standard-state and EoS data, circles pointed to by arrows show species described via the reaction-defined data and a black arrow between sectors M and E shows a "user's override" of data for a mineral included into write-protected layer. See text for explanation of letters.



A combined thermochemical, EoS and reaction-defined database framework (Figure 1) may consist of a "kernel" part, incorporating:

A) standard-state thermochemical values for chemical elements (*e.g.* CODATA-recommended, see [16]);

B) thermochemical data for monoatomic and diatomic gases and liquids [17], optionally enhanced with critical parameters for fugacity corrections at elevated P,T using the "corresponding states" theory [18];

C) selection of well-established thermochemical properties and $C_{p,\mathrm{m}} = \mathrm{f}(T)$ coefficients for the relevant mineral phases [14,19];

D) standard-state properties with HKF EoS parameters for aqueous ions and selected aqueous complexes [11].

The data in "kernel" database must be "frozen" (*i.e.* described and write-protected by the development team) in the sense that they cannot be modified in any modelling applications, but only "overridden" at the user's discretion. An "intermediate" layer of the hybrid database would then include:

E) data for minerals (either in thermochemical or reaction formats) in cases when measured solubility products contradict with thermochemical properties obtained from calorimetry [20], or no calorimetric data are known;

F) re-fitted HKF EoS or reaction-defined data for aqueous ions with large discrepancies in published $\Delta_{\mathrm{r}} G_{\mathrm{m}}^{\circ}$ (298) values (*e.g.* Eu^{+3} [21]);

G) HKF EoS and/or reaction-defined data for the majority of aqueous complexes, sets of which depend on the chosen model of ionic strength corrections [22];

H) reaction-defined data for well-established surface complexes on amphoteric or permanent-charge mineral-water interfaces for surface complexation models [3];

J) a set of selected "model reactions" made of "kernel" database species, intended to facilitate construction of isoelectric/isocoulombic reactions, but not accessible directly for calculations of equilibria or speciation.

Reaction-defined species should be represented via isoelectric reactions with estimated $\Delta_{\mathrm{r}} S_{\mathrm{m}}^{\circ}$ (298) and $\Delta_{\mathrm{r}} C_{p,\mathrm{m}}^{\circ}$ (298) values, to minimise uncertainty at increasing T. Just as the kernel part, the intermediate layer of thermodynamic database must also be maintained and write-protected by the developers team.

A "user's extension" part of the built-in database would comprise an outermost "rim" fully open to any model-specific extensions, where:

K) data for missing species can be added mainly in the reaction-defined format;

L) threads of thermodynamic data can be created for the "exotic" (*i.e.* not present in the kernel database) chemical elements or ligands, as well as their minerals, gases, ions and complexes needed for a specific modelling exercise;

M) some "overriding" data can be put by the modelling experts who disagree with choices made by the developers of the "intermediate" and kernel database.

Application-specific data is to be represented preferably in isocoulombic/isoelectric reaction-defined format, if direct thermochemical or EoS data are absent or difficult to estimate. This means of consistent database extension is transparent and ensures compatibility with the kernel data set and between different model applications.

A prerequisite of integrating the hybrid database framework into model calculations of equilibria is that, for a given temperature (pressure) of interest:

1) $g^{o}(T)$ values are calculated separately (using appropriate algorithms) for all the kernel database, thermochemical and EoS-represented species, and then recursively for the reaction-defined species of intermediate layer;

2) $\Delta_{r}G^{o}_{m}(T)$, $\log_{10}K(T)$ are calculated for all the "reaction-format" items;

3) by algebraic combination, the $g^{o}(T)$ values for the user's extension reaction-defined species are obtained.

Recursive calculations must be performed because some reaction-defined data records refer to other reaction-defined species.

Such a structure of thermodynamic database was provisionally implemented in the GEM-Selektor code (currently developed at LES PSI). It shows a much higher flexibility and convenience for the pragmatic modeller than any other, purely $\log_{10}K$ or purely thermochemical database. It can also be enhanced by implementation of relevant techniques for prediction of entropies and heat capacities of reactions or components, as described in [2,23]. The proposed structure avoids a step of fitting $\Delta_{r}G^{o}_{m}(T)$ or $\log_{10}K(T)$ values generated from reaction-defined format into $C_{p,\mathrm{m}}(T) = \mathrm{f}(T)$, EoS or $\log_{10}K = \mathrm{f}(T)$ coefficients. In this way, a much greater transparency of database extensions can be achieved, and alternative temperature corrections will be easier to compare.

Implementation of a hybrid thermodynamic database also facilitates investigation and comparison of temperature corrections to thermodynamic data by the alternative extrapolation techniques. This is done by constructing several database records of different formats, then calculating and plotting the data automatically at certain increments ΔT within a given temperature interval (at fixed P or P_{SAT}). One can perform "blind tests" to discover the extrapolation which best reproduces the available experimental data for elevated temperatures, or simply check the predicted temperature trends.

Uncertainty propagation in the simplest temperature extrapolations

Table 1 lists some simple temperature extrapolations in order of increasing demand to input data, plus assessments of error propagation in $\log_{10}K(T)$, provided that the extrapolation is appropriate. For the generic three-term extrapolations, it follows that the error in $\Delta_{r}C^{o}_{p,\mathrm{m}}(298)$ is two to three times larger than that in $\Delta_{r}S^{o}_{m}(298)$ produces about the same magnitude of uncertainty at *T*, acceptable in practice if $\delta\log_{10}K(T) < \delta\log_{10}K(298)$ in the whole temperature interval of interest. If parameters of three-term extrapolation are given (*e.g.* fitted from experimental data) then one can estimate how much error at *T* of interest is introduced by the less precise two-term and one-term extrapolations, by taking errors equal to zeroed-off $\Delta_{r}C^{o}_{p,\mathrm{m}}(298)$ and $\Delta_{r}S^{o}_{m}(298)$, respectively. As these numbers for some formation or redox reactions may exceed 100 or 300 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, the one- and two-term extrapolations

Table 1. The simplest temperature extrapolations and associated uncertainty propagation of $\log_{10}K(T)$ and $\Delta_r G^\circ_m(T)$

No. of terms	Fixed parameters	Zero parameters	Other parameters	Comments, examples
One	$g^\circ(T) = \Delta G^\circ_m(298)$	$\int_{298}^{T} \Delta S^\circ_m(T)dT = 0$	$-(T-298)\Delta S^\circ_m(298) = \int_{298}^{T}\int_{298}^{T} \frac{\Delta C^\circ_{p,m}(T)}{T} dTdT$	For some aqueous complexes ($CaCO_3$,aq to 250°C); Not recommended
One[A]	$\ln K(T) = \ln K^\circ(298)$	$\Delta_r H_m(T) = 0$, $\Delta_r C_{p,m}(T) = 0$	$\Delta_r G_m(T) = -RT \ln K^\circ(298)$; $\Delta_r S_m(T) = R \ln K^\circ(298)$	UO_2,cr = UO_2,aq; $0.5H_2O$,l = $>O_{0.5}H$
One[B]	$\Delta_r G_m(T) = \Delta_r G^\circ_m(298)$	$\Delta_r S_m = 0$, $\Delta_r C_{p,m}(T) = 0$	$\ln K(T) = -\Delta_r G^\circ_m(298)/(RT)$; $\Delta_r H_m(T) = \Delta_r G^\circ_m(298)$	SiO_2(cr) = SiO_2(aq); isocoulombic reactions
Two[C]	$\Delta_r S_m(T) = \Delta_r S^\circ_m(298)$	$\Delta_r C_{p,m}(T) = 0$	$\Delta_r H_m(T) = \Delta_r H^\circ_m(298) = \Delta_r G^\circ_m(298) + T\Delta_r S^\circ_m(298)$; $\Delta_r G_m(T) = \Delta_r G^\circ_m(298) - (T-298)\Delta_r S^\circ_m(298)$	Good for isocoulombic and isoelectric reactions
Three[D]	$\Delta_r C_{p,m}(T) = \Delta_r C^\circ_{p,m}(298)$	Second and higher $\Delta_r C_{p,m} = f(T)$ coefficients equal zero	$\Delta_r S_m(T) = \Delta_r S^\circ_m(298) + \ln(T/298)\Delta_r C^\circ_{p,m}(298)$; $\Delta_r H_m(T) = \Delta_r H^\circ_m(298) + (T-298)\Delta_r C^\circ_{p,m}(298)$; $\Delta_r G_m(T) = \Delta_r G^\circ_m(298) - (T-298)\Delta_r S^\circ_m(298) +$ $[T - 298 - T\ln(T/298)]\Delta_r C^\circ_{p,m}(298)$	Best for isoelectric reactions, good for generic reactions up to 150°C

Note: δ denotes the absolute uncertainty of the respective value, *e.g.* $\log_{10}K(T) \pm \delta\log_{10}K(T)$.

[A] $\delta\log_{10}K(T)$ = const, while $\delta\Delta_r G_m(T) = T/298 \cdot \delta\Delta_r G^\circ_m(298)$.

[B] Valid for many kinds of isoelectric reactions [24]; decreasing $\delta\log_{10}K(T) = 298/T \cdot \delta\log_{10}K^\circ(298)$ error propagation; at T = 596 K, $\delta\log_{10}K(T) \approx ½\delta\log_{10}K(298)$, while $\delta\Delta_r G^\circ_m(T)$ = const.

[C] $\delta\log_{10}K(T) = \delta\log_{10}K(298) + (T - 298)/(2.303RT) \cdot \delta\Delta_r S^\circ_m(298)$; this Van’t Hoff extrapolation at 596 K and $\delta\Delta_r S^\circ_m(298) = 10\ J\cdot K^{-1}\cdot mol^{-1}$ results in $\delta\Delta_r G^\circ_m \approx 3$ kJ/mol, or $\delta\log_{10}K(T) \approx 0.3$.

[D] $\delta\log_{10}K(T) = \delta\log_{10}K^\circ(298) + [(T - 298)/(2.303RT) \cdot \delta\Delta_r S^\circ_m(298) + [T - 298 - T\ln(T/298)]/(2.303RT) \cdot \delta\Delta_r C^\circ_{p,m}(298)$; at T = 596 K, $\delta\Delta_r S^\circ_m(298) = 0$ and $\delta\Delta_r C^\circ_{p,m}(298) = 25\ J\ K^{-1}mol^{-1}$, one obtains again $\delta\Delta_r G^\circ_m(T) \approx 3\ kJ\cdot mol^{-1}$, or $\delta\log_{10}K(T) \approx 0.3$.

may in such cases produce $\delta\log_{10}K(T) > \delta\log_{10}K(298)$ even within the relatively small temperature interval below 50-70°C. Hence, for the non-isoelectric formation reactions, the estimated values of $\Delta_r C^o_{p,m}(298) > 25$ J·K^{-1}·mol^{-1} and $\Delta_r S^o_m(298) > 10$ J·K^{-1}·mol^{-1} must always be used.

The constant $g^o(T) = \Delta_r G^o_m(298)$ extrapolation, often provisionally used in GEM calculations of geochemical equilibria for the components with no other standard molar properties known, in general, must be avoided. Either the values of $C^o_{p,m}(298)$ and $S^o_m(298)$ must be predicted (there are many methods available, see [2,25]), or the component must be described in the reaction–defined format.

Examples and discussion

For some important neutral aqueous species, the simplest one-term approximation of dissolution or exchange reaction appears to be precise over a wide temperature interval. Given thermochemical data for the mineral or another similar aqueous species, the unknown thermodynamic properties of aqueous complex can be reaction-defined at any T or, at least, can help to construct other isoelectric/ isocoulombic reactions. Yet, individual analysis is needed because in some cases, the $\log_{10}K(T)$ = const one-term extrapolation works, while often, the $\Delta_r G_m(T)$ = const extrapolation is appropriate. Eq. (1):

$$UO_2\ (cr) \rightleftharpoons UO_2\ (aq) \quad (\log_{10}K_1) \tag{1}$$

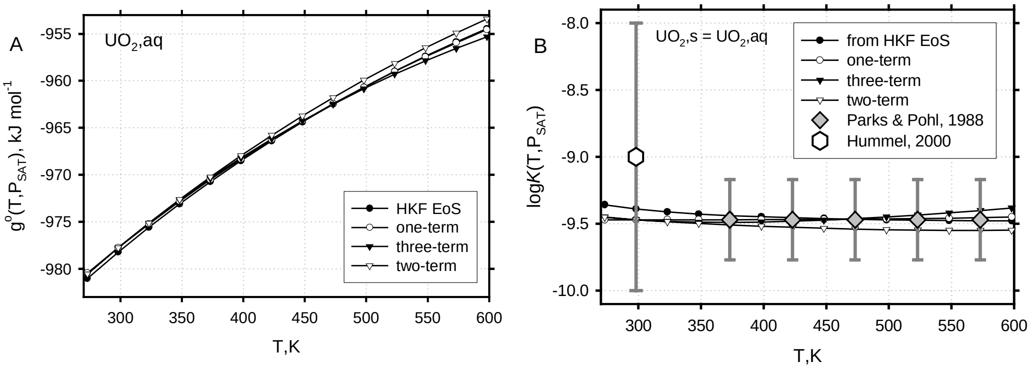
is an example of a purely entropic process described by $\log_{10}K(T)$ = const extrapolation. Stoichiometry of the neutral U^{IV} hydroxocomplex, dominant at pH > 4 in the UO_2-H_2O system, is more often written as $U(OH)_4(aq)$ [14] than $UO_2(aq)$ [26]. The $\log_{10}K(T)$ = const extrapolation permits to calculate standard molar properties of the above reaction and that of the $UO_2(aq)$ species (Table 2). Figure 2 compares $\Delta_r G^o_m(T)$ for $UO_2(aq)$ and $\log_{10}K_1(T)$, obtained using HKF EOS data [26], one-, two- and three-term extrapolations. Experiments on hydrothermal solubility of uraninite [27] showed remarkably constant $\log_{10}K_1 \approx -9.47\pm0.3$ at T = 100 to 300°C. This is consistent precise to 1 log unit with $\log_{10}K^o_1(298) = 8.7$ [28] or 9.0±1 selected in [20]. In view of existing problems with UO_2 solubility at low temperatures [20], we can conclude that the one-term $\log_{10}K_1(T)$ = const extrapolation propagates no error at T < 600 K.

Table 2. Thermodynamic properties of Eq. (1), $\log_{10}K_1(298) = -9.47 \pm 1.0$, and its components

Parameter of reaction	Units of measure	One-term extrapolation	Three-term extrapolation	Parameter of species	UO_2 (solid) [26, Table 2]	UO_2,aq from one-term extr.
$\Delta_r G^o_m(298)$	kJ mol^{-1}	54.05	54.05	$\Delta_f G^o_m(298)$	-1 031.816	-977.762
$\Delta_r H^o_m(298)$	kJ mol^{-1}	0	-1.128	$\Delta_f H^o_m(298)$	-1 084.99	-1 084.99
$\Delta_r S^o_m(298)$	J K^{-1} mol^{-1}	-181.3	-185.084	$S^o_m(298)$	77.0	-104.3
$\Delta_r C^o_{p,m}(298)$	J K^{-1} mol^{-1}	0	16.32	$C^o_{p,m}(298)$	63.58	63.58
A		-9.47	-15.3778	a	62.7726	
B		0	313.131	b	0.03174	
C		0	0.852564	c	-769 438	

Notes: A, B and C are coefficients of the equation $\log_{10}K(T) = A + BT^{-1} + C\ln T$.
a, b and c are coefficients of the equation $\Delta_r C^o_{p,m}(T) = a + bT + cT^{-2}$.
$\Delta_r S^o_m(298)$ and $\Delta_r C^o_{p,m}(298)$ for three-term extrapolation were found from standard molar properties of UO_2(cr) and that of UO_2(aq) [26, Table 1].

Figure 2. Comparison of temperature extrapolations for $g^0(T)$ and $\log K(T)$ for the UO_2,aq species, calculated using the ReacDC and RTparam modules of GEM-Selektor code

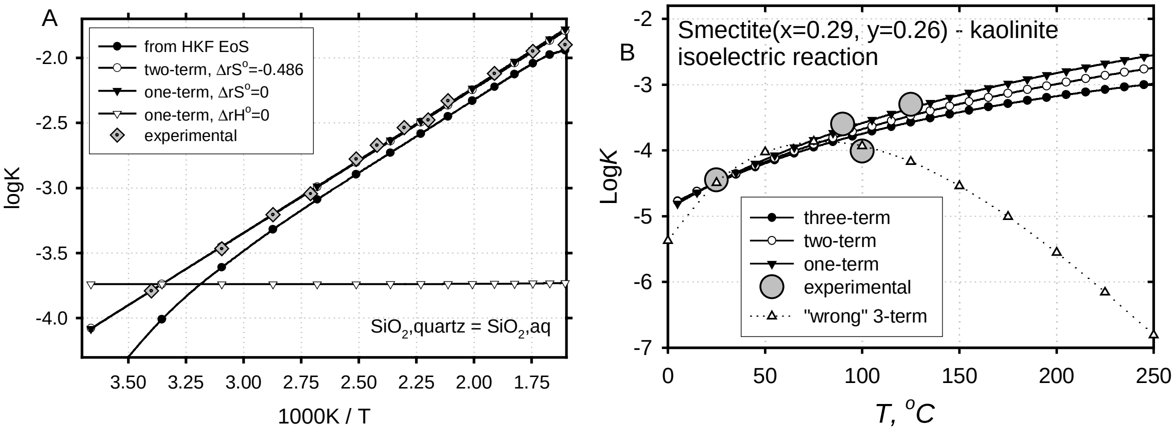


Dissolved silica SiO_2(aq) is another important aqueous species. Knowledge of its standard molal properties permits, for instance, to construct hydrolysis-type reactions between kaolinite and mica-like clay minerals to describe hydrothermal solubility of smectites and illites [29]:

$$K_x(Mg_yAl_{2-y})(Al_{x-y}Si_{4-x+y})O_{10}(OH)_2,cr + (x + 2y)H^+ + \{(2 + x - 6y)/2\}H_2O \rightleftharpoons \\ xK^+ + yMg^{+2} + (2 - 2x + 3y)SiO_2(aq) + \{(2 + x - 2y)/2\}Al_2Si_2O_5(OH)_4,cr \qquad (2)$$

Thermochemical properties of kaolinite are known [19], hence, Eq. (2) can help to determine standard molar properties of *e.g.* smectite (x = 0.29, y = 0.26) by setting up a three-term extrapolation trend [30]. However, usage of $S^{\circ}_{\mathrm{m}}(298)$ and $C^{\circ}_{p,\mathrm{m}}(298)$ values for SiO_2(aq) from SPRONS92.DAT [31] lead to erroneous values $S^{\circ}_{\mathrm{m}}(298) = 311$ and $C^{\circ}_{p,\mathrm{m}}(298) = -516\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ for smectite if experimental $\log_{10}K(T) = f(T)$ dependence was applied. Conversely, if the predicted values $S^{\circ}_{\mathrm{m}}(298) = 255$ and $C^{\circ}_{p,\mathrm{m}}(298) = 306\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ were taken for smectite, then an erroneous temperature trend is obtained for $\log_{10}K(T)$ [Figure 3(b)].

Figure 3. **Temperature extrapolations of $\log_{10}K(T)$ for SiO_2(aq) species (A), reaction (3), and smectite (B), reaction (2). Experimental quartz solubility data was taken from App. 1 of Ref. [32], and that for smectite from [29]. The "wrong" three-term extrapolation was calculated using $\Delta_r S^{\circ}_{\mathrm{m}}(298)$ and $\Delta_r C^{\circ}_{p,\mathrm{m}}(298)$ values derived from $S^{\circ}_{\mathrm{m}}(298)$ and $C^{\circ}_{p,\mathrm{m}}(298)$ of smectite predicted in [30] and HKF EoS values [26] for SiO_2(aq).**



Thermodynamic data involved in the reaction in Eq. (2) can be made consistent by replacing the data [31] for SiO_2(aq) with its properties derived from the one-term extrapolation at $\Delta_r S^\circ_m(298) = 0$ for a reaction:

$$SiO_2(cr) \rightleftharpoons SiO_2(aq) \qquad (\log K_3) \tag{3}$$

Rimstidt [32] proposed a regression log m = -0.0254(±0.0247) – 1107.12(±10.77)/T for solubility of α-quartz up to 300°C, yielding $\log K_3(298) = -3.74\pm0.1$, $\Delta_r C^\circ_{p,m}(298) = 0$ and $\Delta_r S^\circ_m(298) = -0.486\pm0.49$. Once $\left|\Delta_r S^\circ_m(298)\right| < \delta\Delta_r S^\circ_m(298)$ and both are small, setting $\Delta_r S^\circ_m(298) = 0$ would increase $\delta \log K_3(T)$ by only 0.03 units at $T = 600$ K. Figure 3(a) shows temperature trends for $\log K_3(T)$ in comparison with some experimental data. For SiO_2(aq), excellent one-term extrapolation leads to $S^\circ_m(298) = 41.5$; $C^\circ_{p,m}(298) = 44.6$ J·K^{-1}·mol^{-1}, the same as that of quartz. Incorporation of that into a three-term extrapolation of Eq. (2), using independently predicted $S^\circ_m(298)$ and $C^\circ_{p,m}(298)$ values of smectite [30], now yields a quite consistent temperature trend [Figure 3(b)] – in fact, a $\Delta_r S^\circ_m = 0$ one-term extrapolation may be even better.

Generic formation reactions, taken in the three-term extrapolation, can provide good fits up to 200°C for carbonate, sulphate and phosphate complexes of actinides and rare earth elements. For instance, the reaction considered in [2] with experimental $\log_{10}K(T)$ values [33] up to 300°C:

$$UO_2^{2+} + CO_3^{2-} \rightleftharpoons UO_2CO_3(aq) \qquad (\log_{10}K_4) \tag{4}$$

can be converted into isoelectric form (ie) by adding a model reaction, $CO_2(aq) + H_2O \rightleftharpoons CO_3^{2-} + 2H^+$:

$$UO_2^{2+} + CO_2(aq) + H_2O \rightleftharpoons UO_2CO_3(aq) + 2H^+ \qquad (\log_{10}K_5) \tag{5}$$

shown to provide a good two-term extrapolation up to 300°C (see [2], Figure X.4). In the “hybrid” TDB (see *e.g.* Figure 1), many alternative extrapolations can be constructed in order to describe thermodynamic properties of the “reaction-defined” species UO_2CO_3(aq) if the “kernel” thermochemical or EoS data records for other involved species, including UO_2^{2+} ion, are available [11,26]. Isocoulombic reactions:

$$UO_2^{2+} + CaCO_2(aq) \rightleftharpoons UO_2CO_3(aq) + Ca^{2+} \qquad (\text{ica } \log_{10}K_6) \tag{6}$$

$$UO_2^{2+} + CaCO_3(cr) \rightleftharpoons UO_2CO_3(aq) + Ca^{2+} \qquad (\text{ic, } \log_{10}K_7) \tag{7}$$

have also been constructed for comparison (see Figure 4, Tables 3 and 4). A surprising result is that the one-term extrapolation ic-1-t-$\Delta_r H_m$ of $\log_{10}K_7$ at $\Delta_r H_m(T) = 0$ [Eq. (7)] yields an excellent description of $g^o(T)$ for UO_2CO_3(aq) species up to 300°C [Figure 4(d)], an even better one than that provided by the three-term extrapolation of $\log_{10}K_4$ for the formation reaction in Eq. (4). For $\log_{10}K_4$, one- and two-term extrapolations are, however, unsatisfactory.

Isoelectric reactions are also helpful for defining temperature corrections for surface complexes and pH of zero charge [3,34]. At present, this seems to be the only possibility, because no equation of state for surface species similar to HKF EoS has been suggested so far. Elemental stoichiometry and standard molal properties of oxide surface species, consistent with that for gases, minerals and aqueous ions, can be conveniently determined on the basis of a reaction $0.5H_2O(\text{solvent}) \rightleftharpoons O_{0.5}H(\text{surface})$ for

Figure 4. Various temperature extrapolations for the UO_2CO_3(aq) complex. Data in Tables 3 and 4.

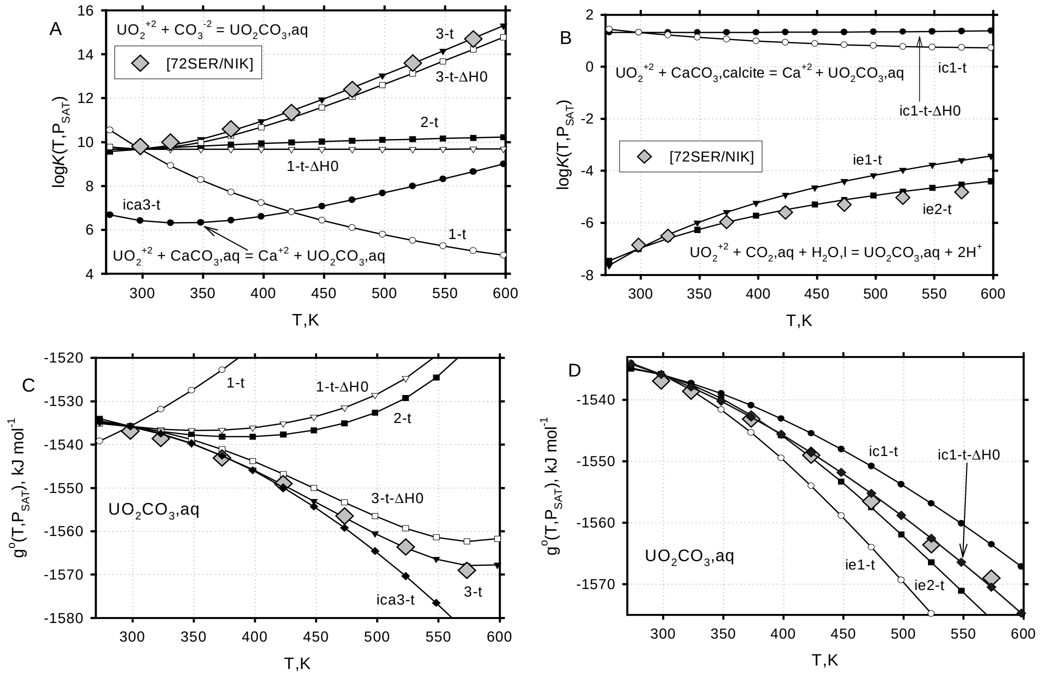


Table 3. Properties of UO_2CO_3,aq species

Parameter	From 3-t extr, Eq.(4)	From ic1-t-$\Delta_r H^o_m$ extr, Eq. (7)
$\Delta_r G^o_m$(298) (kJ mol^{-1})	-1 535.85	**-1 535.86**
$\Delta_r H^o_m$(298) (kJ mol^{-1})	-1 688.25	-1 683.33
S^o_m(298) (J K^{-1}mol^{-1})	57.12	75.13
$C^o_{p,m}$(298) (J K^{-1}mol^{-1})	247.74	152.46

Table 4. Parameters of temperature extrapolations (reactions 4 to 7) involving UO_2CO_3(aq) species

Parameter of reaction	$\log_{10}K^o$(298)	$\Delta_r H^o_m$(298)^a	$\Delta_r S^o_m$(298)^b	$\Delta_r C^o_{p,m}$(298)^b
r.(4) 3-t	9.68±0.04	6.0±6.0	205.44	499.0
r.(4) 2-t	9.68	6.04	205.44	0
r.(4) 1-t	9.68	-55.196	0	0
r.(4) 1-tΔH0	9.68	0	185.13	0
r.(6) ica3-t	6.424	-11.8	83.4	355
r.(5) ie2-t	-7.0±0.05	28.9±2.0	-37.08	0
r.(5) ie1-t	-7.0	39.96	0	0
r.(7) ic1-t	1.32	-7.535	0	0
r.(7) ic1-t-ΔH0	**1.32**	0	25.27	0

[a] kJ mol^{-1}

[b] J K^{-1}mol^{-1}

Standard properties for other aqueous species [11,26], calcite [19] were used.

the amphoteric neutral functional group $>O_{0.5}H^o$. This reaction states that one water molecule attached to a surface creates two $>O_{0.5}H^o$ groups at reference site density Γ^o. The assumption that Γ^o is independent of temperature is equivalent to the statement that (precisely) $\log_{10}K(T) = 1.74436$ and $\Delta_r G^o_m(298) = -9.957$ kJ mol^{-1}, $\Delta_r H^o_m(T) = 0$, $\Delta_r C^o_{p,m}(T) = 0$, $\Delta_r S^o_m(T) = 33.395$ J K^{-1}mol^{-1} for this reaction [3]. From these numbers and standard molar properties of H_2O,l, the molar properties of $>O_{0.5}H$ functional group can be determined at 298.15 K and other temperatures. Next, properties of the protonated surface species $>O_{0.5}H_2^+$ can be defined from the reaction $>O_{0.5}H_2^+ \rightleftharpoons >O_{0.5}H^o + H^+$,aq using one-term extrapolation at $\Delta_r S^o_m(T) = 0$, $\log_{10}K(298)$ of which can be predicted for different oxides. Properties of other surface species can be found from Schoonen's reaction $>O_{0.5}H_2^+ + OH^-$,aq $\rightleftharpoons >O_{0.5}H^o + H^+$,aq + H_2O [34] and similar isoelectric reactions involving adsorbed cations or anions [3], provided that more hydrothermal adsorption data becomes available. Generic formation reactions for surface complexes can provide good fits up to 200-250°C, but only in the three-term temperature extrapolation.

Conclusions

The simplest one-, two- and three-term temperature extrapolations of equilibrium constants reveal a great predictive potential for isoelectric/isocoulombic reactions, which can and should be explored and extensively used in geochemical modelling by LMA and/or GEM algorithms.

This can be done efficiently via implementation of a built-in "hybrid" database combining the protected "kernel" thermochemical/EoS data for substances with the "extension" reaction-defined data for other species.

An appropriate choice of the model substances and reactions to build the isoelectric reactions can define temperature corrections for *e.g.* actinide species that will not create too large uncertainty up to 200–300°C even in the simplest, one-term temperature extrapolations, when only $\log K(298)$ is known.

For non-isoelectric reactions (complexation, dissolution), the one- and two-term extrapolations may produce large errors above 50-150°C; hence, three-term extrapolations must be used, enhanced with prediction of $\Delta_r C^o_{p,m}(298)$, $\Delta_r S^o_m(298)$ of reaction or $C^o_{p,m}(298)$, $S^o_m(298)$ of species of interest.

Implementation of software tools for estimation of $C^o_{p,m}(298)$, $S^o_m(298)$ properties using the NEA TDB-recommended techniques [2] will also permit reliable user's extensions of the "hybrid" database.

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REFERENCES

[1] P. Wersin, NAGRA unpublished internal report, Wettingen, 35 p. (2000).

[2] I. Puigdomenech, J.A. Rard, A.V. Plyasunov, I. Grenthe, "Modelling in Aquatic Chemistry", Chapter X, OECD Paris (1997), pp. 427-493.

[3] D.A. Kulik, *Geochim. Cosmochim. Acta*, 64, 3161-3179 (2000).

[4] D.L. Parkhurst, C.A.J. Appelo, "User's Guide to PHREEQC (Version 2)", USGS WRIR 99-4259, Denver (1999), 312 p.

[5] S.M. Serkiz, J.D. Allison, E.M. Perdu, *et al.*, *Water Res*., 30, 1930-1933 (1996).

[6] Y.K. Kharaka, W.D. Gunter, P.K. Aggarwal, *et al.*, "SOLMINEQ.88: A Computer Program for Geochemical Modeling of Water-rock Interactions", USGS WRIR 88-4227, Menlo Park (1988), 207 p.

[7] F.J. Pearson, U.R. Berner, W. Hummel, "NAGRA Thermochemical Database II", Supplemental data 05/92, NAGRA NTB 91-18 (1992), 284 p.

[8] W. Hummel, *et al.*, "NAGRA-PSI TDB", Paul Scherrer Institut (2001), in preparation.

[9] F.J. Pearson, J.D. Avis, "PMATCH: A Program to Manage Thermochemical Data, Version 1.21", NAGRA unpublished internal report, Wettingen (1989), 62 p.

[10] J.W. Johnson, E.H. Oelkers and H.C. Helgeson, *Computers Geosci*., 18, 899-947 (1992).

[11] E.L. Shock, D.C. Sassani, M. Willis, D.A. Sverjensky, *Geochim. Cosmochim. Acta*, 61, 907-950 (1997).

[12] I.K. Karpov, K.V. Chudnenko and D.A. Kulik, *Amer. J. Sci*., 297, 767-806 (1997).

[13] T.J. Wolery, K.J. Jackson, W.L. Bourcier, *et al.*, "Chemical Modeling in Aqueous Systems II", Chapter 8, *Amer. Chem. Soc. Symp. Series*, 416, 104-127 (1990).

[14] I. Grenthe, J. Fuger, R.J.M. Konings, *et al.*, "Chemical Thermodynamics of Uranium" Elsevier, Amsterdam (1992), 715 p.

[15] R.J. Silva, G. Bidoglio, M.H. Rand, *et al.*, "Chemical Thermodynamics of Americium", Elsevier, Amsterdam (1995), 375 p.

[16] J.D. Cox, D.D. Wagman, V.A. Medvedev, "CODATA Key Values for Thermodynamics", Hemisphere, New York (1989), 271 p.

[17] R.C. Reid, J.M. Prausnitz, T.K. Sherwood, "The Properties of Gases and Liquids", McGraw Hill, New York (1977), 592 p.

[18] D.K. Nordstrom, J.L. Munoz, "Geochemical Thermodynamics", 2nd ed., Blackwell, Boston (1994), 477 p.

[19] R.A. Robie, B.S. Hemingway, USGS Bulletin 2131, (1995), 461 p.

[20] W. Hummel, PSI internal report TM-44-00-03, Paul Scherrer Institut (2000), 33 p.

[21] E. Curti E., PSI internal report TM-44-00-04, Paul Scherrer Institut (2000), 34 p.

[22] I. Grenthe, A.V. Plyasunov, K. Spahiu, "Modelling in Aquatic Chemistry", Chapter IX, OECD Paris (1997), pp. 325-426.

[23] D.A. Sverjensky, E.L. Shock, H.C. Helgeson, *Geochim. Cosmochim. Acta*, 61, 1359-1412 (1997).

[24] Y. Gu, C.H. Gammons, M.S. Bloom, *Geochim. Cosmochim. Acta*, 58, 3545-3560 (1994).

[25] S.K. Saxena, "Modelling in Aquatic Chemistry", Chapter VIII, OECD Paris (1997), pp. 289-323.

[26] E.L. Shock, D.C. Sassani, H. Betz, *Geochim. Cosmochim. Acta*, 61, 4245-4266 (1997).

[27] G.A. Parks, D.C. Pohl, *Geochim. Cosmochim. Acta*, 52, 836-875 (1988).

[28] T. Yajima, Y. Kawamura, S. Ueta, Mat. Res. Soc. Sympos. Proc. 353, 1137-1142 (1995).

[29] S.U. Aja, *European J. Mineral*., 7, 325-333 (1995).

[30] D.A. Kulik, S.U. Aja, Proc. 5th Int. Symposium on Hydrothermal Reactions, 288-292 (1997).

[31] E.L. Shock, H.C. Helgeson, D.A. Sverjensky, *Geochim. Cosmochim. Acta*, 53, 2157-2183 (1989).

[32] J.D. Rimstidt, *Geochim. Cosmochim. Acta*, 61, 2553-2558 (1997).

[33] E.I. Sergeyeva, A.A. Nikitin, I.L. Khodakovskiy and G.B. Naumov, "Experimental Investigation of Equilibria in the System UO_3-CO_2-H_2O in 25-200°C Temperature Interval", *Geochem. Int*., Vol. 4, 900-910 (1972).

[34] M.A.A. Schoonen, *Geochim. Cosmochim. Acta*, 58, 2845-2851 (1994).

SOLUBILITY CALCULATIONS AND THEIR INTERPRETATION IN PA

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Abstract

Typical problem areas encountered in the derivation of solubility limits on the basis of thermodynamic predictions are elucidated with the help of characteristic examples. For each of the examples an interpretation in view of the requirements of performance assessment is made and measures to resolve the problems met are proposed. On the basis of the selected examples its concluded that further activities should primarily focus on the determination of solubility-limiting phases and on a better understanding of system key parameters like the redox potential. For trace elements it is suggested to explore potential effects which are associated with the formation of solid solutions.

Introduction

Maximum dissolved concentrations of an element, a key component of the source term, are important pillars in the performance assessment (PA) for radioactive waste repositories. In most cases well-established principles of thermodynamic equilibrium are applied to derive quantitative results. These thermodynamic principles are quite straightforward, delineating that the most stable solid phase produces the lowest solute concentration (for a given element). Provided that all required thermodynamic data are available, maximum concentrations in solutions ("solubility limits") are "relatively simple", predictable by using geochemical standard procedures.

Unfortunately, real chemical systems do not always behave as simply as the basic principles lead us to believe. Many uncertainties, ambiguities or lack of knowledge make the "relatively simple" predictions of solubility limits much more difficult. The modeller may be faced with unknown and/or ill-defined chemical processes, with incomplete and questionable thermodynamic data, with solid phases that are not ascertained and (thermodynamically) badly characterised, with surfaces including non-quantifiable reactivities, etc. In many cases the kinetics of postulated equilibria/reactions may not be quantified sufficiently well. This is for example important when the usually very slow formation of very stable minerals needs to be considered. Another source of uncertainty is associated with system mass balances, including their changes (*e.g.* by moving groundwater), and with system key parameters like pH, $p_{\mathrm{CO_2}}$, redox potential, temperature and pressure.

Such imponderable problems may strongly aggravate or even hamper quantitative predictions. Uncertainties and lack of knowledge have a particularly strong impact on the quality of predictions for trace elements (those elements of a chemical system which exhibit several orders of magnitude lower concentrations than the major constituents), a class to which most of the radiotoxic relevant isotopes belong. Personal experience from several studies reveals that the application of basic thermodynamic principles alone is not always sufficient to answer key questions such as the maximum concentration of relevant nuclides.

How to derive reliable solubility limits necessary for PA under these not very promising circumstances? Most organisations which contribute to this research/application area rely on the principle of conservatism. In a first step, an "estimate" for the solubility limit is obtained from thermodynamic equilibrium calculations. Thereby it is evident that high quality and as complete as possible thermodynamic databases will produce high quality "estimates". In our opinion it is then indispensable to analyse and to interpret these "estimates" in light of the above-mentioned uncertainties and difficulties and to supply a range to the calculated estimates. Usually, the upper limit of such a range is selected by PA (in specific cases it may be the lower limit). Therefore, it is essential to support a range as narrow as possible using sufficiently reliable additional information, sound estimates, sensible assumptions, good analogies, etc.

It is the aim of this contribution to elucidate characteristic problem areas encountered in deriving solubility limits and to propose approaches which finally lead to defendable maximum concentrations acceptable by PA.

Areas of good knowledge

The good news first. In general we notice that the chemical behaviour of solutes is very well known. Major aqueous complexes of most elements as well as their formation constants are characterised to a sufficient degree. As an example, formation constants of tetravalent cations as included in the updated

NAGRA/PSI database [1] are shown in Table 1. We conclude that speciation in solution (the distribution of an element among the relevant species) is not a major problem when deriving PA-relevant solubility limits (exceptions exist).

Table 1. Formation constants of complexes (and solids) of tetravalent cations (taken from the updated NAGRA/PSI thermochemical database) are shown to document our present state of the art in the thermodynamics of solutes. Rounded values without uncertainty ranges are given for reasons of clarity, full numbers including uncertainty ranges are provided in [1].

	$\log_{10}K^{\circ}$					
	Th^{4+}	U^{4+}	Np^{4+}	Pu^{4+}	Zr^{4+}	Sn^{4+}
$MO_2(cr) + 2H_2O \rightleftharpoons M(OH)_4(aq)$					-11.6	-8.0
$MO_2(am) + 2H_2O \rightleftharpoons M(OH)_4(aq)$	-8.5	-9	-8.3	-10.4		-7.3
$M^{4+} + H_2O \rightleftharpoons MOH^{3+} + H^+$	-2.4	-0.5	-0.3	-0.8	0.3	
$M^{4+} + 4H_2O \rightleftharpoons M(OH)_4(aq) + 4H^+$	-18.4	-9	-9.8	-8.4	-9.7	
$M(OH)_4(aq) + H_2O \rightleftharpoons M(OH)_5^- + H^+$					-6.3	-8.0
$M^{4+} + 4CO_3^{2-} \rightleftharpoons M(OH)_4^{4-}$		35.2	36.7	35.9		
$M^{4+} + 5CO_3^{2-} \rightleftharpoons M(OH)_5^{6-}$	29.8	34.1	35.6	34.5		
$M^{4+} + CO_3^{2-} + 3H_2O \rightleftharpoons M(CO_3)(OH)_3^- + 3H^+$	-3.1					
$M^{4+} + SO_4^{2-} \rightleftharpoons MSO_4^{2+}$	7.6	6.6	6.9	6.9	7.0	
$M^{4+} + 2SO_4^{2-} \rightleftharpoons M(SO_4)_2(aq)$	11.6	10.5	11.1	11.1		
$M^{4+} + HPO_4^{2-} \rightleftharpoons MHPO_4^{2+}$	13					
$M^{4+} + F^- \rightleftharpoons MF^{3+}$	8.0	9.3	9.0	8.8	10.2	
$M^{4+} + 2F^- \rightleftharpoons MF_2^{2+}$	14.2	16.2	15.7	15.7	18.5	
$M^{4+} + 3F^- \rightleftharpoons MF_3^+$	18.9	26.1			24.7	
$M^{4+} + 4F^- \rightleftharpoons MF_4(aq)$	22.3	25.6			30.1	
$M^{4+} + Cl^- \rightleftharpoons MCl^{3+}$		1.7	1.5	1.8	1.5	

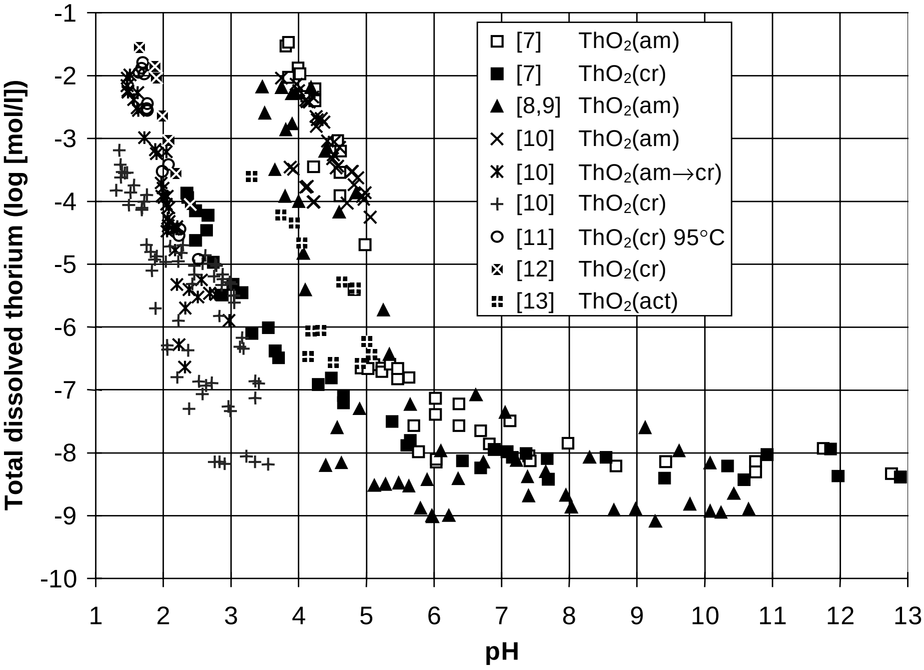
However, additional information concerning the nature and formation constants of ternary complexes including OH^-, CO_3^{2-}, Cl^-, SO_4^{2-}, the formation constants of sulphide and phosphate complexes, the role of organic ligands and the formation of polymeric species (*i.e.* polynuclear hydroxides) are still highly desirable.

The ThO_2 problem

Solubility measurements on the ThO_2-H_2O system from different authors covering the whole pH range are shown in Figure 1. The pattern obviously reveals that two different solids may be responsible for $ThO_2(s)$ solubility at pH < 6. Under alkaline conditions the solubility differences level out and total

Figure 1. $ThO_2(s)$ solubilities from various authors

There is a clear indication that two solids [$ThO_2(cr)$ and $ThO_2(am)$] exist below pH ~ 6, but the patterns suggest that only one solid is responsible for Th concentrations in the alkaline branch



dissolved Th is described by the pH-independent concentration $10^{-8.5\pm0.6}$ mol/l. Experimental details may be taken from the original sources or from [1,2]. From these data we independently derived the formation/solubility constants:

$$\log_{10}K_{s,0}(ThO_2(\text{crystalline})) = 1.8$$

$$\log_{10}K_{s,0}(ThO_2(\text{amorphous})) = 12$$

$$\log_{10}\beta_4(Th(OH)_4(aq)) = -18.4$$

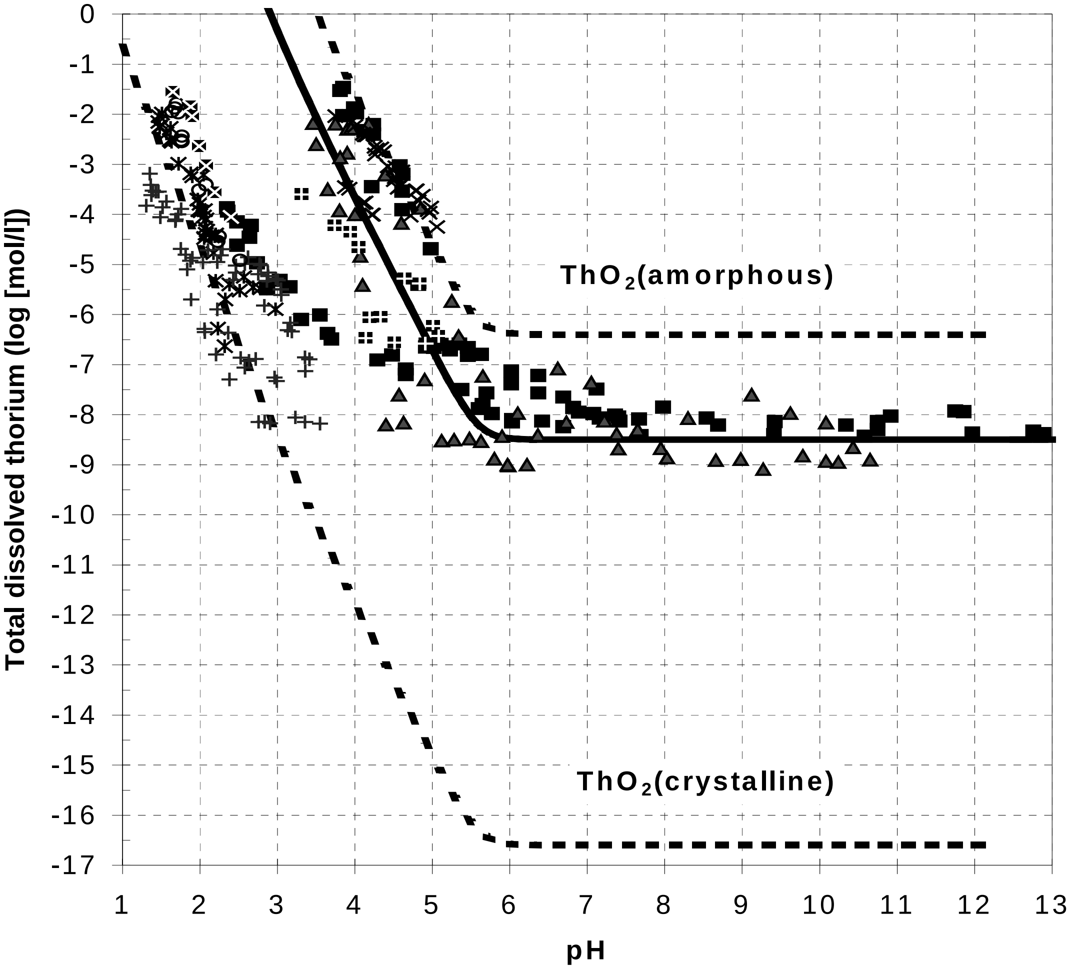
and calculated the dashed lines given in Figure 2. It is obvious that both the crystalline oxide and the amorphous oxide solubility constant do not reproduce measured concentrations in the alkaline region.

Interpretation

- Predictions based on solubility constants of $ThO_2(cr)$ and $ThO_2(am)$ derived at low pH do not reproduce experimental findings at elevated pH conditions.
- It seems that the surface of crystalline ThO_2 converts to a solid which behaves like an amorphous oxide (*cf.* discussion in [2]).
- We have to agree that the ThO_2-H_2O system is not fully resolved in terms of quantitative equilibrium thermodynamics. Note that a similar picture seems to escape from available UO_2-H_2O data [1].

Figure 2. Predictions of ThO_2(s) solubilities based on solubility constants of ThO_2(cr) and ThO_2(am)

The predictions do not reproduce experimental findings in alkaline solutions (dotted lines). The solid line is a pragmatic compromise, representing the solubility of an ill-defined solid with the composition "ThO_2".



How to resolve this issue in PA?

- In the alkaline pH region a maximum Th concentration of $10^{-8.5\pm0.6}$ mol/l is defendable through independent experimental observations.

- $Th(OH)_4$(aq) is the only solute which contributes to this maximum concentration. Accordingly, the sum $\log_{10}K_{s,0}(ThO_2(s)) + \log_{10}\beta_4(Th(OH)_4(aq))$ must correspond to 8.5±0.6.

- Select a formation constant in such a way that it reproduces observed solute concentrations in the pH range relevant for PA (in this specific case the selection is $\log_{10}K_{s,0}(ThO_2(s)) = 9.9$).

Note the dilemma: the pragmatically selected solubility constant does not reproduce Th solubilities at low pH and is not consistent with independently measured thermodynamic properties of ThO_2(cr).

Uranium solubility: An iron problem?

Uranium solubility was modelled in hyper-alkaline cement pore water (pH 12.6) as a function of the system redox state (Eh). According to the thermodynamic database, only very few uranium complexes may become relevant at these extreme conditions:

U(VI): $UO_2(OH)_3^-$
$UO_2(OH)_4^{2-}$
$(UO_2)_3(OH)_7^-$
U(IV): $U(OH)_4(aq)$.

The calculation reveals that in addition to these complex formation reactions, two key equilibria determine the solubility behaviour of uranium:

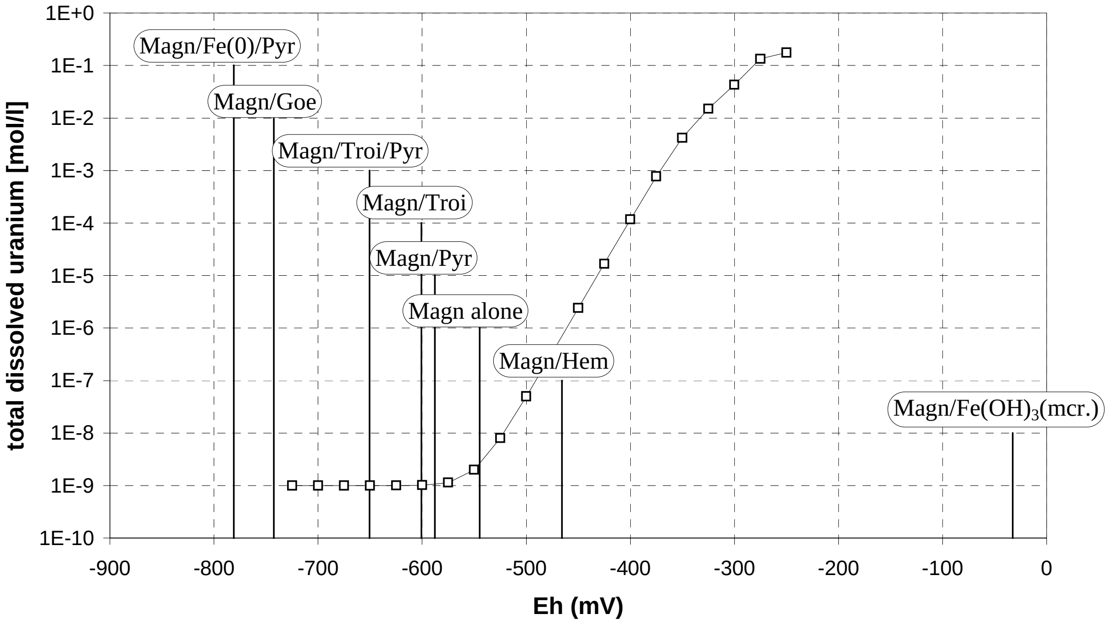
$$UO_2^{2+} + 4H^+ + 2\,e^- \rightleftharpoons U^{4+} + 2H_2O$$

$$UO_2(s) + 2\,H_2O \rightleftharpoons U(OH)_4(aq).$$

Note that $UO_2(s)$ is the only solid phase (included in the database) which may become stable at reasonable low Eh values. The solid curve in Figure 3 gives an impression of the exceptional redox sensitivity of uranium solubility under cement pore water conditions.

Figure 3. **Solubility of uranium in cementitious environments (pH 12.6) as a function of the system redox potential**

Eh itself is defined by the solubility of the principal corrosion product magnetite and, most likely, by the solubility of additional iron (and/or sulphur) bearing phases which may form/be present under given conditions. Conceivable phase assemblies (indicated in the boxes) cover a rather broad Eh range. A key issue in PA applications is to make an unambiguous decision on the redox-controlling phase assembly.



Interpretation

Present PA scenarios assume that the system Eh is defined by the Fe^{3+}/Fe^{2+} redox couple and that magnetite is the principal corrosion product of the vast amounts of steel disposed of together with the radioactive waste. This imposes several restrictions to the derivation of maximum concentrations for uranium:

- Uranium solubility critically depends on Eh. It is hardly possible to derive a reliable solubility limit in the light of the uncertainties imposed by the redox potential.

- Eh itself is defined by the solubility of magnetite and, most likely, by the solubility of additional iron (and/or sulphur) bearing phases which may form/be present under given conditions. Concerning Eh definition we may select from several potential candidates presently included in the database:

Elemental iron	Fe(0)
Goethite	FeOOH
Hematite	Fe_2O_3
Hydroxide(s)	$Fe(OH)_3$(mcr, am)
Siderite(s)	$FeCO_3$(cr, precip.)
Melanterite	$FeSO_4 \cdot 7H_2O$
Triolite	FeS
Pyrite	FeS_2
Elemental sulphur	S(0)

A series of conceivable solid phase combinations (indicated in Figure 3, together with their resulting equilibrium Eh represented as vertical lines) covers an Eh range from -780 to -35 mV. Unfortunately, our present knowledge base is not sufficient to make an unambiguous decision on the redox-controlling phase assembly. Although strong indications from thermodynamic principles point to very low Eh, we cannot firmly exclude more positive potentials as, for example, the -35 mV from the combination magnetite/$Fe(OH)_3$(microcr.).

We conclude that a better understanding of the iron (and sulphur) system is essential. This primarily encompasses the nature (of course including the thermodynamic properties) of iron compounds, solids and/or solid solutions formed (thermodynamically and/or kinetically) under given conditions as well as properties and reactivities of active surfaces which may be present.

How to resolve this issue in PA?

- Under the given prerequisites it would be important to find arguments which help defend low Fe^{3+} concentrations (and consequently a low Eh) in solution. In cementitious environments such arguments could be based on the capacity of hydrated calcium aluminate ferrite phases to bind iron. Although not very well characterised from a quantitative thermodynamic point of view, these phases are known to produce very low Fe(III) concentrations.

- Several experimental studies [3,4] demonstrate very low concentrations of dissolved U in non-reducing cementitious systems, contradicting the predictions as shown in Figure 3. Even though the nature of the limiting solids as well as their thermodynamic properties are not available, the experimental observations may directly flow into PA.

Radium is very soluble?

The presently available database includes only a few species and solids, namely $RaCl^+$, $RaOH^+$, $RaSO_4(aq)$, $RaCO_3(aq)$, $RaSO_4(s)$ and $RaCO_3(s)$, all taken from [5]. A prediction of Ra solubility in the reference cementitious system (pH 12.6, total CO_3^{2-} $1\cdot10^{-5}$ mol/l, total SO_4^{2-} $1\cdot10^{-4}$ mol/l) produces Ra concentrations of $1\cdot10^{-5}$ mol/l, as long as sulphate is not reduced to sulphide. Much higher Ra concentrations would be expected in the absence of sulphate (of the order of 10^{-2} mol/l).

Interpretation

Radium concentrations for cementitious systems predicted solely on the basis of available thermodynamic data seem unreasonably high and would offer serious problems for PA.

- It is not promising to improve the quality of existing data, nor is it likely that "new" sparingly soluble Ra bearing solid phases will be discovered.

- To defend sufficiently low Ra concentrations requires taking measures which go beyond the application of thermodynamics for pure phases. Such measures may include additional system information and/or new conceptual models for defining maximum concentrations.

How to resolve this issue in PA?

The basic idea is to utilise potential effects which are associated with the formation of solid solutions. A rough description of this idea is given below:

- *Hypothesis*: The well known calcium aluminate (mono) sulphates (AFm) may form solid solutions with corresponding Ra-bearing phases. This hypothetical solid solution would have the end-members:

$$C_3A.CaSO_4.12H_2O \text{ — } C_3A.RaSO_4.12H_2O$$

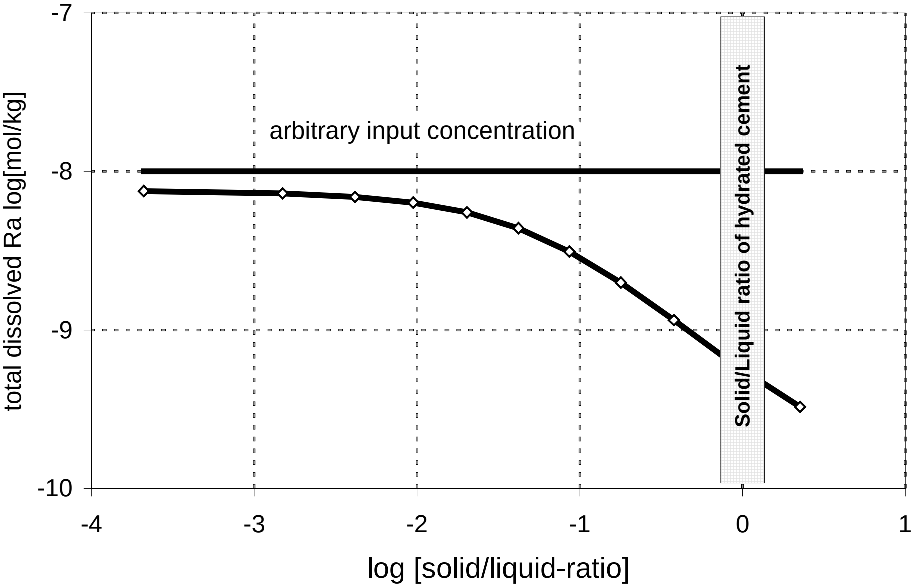
(the shorthand notation C_3A stands for $3CaO.Al_2O_3$). Up to now, the existence of the Ra end-member has not been verified, but many other end-members including a variety of divalent cations are known [6].

We assume identical stabilities for both end-members and model the solubility of this hypothetical ideal solid solution in aqueous solutions with increasing amounts of AFm phases but constant amounts of Ra. The results of this exercise are shown in Figure 4. Up to about 10 g/kg of water (16 mmoles of AFm) no significant effect is observed, but at high solid/liquid ratios the solid solution acts as a sink for the traces of Ra. Such a dependence on the solid/liquid ratio is not expected, when a "pure" Ra-bearing solid like $RaSO_4(s)$ is the limiting phase.

We conclude from this exercise that it may be essential for PA to verify the formation of solid solutions. In particular cases this would make it possible to utilise large mass ratios for defending considerably lower maximum concentrations. In PA, large mass ratios (*i.e.* matrix material/ inventory) are typical for trace elements like radium.

Figure 4. Solubility of radium for a hypothetical Ra-bearing solid solution

An arbitrarily selected amount of Ra^{2+} *(*10^{-8} *mol/kg of water) is "titrated" with solid AFm (*$C_3A.CaSO_4.12H_2O$*) from a dilute suspension (*$3\cdot10^{-4}$ *mol/kg of water) up to a solid/liquid ratio corresponding to cementitious materials (3.6 mol/kg of water). At high AFm concentrations the solid solution acts as a sink for Ra. Such behaviour is not observed for "pure" phases (indicated by the horizontal line).*



Conclusions and recommendations in view of PA

Complete thermodynamic databases of high quality are indispensable, but applying them does not always satisfy the PA needs for "solubility limits". Missing knowledge in the behaviour of solutes (speciation) does not produce major uncertainties. In general, sufficient data of reasonable quality are available for this class of compound.

Further activities should desirably focus on answering the essential question "What is the solubility limiting solid phase?" An ideal result of such activities would identify and quantify those solid phases which really form at given conditions (a minimum requirement would be that such phases not contradict the available experimental observations). An important result would also be to identify those solid phases which do not form at given conditions (high temperature phases, kinetically hindered phases, exotic laboratory solids, etc.).

Activities should also focus on a better understanding of system key parameters like Eh, pH and p_{CO_2}. The impact of a non-adequate Eh definition may well exceed uncertainties associated with particular thermodynamic radionuclide data. Referring to the given example we conclude that investigations on iron-bearing phases, including their surface reactivities as well as the role of the sulphur system, would be desirable tasks.

The thermodynamic description of trace element behaviour is a very difficult task. There is ample evidence that for these elements the formation of solid solutions with major elements is rather the rule than the exception. It is therefore not adequate to perform solubility calculations using pure phases alone. Models to describe solid solution behaviour are available and scoping calculations indicate substantial benefits for PA, especially in cases where large mass ratios between major and trace elements are in operation. However, data for this class of mixed compounds are largely missing. Two steps are necessary to improve this situation for PA. Its of utmost importance to prove the formation of solid solutions at given chemical conditions (the analytical tools to do so are widely used today, *e.g.* XAFS techniques). It is then of secondary importance to estimate or measure formation constants of verified solid solutions.

Acknowledgement

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REFERENCES

[1] W. Hummel, U. Berner, E. Curti, F.J. Pearson, T. Thoenen, NAGRA /PSI Thermochemical Database 01/01, PSI Bericht Nr. 01-xx, Paul Scherrer Institute, Villigen, Switzerland (in review procedure).

[2] V. Neck, J.I. Kim, “Solubility and Hydrolysis of Tetravalent Actinides”, *Radiochimica Acta*, 89, 1-16 (2000).

[3] L.P. Morony, F.P. Glasser, “Reactions between Cement Components and U(VI) Oxide”, *Waste Management*, 15/3, 243-403 (1995).

[4] R.J. Serne, D. Rai, P.F. Martin, A.R. Felmy, L. Rao, S. Ueta, “Leachability of Nd, U, Th and Sr from Cements in a CO_2-free Atmosphere”, Mat. Res. Soc. Symp. Proc., Vol. 412, 459-467 (1996).

[5] D. Langmuir, A.C. Riese, “The Thermodynamic Properties of Radium”, *Geochim. Cosmochim. Acta*, 49, 1593-1601 (1985).

[6] H. Pöllmann, “Immobilization of Pollutants in Waste Disposal by Forming Mineral Reservoirs”, in *Process Mineralogy XII – Applications to Environment, Precious Metals, Mineral Benefication, Pyrometallurgy, Coal and Refractories*, W. Petruk and A.R. Rule, eds., The Minerals, Metals & Materials Soc., 3 (1994).

[7] H.C. Moon, “Equilibrium Ultrafiltration of Hydrolysed Thorium(IV) Solutions”, *Bull. Korean Chem. Soc*., 10, 270 (1989).

[8] A.R. Felmy, D. Rai, M.J. Mason, “The Solubility of Thorium(IV) Oxide in Chloride Media: Development of an Aqueous Ion-interaction Model”, *Radiochimica Acta,* 55, 177-185 (1991).

[9] J.L. Ryan, D. Rai, “Thorium(IV) Hydrous Oxide Solubility”, *Inorganic Chemistry*, 26, No. 24, 4140-4142 (1987).

[10] D. Rai, D.A. Moore, C.S. Oakes, M. Yui, “Thermodynamic Model for the Solubility of Thorium Dioxide in the Na^+-Cl^--OH^--H_2O system at 23°C and 90°C, *Radiochimica Acta*, 88, 297-306 (2000).

[11] C.F. Baes, N.J. Meyer, C.E. Roberts, *Inorganic Chemistry*, 4, 518 (1965).

[12] T. Bundschuh, R. Knopp, R. Müller, J.I. Kim, V. Neck, Th. Fanghänel, “Application of LIBD to the Determination of the Solubility Product of Thorium(IV)-colloids”, *Radiochimica Acta*, 88, 625-629 (2000).

[13] E. Östhols, J. Bruno, I. Grenthe, “On the Influence of Carbonate Mineral Dissolution: III. The Solubility of Microcrystalline ThO_2 in CO_2-H_2O Media, *Geochim. Cosmochim. Acta*, 58/2, 613-623 (1994).

DIFFICULTIES ENCOUNTERED IN THE JAPANESE PERFORMANCE ASSESSMENT PROGRAMME USING THERMODYNAMIC DATA

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Abstract

The Japan Nuclear Cycle Development Institute (JNC) published a second progress report (the H12 report) concerning HLW disposal in Japan in November 1999. This report was instrumental in establishing confidence in the concept of a high-level radioactive waste (HLW) disposal system and paved the way for the creation of an implementation body in 2000.

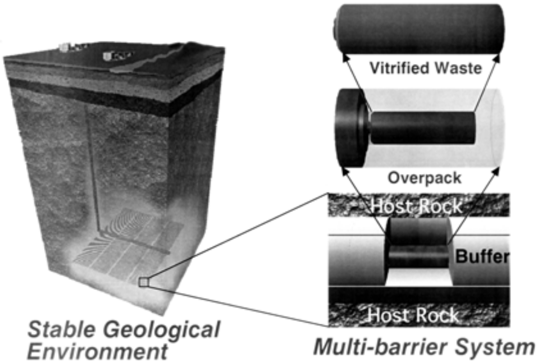
JNC developed an in-house thermodynamic database of radioactive elements (JNC-TDB) for the performance analysis of the H-12 report. The database development was focused on the repository condition, reducing and various CO_2 conditions.

This paper presents the difficulties encountered to increase confidence in JNC-TDB for performance analysis learned from studies undertaken for the H12 report. Those are related to increase reality, reliability and the relevant amount of data under expected repository conditions.

Introduction

The objective of the H12 report [1] for a HLW geological disposal in Japan is specified to present the technical reliability of HLW geological disposal based on the progress made since the publication of the first progress report [2] in 1992. The H12 [1] report also provided a scientific and technical basis for site selection and formulation of the regulatory infrastructures. The performance assessment in the H12 report required data for dissolution rate of vitrified waste, thermodynamic database and sorption/diffusion database of radioactive elements, which were used to analyse the performance of the EBS (vitrified waste, compacted bentonite) and the geosphere (rocks) under expected repository conditions. The repository concept in H12 report is shown in Figure 1.

Figure 1. Disposal concept



This report presents the difficulties encountered to increase confidence in the JNC-TDB for performance analysis learned from studies undertaken for the H12 report following the status of the JNC-TDB development.

Status of JNC-TDB development for performance assessment

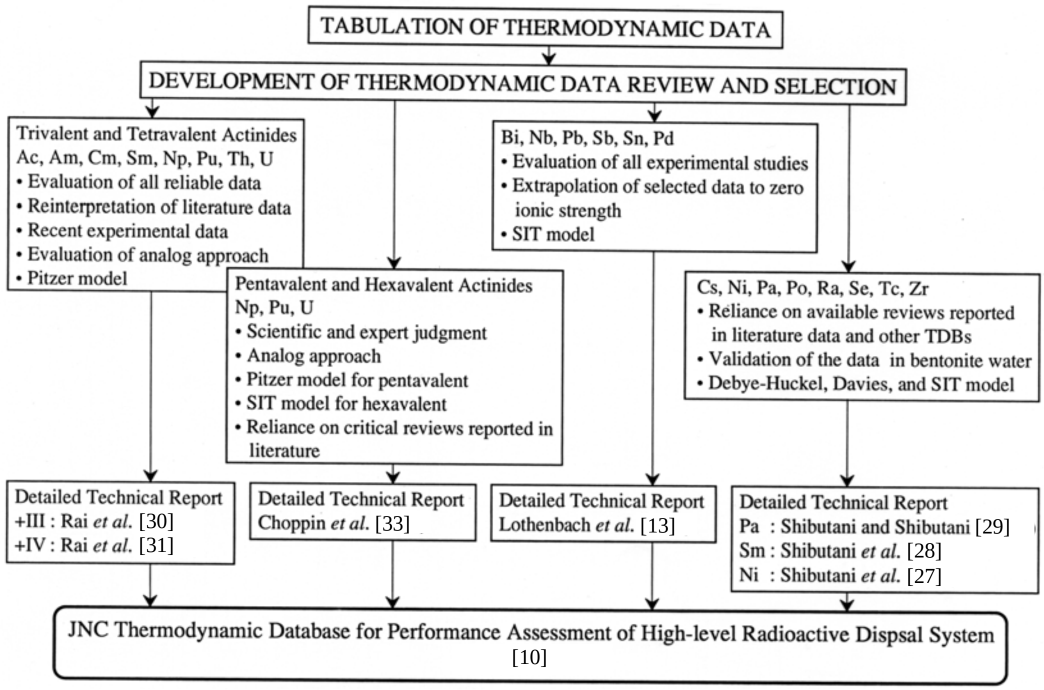
Status of JNC-TDB development

Critically reviewed thermodynamic databases with a traceable data selection are rare, and ongoing projects are slow to progress. International efforts have been undertaken, *e.g.* by the International Atomic Energy Agency (IAEA) and the Nuclear Energy Agency (NEA). The IAEA project “The Chemical Thermodynamics of Actinide Elements and Compounds” [3] came to a close after the last publication in 1992. The OECD/NEA TDB project has a high quality review standard and includes international reviewers, but its progress remains slow. During H-12 report work, only the OECD/NEA TDB for uranium [4] and americium [5] was available. Databases for technetium, neptunium and plutonium were close to completion, but were not sufficiently so as to be included in the H12 report. JNC thus determined to start its own project to develop a thermodynamic database for radioactive elements (JNC-TDB). International experts assisted JNC with the aim of a developing critically reviewed database for a large number of elements: Ac, Am, Cm, Np, Pu, Sm, Th, U, Bi, Nb, Pb, Pd, Sb, Sn, Cs, Ni, Pa, Po, Ra, Se, Tc and Zr. These elements were selected on the basis of their potential hazard index reported in Ref. [6]. Key reactions in the solubility estimation of radioactive elements for the performance analysis of the geological disposal system are oxidation/reduction, hydrolysis, carbonate, sulphate, phosphate and chloride.

In the first progress report for HLW disposal in Japan [2], a thermodynamic database for radioactive elements, PNC-TDB_H-3, [7] was used to estimate the solubility.

At the initial stage of the JNC-TDB development, general review guidelines were established for evaluating reported experimental procedures and data interpretation techniques. However, as might be expected of such a large technical undertaking, and because of funding and time limitations and the quality and extent of available data, it was not possible to critically evaluate and use the same evaluation criteria as agreed for each element. The general procedure for data collection and the review process for different elements is shown in Figure 2. In all cases, an effort was made to tabulate the totality of the available data.

Figure 2. General technical approach, review, process and technical output for developing the JNC-TDB for performance assessment



In the case of trivalent [Ac(III), Am(III), Cm(III), Np(III), Pu(III) and Sm(III)] and tetravalent [Th(IV), U(IV), Np(IV) and Pu(IV)] actinides and rare earths, decisions were made primarily based on recent experimental data obtained in simple systems and validated in mixed and complex systems where the Pitzer model [8] was used. In the case of pentavalent actinides [Np(V) and Pu(V)], recently obtained data for Np(V) [9] using the Pitzer model approach were used as the basis for both Np(V) and Pu(V). In the case of hexavalent actinides [U(VI), Np(VI), Pu(VI)], recently available U(VI) data [4] were the primary reference source. In the case of Bi, Nb, Pb, Pd, Sb and Sn, all available experimental data were evaluated, and selected experimental data were extrapolated to zero ionic strength using the specific ion interaction theory (SIT) model which has been described in the literature [4,5]. Data for the remaining elements were tabulated by JNC staff members primarily using existing compilations. For Ra and Po, the thermodynamic data sets are the same as in the PNC-TDB_H-3, because no new thermodynamic data have been reported since 1992. For Tc, the OECD/NEA database will be adopted by the JNC-TDB in the near future. For Ni, Zr and Se, the thermodynamic data reported by Cross, *et al.* [26] were the primary reference data, which are the same as those in the PNC-TDB_H-3.

Data selection for the JNC-TDB was determined based on the following three criteria:

i) confirmation of the reliability and traceability of thermodynamic data;

ii) data selections were carried out by using a suitable method for activity correction based on some experiments which were adequate to obtain thermodynamic data;

iii) expert review of the data selected from other thermodynamic databases.

The frozen JNC-TDB [10] improved the traceability of the origin of the thermodynamic data and its scientific reliability by verifying the original studies from the following points of view:

- identification of the solubility limiting solid phase;
- description of pH, redox condition and concentration of the ligands;
- ionic strength and electrolyte media used in the experiments;
- extrapolation of activity to zero ionic strength.

Additionally, the most recent information was incorporated. Consequently, the JNC-TDB was also improved in relation to the following points:

- Traceability of all data was assured except for a few elements.
- Carbonate and hydroxy-carbonate complexes of the tetravalent actinides were incorporated, which have recently been reported [11,12] and were important for high carbonate systems such as pore water in compacted bentonite. This development for tetravalent actinides was an expansion of the Th thermodynamic data used for the safety assessment of the Waste Isolation Pilot Plant (WIPP) in the United States.
- Thermodynamic data for americium were mostly based on the OECD/NEA database [5] whose high reliability is internationally recognised.
- Thermodynamic data for palladium, lead and tin were re-evaluated from original experimental values basically following the procedures of the NEA-TDB [13].
- For the trivalent lanthanide (Sm) and actinides (Ac, Pu and Cm), available thermodynamic data were limited and reliability of the data has not been established. Therefore, they were represented by the data for Am(III) based on chemical analogy.

In developing the JNC-TDB, an equilibrium constant of 25ºC and an ionic strength of $I = 0$ were established. However, the parameters concerning activity correction have not yet been sufficiently determined. Therefore, Davies activity coefficient formula, which does not depend on the type of soluble chemical species, was adopted. This formula is applicable up to the ionic strength of approximately 0.5 molal [14]. It was thus applicable to the fresh-reducing-high pH groundwater (reference groundwater in the H12 report) whose ionic strength is 0.02 molal.

Derived solubilities of radioactive elements

The solubilities of radioactive elements in pore water of compacted bentonite are determined by the following procedure:

- Estimate the solubility by using the geochemical code PHREEQE [15] with an appropriate thermodynamic database of the JNC-TDB and assuming a solubility-limiting solid phase.
- Values measured in experiments are used where they are available and greater than the calculated values.
- Effects of co-precipitation are considered for a relevant element (Ra).

The solubilities of safety-relevant elements in pore water determined for fresh-reducing-high pH groundwater are listed in Table 1 [16]. In the selection of solubility-limiting solid phases, thermodynamic stability and observations in solubility experiments are taken into account.

Table 1. Solubilities of safety-relevant elements in fresh-reducing-high pH pore water

Element	Solubility (mol 1^{-1} at 25°C)	Limiting solid[*3]	Dominant species[*3]
Se	3×10^{-9}	$FeSe_2$(cr)	HSe^-
Zr	1×10^{-6} [*1]	ZrO_2(am)	$Zr(OH)_4$(aq)
Nb	1×10^{-4} [*1]	Nb_2O_5(am)	$Nb(OH)_6^-$
Tc	4×10^{-8}	$TcO_2 \cdot 2H_2O$(am)	$TcO(OH)_2$(aq)
Pd	1×10^{-9} [*1]	Pd(cr)	$Pd(OH)_2$(aq)
Sn	5×10^{-6} [*1]	SnO_2(am)	$Sn(OH)_5^-$, $Sn(OH)_4$(aq)
Cs	Soluble	–	Cs^+
Sm	2×10^{-7}	$SmOHCO_3$(cr)	$Sm(CO_3)_2^-$, $Sm(CO_3)_3^{3-}$, $SmCO_3^+$
Pb	2×10^{-6}	$PbCO_3$(cr)	$PbCO_3$(aq), $Pb(CO_3)_2^{2-}$
Ra	1×10^{-12} [*2]	Ra-Ca-CO_3	Ra^{2+}
Ac	2×10^{-7}	$AcOHCO_3$(cr)	$Ac(CO_3)_2^-$, $Ac(CO_3)_3^{3-}$, $AcCO_3^+$
Th	5×10^{-6}	ThO_2(am)	$Th(OH)_3CO_3^-$
Pa	2×10^{-8}	Pa_2O_5(s)	$PaO(OH)_3$(aq)
U	8×10^{-9}	UO_2(am)	$U(OH)_2(CO_3)_2^{2-}$, $U(OH)_4$(aq)
Np	2×10^{-8}	NpO_2(am)	$Np(OH)_2(CO_3)_2^{2-}$, $Np(OH)_4$(aq)
Pu	3×10^{-8}	PuO_2(am)	$Pu(OH)_2(CO_3)_2^{2-}$, $Pu(CO_3)_2^-$, $Pu(CO_3)_3^{3-}$, $PuCO_3^+$
Am	2×10^{-7}	$AmOHCO_3$(cr)	$Am(CO_3)_2^-$, $Am(CO_3)_3^{3-}$, $AmCO_3^+$
Cm	2×10^{-7}	$CmOHCO_3$(cr)	$Cm(CO_3)_2^-$, $Cm(CO_3)_3^{3-}$, $CmCO_3^+$

[*1] Measured value

[*2] The observations of groundwater are adopted as conservative value, based on the comparison with solubility calculated using simple co-precipitation model of Ra with Ca.

[*3] (cr): crystalline, (am): amorphous, (s): solid that can not be identified as either crystalline or amorphous in the original literature, (aq): aqueous species with neutral charge [10]

Validity of the databases

The validity of the JNC-TDB was verified through independent experiments. Examples of validation activities are described below. The validity of thermodynamic data for trivalent actinides such as Am(III) was shown through comparison with studies by Rai, *et al.* [17] using Am-doped glass. The validity of thermodynamic data for Pu was also shown though our study on the leaching behaviour of Pu released from the Pu-doped glass, which indicated that the maximum Pu concentration was limited by PuO_2(am) in the pH range more than 6 as shown in Figure 3 [18]. The following coupled experiment was also performed at JNC to validate the leaching rates of glass, thermodynamic database and Kd model (values) simultaneously. Ashida, *et al.* [19] studied the coupled behaviour of Pu released from the Pu-doped glass surrounded by the compacted bentonite saturated with distilled water. The experimental results are shown in Figure 4. Under these conditions, leaching of Pu from the glass, diffusion and sorption of Pu in the compacted bentonite occur simultaneously. The experimental results were interpreted by transport modelling using individual parameters; leaching rate of the glass, solubility, sorption and diffusion coefficient of Pu. The modelled diffusion profile is similar to experimental results, as shown in Figure 4.

Figure 3. Solubility measurements by Pu-doped glass

● Experimental results of leaching experiment with crushed Pu-doped glass
× Solubility measurements of PuO_2(am) [32]

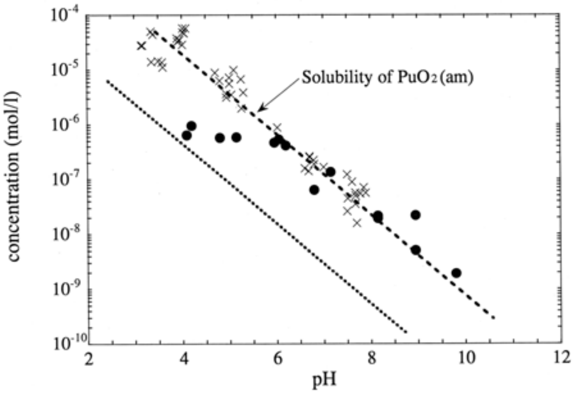
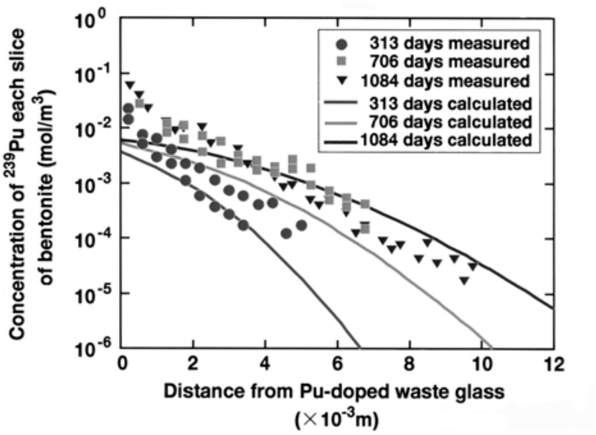


Figure 4. Results of coupled experiments using Pu-doped glass with compacted bentonite (ρ = 200 kg/m^3)



Difficulties encountered during JNC-TDB development and its use for performance assessment

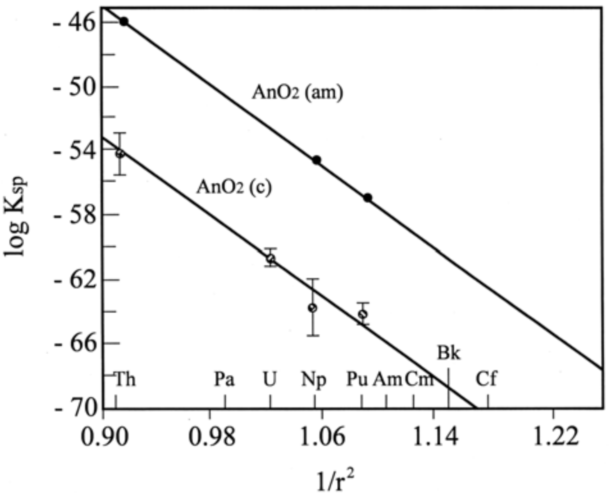
Difficulties involving the use of the JNC-TDB in H12 performance assessment work are categorised into three types to increase the confidence in the TDB; first to increase reality, second to increase reliability and third to increase the relevant amount of data under expected repository conditions. The difficulty of "increasing reality" is related to the availability of thermodynamic data of naturally observed minerals, *e.g.* crystalline phases, co-precipitation or solid-solution. For example, this difficulty has been generated by TDB validation studies by using glass-leaching experiments as discussed below. The second issue, that of increasing reliability, is related to the availability of existent thermodynamic data, *e.g.* redox reaction of actinides and FPs, use of chemical analogue or theory, colloid/organic effects. The third problem, increasing the relevant amount of data, is related to a lack of data under expected repository conditions, reducing and variable CO_2 conditions.

Difficulty to increase reality

Reality in performance assessment is required to rationalise the EBS design and to confirm a margin of safety by conservative assessment. The solubility limit is critically important for the EBS design relying on the diffusion retardation processes. Difficulties to increase reality are: limitation of data for crystalline phase (*e.g.* U,Th), development of data for co-precipitation of actinides (silicate, iron, carbonate minerals; Th, Am, Cm, Ra) and FPs (*e.g.* Fe-S-Se) and validation of TDB by using vitrified waste.

The present performance assessments have adopted the amorphous phases in general for the solubility-limiting solid phases of actinides under the consideration of conservatism, however, thermodynamics indicates that the crystalline phases are more stable. The differences in solubility products between amorphous and crystalline phase are shown in Figure 5 [20].

Figure 5. Variation of solubility products of actinide dioxides [20]



The solubility differences between amorphous and crystalline phases are several orders of magnitude, so the studies on the transformation from amorphous to crystalline phase in the long-term are important. Thermodynamic data are also extremely limited regarding the effects of temperature on crystallinity of actinide oxide phases in aqueous solutions. Other viewpoints include the development of data for co-precipitation or solid solution. Since Se is a critical element in performance analysis due to the formation of anions non-sorptive to geological materials and its solubility is key parameter, we expected the formation of Fe-Se or Fe-Se-S minerals whose solubility is much lower than Se(cr). The TDB validation studies using Th-doped glass leaching experiments also indicate the formation of an actinide-bearing silicate compound. The three examples mentioned above are described below.

For transformation of amorphous to crystalline phase, Rai, *et al.* [21] have conducted solubility experiments using Th oxide phases as a representative of actinide(IV) oxides. The experiments were performed as a function of pH and time and at 0.1 M NaCl for ThO_2(am) at 23°C, ThO_2(am→cr), a thermally transformed amorphous Th hydrous oxide at 90°C and ThO_2(cr) at 23°C and 90°C. Experimental ThO_2(am→cr) and ThO_2(cr) solubilities at 90°C were shown in Figure 6 as a function of pH. Results show that when ThO_2(am) is heated at 90°C, it transforms to a relatively insoluble and crystalline solid, ThO_2(am→cr), as shown in Figure 7. At a fixed pH, the observed solubility of ThO_2(am) is more than 11 orders of magnitude greater than those for ThO_2(cr) at 23°C or of ThO_2(am→cr) and ThO_2(cr) at 90°C. Solubility data were interpreted using the Pitzer ion-interaction model. At 90°C, the K_{sp} (solubility product) for a relatively less crystalline phase, ThO_2(am→cr), $10^{-49.2}$, is several orders of magnitude lower than that for ThO_2(am) at 23°C, $10^{-44.9}$.

Figure 6. Experimental ThO_2(am→cr) and ThO_2(cr) solubilities in 0.1 M NaCl at 90°C

ThO_2(am→cr) data are for sample Sets I to III that were originally equilibrated at 23°C and then equilibrated at 90°C. The lines represent predicted solubilities of various Th solid phases.

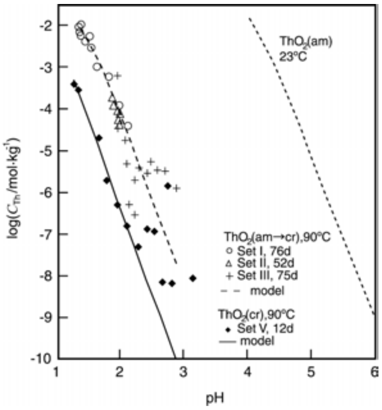
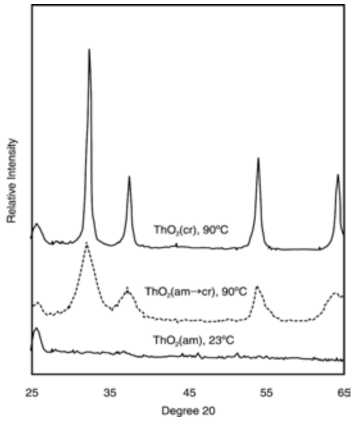


Figure 7. X-ray diffraction patterns for the solid ThO_2 phases examined in this study

(am) = amorphous, (am→cr) = transformation of amorphous phase when heated to 90°C, (cr) = fully crystalline phase prepared by firing thorium oxalate at 750°C



Another example is related to co-precipitation or solid solution.

Concerning Se solubility, the Fe-S-Se compound is likely the solubility-limiting solid phase in the long term. First, Se solubility measurements were conducted under reducing conditions in order to identify a Se solubility-limiting solid phase in the Fe-Se system [22]. Two types of Se solubility measurements were performed under reducing conditions. The first experiment was conducted in bentonite (Kunigel V1) coexistence condition. In the first experiment, an Se concentration in an aqueous phase of approximately 10^{-8} mol/l was obtained. The second experiment was conducted in an Fe-Se system without bentonite. A higher temperature, 80°C, was adopted in the second experiment, because at the former experimental temperature, 60°C, a phase equilibrium was not reached during the experimental period. The Se concentration decreased with time as shown in Figure 8. However, a phase equilibrium was still not reached. Se concentrations in some samples are below the detection limit level (4×10^{-9} mol/l) of the ICP-MS. Several Se solids were identified as shown in Figure 9. Though Se(cr) was dominant in the initial stage, this solid phase was gradually transformed to Fe-Se solids ($FeSe_2$,FeSe). Therefore, it is suggested that $FeSe_2$, which is the most thermodynamically stable phase, will be a solubility-limiting solid phase in the Fe-Se system in the long term.

Figure 8. Se concentration as a function of time in two types of experiments

1st – with bentonite, 2nd – Fe-Se system, ND – detection limit of ICP-MS

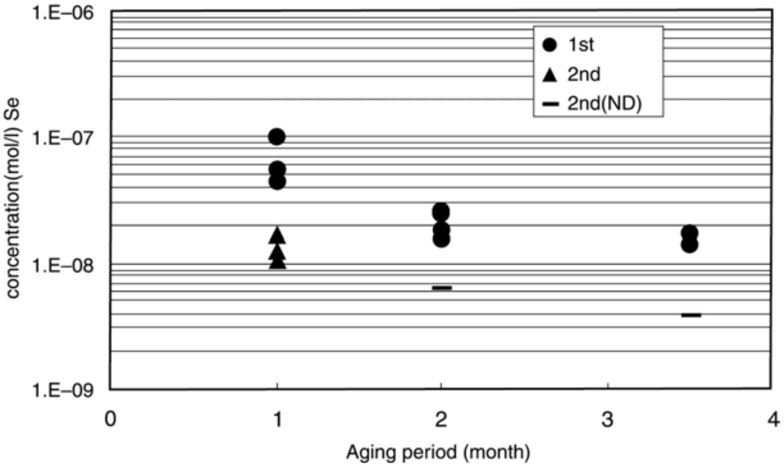
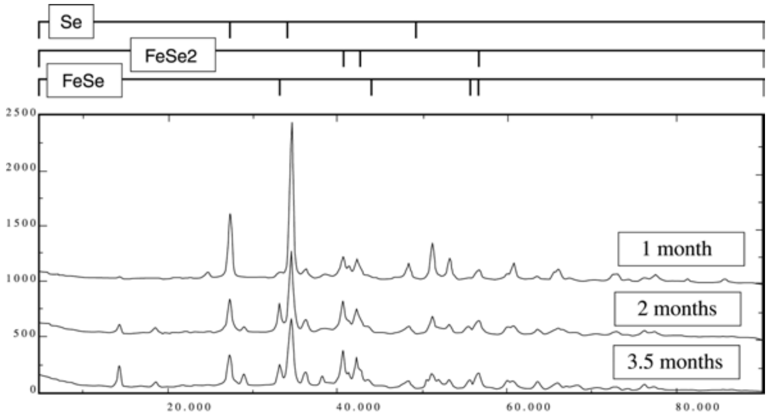


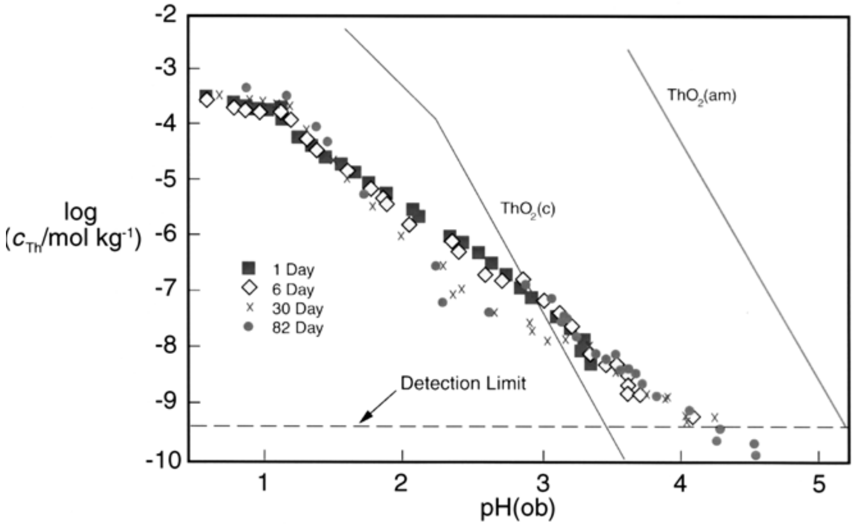
Figure 9. X-ray diffraction patterns for Se solid phase (initial pH 7)

The solid phase transformed for the ageing period. Comparing Se(cr) and Fe-Se solids, Se(cr) relatively decreased.



Dissolution behaviour of Th from Th-doped glasses as a function of pH and carbonate concentrations was studied. It was found that in the absence of strongly complexing ligands such as carbonate, the observed concentrations of Th in solution were measurable only under acidic conditions. The comparison of the predicted Th concentrations based on the JNC-TDB [10] showed that the observed aqueous Th concentrations are lower than those expected in equilibrium with ThO_2(am) or ThO_2(cr) in the low pH range as shown in Figure 10 [23]. The observed Th concentrations might result from Th reaction with silicate both in the aqueous and solid phase and indicated the solubility-limiting phase, $ThSiO_4$(s).

Figure 10. Aqueous Th in glass/water suspensions



Difficulty to increase reliability

Reliability in the existent thermodynamic data is important for the interpretation of radionuclide migration and the variation of transport parameters for performance assessment. Difficulties to increase reliability are: availability of data for redox equlibria of actinides (*e.g.* U, Pu) and FPs, availability of chemical analogy and theory to evaluate TDB, colloid/organic effects and validation of TDB by using vitrified waste.

The difference in redox states of actinides (*e.g.* Pu, U) and FPs affects the setting of migration parameters. Table 2 shows the results of Pu speciation analysis in fresh-reducing-high pH (FRHP) and saline-reducing-high pH (SRHP) pore water in the H12 report using the JNC-TDB and HATCHES Ver. 12. The JNC-TDB predicts dominant redox state of Pu, trivalent, whereas HATCHES predicts tetravalent. These differences in redox state cause the difference in solubility and distribution coefficient (Kd) setting for performance assessment; however, it is very difficult to determine the redox state of Pu in neutral pH range under reducing conditions. Another example is to confirm the colloid/organic effects on the solubility and consequently derived thermodynamic data. JNC has conducted gold colloid (15 nm) transport experiments using highly compacted bentonite and confirmed that the highly compacted bentonite filtrates gold colloid as shown in Figure 11 [24]. Therefore, based on the repository concept of the H12 report, the solubility and consequent TDB derivation should be based on experiments by carefully avoiding colloid effects. Some natural organics are larger in size than gold colloids, in which case the solubility measurements should be conducted by considering the size effects of natural organics.

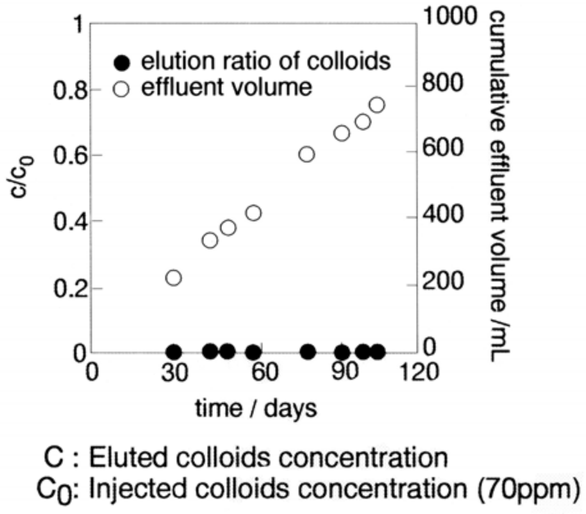
Table 2. Comparison of Pu speciation analysis between JNC-TDB and HATCHES Ver. 12

	Fresh-reducing-high pH pore water (FRHP) pH = 8.4, Eh = -276 mV Total C = 1.6e-2 (dominant; HCO_3^-)		Saline-reducing-high pH pore water (SRHP) pH = 7.8, Eh = -309 mV Total C = 2.2e-2 (dominant; $CH_4(aq)$)	
JNC-TDB	$Pu(III)(CO_3)_2^-$ $Pu(IV)(OH)_2(CO_3)_2^{2-}$ $Pu(III)(CO_3)_3^{3-}$ $Pu(III)CO_3^+$	(47%) (24%) (17%) (11%)	$Pu(III)OH^{2+}$ $Pu(III)CO_3^+$ $Pu(III)(OH)_2^+$	(39%) (26%) (20%)
HATCHES Ver. 12	$Pu(IV)(CO_3)_3^{2-}$ $Pu(IV)(CO_3)_4^{4-}$	(71%) (29%)	$Pu(IV)(CO_3)_3^{2-}$ $Pu(IV)(CO_3)_4^{4-}$	(56%) (44%)

* Difference from data for Pu(IV) complexation.

Figure 11. Colloidal transport through the compacted sand-betonite mixture

Colloid filtration by compacted sand-bentonite mixture containing 50 wt.% sand and saturated with 0.5 M NaCl solution at dry density 1 800 kg/m^3 [24]

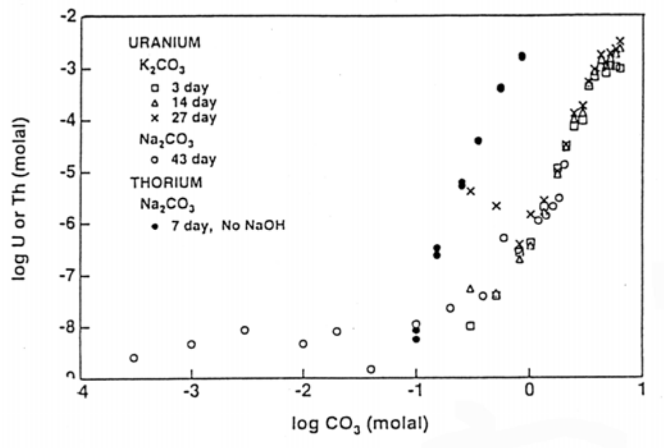


Difficulty to increase the relevant amount of data under repository conditions

The lack of thermodynamic data relevant for repository conditions, reducing and various CO_2 conditions and higher temperatures should be noted. Ionic strength should also be considered if a repository with high salinity is selected.

It is not easy to obtain the correct data under well-controlled reducing conditions. The failures of redox-sensitive actinide solubility experiments have very often been found to be related to the control of reducing conditions. Thermodynamic data for actinides(IV) carbonate complexes have been developed (*e.g.* U(IV) and Th(IV) by Rai, *et al.* [25], Np(IV) by Rai, *et al.* [11], Pu(IV) by Rai, *et al.* [12]). An example of the comparison of Th(IV) and U(IV) hydrous oxide solubility dependencies on carbonate concentration are shown in Figure 12 [25]. These thermodynamic data need to be developed under well-controlled conditions and validated through independent experiments.

Figure 12. Comparison of the solubility of $UO_2 \cdot xH_2O(am)$ and $ThO_2 \cdot xH_2O(am)$ at different equilibration periods in carbonate solutions containing 0.01 M NaOH, unless otherwise noted [25]



The difficulties concerning ionic strength corrections and temperature dependencies of thermodynamic data require more international efforts to develop a theoretical model and a related database.

Conclusion

The JNC in-house thermodynamic database (JNC-TDB) for radioactive elements has been developed for performance assessment as outlined in the H12 report. Development of the JNC-TDB has been focused on the repository condition, reducing and various CO_2 conditions, *e.g.* actinide(IV)/(III) and their carbonate complexes.

The validity of the JNC-TDB was verified through independent experiments *e.g.* glass leaching, solubility experiments.

The difficulties of the use of the JNC-TDB encountered in H12 performance assessment work are categorised into three types to increase the confidence in the TDB: first to increase reality, second to increase reliability and third to increase the relevant amount of data under expected repository conditions. The difficulty of increasing reality is related to the availability of thermodynamic data of naturally observed minerals, *e.g.* crystalline phases, co-precipitation or solid solution. The second, increasing reliability, is related to the availability of existent thermodynamic data, *e.g.* redox reaction of actinides and FPs, use of chemical analogue or theory, colloid/organic effects. The third problem, that of increasing the relevant amount of data, is related to a lack of data under expected repository conditions, reducing and variable CO_2 conditions. The above-categorised difficulties have been tackled gradually by recent studies. If more reliable and realistic performance assessment is required in the near future, such activities should be accelerated on an international scale.

Acknowledgement

The author thanks the JNC staffs for their efforts in developing the JNC-TDB for the H12 report.

REFERENCES

[1] "H12 Project to Establish Technical Basis for HLW Disposal in Japan", Japan Nuclear Cycle Development Institute, Project Overview Report, JNC TN 1400 99-010 (1999).

[2] "Research and Development on Geological Disposal of High-level Radioactive Waste: First Progress Report", Power Reactor and Nuclear Fuel Development Corporation, PNC TN 1410 93-059 (1992).

[3] J. Fuger, I.L. Khodakovsky, E.I. Sergeyeva, V.A. Medvedev and J.D. Navratil, "The Chemical Thermodynamics of Actinide Elements and Compounds: Part 12. The Actinide Aqueous Inorganic Complexes", International Atomic Energy Agency, Vienna, Austria (1992).

[4] I. Grenthe, J. Fuger, R.J.M. Konings, R.J. Lemire, A.B. Muller, C. Nguyen-Trung and H. Wanner, "The Chemical Thermodynamics of Uranium", OECD Nuclear Energy Agency, Amsterdam: North-Holland (1992).

[5] R.J. Silva, G. Bidoglio, M.H. Rand, P.B. Robouch, H. Wanner and I. Puigdomenech, "Chemical Thermodynamics of Americium", OECD/NEA, Elsevier (1995).

[6] "Current Status of Research and Development on Geological Disposal (FY1989)", PNC Technical Report, PNC TN1410 91-009 (1991) (in Japanese).

[7] M. Yui, H. Makino, T. Ashida, H. Umeki, K. Ishiguro and A. Neyama, "Dissolution Behavior of Vitrified Waste and Evaluation of Radionuclides Solubilities in Near-field Porewater Chemistry", PNC Technical Report, PNC TN8410 92-161 (1992) (in Japanese).

[8] K.S. Pitzer, "Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations", *The Journal of Physical Chemistry*, Vol. 77, No. 2, pp. 268-277 (1973).

[9] T. Fanghäenel, V. Neck and J.I. Kim, "Thermodynamics of Neptunium(V) in Concentrated Salt Solutions: II. Ion Interaction (Pitzer) Parameters for Np(V) Hydrolysis Species and Carbonate Complexes", *Radiochimica Acta*, Vol. 69, pp. 169-176 (1995).

[10] M. Yui, J. Azuma and M. Shibata, "JNC Thermodynamic Database for Performance Assessment of High-level Radioactive Waste Disposal System", JNC Technical Report, TN8400 99-070 (1999).

[11] D. Rai, N.J. Hess, A.R. Felmy, D.A. Moore and M. Yui, "A Thermodynamic Model for the Solubility of NpO_2(am) in the Aqueous K^+-HCO_3^--CO_3^{2-}-OH^--H_2O System, *Radiochimica Acta*, 84, pp. 159-169 (1999).

[12] D. Rai, N.J. Hess, A.R. Felmy, D.A. Moore and M. Yui, “A Thermodynamic Model for the Solubility of PuO_2(am) in the Aqueous K^+-HCO_3^--CO_3^{2-}-OH^--H_2O System, *Radiochimica Acta*, 86. pp. 89-99 (1999).

[13] B. Lothenbach, M. Ochs, H. Wanner and M. Yui, “Thermodynamic Data for the Solubility and Speciation of Sn, Sb, Pb, Bi, Nb, and Pd in Aqueous Solution”, JNC Technical Report (1999).

[14] W. Stumm and J.J. Morgan, “Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters”, 3rd ed., John Wiley & Sons, Inc. (1996).

[15] D.L. Parkhurst, D.C. Thorstnsen and L.H. Plumer, “PHREEQE – A Computer Program for Geochemical Calculations”, US Geological Survey, Water-resources Investigations 80-96 (1980).

[16] J. Azuma, M. Shibata, M. Yui, T. Shibutani, S. Notoya and Y. Yoshida, “Solubility and Speciation of Radioactive Elements of High-level Radioactive Waste Disposal System”, JNC Technical Report TN8400 99-071 (1999) (in Japanese).

[17] D. Rai, J.A. Schramke, D.A. Moore and G.L. McVay, “Americium Concentrations in Solutions Contacting Americium-doped Glass”, *Nuclear Technology*, 75 (1986).

[18] M. Yui, T. Shibutani, M. Shibat, D. Rai and M. Ochs, “A Plutonium Geochemical Database for Performance Analysis of High-level Radioactive Waste”, *Plutonium in the Environment*, Vol. 1, pp. 159-124 (2001).

[19] T. Ashida, Y. Kohara and M. Yui, “Migration Behavior of Pu Released from Pu-doped Glass in Compacted Bentonite”, *Radiochimica Acta*, 66/67, 359-362 (1994).

[20] D. Rai, J.L. Swanson and J.L. Ryan, “Solubility of $NpO_2.xH_2O$(am) in the Presence of Cu(I)/ Cu(II) Buffer”, *Radiochimica Acta*, 42, pp. 35-41 (1987).

[21] D. Rai, N.J. Hess, D.A. Moore, C.S. Oakes and M. Yui, “Thermodynamic Model for the Solubility of Thorium Dioxide in the Na^+-Cl^--OH^--H_2O System at 23°C and 90°C, *Radiochimica Acta* (2000).

[22] H. Tachikawa, H. Kitao, I. Yanagisawa, S. Kataoka, M. Shibata and M. Yui, “Solubility Measurement of Selenium Under Simulated Geological Disposal Environment”, presented at MRS’2000 (2000).

[23] D. Rai, private communication (2001).

[24] S. Kurosawa, M. Yui and H. Yoshikawa, “Experimental Study of Colloid Filtration by Compacted Bentonite”, Mat. Res. Soc. Symo. Proc., Vol. 465, pp. 963-970 (1997).

[25] D. Rai, A.R. Felmy, D.A. Moore and M.J. Mason, “The Solubility of Th(IV) and U(IV) Hydrous Oxides in Concentrated $NaHCO_3$ and Na_2CO_3 Solutions”, Mat. Res. Soc. Synp. Proc., Vol. 353, pp. 1143-1150 (1995).

[26] J.E. Cross, F.T. Ewart and C.J. Tweed, “Thermodynamic Modelling with Application to Nuclear Waste Processing and Disposal”, AERE-R 12324 (1987).

[27] S. Shibutani, "Solubility Measurement of Trivalent Lanthanide for Performance Assessment", PNC Technical Review No. 97, pp. 67-75 (1996) (in Japanese).

[28] S. Shibutani, "Development of Thermodynamic Database of Ni for Performance Assessment of Geological Disposal System of High-level Radioactive Waste", PNC Technical Report PNC TN8410 96-257 (1996) (in Japanese).

[29] T. Shibutani and S. Shibutani, "Database Development of Chemical Thermodynamics of Protactinium for Performance Assessment of HLW Geological Disposal System", PNC Technical Report PNC TN8410 98-052 (1998).

[30] D. Rai, L. Rao, H.T. Wegner, A.R. Felmy, G.R. Choppin and M. Yui, "Thermodynamic Data for Predicting Concentrations of Pu(III), Am(III) and Cm(III) in Geologic Environments", JNC Technical Report JNC TN8400 99-009 (1999).

[31] D. Rai, L. Rao, H.T. Wegner, A.R. Felmy, G.R. Choppin and M. Yui, "Thermodynamic Data for Predicting Concentrations of Th(IV), U(IV), Np(IV) and Pu(IV) in Geologic Environments", JNC Technical Report JNC TN8400 99-010 (1999).

[32] D. Rai, R.J. Serne and D.A. Moore, "Solubility of Plutonium Compounds and Their Behavior in Soils", *Soil Sci. Soc. Am. J.*, 44(3), pp. 490-495 (1980).

[33] G.R. Choppin, M. Brounikowski, J. Chen, J. Byegard, D. Rai and M. Yui, "Thermodynamic Data for Predicting Concentrations of AnO_2^+ and AnO_2^{2+} Species in Geologic Environments", JNC Technical Report JNC TN8400 99-012 (1999).

DISCUSSION

The following general discussion was held after the presentations in the first half of Session III.

I. Grenthe advanced an argument concerning the use of conservative or realistic solubility values. He said that it is not advisable to use conservative values and he referred to the Th example presented by T. Fanghänel. He particularly commented that, unless the process occurring in your system is understood, the conservative value must not be used.

H. Wanner answered that this issue, conservative vs. realistic, has arisen many times before and that he agreed with J. Bruno regarding the use of realistic values but that it is of the utmost importance to assess the uncertainties associated with the realistic values used. In fact, he affirmed, the assessment of the uncertainties is one of the more difficult aspects of performance assessment.

M. Askarieh said that the problem of the quantification of the uncertainties can only be saved by using conservative values. Therefore conservative becomes pragmatic. There are so many sources of uncertainty, such as the data, the model construction, the definition of the scenarios, etc., that it is more operative to use conservative values than to try to assess the uncertainty associated with every data, every model, every scenario.

I. Grenthe remarked that a justification is needed in order to predict with conservative values.

J. Bruno commented on the use of solid-solution approaches in performance assessment. He said that ten years ago none of the performance assessment approaches would have used solid solutions because they were assumed to be non-conservative. Scientists, on the other hand, determined that it is too difficult to quantify solid solutions in our field, and he referred to T. Fanghänel for comments.

At this point *T. Fanghänel* said that he did not mean to imply that it was too difficult to apply solid-solution models, but that to use ideal mixing models resulted in too-low solubility values. He pointed out that real solid-solution models should be used to describe these types of systems, an extremely difficult task to accomplish given the lack of data.

J. Bruno argued that there is certainly a lack of values for the parameters needed to describe this type of interaction by using real mixing models, but that the possibility exists of going a step forward by looking at natural systems. He stated that in none of the natural systems studied did the real solid-solution models produce better predictions that the ideal solid-solution models. Therefore, it seems that the use of ideal mixing is perhaps not the solution, but it does contribute toward solving the problem and that we should not be put off by the problem before encountering it.

D. Kulik pointed out that when dealing with solid solutions we should differentiate between the solids formed by mixing two metals at similar molar fractions from those where one of the metals is present at trace levels. In this latter case, the use of ideal mixing models is reasonable. Moreover, the error when using ideal mixing decreases as the molar fraction of the trace decreases, and in our systems the molar fraction of the radioelements is expected to be very low.

H. Wanner pointed out that one of the issues of concern is how the TDB projects, such as NEA TDB, can help solve the solid-solutions problem.

J. Alonso said that the point made by J. Bruno concerning the neglect of the use of solid-solution models in performance assessment due to the lack of conservatism is not a good argument. Performance assessment is sometimes biased by conservatism but what is really important is uncertainty.

B. Schwyn argued that there is a very good tool in performance assessment to deal with this type of problem: sensitivity analysis. By using sensitivity analysis one can see how useful an approach is and whether it is needed or not. One can also determine whether in that particular case there is a need for additional research on solid-solution models.

G. Ouzounian supported J. Alonso's comments concerning the performance assessment approach and welcomed the global geochemical approach in J. Bruno's presentation. He found it interesting to analyse all the issues arising in performance assessment: canister, bentonite, waste and environment, and not to focus only on the explanation of a given experiment performed in the laboratory. He summarised by saying that the most important thing is the definition of a given environment and the understanding of the main parameters that control the behaviour of the radionuclides in that environment. In this sense, TDB can help in the analyses of this environment.

C. Tweed answered the question posed by H. Wanner regarding the implication of the NEA TDB project in assisting the solid-solution models. She said that NEA TDB should provide data needed to highlight the formation of solid solutions but that at this point the thermochemical databases such as NEA TDB probably end their job. This is due to the fact that disposal scenario issues are country-dependent and therefore databases such as NEA TDB must assist all possible scenarios, but that it is not their job to define such scenarios. What is very important for a given waste concept can be of no interest for another.

K. Guerman pointed out that while the influence of T on the solubility of radionuclides had been assessed, no one has commented on the effect of the radiation dose. It has been observed that it has an influence on the solubility of Tc, for example.

R. Ewing commented that it is difficult in performance assessment to decide what is conservative because the assumption of a conservative value for a given parameter does not ensure that the results of the simulations conducted by using that value are going to be conservative. In performance assessment, he said, sensitivity analyses are more dependent on the assumptions than on the data used. Therefore, it is important to realise that the uncertainty associated with the assumption is larger than the uncertainty associated with the data and that the choice of the boundary conditions is extremely relevant. He pointed out that one of the problems is that performance assessment uses a different language and that we should work together in approaching both views of the problem. It could be very helpful to receive information from those carrying out performance assessment on how they conduct their analyses in order to increase mutual understanding.

M. Askarieh said that performance assessment is not predicting but rather estimating limits for the consequences, impacts, etc. An important aspect that has not been commented on is the time dependency of the phenomena.

I. Grenthe saw a contradiction between increasingly understanding the phenomena and using conservative approaches that seem to use reduced knowledge.

J. Bruno expressed his opinion that performance assessment is not understanding but predicting and that the important aspect in performance assessment is to know what the consequences of a given scenario will be. Therefore there are two requirements to fulfil: 1) peer review, in the sense that you have to convince your peers that you are understanding the processes underlying your predictions; therefore you must use "hard" data in your models, and to adequately convince the peer reviewers it is very helpful to compare results with evidences from natural systems and 2) regulation, in the sense that the exercises need to be correct for the regulators to ultimately approve them.

J. Alonso said that conservatism must not be taken as an excuse to stop research but that sometimes it is the only way to approach the right solution for performance assessment. He also agreed with M. Askarieh regarding the fact that performance assessment is not prediction.

To finish the session, *H. Wanner* thanked the speakers for their contributions and asked them to give their view on how the NEA TDB project should continue.

D. Kulik summarised by saying that the important thing is to increase confidence and that the only way to decrease uncertainty is a proper scientific understanding.

U. Berner said that NEA TDB should help those using the data in two ways: 1) by determining important solids and 2) by determining the important parameters.

J. Bruno proposed the continuation of NEA TDB as well as the organisation of a workshop or the edition a publication dealing with the subject of how to bridge the gap between the compilations and the use of data contained therein.

M. Yui said that performance assessment is essentially "assessment", assessment is supported by prediction, prediction depends on understanding and understanding must be based on data. Some work could be done on other waste forms such as vitrified waste and not only on spent fuel.

How Does Performance Assessment Use the Data?

Chair: C. Palmer

THE DETERMINISTIC APPROACH

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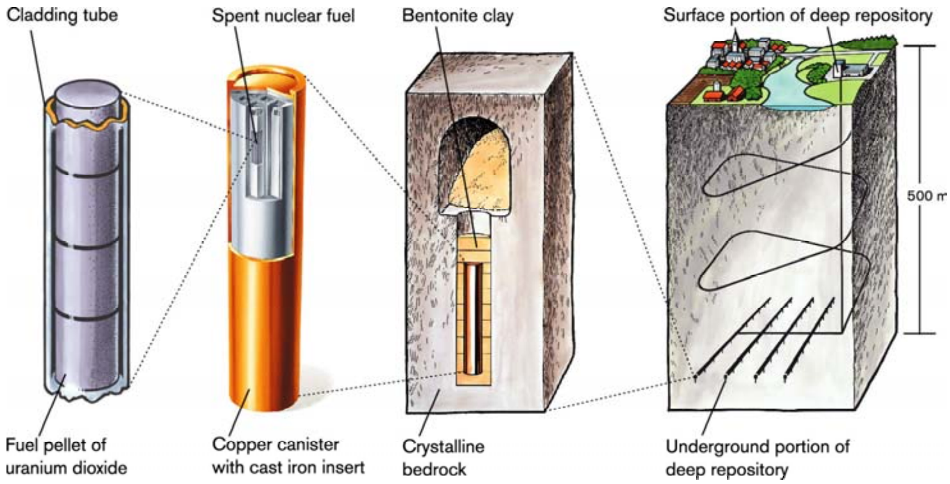
Abstract

This paper describes how solubility limits were used in the SR 97 safety assessment. In the canister defect scenario, some waste canisters are assumed to have initial penetrating defects. Water from the surrounding rock may come into contact with the spent fuel and radionuclides may be released. Solubility is an important mechanism which may reduce the transport of radionuclides from the canister. In SR 97 solubility limits were calculated for three different groundwaters as well as for an assumed bentonite porewater. Variation studies were done for the major parameters (pH, Eh and alkalinity). One realistic and one pessimistic solubility were selected for each radioelement. Total dose calculations show that variations in solubility limits have no impact on the overall dose. However, variations in solubility limits do have an impact on the release of the individual radionuclides, especially those that are long-lived.

Introduction

In preparation for upcoming site investigations for the location of a deep repository for spent nuclear fuel, SKB has carried out the long-term safety assessment (SR 97) [1] of a repository of the KBS-3 type. The KBS-3 repository for spent nuclear fuel is designed primarily to isolate the waste. If the isolation should for any reason be breached, a secondary purpose of the repository is to retard the release of radionuclides. This objective is achieved with a system of barriers (see Figure 1).

Figure 1. KBS-3 repository



The fuel is placed in corrosion-resistant copper canisters. Inside the five-metre-long canisters is a cast iron insert that provides the necessary mechanical strength.

The canisters are surrounded by a layer of compacted bentonite clay. The bentonite protects the canister mechanically in the event of small rock movements and prevents groundwater and corrosive substances from reaching the canister.

The canisters with surrounding bentonite clay are placed at a depth of about 500 metres in the crystalline bedrock, where mechanical and chemical conditions are stable from a long-term perspective.

If any canister should be damaged, the chemical properties of the fuel and the radioactive species (for example their poor solubility in water) put severe limitations on the transport of radionuclides from the repository to the ground surface.

The repository is thus built up of several barriers which support and complement each other. The safety of the repository must be adequate even if one barrier becomes defective or fails to perform as intended. This is the essence of the multiple-barrier concept.

In the SR 97 safety assessment the future evolution of the repository system is analysed in the form of five scenarios. The first is a base scenario where the repository is postulated to be built entirely according to specifications and where present-day conditions in the surroundings, including climate, persist. The four other scenarios show the evolution if the repository contains a few initially defective canisters, in the event of climate change, in the event of earthquakes and in the event of future inadvertent human intrusion.

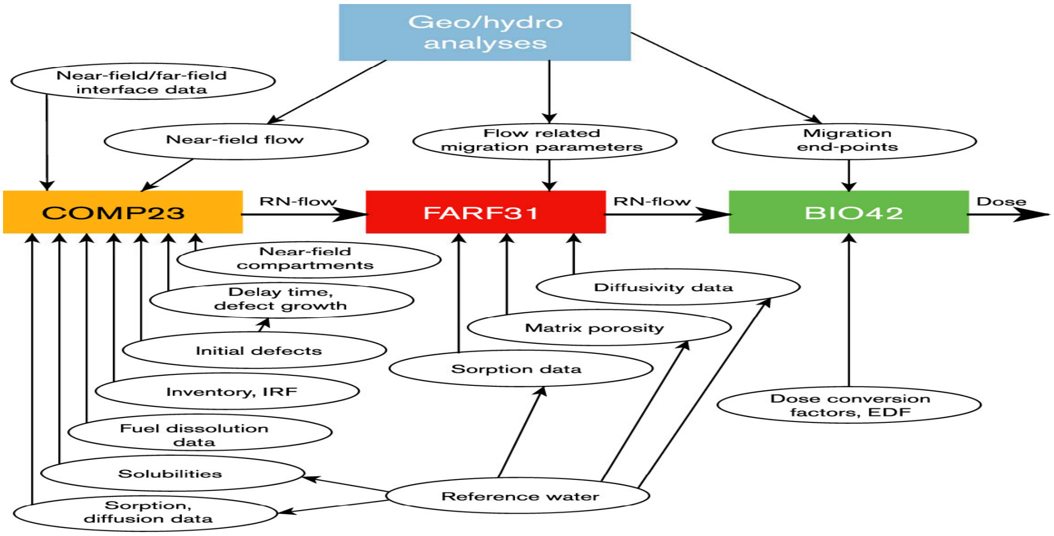
Only the canister-defect scenario is discussed in this paper.

Canister-defect scenario

In the canister defect scenario, a few canisters are postulated to have initial defects in the copper shell. Otherwise, as for the base scenario, the repository is assumed to be designed according to specifications, and present-day conditions in the surroundings are assumed to persist. The evolution in and around the majority of canisters, which are assumed to be undamaged, is thereby expected to be the same as for the base scenario and is therefore not dealt with in the canister-defect scenario. Instead, all relevant aspects of the evolution of the damaged canisters are dealt with in detail, along with radionuclide migration from damaged canisters in the buffer/backfill, geosphere and biosphere.

Once water comes into contact with the waste form the spent fuel may be dissolved/altered and radionuclides may be released. The radionuclide release from the repository is calculated with a series of connected models (Figure 2). For most of the data going into the models one realistic and pessimistic value were selected [2]. The pessimistic values were used to evaluate the system sensitivity.

Figure 2. SR 97 – model chain



Solubility calculations

In SR 97, data from three real sites were used. These were Aberg (Äspö), Beberg (Finnsjön) and Ceberg (Gideå). The groundwater at Aberg is fairly high in chloride and low in carbonate, Beberg water is high in carbonate, while Ceberg water is low in both chloride and carbonate, but with a rather high pH (9.3). Along with these waters, solubility calculations were done for an assumed bentonite porewater, which is high in carbonate and pH.

The solubility calculations were done with the EQ3NR-code using the NAGRA TDB [3,4] with some additions and modifications. Solubilities of all relevant radionuclides were calculated for all reference waters. The dependence on the major parameters (pH, Eh, alkalinity and temperature) was investigated by changing these parameters one at the time. One realistic and one pessimistic solubility were calculated for each radioelement. The realistic value was taken as the highest of the site-specific water and the bentonite porewater for each site, while the pessimistic value was taken as the highest calculated solubility from all the cases. The calculated solubilities can be found in Table 1. Details about the calculations can be found in [5].

Table 1. Calculated soubilities

Element	Aberg	Beberg	Ceberg	Bentonite	Range	Pessimistic
pH	7.70	7.90	9.30	9.21	Aberg uncertainties	Maximum value
pe	-5.21	-4.23	-3.41	-6.51		
Ni	$5.15\cdot10^{-6}$	$9.73\cdot10^{-6}$	$2.07\cdot10^{-8}$	high	$1\cdot10^{-5}$-$1\cdot10^{-1}$	High
Se	$7.34\cdot10^{-10}$	$3.52\cdot10^{-11}$	$9.80\cdot10^{-12}$	$2.59\cdot10^{-9}$	$4\cdot10^{-11}$-$4\cdot10^{-9}$	High
Sr	$6.88\cdot10^{-3}$	$3.09\cdot10^{-3}$	$3.05\cdot10^{-5}$	$1.21\cdot10^{-4}$	$6\cdot10^{-7}$-$4\cdot10^{-2}$	$4\cdot10^{-2}$
Zr	$2.48\cdot10^{-9}$	$2.51\cdot10^{-9}$	$2.51\cdot10^{-9}$	$2.50\cdot10^{-9}$	$2\cdot10^{-9}$-$3\cdot10^{-9}$	$3\cdot10^{-9}$
Nb	$6.08\cdot10^{-5}$	$7.44\cdot10^{-5}$	$1.39\cdot10^{-3}$	$1.37\cdot10^{-3}$	$2\cdot10^{-5}$-$4\cdot10^{-2}$	$4\cdot10^{-2}$
Tc	$7.14\cdot10^{-9}$	$7.92\cdot10^{-9}$	$7.27\cdot10^{-9}$	$7.67\cdot10^{-9}$	$4\cdot10^{-9}$-$5\cdot10^{-8}$	$5\cdot10^{-8}$
Pd	$4.21\cdot10^{-9}$	$4.17\cdot10^{-9}$	$4.18\cdot10^{-9}$	$4.17\cdot10^{-9}$	$4\cdot10^{-9}$-$8\cdot10^{-9}$	$8\cdot10^{-9}$
Ag	$2.96\cdot10^{-5}$	$9.39\cdot10^{-7}$	$7.12\cdot10^{-7}$	$4.64\cdot10^{-20}$	$3\cdot10^{-5}$-$3\cdot10^{-5}$	$3\cdot10^{-5}$
Sn	$5.52\cdot10^{-10}$	$6.03\cdot10^{-10}$	$4.68\cdot10^{-9}$	$4.49\cdot10^{-9}$	$1\cdot10^{-10}$-$1\cdot10^{-5}$	$1\cdot10^{-5}$
Sm	$2.13\cdot10^{-6}$	$2.69\cdot10^{-7}$	$2.91\cdot10^{-7}$	$8.03\cdot10^{-7}$	$3\cdot10^{-7}$-$2\cdot10^{-5}$	$2\cdot10^{-5}$
Ho	$6.27\cdot10^{-6}$	$1.52\cdot10^{-6}$	$1.97\cdot10^{-6}$	$5.58\cdot10^{-6}$	$2\cdot10^{-6}$-$6\cdot10^{-5}$	$6\cdot10^{-5}$
Ra	$2.86\cdot10^{-7}$	$5.02\cdot10^{-7}$	$1.20\cdot10^{-4}$	$4.57\cdot10^{-8}$	$2\cdot10^{-7}$-$2\cdot10^{-6}$	$2\cdot10^{-4}$
Th	$2.40\cdot10^{-10}$	$1.17\cdot10^{-9}$	$2.40\cdot10^{-10}$	$1.22\cdot10^{-9}$	$2\cdot10^{-10}$-$5\cdot10^{-10}$	$2\cdot10^{-9}$
Pa	$3.16\cdot10^{-7}$	$3.16\cdot10^{-7}$	$3.16\cdot10^{-7}$	$3.16\cdot10^{-7}$	$3\cdot10^{-7}$-$3\cdot10^{-7}$	$4\cdot10^{-7}$
U	$1.27\cdot10^{-7}$	$1.29\cdot10^{-7}$	$1.29\cdot10^{-7}$	$1.28\cdot10^{-7}$	$2\cdot10^{-8}$-$2\cdot10^{-7}$	$2\cdot10^{-7}$
Np	$7.00\cdot10^{-9}$	$1.05\cdot10^{-7}$	$8.39\cdot10^{-9}$	$5.87\cdot10^{-8}$	$5\cdot10^{-9}$-$6\cdot10^{-8}$	$2\cdot10^{-7}$
Pu	$6.56\cdot10^{-9}$	$5.35\cdot10^{-10}$	$1.03\cdot10^{-10}$	$1.38\cdot10^{-10}$	$1\cdot10^{-10}$-$3\cdot10^{-6}$	$3\cdot10^{-6}$
Am	$6.87\cdot10^{-7}$	$9.36\cdot10^{-8}$	$4.89\cdot10^{-8}$	$9.34\cdot10^{-8}$	$1\cdot10^{-7}$-$7\cdot10^{-6}$	$7\cdot10^{-6}$
Cm	$2.22\cdot10^{-7}$	$2.02\cdot10^{-9}$	$9.01\cdot10^{-10}$	$1.66\cdot10^{-10}$	$1\cdot10^{-11}$-$2\cdot10^{-6}$	$2\cdot10^{-6}$

Importance of uncertainties

The importance of uncertainties in parameters was studied by keeping all parameters at their best-estimate value and changing them to the pessimistic value one by one, while the maximum dose from the repository was calculated. Figure 3 shows the result of this for all the parameter groups in the assessment.

This shows that uncertainties in solubilities have no impact whatsoever on the maximum dose in the assessment. This is not surprising, since radionuclides without solubility limits (*i.e.* ^{129}I) are the main dose contributors. Does this mean that we do not have to care about solubilities in performance assessment? No, since the reason why radionuclides with high solubilities always dominates the dose, is that solubility limits are a very effective and very reliable barrier.

The importance of solubilities for the maximum dose from the individual radionuclides was also calculated. Both from a case where all parameters were kept at their realistic values and the solubilties were increased to their pessimistic values as well as from a case with all parameters at their pessimistic values where the solubilties were decreased to their realistic values. The results from these calculations can be found in Table 2 and 3. Dose P/B is the relation between maximum dose for the case with the pessimistic solubility and the dose from the case with all parameters at their best estimate values. Dose B/P is the relation between maximum dose for the case with the best estimate solubility and the dose from the case with all parameters at their pessimistic values. Sol. B/P and P/B are the relations between

Figure 3. Importance of uncertainties in the overall assessment

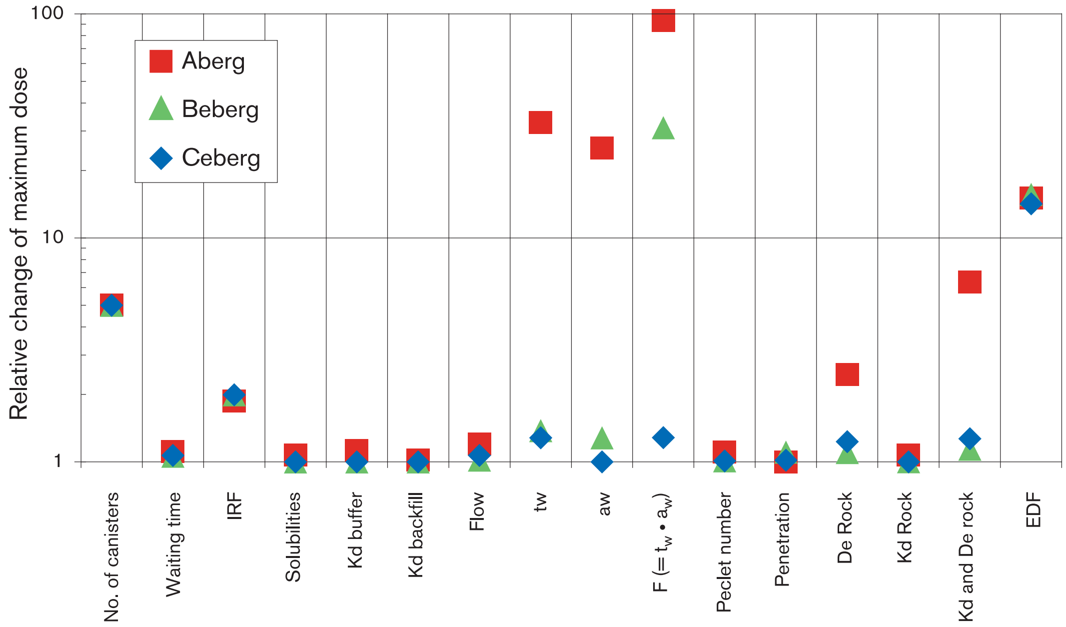


Table 2. Relation between maximum dose from individual radionuclides for a case with pessimistic solubilities and a case with all parameters at best-estimate values

	^{242}Pu	^{238}U	^{234}U	^{230}Th	^{226}Ra	^{245}Cm	^{241}Am	^{237}Np	^{233}U
Dose P/B	1.4	1.6	1.6	1.6	1.2	1	1	1	1
Sol. P/B	460	1.6	1.6	8.3	700	9	10	29	1.57
	^{229}Th	^{243}Am	^{239}Pu	^{235}U	^{231}Pa	^{108m}Ag	^{166m}Ho	^{94}Nb	^{59}Ni
Dose P/B	1	1	1	1	1	1	1	1	1
Sol. P/B	8.3	10	460	1.6	1.3	1	10	660	High
	^{63}Ni	^{107}Pd	^{240}Pu	^{79}Se	^{151}Sm	^{126}Sn	^{90}Sr	^{99}Tc	^{93}Zr
Dose P/B	1	1.9	1	1.2	1	5.5	1	2.7	1.2
Sol. P/B	High	1.9	460	High	9.4	18 000	5.8	7	1.2

Table 3. Relation between maximum dose from individual radionuclides for a case with best-estimate solubilities and a case with all parameters at pessimistic values

	^{242}Pu	^{238}U	^{234}U	^{230}Th	^{226}Ra	^{245}Cm	^{241}Am	^{237}Np	^{233}U
Dose B/P	0.4	0.6	0.6	0.6	1	1	1	0.96	1
Sol. B/P	0.002	0.6	0.6	0.1	0.0014	0.1	0.1	0.035	0.6
	^{229}Th	^{243}Am	^{239}Pu	^{235}U	^{231}Pa	^{108m}Ag	^{166m}Ho	^{94}Nb	^{59}Ni
Dose B/P	0.8	1	0.04	0.1!	1	1	1	0.6	0.6
Sol. B/P	0.12	0.1	0.002	0.6	0.8	1	0.1	0.0015	Low
	^{63}Ni	^{107}Pd	^{240}Pu	^{79}Se	^{151}Sm	^{126}Sn	^{90}Sr	^{99}Tc	^{93}Zr
Dose B/P	1	0.5	0.3	0.64	1	0.003	1	0.15	0.8
Sol. B/P	Low	0.5	0.002	Low	0.1	5e-5	0.2	0.14	0.8

the solubility values. The results show a linear dependence between dose and solubility for very long-lived radionuclides. Radionuclides with a half-life shorter than 10 000 years are generally not affected by variations in solubility. Solubility may have an effect on the release of radionuclides with a half-life in the range of 10 000-100 000 years.

Conclusion

The results from this study are strongly dependent on the KBS-3 geometry and the characteristics of the investigated sites. However, it still gives some advice where future efforts should be focused. Short-lived (<10 000 years) nuclides are generally not affected by solubility. Very long-lived ones are generally not a safety problem. Therefore, high quality databases are most needed for radionuclides with half-lives in the range of 10 000-100 000 years. ^{239}Pu, ^{99}Tc and ^{126}Sn are nuclides which can be of potential importance in performance assessment. The release of those nuclides may be affected by solubility, especially if there is a failure in any of the other barriers.

REFERENCE

[1] "Deep Repository for Spent Nuclear Fuel. SR 97 – Post-closure safety", Main report, Vol. I, Vol. II and Summary, SKB Technical Report TR-99-06 (1999).

[2] J. Andersson, "Data and Data Uncertainties. Compilation of Data and Data Uncertainties for Radionuclide Transport Calculations", SKB Technical Report TR-99-09 (1999).

[3] F.J. Pearson, Jr., U. Berner, "NAGRA Thermochemical Data Base I. Core Data", Technical Report 91-17 (1991).

[4] F.J. Pearson, Jr., U. Berner, W. Hummel, "Nagra Thermochemical Data Base II. Supplemental Data 05/92", Technical Report 91-18 (1992).

[5] J. Bruno, E. Cera, J. de Pablo, L. Duro, S. Jordana, D. Savage, "Determination of Radionuclide Solubility Limits to be Used in SR 97. Uncertainties Associated to Calculated Solubilities", SKB Technical Report TR 97-33 (1997).

THE PROBABILISTIC APPROACH

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This paper was presented orally, but was unfortunately not available at the time of publication.

DATA COLLECTION FORM: THE LINK BETWEEN MIGRATION STUDIES AND PERFORMANCE ASSESSMENT – BELGIAN CASE

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Abstract

The thermochemical databases of the NEA (TDB) are used in support of the determination of solubility values for performance assessment (PA). PA uses solubility to define the concentration limit at which radionuclides migrate from the near-field to the far-field of the repository. Being different from a thermodynamically defined solubility, a concentration limit can be equal to the solubility of pure phases but can also be imposed by other processes, *e.g.* formation of colloids or solid solutions. This paper illustrates a way that the TDB is utilised to interpret some migration experiments through geochemical and solute transport modelling. As a result, some meaningful migration parameters are derived based on both experimental observations and the application of the TDB.

Introduction

In Belgium, boom clay is being studied as a candidate host rock for radioactive waste disposal. To assess the safety, PA calculations are performed with input parameters representing the relevant geological, hydrogeological, physical and chemical processes that likely occur in the repository and the geological surroundings when the radionuclides will be released from the waste packages. The result of PA is therefore heavily dependent on input parameters. To assure the traceability of the parameter derivation, the input parameters are compiled in data collection forms (DCF) [1] following a working instruction within the SCK•CEN's quality assurance system. The DCF are the result of a discussion between the researchers, so-called experts, who perform experiments and calculations to derive the parameters and the performance assessors who use the parameters to carry out the PA calculations.

PA determines which parameters are needed based on the relevant migration processes that might occur under repository conditions. In boom clay, the migration of radionuclides is mainly controlled by molecular diffusion because of the plasticity and the very low hydraulic conductivity of the clay formation [2]. Therefore PA requires parameters that describe a diffusive transport of radionuclides in clay, namely, pore diffusion coefficient (D_p), diffusion accessible porosity (η) and retardation factor (R). PA also needs the concentration at which radionuclides diffuse into the clay, *i.e.* the source term, which in a lot of cases can be solubility limited. The geochemistry of boom clay is in favour of chemical reduction, hydrolysis reaction and precipitation of radionuclides because of a slightly alkaline pH and a reducing redox potential [3]. The solubility of radionuclides under boom clay conditions is therefore an important parameter.

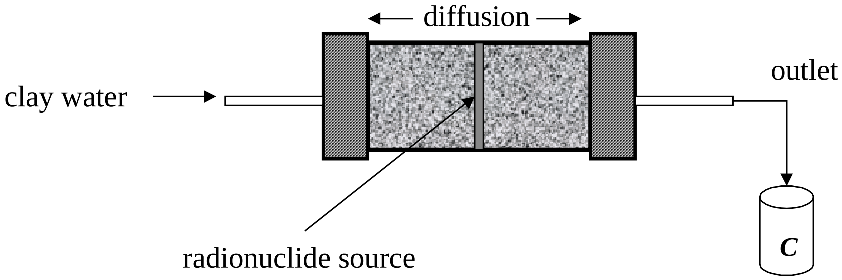
The general procedure for deriving solubility values involves literature survey, experimental measurements and geochemical calculations. As a result, a set of solubility values is collected for each radionuclide. Since PA needs a single value for solubility, an appropriate probability density function (PDF) is thus assigned to the data set and a best-estimate value is obtained. For those radionuclides whose TDB are available, we use TDB as one of the data sources to calculate solubility using a geochemical computer code.

Although the TDB provide high-quality data for solubility calculations, it is problematic to apply the results of solubility calculations directly into PA. The main problem is that the pure solubility controlling phases predicted using the TDB might not form under *in situ* geochemical conditions and in a time scale of interest. Even if the pure phases do form, we still have little guidance in deciding which phase is relevant under the geochemical conditions considered. Migration experiments at this point can provide complementary information to the solubility calculations and eventually support the selection of solubility values. This paper shows some results where the TDB is applied in conjunction with migration experiments to derive meaningful solubility values for PA.

Migration experiments

The experimental set-up is shown in Figure 1. A clay core of 7 cm made of two 3.5 cm plugs is confined in a stainless steel cell between two porous filter plates. A few microlitres of concentrated radionuclide solution are spiked on a filter paper that is then sandwiched between the two plugs. From one end of the cell, a constant flow of boom clay pore water is percolated through the core, and the liquid samples are collected periodically at the outlet of the cell for concentration measurement. The system is sealed and is considered to be anaerobic.

Figure 1. Percolation experiment with an impulse radionuclide source. The hydraulic pressure difference ΔP is in a range of 0.7 to 1 MPa; the dimension of the clay core is $\varnothing 3.8 \times 7$ cm.



Solubility calculations

The TDB are used to calculate the solubility of five radionuclides, *i.e.* uranium, americium, technetium, neptunium and plutonium under the geochemical conditions prevailing in boom clay. The geochemical computer code used is The Geochemist's Workbench® (GWB) [4]. The data of Gibbs free energy of formation are downloaded from the NEA TDB web site and converted to formation constants in the GWB database format. The database conversion and process are conducted using NEA2GWB, a software developed in-house. The current version of NEA2GWB uses Davies equation for ionic strength corrections.

The pore water composition used for the solubility calculations is given in Dierckx [3]. The pore water is of the sodium bicarbonate type ($NaHCO_3$ about 0.015 molal) with a CO_2 partial pressure of $10^{-2.42}$ atm at an *in situ* temperature of 16°C. Since the solubility calculations are performed for a temperature of 25°C, we used a higher p_{CO_2} of $10^{-2.31}$ atm so that the total bicarbonate concentration reaches 0.015 molal as measured in the real pore water. The redox potential applied is -275 mV (E_h) which corresponds to the potential imposed by pyrite oxidation at pH of 8.2. The *in situ* redox measurements in boom clay have been quite elusive but generally gave a value lower than -300 mV.

The solubility calculations were conducted for a dissolution process by equilibrating solubility controlling phases with the pore water at the saturation index (SI) = 0. In a chemical equilibrium calculation, once a radionuclide is supersaturated in terms of several minerals, the most stable mineral with the greatest SI would precipitate [5]. However, this mineral does not necessarily form in reality because it may not have the time to nucleate and grow. To scope all the possible radionuclide-containing minerals that might precipitate, we performed a separate calculation to search for all the phases having a SI greater than 0 if a sufficient amount of radionuclides are present. At the stage of solubility calculations, we are not able to decide which phase will impose the solubility. We therefore calculate solubility values for all phases that could be supersaturated under the geochemical conditions considered. The detailed procedure for calculations and the results are given in Wang, *et al.* [6].

Transport modelling

Radionuclide transport as measured in the experimental set-up (Figure 1) can be described by an advection-diffusion equation:

$$\frac{\partial C}{\partial t} = D_{app}\frac{\partial^2 C}{\partial x^2} - V_{app}\frac{\partial C}{\partial x}$$

with:

C: the concentration of radioisotope in the liquid
t: time of the percolation
x: the distance from the source
D_{app}: apparent diffusion coefficient
V_{app}: apparent velocity

The apparent diffusion coefficient (D_{app}) and the apparent velocity (V_{app}) are calculated according to the equations:

$$D_{app} = \frac{D_p}{R} \text{ and } V_{app} = \frac{V_D}{\eta R}$$

where D_p is the pore diffusion coefficient taken as 2×10^{-10} m^2·s^{-1} for all radionuclides and V_D the Darcy velocity which is related to the hydraulic conductivity, hydraulic pressure difference and the length of the clay core.

The outlet concentration of radionuclide can be simulated with two different initial source conditions, namely, an impulse source condition and a solubility-limited source condition. The impulse source condition considers that the initial concentration of radionuclide is equal to that of the impulse source, *i.e.*:

$$C\,(x = 0, t = 0) = C_0 \qquad \text{(impulse source)}$$

where C is the concentration of the radionuclide, x the distance from the source position, t the time and C_0 the concentration of the impulse source.

The impulse source condition has proved to be adequate only for the radionuclide species with simple chemistry, *e.g.* caesium. For radionuclides with complex speciation and redox chemistry, the source condition may change drastically as soon as the source makes contact with the clay that plays as a reduction front.

To take speciation change and the precipitation of radionuclides into account, we can assume that the radionuclides are reduced, hydrolysed and precipitated at the source position from the start of the experiment. The concentration at which the radionuclides diffuse into the clay is thus limited by the solubility of the precipitated phase. The corresponding initial condition can be expressed as:

$$C\,(x = 0, t \geq 0) = S \qquad \text{(solubility limited source)}$$

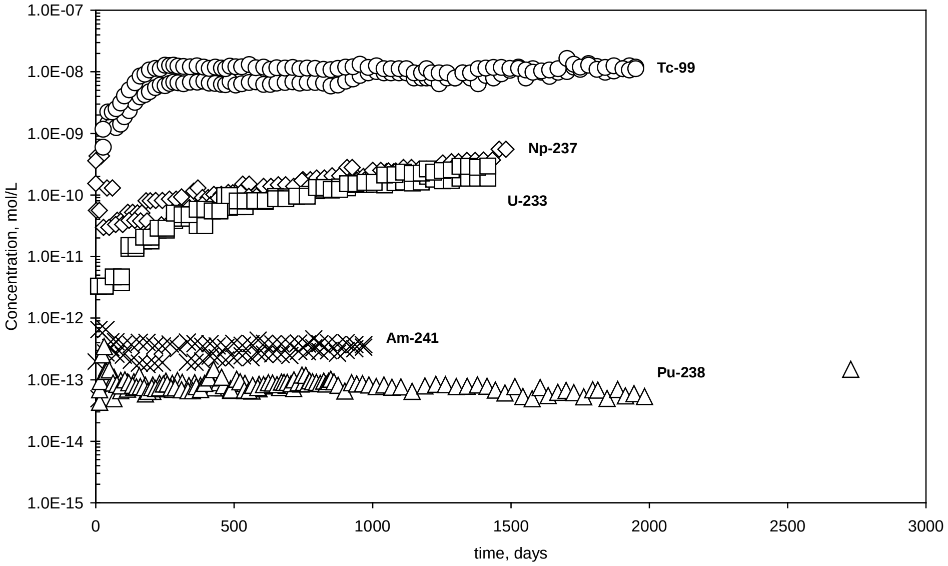
where S is the solubility of the precipitated phase.

The transport simulations using the solubility-limited source condition are performed with the numerical code Xt [7] which is coupled with the GWB. Analytical solutions for the transport equation with the appropriate boundary conditions of the experiments are also available [8]. The results of the numerical simulations and the analytical solutions of the problem are comparable.

Results and discussions

Results from solubility calculations using the TDB are summarised in Table 1. More than one radionuclide-containing mineral can be supersaturated in the pore water of boom clay if the radionuclide concentration is high enough. As already discussed, the results obtained here are useless for PA if we cannot figure out which mineral will impose the solubility of the concerned radionuclide. In addition, the standard data collection procedure is not applicable to the results of Table 1 since no PDF can be assigned. We thus turn to the migration experiments for additional information to support the selection of solubility values. Figure 2 presents the outlet concentration profiles of five radioisotopes as a function of time.

Figure 2. Concentrations of radioisotopes (^{99}Tc, ^{233}U, ^{237}Np, ^{238}Pu and ^{241}Am) at the outlet of the percolation cells



Concentration of percolated radioisotopes is in general low and reaches somewhat of a plateau as a function of time. Mass balance calculations for these experiments showed that all five injected radioisotopes are quantitatively retained by the clay, *i.e.* there is no impulse like breakthrough of the isotopes within 3 to 10 years of experimental time. This fact also demonstrates that the impulse initial condition does not apply to the data shown in Figure 2.

Since the radioisotopes are apparently retained but retardation is smaller or non-existent. We applied the solubility-limited source as the initial condition for the transport simulations. Figures 3 to 5 show the results of the simulation for ^{233}U, ^{99}Tc and ^{237}Np. The general strategy of the simulation is to fit the plateau value of concentration as the solubility of the radionuclides while changing the retardation factor. Other parameters remain constant.

The two uranium data sets (Figure 3) fall in a range of retardation factor of 60 to 100 if a solubility value of 5×10^{-10} M was used. This fitted solubility value happens to be in good agreement with the solubility of UO_2(c) given in Table 1. We therefore concluded that the solubility-controlling phase for uranium under boom clay conditions might be the uraninite mineral. Other minerals with higher solubility values listed in Table 1 do not likely form. The migration of uranium in boom clay can thus be characterised as a combined process involving a solubility-limited source term and a moderate sorption.

Table 1. Solubility of U, Am, Tc, Np and Pu (mol/L) in boom clay water at pH 8.2 and E_h -275 mV

Database: NEA TDB (downloaded form the NEA website)

U		**Am**		**Tc**		**Np**		**Pu**[§]	
UO_2	$4\ 10^{-10}$	$AmOHCO_3$	$1\ 10^{-7}$	TcO_2	$4\ 10^{-13}$	NpO_2	$3\ 10^{-20}$	PuO_2	$1\ 10^{-17}$
$USiO_4$	$1\ 10^{-9}$	$Am_2(CO_3)_3$	$7\ 10^{-7}$	Tc	$1\ 10^{-11}$	NpO_2(am)	$5\ 10^{-9}$	$PuPO_4$	$9\ 10^{-15}$
$UO_{2.25}$	$5\ 10^{-8}$	$Am(OH)_3$	$1\ 10^{-5}$	TcO_2:1.6H_2O	$4\ 10^{-9}$			PuO_2 (am)	$1\ 10^{-11}$
$UO_{2.25}(\beta)$	$5\ 10^{-8}$	$Am(OH)_3$(am)	$7\ 10^{-4}$					$Pu(OH)_3$	$6\ 10^{-8}$
$UO_{2.3333}(\beta)$	$4\ 10^{-7}$								
UO_2(am)*	$4\ 10^{-5}$								
U_3O_8	$4\ 10^{-3}$								
$UO_{2.6667}$	$4\ 10^{-3}$								

* $\Delta_f G_m^o$ = -1 003.6 kJ·mol^{-1}. The data was discussed but not selected by TDB.

[§] The results for plutonium are questionable since the $Pu(OH)_4$(aq) species was not selected in the TDB.

Figure 3. Experimental and simulated concentration profiles of ^{233}U at the outlet of the percolation cell

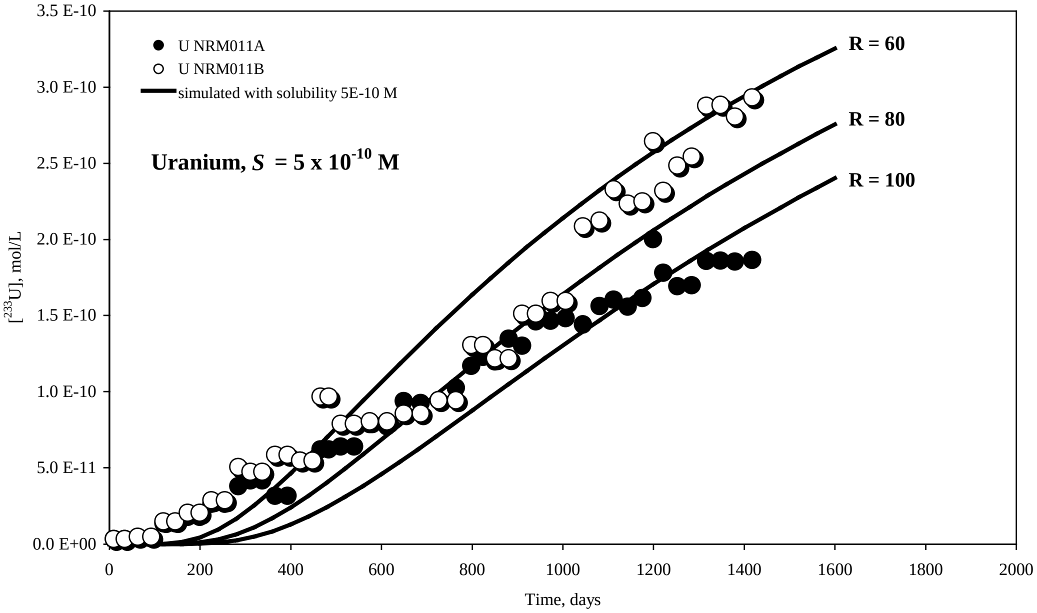


Figure 4. Experimental and simulated concentration profiles of ^{99}Tc at the outlet of the percolation cell

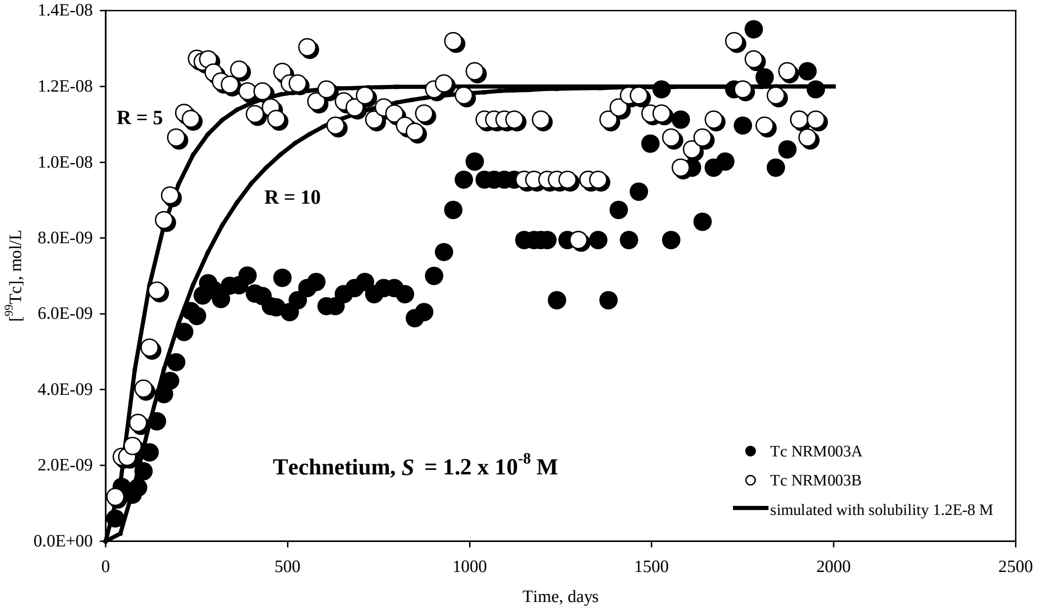
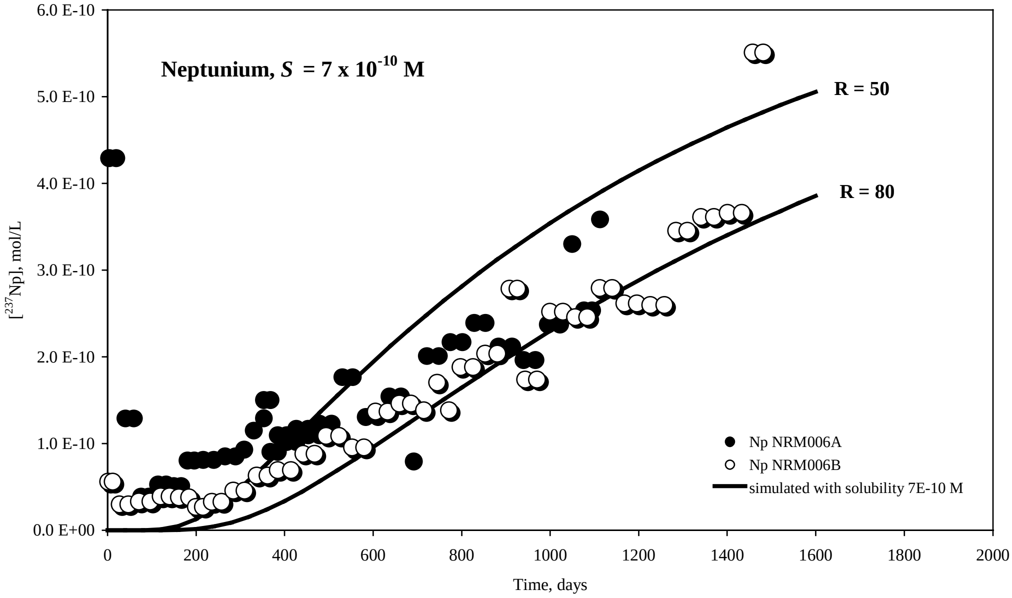


Figure 5. Experimental and simulated concentration profiles of ^{237}Np at the outlet of the percolation cell



The technetium breakthrough is much faster (Figure 4). Under the time frame of 1 000 days, the two data sets deviate from each other, but later converge towards a plateau concentration of 1.2×10^{-8} M. This value is considered as the concentration limit at the source term which is close to the solubility of $TcO_2 \cdot 1.6H_2O$ (Table 1). Although the two data sets are quite different, it can be due to some artefacts of the experiment, the slopes of the data can still be fitted well with a range of R value of 5 ~ 10. Thus the migration of technetium is about 10 times faster than uranium. The solubility-controlling phase formed during the experiment is likely a hydrated technetium oxide but not the well-crystalline TcO_2 or the metallic Tc since the latter two phases have much lower solubility values.

The case of neptunium is similar to that of uranium (Figure 5) in terms of both solubility and retardation. The fitted solubility is 7×10^{-10} M, that is, close to the solubility of the hydrated NpO_2(am) selected in the TDB.

The cases of americium and plutonium cannot, however, be addressed with the same strategy. The measured concentration limit of americium (Figure 2) is much lower than the solubility of any solid phases listed in Table 1. This is probably an indication that americium migration is controlled by other processes than solubility, *e.g.* colloid formation and/or the formation of a solid solution that may result in a very low apparent aqueous concentration of americium. The interpretation of the plutonium case is somehow hindered by the fact that the data for the species of $Pu(OH)_4$(aq) is not selected by the TDB. Since the $Pu(OH)_4$(aq) species is crucial under the reducing conditions of boom clay, we will not attempt to interpret the plutonium case until the $Pu(OH)_4$(aq) data become available.

Although the cases of americium and plutonium cannot be fully interpreted at the moment, the migration behaviour of the two elements is apparently quite similar (see Figure 2). The concentrations are extremely low (~ 10^{-13} M) and remain constant for very long time (3 to 10 years). According to these features, a concept of "operational solubility" is introduced to the data collection [1]. Operational solubility considers that americium and plutonium are present as non-retarded species in the aqueous phase, *i.e.* $R = 1$ with solubility values that are equal to the outlet concentration measured from the percolation experiments. In this way, we are able to provide PA with a workable parameter set which is derived from long-term and reproducible experiments. The mechanisms behind the operational solubility are, however, not understood.

Fitting the solubility values and the retardation factors from the migration data as described in this paper is an *ad hoc* way to extract the parameters necessary for PA. On one hand, we are not able to verify the formation of the solubility-limiting phases, and on the other the concept of the retardation factor is an oversimplified notion for describing sorption process. The initial conditions for transport simulation are only approximate, *e.g.* we assumed that the radionuclide concentration is limited by a solubility at the start of the experiment ($t = 0$), but in reality the solubility-controlling phase may only form after a certain period of time because of slow kinetics. In the beginning stage of the experiment radionuclides may diffuse into the clay at a much higher concentration than the solubility. This may explain why some data points cannot be fitted at the early stage of the experiments (see Figure 5).

Conclusions

Through the application of the TDB in geochemical and the transport modelling, we are able to postulate the retention mechanisms of the radionuclides studied in boom clay. The radionuclides are likely immobilised rather than retarded in the reducing boom clay. The solubility values as can be derived from the TDB are crucial for deriving the retardation factor of uranium, technetium and neptunium. In the case of americium, the formation of a pure solubility-controlling phase is unlikely based on the comparison between the experimental results and the TDB data. The present TDB data of plutonium does not allow a conclusive interpretation for the migration behaviour of plutonium in boom clay. Operational solubility values derived from the experiments are therefore applied to the cases of americium and plutonium.

The TDB data as applied to the selection of solubility values can only be used if a pure solubility-controlling phase is formed. It is in general difficult to verify the formation of a pure radionuclide precipitate; the application of the TDB to the migration experiments is therefore hardly mechanistic. In addition, precipitation is only one of the many immobilisation processes [9], databases of other processes are also needed, *e.g.* formation of colloids and solid solutions.

Acknowledgements

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REFERENCES

[1] J. Marivoet, G. Volckaert, S. Labat, P. De Cannière, A. Dierckx, B. Kursten, K. Lemmens, P. Lolivier, D. Mallants, A. Sneyers, E. Valcke, L. Wang and I. Wemaere, “Values for the Near Field and Clay Parameters Used in the Performance Assessment of the Geological Disposal of Radioactive Waste in the Boom Clay Formation at the Mol Site”, Volume 1, 2, SCK•CEN Report, R-3344, Mol, Belgium (1999).

[2] P. De Cannière, H. Moors, P. Lolivier, P. De Preter and M. Put, “Laboratory and *In Situ* Migration Experiments in the Boom Clay”, EUR 16927EN (1996).

[3] A. Dierckx, “Boom Clay *In Situ* Porewater Chemistry”, SCK•CEN Report, BLG-734, Mol, Belgium (1997).

[4] C.M. Bethke, “The Geochemist’s Workbench, Release 3.1, A User’s Guide to Rxn, Act2, Tact, React, and Gtplot”, Hydrogeology Program University of Illinois (2000).

[5] C.M. Bethke, “Geochemical Reaction Modeling”, Oxford University Press, New York (1996).

[6] L. Wang, A. Dierckx and P. De Cannière, “Speciation and Solubility of Radionuclides in Boom Clay: Calculations Performed with the Geochemist’s Workbench 3.1, Database LLNL’s Version 8, Release 6”, SCK•CEN Report, R-3508, Mol, Belgium (2000).

[7] C.M. Bethke, “The Xt Model of Transport in Reacting Geochemical Systems”, Reference Manual for X1t, X2t and Xtplot, Release 2.1 (2000).

[8] M. Aertsens, M. Put and L. Wang, “Modelling and Interpretation of Migration Experiments, Task 2.11”, in *Geological Disposal of Conditioned High-level and Long-lived Radioactive Waste*, progress report to NIRAS/ONDRAF for the second semester of 1998, SCK•CEN Report, R-3371, Mol, Belgium (2000).

[9] M. Heath, “Conclusions of Working Group 4: Immobilisation, Geological Evidence and Theoretical Bases for Radionuclide Retention”, Workshop proceedings, Oskarshamn, Sweden, 7-9 May 2001, OECD/NEA, Paris (2001).

DISCUSSION

J. Bruno acted as moderator of the discussion for this sub-session.

J. Alonso asked about the relevance of the consistency in thermochemical databases, given that in some cases databases from different sources are combined to perform simulations.

P. Sellin answered that SKB uses an internally consistent database for each element. However, he said that it is very difficult to guarantee the global consistency of a database and that currently there are no totally consistent databases available.

J. Bruno added on this subject that it is quite difficult to guarantee the consistency of the whole thermochemical databases and that one of the issues of concern in projects such as NEA TDB should be to provide a consistent database for all important elements and not only for radionuclides. He insisted on the relevance of ensuring the consistency of the database for major elements, although he made it clear that the consistency of a database does not ensure the quality of the data it contains.

G. Ouzounian asked the speakers whether the uncertainties associated with the calculations have emerge from the thermochemical database used or from a lack of knowledge of the system.

C. Palmer answered that in their case the major uncertainty is related to the lack of a complete mechanistic understanding of the system.

L. Wang added that solubilities only apply if dissolution is larger than the solubility limit. In their case he said that the uncertainty associated to the rate of dissolution of the vitrified waste is much larger than the solubility limit.

P. Sellin said that the uncertainty associated with the thermochemical database used is not very important given that the number of species and solid phases playing a role in the system is limited even over a wide range of geochemical conditions. In this case, the uncertainty comes mainly from a lack of knowledge concerning the evolution of the near field and from the selection of the solubility-limiting phase.

K. Spahiu wished to clarify the phrase “consistent database”. He ensured that the NEA databases are internally consistent given that no data for a given species are selected until the data for the basic components have been selected. This procedure avoids artificial errors introduced by the selection of different basic data eventually conducted by different experts.

L. Wang addressed the lack of auxiliary data for water rock interaction (WRI). Solubility calculations for radionuclides are performed at different conditions which are obtained from WRI calculations. Therefore the data set used for conducting the WRI calculation directly affects the radionuclide solubility calculations.

R. Ewing commented on the probabilistic approach. He said that the procedure of repeated sampling to obtain a probability distribution is not the right way to assess the uncertainty of the analyses. What this procedure provides is the uncertainty in the sampling.

C. Palmer added that the important thing is to justify the range of conditions that you measure in order to support your probabilistic approach.

I. Grenthe commented on the internal consistency of the databases and illustrated this with an example on how the $\Delta_f G_m^o$ of formation of different U species will change depending on the $\Delta_f G_m^o$ of formation of the uranyl ion, but that the value of $\log_{10}K$ will not change.

U. Berner pointed out the relevance of chemical and “not only mathematical” consistency. This means that we should look for analogue systems in which the species or solids suggested are present.

C. Palmer said that what YMP ensured is that the same database was used in any performance assessment calculation. For this purpose YMP integrated auxiliary data from SUPCRT with the NEA TDB database.

H. Wanner assured that the NEA TDB databases are internally consistent and encouraged every one to read the introduction of the NEA TDB books in order to have a description of how the database has been constructed and how internal consistency is ensured. If one requires data from other systems that have not been reviewed by NEA then it is left to the user to look for a set of consistent data.

L. Wang said that he did not mean to imply that the NEA TDB database was inconsistent, but rather that most of the major data he needed was not in there.

J. Bruno commented that we can not ensure that, for example, the NAGRA and the NEA TDB databases are consistent and this can be an important point. Perhaps the testing of the consistency of these databases must be done in-house but it definitely must be done somewhere.

I. Grenthe raised the issue of the compilations of data for Cu and Ni. The reviewers not only use the available chemical information, but also their chemical knowledge. Databases contain much more information than normally believed.

R. Arthur said that the question of the databases should go beyond internal consistency. We must ask how to integrate databases that are used for radioelements with those on major elements. This integration can be difficult. For example, the merging of the NEA TDB database and the EQ3/6 database is questionable due to the different standard states defined in both TDBs. The auxiliary data used for the calculation of the data in EQ3/6 are different from those used in the NEA work in some cases.

H. Wanner expressed his opinion that these differences in the fundamental values are very small in most cases. He asked what values present discrepancies and how large those discrepancies really are.

T. Fanghänel, in relation to the question raised by R. Arthur, answered that the standard states in EQ3/6 and in NEA are perfectly identical.

R. Arthur, however, said that most of the data in EQ3/6 comes from SUPCRT, where the standard state is at the pressure of interest, whereas in the NEA TDB it is at 1 bar.

At this point a discussion on the differences between the standard states began, but it had to be concluded due to time limitations.

PANEL SESSION

TDB Input in Performance Assessment

PANEL SESSION

Panel members
Moderator: Jörg Hadermann, PSI (Switzerland)
Jesús Alonso, ENRESA (Spain)
Margit Snellman, POSIVA (Finland)
Eric Giffaut, ANDRA (France)
Bill Glassley, LLNL (USA)
Cherry Tweed, Harwell IBC (UK)

J. Hadermann welcomed everybody to the special panel session. He introduced the members of the panel session. He offered each of them the floor to give a short statement that would be the catalyst for an open discussion. He structured the discussion having made a list of topics that each speaker should be addressing and asked them to focus the discussion on those topics.

(*In the following the initial contributions from the members of the Panel Session are reported verbatim*.)

J. Alonso (ENRESA)

"The main aim here is to identify the objectives of the TDB project, to have clear what are the criteria for the selection of new topics. A key point is to reach a balance between what is needed now and how we should approach the solution. A closer interaction of PA with scientific work is needed: PA must not be seen as the final state of the analyses, in a pyramidal way, but as participating in the whole pyramid structure. PA is comprehensive and extends to the full chain of data, models and, of course, uncertainties. Uncertainty analyses are fundamental in PA, as they help to build confidence on the results of the analyses. This type of analyses must not be only the responsibility of PA but of all the actors along all the process chain, starting with the scientists. PA is mainly concerned with the consequences of waste disposal. PA aims at showing that regulatory criteria are met and in this manner at providing the information needed for decision-making. This is a very long process and there is still a long way to go. PA and scientific developments do not have immediate, but rather long-term, milestones.

Another topic of interest is the dichotomy between simplicity and complexity. People responsible for PA are rather keen on simple models. I personally think that simple models are good as the final chain of the process. But this must not exclude the analyses of the complexity of the problem. The point is where to cut this complexity. Once we arrive at the understanding of the behaviour of the whole system, we will be able to build up a simple model, and modellers will be in a better position.

What is the role of complex models? In my opinion complex models must provide a very detailed explanation of how the system works. However, it is not possible to implement all the parameters of these models and we must combine information from experiments and natural systems with the application of expert judgement. So, the more general usefulness of TDB and PA is to provide a good framework for the application of expert judgement. What PA asks from TDB is data, models, even if those models depend on the position we are in the PA pyramid. But this is not enough, we need of the assessment of uncertainties derived from scenarios, systems, etc., which have not only statistical meaning. Science must provide the fundamental understanding of these processes for the sake of scientific consistence of the assessment. Conservatism is not the reality of PA, but perhaps it is the only runaway from uncertainty in bounding the consequences. This, though, must not be an excuse for the relaxation of science. The repository system is a multi-barrier system for the confinement of RN. It is not simple to analyse the sensitivity of these systems, to identify what is or is not important. For example, we can obtain reasonable results without considering solubility limits, but this has no sound scientific basis. What are topics of interest for PA in the near future? Confidence building, understanding the phenomena, etc. The first group of topics deals with the chemical barrier. First, we have to fill in the existing gaps in the database: quality assurance, role of organic complexation, co-precipitation processes. The second group of topics deals with chemical phenomenon in other barriers: related to mobilisation of RN, degradation of waste forms, transport in colloidal form, retention of RN in solid solutions. The behaviour of the physical barriers, including the stability of the main components: corrosion of the canister, alteration/dissolution of bentonite (buffer material), neo-formation of mineral phases, coatings, general pore-water interactions. It is also of major concern the buffering capacity of the different barriers: pH or redox transients.

One important issue is the dissemination of knowledge. NEA TDB has been very active in this sense; it is an example to follow. I would recommend continuing in this way. Potential activities of the project will be to help to apply thermodynamic laws and data in actual PA. How to support the expert judgement to apply thermodynamic data to real complex systems?"

Open discussion

K. Spahiu rose the point on the estimation of the data. Data estimation is conducted to fill in the gaps of the existing TDB. The point is how to estimate the data?

J. Hadermann said that it is the responsibility of the user to obtain the expertise to properly estimate the data for a specific application.

I. Grenthe said that he had tried to illustrate that estimations can have a good scientific basis. It is the first way to go when no data are available. It can be very useful for experimental planning. In this area, where experiments are expensive, one wants to concentrate all efforts on the most important issues, and estimations can provide some guidance in this regard. As always, it is an iterative procedure. There are good and poor methods of estimation; by referring to the literature one can identify which methods are less promising than others.

K. Spahiu said that, of course, there are good methods of estimation, such as the ones shown in “Modelling of Aquatic Chemistry” but some other examples to follow would be very useful.

M. Askarieh commented that most of the aspects dealt with by J. Alonso are not within the scope of the NEA TDB Project.

G. Ouzounian said that what can be done is to communicate to the NEA TDB Management Board the issues raised by J. Alonso, for a further decision as to whether to take them on board.

J. Alonso asked whether, regarding the stability of the bentonite barrier, the NEA TDB Project activities could not suggest methods or data to tackle that issue.

J. Hadermann commented that unfortunately this workshop is not aimed at providing a response to all the issues in which TDB may play a role. In general, the workshop has been limited to solubility limitations (solid solutions have been addressed to some extent): the source-term. But very little has been said on the use of thermochemical databases in sorption, for example. Not everything is being covered, but this is because that would be impossible within the available time.

J. Hadermann then gave the floor to M. Snellman.

M. Snellman (POSIVA)

“I was asked to comment on ionic strength corrections. The first thing to consider in our PA dealing with saline or brackish conditions is that all standard states must be corrected. Something that came up during this meeting is that ionic strength corrections are best suitable for intermediate ionic strength, not for very low neither for very high ionic strength. They are also best suitable for low charged ions ($q > 2$). According to some of the data presented by T. Fanghänel the POSIVA interest is at ionic strength ranges where Pitzer presents the best results. The main point, discussed by K. Spahiu, was that most of the data we have is for application of extended Debye-Hückel. For high ionic strength this is a problem that must be solved. The SIT approach is not included in geochemical codes. Pitzer data are very limited, especially for An(IV). Natural data that can be used for building confidence in PA is very important and it should be included in future programmes. Some other questions arising from T. Fanghänel and K. Spahiu presentations are that most of the RN of interest are going to be at trace levels in ground water.”

At this point, M. Snellman presented a summary of the advantages and limitations of SIT and Pitzer approaches.

“Improvements to make for the future would be: to introduce the SIT approach into geochemical codes to get rid of the possibility of having erroneous calculations due to the fact that you are using data originally obtained by using SIT; to use different electrolytical models for the data available at very saline conditions; to back-up this information with site-specific data, with site-specific experimental studies.”

Open discussion

I. Grenthe commented that one can generally say that in systems where very weak complexes are formed difficulties may arise to interpret what species are present in solution. The good thing is that these complexes will not have any important effect on the calculations. The other aspect that is important to acknowledge is that activity corrections are important, but even more important is to ascertain that the stoichiometry of the complexes is preserved under different ionic strength, and this is indeed the case. Once the speciation has been ascertained, the main basis of the chemistry has been established and then different ionic strength corrections can be tried. But what is important is to have the same ionic model, independent of the ionic strength.

H. Wanner said that there is a very important conclusion on the ionic strength discussion. He said that it was a very good idea of the initiators of the NEA TDB Project to use SIT. The reason why Pitzer's theory was not used is now clear. It is not feasible to use it for international projects, where the reviewers are obliged to use data from many different sources with all the systematic errors involved, and these prevent being aware of the curvatures as a function of ionic strength.

T. Fanghänel confirmed that indeed the use of SIT was a good choice for the NEA TDB exercise. However, practitioners must be aware of its limitations and be prepared to take a step forward and use other type of models.

J. Hadermann summarised by saying that this was a very good conclusion on ionic strength corrections. J. Hadermann then passed the floor to E. Giffaut.

E. Giffaut (ANDRA)

"I was asked for a speech on applications and limitations of TDB use in PA. I will focus on few points given the extension of the subject. During the workshop everybody agreed on using TDB as PA support. There is also an agreement concerning the compromise with science, at least with the TDB development. The main difficulty is the difference between scientific development and TDB development, and PA itself. The problem is that PA seems to be consistent with the development of knowledge and it is very difficult to assess the appropriate level of knowledge. The level of simplification in PA has to be consistent with the level of knowledge. In order to illustrate this point I will go back to chemical parameters in PA. There are only two geochemical parameters: 1) solubility limits and 2) K_D values. That is, a rather poor level of knowledge is included. The question is why we do not go further in the description of the process, because it seems that TDB have many other information and that numerical tools have developed enough to undertake these calculations. Why in PA is the TDB not directly introduced to assess the solubility limit instead of introducing the solubility limit? For the transport assessment it is important to know the concentration in the aqueous phase. What about the solid phase, in terms of precipitated, sorbed phase, solid solution, etc., which is, in fact the residual of the amount of element that is not in solution? When we talk about the conceptualisation it seems to be possible to define it at steady state, but what about the dynamic processes, with diffusion and similar processes? A good conceptualisation would be that one when you have a problem of upscaling and time extrapolation.

There are some problems in the application of the TDB. One is the existence of in-house TDBs. Everybody has developed a TDB by his own that seems to be used as reference in the different projects. OK, but are we not in a risk of inconsistency when discussing all PA issues together? There is also the problem of including natural systems data, data on concrete, iron data and RN speciation of course. It is important to highlight the dynamic evolution of the disposal in time and in space. It is difficult to split a TDB into a list of radionuclides in one part and natural or major systems in another part.

The PA challenge is to find some non-coupled effects in space and time, a kind of simplification that must be as complete as possible. One question to add is "What is the first input in this PA development? Is it the expert advice or is it the complete development of the PA model?"

TDB cannot be used as a black box and expert advice must be present in PA. The updating of the data is very important. It is not a minor challenge to take a step forward in the data selection given that it is a reference for the existing PA exercises."

Open discussion

J. Hadermann thanked the speaker and inquired on the meaning of "upscaling" given that NEA TDB is defined for a very specific range of conditions.

E. Giffaut answered that TDB is a tool for PA. If it is considered that PA is mainly oriented to transport of radionucleides, then the focus must be on the processes important in time and space and it seems very difficult to propose a simplified model for PA.

J. Small commented on the modelling of dynamic systems. He said that it is different when approaching a surface site as opposed to a deep site, as the latter can be considered to be at steady-state conditions. The approach used in the Drigg site was to model the chemical evolution of the whole site by considering kinetics of corrosion, degradation and cement evolution. Define redox-pH conditions, include the speciation calculations and RN solubilities based on TDB. He stated that they are considering and using NEA TDB directly in a dynamic system. Similar models were used for glass dissolution. He added that they developed a dynamic source-term model for glass leaching and that those effects are driven by kinetic processes. Dynamic systems need kinetic and non-equilibrium effects.

I. Grenthe wanted to address some of the questions of E. Giffaut on TDBs. He stressed that there is no universal TDB. There is a considerable risk when in-house TDBs are developed. In principle, it could be contemplated within the framework of a future TDB project that experts evaluate how the databases are selected in the various in-house TDBs.

L. Wang commented on whether the polynuclear species of $Pu(OH)_4$ are or not different species. This may change all estimations, because all data are determined by using ultra-filtration. The real source of radionuclide leaching should be fragmentation of vitrified glass on the strong alpha and gamma radiation. In these fragments the concentration of the radionuclide is very high. The same applies to Tc. He mentioned recent studies by Grambow, *et al.* suggesting that TcO_2 is not the solubilty-limiting phase. The most stable particles are the polynuclear particles of $Tc(OH)_4$ and in these particles mixed oxidation states are present.

J. Haderman now gave the floor to the next speaker, Bill Glassley, who addressed the issue of coupling with transport.

B. Glassley (LLNL)

"I will present some experience obtained from the Yucca Mountain Project. We are going to concentrate our attention on how technical databases are developed and applied. What we are looking (the speaker showed two overheads) at are two cross-sections at two different times, 85 y and 100 y after closure. The variability is going to persist for the whole life of the repository. Temperature effects are the following: water that migrates down and reaches the repository tunnel will be heated and water vapour migrates, condenses and we will see lake-like features. Mineralogical alteration is going to occur along the flow pathway. Because of chemical and temperature effects, any existing solid solutions are going to change their composition. Carbonates, feldspars and clays that are going to be important in the RN migration are not going to have the same composition that they have today. It is important to understand what will be the chemical and thermal effects and what will be their effect on the solid solutions, and how these changes in the solid solutions are going to affect the behaviour of RN being transported. How sequestration of RN is going to occur. These processes are going to occur independently of whether we are in a saturated or unsaturated zone. The only difference is going to be the orientation of the plume coming off the tunnel and the magnitude of the chemical changes. There is some probability that as RN move through the system, solubility-limiting solid phases may change. We do not know about this, but it is important to know what are the range of changes in our parameters in order to see which mineral species could be responsible for the solubility-limiting in all the range of conditions expectable. Urs Berner has commented on this. When looking at TDB-III the aim could be trying to generate thermodata for a range of potential mineral phases that are going to play any role and develop thermal estimates on how these properties are going to change. What is important are natural systems. They consistently appear to maintain degrees of super-saturation. We need to understand better what these mineral phases are and how this super-saturation affects their formation. Redox non-equilibrium has been also commented upon. Natural systems maintain redox non-equilibrium under many conditions. I would like to encourage those that are developing TDB to develop mechanisms for noting what is the role of super-saturation and the role of kinetics. In the future these are going to be key issues. Given the expertise associated with the development of databases it would be unfortunate not to give the opportunity to this expertise to judge which are going to be the important secondary solid phases."

Open discussion

J. Bruno asked for the evidences of the persistent redox non-equilibrium.

B. Glassley answered that they are everywhere in natural systems. In Yucca Mountain there is a redox non-equilibrium. When you try to reconcile sulphate/sulphide, iron(II)/iron(III), oxygen measurements they are consistently in non-equilibrium. Therefore, some kinetics are involved in these processes.

J. Bruno said that oxygen is never going to be in equilibrium, that is why breathing is possible. But he wondered where this extensive body of evidence of oversaturation could be found.

B. Glassley answered that there is a whole list of cases. The formation of zeolites, for example. Silica super-saturation with respect to quartz persists always, whether in surface waters, deep wells, etc.

J. Bruno asked B. Glassley in turn whether he was aware of the latest advances on the oversaturation of silica in surface waters appearing in science. He added that the Fe(II)/Fe(III) system is always in equilibrium and that if proper measurements are done in groundwater many redox couples can be identified that are in equilibrium, although often lack of equilibrium is invoked to explain our failure to interpret our observations. Maybe this is a limitation on the way systems are observed. Systems are disturbed by our measurements.

B. Glassley replied that this was a possibility that evidence forces us to consider. If it plays a role for silicates, there is no reason to think that it is not going to have any role with the radionuclide solubility-limiting phases. Thus he suggested that proper attention should be paid to it by considering all the available experimental data.

J. Haderman asked whether this could not be a consequence of some temperature changes.

B. Glassley answered that this could be the case in some hydrothermal systems, for example in New Zealand. But that in most systems the fluids go long travelling distances and still non-equilibrium is maintained.

J. Haderman said that he meant temporal changes, too-fast flow compared to kinetics.

B. Glassley accepted that this could be the case.

J. Small went back to redox non-equilibrium. He said that redox can be measured in non-equilibrated groundwater, as many textbooks indicate. Nitrate and Fe(II)/Fe(III) can be measured and a range of Eh calculated from these measures. This is a classic issue. The key issue is how RN behaves in the system: which of these redox couples must we use to calculate the Eh of the system?

B. Glassley said that this was the problem.

J. Bruno commented that there are a lot of textbooks in geochemistry that state that redox non-equilibrium is a fact, But that recently his team had been properly measuring redox equilibrium in groundwater. The main problem encountered was the need to break down the myth of the redox non-equilibrium, something extremely difficult.

J. Hadermann gave the floor to Cherry Tweed.

C. Tweed (HARWELL IBC)

"When we were asked to be members of the panel, we were asked to come without any pre-conceived idea, we were asked to come and listen to the speakers and form our ideas on the basis of the speeches. I was given the job of looking out at TDB requirements of a probabilistic PA and compare it with deterministic PA. I have changed my ideas during the last two days. Within the Swiss and the Swedish programme they conducted thermodynamic calculations and produced a solubility number. I compare those two examples with the experience of UK where we do a probabilistic PA. We extract distribution of values brought together by a consensus of experts and we take into account experimental data, data in the literature, natural systems data, information from waste matrix studies and supporting thermodynamic modelling. I realised that people also use this expert opinion to get deterministic values. I had greatly underestimated the role of validation. Our TDB needs are very similar. We may concentrate on the area of the uncertainty. Is easy to say that if you have a probabilistic PA you have a greater account of uncertainty than in deterministic approach. But from the presentation we have seen it was clear that people doing deterministic PA use a best estimate but also take into account the uncertainty, and in summary we use different procedures but end up with very similar points of view. Sometimes we are actually just deriving reference groundwaters but here we are taking analytical data and using thermodynamical models to get representative *in situ* compositions. We often talk of the role of deriving water compositions by corrosion products. Here again we rely on, not always, thermodynamic data. One of the things is which is the current state of the knowledge. What happens with the databases is that when everything is fine nobody notices, but when something is not working properly or when you need some value that is not included in the database, one starts to blame it on the TDB, without noticing the large amount of work underlying. We have come a long way in the last ten years. In the eighties we were discussing what species of uranium we needed to include in the database and now we are discussing whether we need best estimates or upper limits. It is very important when we look at the future to acknowledge what has actually happened so far and the great steps we have made. There are several issues of interest for future work. We can structure these issues as follows:

1) *Filling gaps*. This is to continue the work we have already done. There are some data which are not good enough to meet the criteria to be included in an internationally recognised database. It would be useful to have recorded somewhere second-class data in addition to the first-class data in the NEA TDB. Another way of filling gaps is to have estimated constants. Acknowledge the limitations but document them. Another point is that we need more solids. The definition of which solid phase we must to include. There is more work to be done on the solid phases.

2) *The "how to"*. How to deal with solid solutions. It is such a big area that it would be unrealistic to expect this project to produce a comprehensive database on this subject. But it would be useful to have a definite guide on how to approach the system. We have heard a lot on SIT and on Pitzer. I would very much value an easy guide on the how to: which constants do you remove? Which effect does it have? What are the errors if you omit to take these constants out? Something that help us to apply SIT or to use it in our models.

3) *Confidence building*. Supporting data, it would be good to have an international consensus on the iron couple, for example. The last is to demonstrate that these databases do work: validation. It would be good for an international body to bring together the successful applications of the thermodynamic modelling so that there is a document for those proposing and regulating."

Open discussion

J. Hadermann thanked the speakers and opened the discussion. He stressed that it is well known that there are two important issues to consider. The first one is that it is not sufficient to perform theoretical studies – measurements are indeed required. In natural systems measurements are a must, there is no way around them, and it is not enough to theoretically model the systems. The second issue is that the scientific community usually takes into account measurements if they show up in the open literature. But a wealth of work is reported elsewhere and it is difficult to adequately integrate this work.

J. Bruno said that Cherry Tweed was right in being optimistic. He said that during the Chemval project the situation was painful when it came to the application of chemical models, validation, etc. He added that since then, quantitative models have came forward. Chemval is not unique in this sense. What is in the books is that nothing happened before the 1940s, but there had been a lot of experimental data. It is an unfortunate reality that some of the data simply fail to make it to the literature. Conversely, it is very easy to set up a myth in the scientific literature. The breaking down of these myths is very hard because of the requirement to invalidate concepts that have been already incorporated to the common knowledge of many people.

I. Grenthe commented about the chapter on the use of SIT in "Modelling of Aquatic Chemistry", because this answers some of the questions that have arisen. One opportunity would be the upcoming 6th Framework Programme within the EC. There are very extensive resources within this framework for the nuclear area. Some of the national representatives attending could work together with the scientific institutions to create a programme for the mentioned framework. It is a good idea to start teaching the decision-makers at this stage because conventional sources of financing are completely overextended.

J. Hadermann brought up the point that within the scientific community the measurement of specific thermodynamic data is not considered to be a great scientific challenge, and therefore the efforts at university level (PhD work) have strongly declined, if not disappeared, to a great extent.

C. Tweed then made the point that this is work which simply has to be done in order to fulfil societal needs and without the hope to win a prestigious prize. As an example, she mentioned the household person doing work which falls into this category (laundering, etc.): absolutely necessary but with little prospect of increasing personal prestige. She added that she hoped not to have given the impression that no additional experiments are needed. She also pointed out that it should be realised that in the NEA TDB books already published, there are many more gaps than the ones that can be filled by experiments. Therefore, there is still a need to look seriously to the “less pure” data and to the role of estimation.

J. Hadermann thanked all the contributors and closed the Panel Session.

CLOSING REMARKS

M. Askarieh summarised by commenting that it had been a very interesting workshop with a broad spectrum of participants (modellers, performance assessment experts and experimentalists) and presentations. He thanked the panel members for their very good job in summarising and raising the more important issues. He highlighted the role of the in-house thermochemical databases: obviously there is an urgent need for thermochemical databases for PA and this is understandable. But this raises the issue of whether, by building up in-house databases, we are somehow contradicting the initial ideas at the foundation of the NEA TDB group some years ago. The NEA TDB project needs to be attentive to the needs of the in-house thermochemical databases. He argued that another important issue was the use of good science or, rather, the need for good science. There is no good thermochemical database without science. The effective use of NEA TDB data will give rise to high-quality performance assessment. The NEA TDB Project has produced five books on thermochemical data. Hopefully in the future more books will be published, but what needs to be disseminated is the good use of these books. Data are taken from the books and applied, perhaps not always in the way that the reviewers intended them to be used. C. Tweed raised the problem of how to fill the gaps and how to build confidence. All these issues will be taken into account by the Management Board of the NEA TDB Project when discussing and designing the future stages of the project.

M. Askarieh thanked ENRESA, particularly J. Astudillo and P. Hernán for facilitating the workshop, J. Bruno and his QuantiSci collaborators for the local organisation of the workshop and Universitat Politecnica de Catalunya for making available the conference room. He also thanked the speakers, the panel members and all the attendees for their contribution to the success of the workshop.

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