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SUMMARY

This final report from the Concerted Action "Joint European Thermodynamic Database for Environmental Modelling – JETDEM" describes the rationale for, and the mechanism by which such a database may be established and managed. The report describes where and how it will fit into the envisaged "Key action 2, Nuclear Fission" within the Fifth Framework Programme of the European Atomic Energy Community (EURATOM) for Research and Training in the Field of Nuclear Energy (1998–2002).

In a first step in chapter 2 geochemical codes and associated databases that are used most widely are assessed. The status of current thermodynamic modelling tools and databases is discussed and summarised.

Chapter 3 outlines data requirements. According to the selected target areas of the JETDEM - project the discussion was restricted to elements of potential radiological significance (actinides and fission products) and other elements which are important for the performance assessment of nuclear waste repository systems. The available information for the various systems is fairly different. While for some elements/systems knowledge is satisfactory, for other systems data are poor or virtually non existent. Moreover the degree of definition from the point of view of thermodynamics is very different for the various systems. Besides systems which fit strictly into the framework of thermodynamics there are thermodynamically „ill defined“ systems which cannot be handled without extra thermodynamic definitions (additional conventions etc.). Data requirements for aqueous species (chemical potentials, enthalpies, entropies, activity coefficients) solids (solid phases and reactions on the interface) and thermodynamically „ill defined“ systems (Kd's, humic/fulvic acids, colloids, biological systems) have been summarized by applying an oxidation state analogy. The state of knowledge for the various quantities is summarized.

Available methods for estimating thermodynamic quantities based on well established chemical theories are summarised in chapter 4. These methods are necessary in order to describe chemical systems when insufficient experimental information is available. However, these methods will always be an adjunct to direct experimental determinations.

Various methods for the:

- estimation of thermodynamic data for solutes in multi-component systems
 - correction of thermodynamic data to standard state conditions
 - estimation and extrapolation of thermodynamic properties for minerals and solid solutions
- are discussed.

Based on the stated data requirements for a Joint European Thermodynamic Database for Environmental Modelling examined in chapter 3, an experimental programme to provide priority fundamental data is proposed in chapter 5. The programme is focused on the following main areas:

- fundamental aspects of actinide chemistry
- redox transformations
- chemical backfills and nuclear waste matrices
- sorption processes and formation of solid solutions

in chapter 6 general problems related to the verification of experimental data and their correlation with the underlying modelling concepts are discussed. An overview of experimental techniques, in particular spectroscopic methods, suitable for data verification and their areas of application are summarised.

In the final chapter (chapter 7) conclusions and recommendations for further research activities are outlined. The focus of JETDEM is on nuclear waste management issues, a field where organisations and scientists in Europe play an internationally leading role. Strategies are outlined and research areas are suggested which need to be sustained in order to preserve this lead and to ensure environmentally sound waste management practices. The following points are considered essential:

- There is a need to establish a central facility with responsibility for the management of a Joint Thermodynamic Database for the nuclear waste, reprocessing and partitioning fields. This facility should act as a hub in a network organisation. An essential element is the availability and efficient dissemination of primary experimental information. In those cases where such data are not available, the centre should establish a system encouraging experimentalists to perform appropriate experimental determinations.
- Goal-oriented research is necessary to find socially, economically and technically acceptable solutions for the handling of radioactive wastes of different types. This requires a move towards multi-disciplinary team building, both in the form of networks and by concentrating resources within those few European research institutions that possess the necessary facilities for handling active material.
- Considerable effort is required to make the research challenges within the nuclear waste management area attractive to new generations of scientists. There is need both for nuclear systems oriented scientists and for specialists from related fields, including the non-nuclear waste sector. A programme for training of young scientists and mobility is necessary to ensure that the European nuclear capability which currently exists is maintained.

1. INTRODUCTION

1.1. OBJECTIVES

This final report from the Concerted Action "Joint European Thermodynamic Database for Environmental Modelling – JETDEM" describes the rationale for, and the mechanism by which such a database may be established and managed.

The report also describes where and how it will fit into the envisaged "Key action 2, Nuclear Fission" within the Fifth Framework Programme of the European Atomic Energy Community (EURATOM) for Research and Training in the Field of Nuclear Energy (1998–2002). The main objectives of this key action are "to enhance the safety of Europe's nuclear installations and improve the competitiveness of Europe's industry. Within these broader objectives, the more detailed aims are to ensure the protection of workers and the public from radiation and the safe and effective management and final disposal of radioactive waste..." The specific objective is "to develop a sound basis for policy choices on the management and disposal of spent fuel and high level and long lived radioactive wastes and on decommissioning and building a common understanding and consensus on the key issues."

Thermodynamic data and the underlying chemical models are the basis for predicting the performance of a nuclear waste repository. Therefore, in the past, considerable effort was made to determine thermodynamic data of species relevant for repository systems. Primary experimental data were evaluated and compiled in database systems. Although in many areas considerable progress has been achieved, there are still areas where our knowledge is insufficient and the available data have high uncertainty, are partly inconsistent and reaction mechanisms are not understood. These key areas where further research is inevitable are identified by this concerted action and are presented in this report.

A multi-disciplinary approach is fundamental to the design and evaluation of technical systems that are required to function over extremely long periods of time, without presenting unacceptable risks for present and future societies. It is only in this way that scarce human expertise and financial resources can be used in an efficient way. The members of the Concerted Action responsible for this report are convinced that the recommendations for further research activities outlined in this report is a means of achieving the strategic goals stated above and also provides important input of new information to the ongoing national nuclear waste programmes within Europe. With these statements and the discussion in the report we have hopefully made it clear that JETDEM is not intended to undertake just a compilation of data.

This report discusses the need for, and the structure and maintenance of a European thermodynamic database to be used primarily for the "validation" of geochemical models for the migration of radionuclides and other solutes from nuclear waste repositories. It is also useful for problems related to other contaminated areas. Within the scope of a Concerted Action we have reviewed ongoing thermodynamic database activities (aqueous and pure substance databases) and also specific areas where the current thermodynamic data are non-existent, or of poor quality. We have identified some of the additional experimental work that is indeed necessary and indicated areas where the database can rely on existing

structure of ongoing research into nuclear waste management and related areas within Europe. Continued strong support to the European institutes where cutting-edge research on radio- and nuclear chemistry, including actinide chemistry is taking place, is essential because few universities have the capacity to tackle such problems. Through a "mobility" programme, these centres will be able to provide the training and research facilities for young university students. A number of research projects suitable for diploma or thesis work are identified in the final JETDEM report. In addition to specialised disciplinary training, the programme outlined will provide young scientists and other participants with the broader perspective required to solve nuclear waste disposal problems.

1.2 SCOPE

The scope of the JETDEM project covers the scientific basis for the radiological and environmental assessment of repositories for nuclear waste. A scientifically founded and accepted approach is, in our view, a necessary element for public acceptance.

The JETDEM project builds on experience from previous research, such as the MIRAGE and CHEMVAL projects supported by the EC, various national and international research programmes and scientific knowledge from a range of different disciplines, chemistry, physics, geology, hydrology, civil engineering etc. An important part of the project is to identify areas where additional experimental effort is required in order to fill the gaps in current knowledge, required for the performance and safety assessment of complex nuclear repository systems. The implementation of repositories for low and intermediate level radioactive wastes is already under way in a number of countries whereas for high level waste in no country the disposal has yet started. Members of the JETDEM team have participated in national programmes of this type and consequently are aware that many problems, (*e. g.* the chemical evolution of the near-field) are common across national boundaries.

1.3. PROBLEM AREAS

Many countries already have programmes for the establishment of nuclear waste repositories. JETDEM has formal and informal links to these programmes and clearly this is the main focus of the Concerted Action. However, there are other areas where thermodynamic data are required urgently.

Decommissioning of nuclear installations. Many of the nuclear facilities in Europe (including the former USSR), USA, and elsewhere have reached the end of their economic and technical life expectancy and decommissioning measures are being underway. Often, contamination extends beyond the main technical parts of the installations or is currently contained by methods not regarded as reliable for long-term safety. Large clean-up programmes are already underway in the US for former nuclear sites (USDOE 1989; USDOE 1990). Programmes of this type are urgently needed in the former USSR, particularly for the decommissioning of nuclear submarines.

Nuclear accidents and poor site management. Areas contaminated by nuclear accidents or poor waste management will have to undergo remediation actions (Eisenbud, 1987). Ten years

after the reactor accident of Chernobyl vast areas are still radioactively contaminated, especially by caesium-137, strontium-90 and actinides. Parts of the population have returned to prohibited areas. Comprehensive help to launch clean-up programmes are needed urgently.

Past mining activities. These include regions affected by the mining and processing of uranium ore (BfS, 1992). For example, the legacy of forty-five years of uranium mining in the southern parts of the former East Germany, has left the local population with an extensive number of mines, rock piles and mill tailings (BMW, 1995; WISMUT, 1994). The WISMUT company mined 220,000 tons of uranium from 1945 to 1990. The mines are characterised by a total shaft length of some 1400 km and reach a depth of up to 1800 m. The mill tailings contain about 100 million m³ of contaminated residue. The primary source of external contamination is from groundwater that has flooded the mine shafts, as well as seepage waters from mines and mill tailing piles. Uranium, its decay products and arsenic are the main potential hazards to the biosphere (BfS, 1992).

Interactions between radionuclides and biological material. Interactions between inorganic metal contaminants and biological materials can be found at many waste deposit sites, where they often govern the speciation and migration of the contaminants. One example is the microbial reduction of U(VI) to insoluble U(IV), or the reverse process which is used for bio-leaching to obtain uranium concentrates from ores. These interactions are only poorly understood on a molecular level, mainly because of their inherent heterogeneity. Biological material can be living or dead: whole plants or parts of them, bacteria, algae, protozoa, fungi, and intermediate or final degradation products. Bio-accumulation of heavy metals or organic substances, bio-catalysed degradation processes (including oxidation and reduction reactions), formation of bio-colloids, sorption onto bio-films on mineral surfaces are examples of microbiological processes. They tend to be very dynamic as compared to most geochemical systems.

Microbiology may be used as a tool to influence sorption and migration processes in order to immobilise the contaminant or to transform it into a state which is either less toxic or has a significantly lower bio-availability. Detailed knowledge of the main mechanisms of bio-accumulation and the binding strength of the bacteria is important for development of remediation technologies for radioactive contaminated sites. Moreover, knowledge acquired in this field may also be very important for nuclear risk assessment such as the transfer of radionuclides from the aquatic environment to living matter such as crops, vegetables, domestic animals and people.

1.4. MODELLING APPROACHES

Numerical simulation of the processes affecting the migration of radioactive contaminants is an integral part of radiological assessment procedures for which chemical equilibrium models are an important part of such models. Because significant and largely unexplained differences were found in "standard" compilations of thermodynamic data the European Community initiated the CHEMVAL project (Falck et al. 1996) which resolved some of the inconsistencies and resulted in a substantial body of new data.

Thermodynamic modelling is an important tool for describing the characteristics of chemical systems in nature and elsewhere. Models are by choice and necessity incomplete and describe

and description of real systems. From this, it follows that modelling may be performed at different levels of sophistication and necessary elements are approximations, estimates and expert judgement, based on the perception of the problem at hand. The challenge is to find a model that represents the physico-chemical phenomena *sufficiently* well, to determine the numerical data required and to estimate the consequences of the inherent uncertainties in the models.

The essential part of modelling is the formulation of objectives for the model, the documentation of the scientific basis for the analysis and the expert judgements and/or assumptions made. The following set of procedures are typically used in the analysis:

Choice of scenarios. A scenario is a postulated sequence of future events. The components of a scenario may be categorised by the definition of Features, Events and Processes (FEP's) based on the current level of understanding of the system and also on hypothetical performance criteria.

Formulation of conceptual models, i.e. the selection of the appropriate scientific theories, models and data that will be used to describe the processes defined in the various scenario descriptions. The process in general involves physical and chemical approximations.

Construction of mathematical models, i.e. the translation of the conceptual models into a suitable numerical form for calculating relevant system properties under the given assumptions.

Calculations. This is seemingly the most straightforward part of the exercise. However, it is essential to use computer codes that are well tested and do not suffer from problems of numerical instability. A particularly difficult problem is the coupling of different processes, e.g. chemical reactions and mass-transport such as advection and diffusion.

There is an obvious relationship between quality assessment and safety performance. This also extends to the type and quality of the thermodynamic data required. Global safety assessments cannot *directly* use the detailed mechanistic models developed in the laboratory. The uncertainty in the global models by far outweighs the uncertainty in the numerical values of most thermodynamic quantities. Nevertheless, precise thermodynamic data are necessary because they provide the scientific understanding of the processes taking place. This is necessary to justify the approximations required in the models used in performance and safety assessment.

1.5. WORKING ASPECTS

A large number of different thermodynamic databases exist today. There are two main reasons for this new activity of JETDEM, the first is to ensure consistency, quality and traceability of the data, the second to ensure that the *particular* data needed for the nuclear waste management are made available. A thermodynamic database needs continuous updating and reassessment as pertinent knowledge advances and new experimental data become available. There is, therefore, need for an institution that provides a forum for scientific discussions of the thermodynamic data used and of the new experimental information that is made available through the scientific literature. Communication should use electronic media, informal or

formal workshops and exchange of scientists. It is also necessary to have an organisation with experience in the management of databases and distribution of information to the users.

2. STATUS OF THERMODYNAMIC DATABASES AND CODES USED FOR THERMODYNAMIC MODELLING

2.1. INTRODUCTION

The overall objective of this concerted action is to establish the mechanism by which a quality assessed thermodynamic database may be built for radiological and environmental assessment. In this sense, a review of the present status of thermodynamic databases used in radioactive waste management has to be carried out in order to define the needs and priorities for future research activities.

Many thermochemical databases have been compiled and used in the last decades and the radioactive waste management agencies have understood from an early stage the need for quality thermodynamic data to support performance assessment calculations.

In order to achieve the above objectives, the first step of the work has been the assessment of those geochemical codes and associated databases that are used most widely and the reasons behind this. Therefore, two questionnaires were distributed among the JETDEM partners, as well as to some other institutions with experience in the measurement, evaluation and use of thermodynamic data. A summary of the response is given below.

2.2. THERMODYNAMIC DATA, SOURCES AND QUALITY ASSURANCE

Thermodynamic data are required for understanding and describing chemical processes in nature. The quality of thermodynamic modelling is dependent upon the quality of these data compiled in the form of databases. This section describes the characteristics of experimental data on which published thermodynamic compilations are based and a methodology for the quality assessment of such data.

Detailed information on the primary experimental data is necessary for a proper quality assessment of published thermodynamic listings. Published information varies with the type of data and also over time. Typically, much less information on experimental details are given in recent publications than in older work and in some cases one cannot ascertain that new data are necessarily more reliable than older values.

Thermodynamic data always refer to a given temperature and a certain standard state where the activities and activity coefficients of reactants/products and the solvent are unity. In order to compare published experimental data obtained in different ionic media it is necessary to employ methods that allow the calculation of activity coefficients of the reactants/products with respect to a common standard state as defined according to IUPAC (International Union for Pure and Applied Chemistry). In the same way, standard state thermodynamic data have to be recalculated to the conditions encountered in the systems to be modelled (which in general are not standard state conditions). Calculations of this type are made using extended electrolyte theories based on the Debye-Hückel (DH) model. All such models are semi-empirical and contain a number of parameters that must be evaluated from experimental data.

differ in the ionic strength range of their applicability and in the number of empirical parameters they contain. It is necessary therefore to evaluate the characteristics of these models in order to estimate the accuracy of the thermodynamic quantities derived.

2.3. EQUILIBRIUM CONSTANT DATA

Equilibrium constants are nearly always determined in an ionic medium of a given composition. For many reactions several published constants are available obtained in different ionic media and at different temperatures. Before the numerical values can be compared with one another they have to be recalculated to a common standard state. This requires a methodology for the calculation of the activity coefficients of reactants/products, as indicated previously.

The methodology for the experimental determination of equilibrium constants deserves a special comment. In order to describe a complicated equilibrium system (a system where there are several species present in comparable concentrations), it is necessary to determine both the composition and the equilibrium constants simultaneously under conditions where the activity coefficients of reactants/products remain constant. This is achieved using a background ionic medium, the concentration of which is much higher than that of the reactants/products. It is also necessary to vary the total concentrations of the reactants/products over as wide a range as possible. Details of the methodology are given in monographs, for example, by Rossotti and Rossotti (1961) and by Beck and Nagypál (1990).

It is not a trivial exercise to derive a comprehensive chemical model for a complex chemical equilibrium system, It requires attention to the experimental details and also a careful analysis of the experimental data. Alternative chemical models may sometimes describe the same set of experimental data. Selection of the 'best' model must then be based on the known characteristics of the ligand(s) and the metal ions (e.g. coordination geometry, preferred coordination number of the metal ions, the nature of the donor/acceptor characteristics etc). It is essential that this type of chemical information be recorded when the selection of the model is made and the corresponding equilibrium data compiled.

In the following sections we discuss the status of current thermodynamic modelling tools and databases.

2.4. QUESTIONS SUBMITTED TO THE PARTICIPANTS

2.4.1. Questions related to geochemical codes

The following questions were posed with the aim of finding the geochemical codes that are used most widely and why, their advantages and disadvantages, their limitations, etc. The information provided by the participants is then collated to provide a summary of the current status.

The questionnaire addressed the following:

1 Which (geo)chemical codes do you usually use in your work?

- 3. What are their limitations? 1 range? Ionic strength corrections?*
- 4. Do you consider them user-friendly?*

2.4.2. Questions related to the main databases used

A similar questionnaire is issued concerning the thermodynamic databases most frequently used by the different groups. From the information obtained it is possible to make some general remarks on the consistency and content of the more common thermodynamic compilations. This is seen as a first step towards achieving, ultimately, one internally consistent thermodynamic database that will integrate all available thermodynamic data for radiological and environmental assessment.

The questionnaire addressed the following:

- 1. What are the main databases that you currently use?*
- 2. Can you give us the complete reference, the last update etc.?*
- 3. What information do the databases include?*
- 4. Does the database include the data source?*
- 5. Advantages and disadvantages of the selected database(s)?*
- 6. Reasons to use this database.*
- 7. Can you consider them to be user-friendly?*
- 8. Database format and compatibility with codes.*
- 9. Have you updated or extended your database with new data?*
- 10. What modifications have you included?*
- 11. Could you reference them?*
- 12. Please, include comments, suggestions not present in the questions above.*

2.5. THE USE AND STATUS OF GEOCHEMICAL CODES AND DATABASES.

2.5.1. Geochemical codes

From the answers given by each group (Appendix 1.), we can see that there are some groups (e.g. Univ. Aberdeen-Reading, KTH and FZR) which have standardised on preferred geochemical codes while other groups (e.g. FZK/INE, QuantiSci, PSI Switzerland and RMC) use various codes for different applications. The latter is necessary when dealing with radically different areas of research where specialised tools are required to provide pertinent information. However, this is not usually the case in radiological assessment and, consequently, the proliferation of geochemical codes results in an unnecessarily large number of associated databases which makes cross-comparison difficult.

One can differentiate between geochemical codes which can be applied generally in low temperature geochemistry and codes designed for use in specific or extreme environments, e.g. high ionic strength, high temperatures and pressures etc.

We can conclude that the PHREEQE family of codes is the most widely used geochemical

friendliness combined with the wide range of capabilities included in the various versions. Furthermore, the fact that the code is maintained by the USGS (PHREEQE) and AEA Technology (HARPHRQ) is perceived as a major advantage by many users. The MINEQL family of codes is the second alternative for multi-purpose geochemical codes. The EQ3/6 code package (maintained by LLNL) is also widely used, and the HALTAFALL family of codes (HALTAFALL, SOLGASWATER, C-HALTAFALL, EC, SED, PREDOM) is a popular complementary tool for chemical modelling because of its graphical post-processing capabilities. This has been enhanced recently by including a useful data pre-processor in the form of the MEDUSA code (KTH). For more specific use other geochemical codes are required (SALT, Thermo-Calc, Dicitra, etc.).

The main outputs from these codes are the aqueous speciation (concentration and activities); saturation indices for minerals; Eh (pe), pH, ionic strength and gas fugacities; redox reactions; solid solutions; surface complexation and ion exchange, and phase diagrams of multi-component systems.

The foremost limitations are temperature and pressure. In general, the ionic strength modelled in surface or groundwaters is within the range of the Davies and Debye-Hückel (DH) corrections for the activity coefficients; that means that usually the ionic strength is lower than $0.3 \text{ mol}\cdot\text{dm}^{-3}$. In systems with considerably higher ionic strength such as brines, codes based on the Pitzer model (*e.g.* EQ3/6 or PHRQPITZ) are applied. For more specific systems, *e.g.* steel-alloys at high temperatures and pressures, other models and databases are available. However, no code is available that can make use of the SIT approach to calculate equilibrium compositions at moderate ionic strength, in spite of the fact that this is the preferred methodology when deriving thermodynamic constants at infinite dilution.

None of the geochemical codes reviewed is able to handle uncertainty in thermodynamic data in its standard form, though Monte Carlo pre-processors can be applied

In general, all the geochemical codes used are considered user-friendly, although data pre-processing and post-processing is still cumbersome. Only, the BACKDOOR and MEDUSA codes have enhanced data processing.

2.5.2. Thermodynamic databases

With respect to thermodynamic databases, individual groups may use up to four different database formats. This is only partly accounted for by the fact that specific databases are required for different areas of research. Leaving aside the obvious duplication of effort, the potential for errors in data transcription/conversion is substantial.

The NEA-TDB database is the preferred compilation for those actinides reviewed to date (U and Am). An other widely used thermodynamic database which includes more elements than the present NEA-TDB is the Nagra Thermochemical Data Base, which is currently maintained by the Paul Scherrer Institute (PSI), and CHEMVAL 6.0.

In order to compile a thermodynamic database including all the information relevant to radiological and environmental assessment, the widely used thermodynamic databases will have to be assessed in order to extract the consistent thermodynamic data and to find for

specific applications, as for instance those used by the Univ. of Uppsala will also have to be reviewed, taking into account the research tasks for which these data are used.

The main information included in the thermodynamic databases is the stoichiometry of the formation/dissociation reactions, equilibrium constants for aqueous species and solid phases, enthalpies and Gibbs energy of formation/dissociation, constants for surface complexation and ion exchange reactions and Pitzer interaction coefficients, of which the latter are only included in databases intended for high ionic strength applications. Importantly most of the databases include the data source though this is often the previous compilation rather than the original experimental measurement.

Another aspect to take into consideration is their compatibility with geochemical codes; PHREEQE, EQ3/6 and MINEQL are widely used and, therefore formatted databases exist. In some cases, the software necessary to translate the data from one database to another format is available, e.g. NEA (HATCHES) into the EQ3/6 format.

The main limitations of the thermodynamic databases arise from the lack of thermodynamic data for geochemically relevant solid phases, the lack of high temperature data and the lack of information permitting activity corrections. In this sense, databases are usually updated with current experimental information arising from on-going research programmes. Temperature corrections are usually approached using the Van't Hoff equation. Ionic strength corrections are approached by SIT methods at moderate ionic strength ($I < 3$ molal) and by using the Pitzer approximation at higher ionic strength e.g. salt brines. Only a small variant of the CHEMVAL 6.0 database, however, contains a set of specific interaction coefficients for use in SIT corrections and this is not being maintained. The NEA-TDB compilations also provide these coefficients in the appendices.

A short description of the main characteristics and limitations of the databases most used by the participants is given in the sub-sections below.

2.5.2.1. NEA-TDB

This database is the most widely used, largely owing to the recent publications of selected thermodynamic data for U and Am (Grenthe et al., 1992 and Silva et al., 1995 respectively). In addition to the stability constants of aqueous complexes and the solubility product of solid phases, it includes Gibbs free energies, enthalpies of formation, and entropy and heat capacity data for U and Am. Since comparable effort is being carried out under the auspices of NEA on other elements such as Tc, Np, Pu, (to be published during 1999) it is likely that this database will continue to be used extensively.

The NEA database is compatible with the most widely used geochemical codes listed previously and the ultimate data sources are included, at least for U and Am. It should be noted that the database contains information of highly variable quality as the majority of entries have not been reviewed to the extent of data for U and Am. Further, the methods used for activity corrections (mainly Davies, some SIT) are not consistent throughout. This constraint also holds true for several of the other databases listed below.

2.5.2.2. CHEMVAL 6.0

This database is more extensive than that above and can be considered well documented and tested within international programmes. However, it was conceived as a project database and now that CHEMVAL has been completed it is no longer maintained. Consequently, there is no formal mechanism to correct errors that have been detected in a recent release.

It differentiates between master species and reacting species, it gives equilibrium constants for aqueous species and solid phases at several temperatures, surface complexation and ion exchange reactions and enthalpies of reaction. This database is also compatible with the most widely used geochemical codes and the ultimate data source is included. A variant sub-set of the main database has been produced using the SIT method for ionic strength correction.

2.5.2.3. NAGRA TDB

This database includes a large number of elements as in the previous example. It attempts to distinguish between 'Core' data and Supplementary data (Pearson and Berner, 1991; Pearson et al., 1992), a somewhat subjective exercise as Core data will depend on the application.

For each species this database gives the stoichiometry of the dissociation reaction, the dissociation constant for aqueous species and the solubility constant for solid phases at different temperatures together with the enthalpy and Gibbs free energy of formation.

This database does not provide either volume data nor SIT and Pitzer coefficients but is compatible with the most widely used geochemical codes. The data source is included in the database.

2.5.2.4. HATCHES-NEA 7.0

This database is being maintained by AEA Technology and is compatible with the HARPHRQ code. It contains data for more than 1300 aqueous species and 850 solid phases.

It utilises the Microsoft Access database system and includes information on data sources and derivation. It has quite a strict quality assurance procedure to minimise errors and ensure internal consistency. The database management system includes automatic output conversion to EQ 3/6 and PHREEQE format. The database is updated regularly and distributed by the NEA.

2.6. CONCLUSIONS

The main conclusions arising from this survey on the use and status of modelling tools and databases are the following:

- The use of geochemical modelling codes is widespread throughout Europe.

- The most widely used codes (PHREEQE family, MINTEQA and EQ 3/6) are based on development work carried out at US institutions though maintained by European organisations.
- The extensive code testing performed during the CHEMVAL I and II exercises has given a high degree of confidence and consensus regarding the reliability of modelling tools.
- Most of the codes have associated thermodynamic databases in highly variable formats. This creates a great deal of confusion as these databases are being refined further by individual users without much evidence of traceability.
- The testing of geochemical modelling tools performed via the CHEMVAL I and II exercises and in conjunction with some of the Natural Analogue projects (Poços de Caldas, El Berrocal, Oklo and Palmottu) has generated a degree of consensus regarding the use and limitations of current databases.
- The NEA-TDB databases for U and Am represent the standard which most of the current thermodynamic databases would like to attain as more TDB compilations become available.
- Confidence in geochemical modelling codes and databases arises where the tools are maintained by research organisations and are widely available through the NEA data bank, for example, EQ 3/6 (by Lawrence Livermore National Lab.) and HARPHRQ (by AEA Technology).
- There is still much work to be done in order to improve the user friendliness and compatibility of the various codes and databases being used in Europe.
- There is a need to establish an active mechanism in order to be able to integrate the experimental data now being produced in research laboratories into a European thermodynamic database which is maintained on a regular basis. The time lapse between publication of thermodynamic data and integration in a correctly assessed thermodynamic database can be five years or more.

A thermodynamic database cannot be “European” in the sense that its content has a particular European dimension. “European” should therefore be understood as an activity supported by the European Community, where the responsibility for the organisation, management and quality assessment/assurance rests within the European research community. As indicated in the previous sections of this report there are a number of databases used within the nuclear waste management area – in addition to the ones already mentioned there are different organisations with a responsibility for the collection and management of databases. The best known is CODATA located in Paris (and IUPAC). The first organisation provides quality assessed data, mainly for solid phases, the latter makes compilations of thermodynamic equilibrium data but without quality assessment. It is essential that the JETDEM activity builds on the databases already in existence and that additions to them are made in such a way that internal consistency is assured. JETDEM will provide a *subset* of thermodynamic data of particular relevance to nuclear waste management and the first priority within the programme will be to define this subset in order to achieve the objectives within a reasonable time. As part of the current Coordinated Action some of these objectives have been identified and they

are outlined in the following subsections. However, additional information is needed and this must be provided by the present users of thermodynamic databases.

The quality assessment of old and new data will be an important element in JETDEM. It will not be practical to have a small group of experts doing this delicate and time-consuming work. The scientists within JETDEM will, through discussions with users and other organisations working with evaluation of thermodynamic data, propose a set of procedures for data evaluation, recalculation of standard state data to the actual system conditions (and vice versa), methods for estimation of thermodynamic quantities where no experimental information is available, etc. It is only if these “standard” procedures are accepted and used by a majority of the scientific community that the JETDEM activity can be managed in the way we foresee.

Implicit in the statements above is that the data assessment within JETDEM is a *network* activity, managed by a small core organisation. As indicated in section 4, a substantial amount of work has already been made on the development of such “standard procedures” by members of the present JETDEM team, and they are currently used *e.g.* within OECD/NEA.

A specific and very important task within JETDEM will be to ensure consistency between the various components of the thermodynamic databases (high temperature mineralogy, high ionic strength).

3. DATA REQUIREMENTS

3.1. INTRODUCTION

According to the selected target areas of the JETDEM project the following discussion is restricted to elements of potential radiological significance (actinides and long-lived fission products) and other elements which are important for the performance assessment of nuclear waste repository systems.

A unifying theory, which allows the calculation of thermodynamic data *ab initio*, is not yet available, though in some cases it may be possible to estimate data by analogy or empirical correlation. Therefore, the primary source for thermodynamic data is an experimental determination.

Information available for the various systems of interest differs considerably. Whereas for some elements/systems knowledge is satisfactory, for others data are poor or non-existent. Moreover, the degree of definition from the point of view of thermodynamics varies between the fields of radiochemistry, geochemistry and materials science. Thermodynamically ill-defined systems cannot be handled without additional conventions. Therefore, the discussion is structured as follows:

- **Aqueous species**
 - chemical potentials, enthalpies, entropies
 - activity coefficients
- **Solids**
 - homogeneous
 - “pure” solids, double salts, hydrates
 - solid solutions
 - interface
 - sorption (e.g. surface complexation)
 - ion exchange
- **Thermodynamically ill-defined systems**
 - mineral chemistry
 - naturally occurring organics including humic/fulvic acids
 - colloids
 - components of engineered systems
 - biological systems

3.2. AQUEOUS SPECIES

Data are generally lacking for temperatures and pressures other than ambient conditions. Data at elevated temperatures are missing though these are essential for understanding processes such as HLW corrosion where the temperature may reach 150°C, or interactions in flooded mines (temperatures up to 70°C and pressure up to 20 MPa). There are only a very few

3.2.1. Chemical potentials, enthalpies, entropies

The state of knowledge is summarised in Table 3.1.

Actinides

As far as simple actinide ions are concerned, the status is regarded as satisfactory although in some instances the necessary reconciliation of emf and calorimetry data leads to entropy values with considerable uncertainty. Knowledge of the aqueous chemistry and, hence, of the chemical potentials of simple inorganic complexes (complexes with ligands such as OH^- , CO_3^{2-} , SO_4^{2-} , halides, phosphates etc.), with the exception of phosphates, is fairly complete at ambient temperature (25°C). Data on the formation of mixed (ternary) complexes are not so well established. For the four elements, U, Np, Pu and Am, available data are being compiled and critically evaluated in the recently published (or soon to be available) NEA Thermodynamic Databases (Grenthe et al. 1992, Silva et al 1995). The state of knowledge is different for the various oxidation states of actinides. Whereas the tri-, penta- and hexavalent actinide complexes are reasonably well known, data are scarce for the tetravalent actinides due to their low solubilities and tendency to form colloids. Further data on both actinide(VI) and (IV) complexes are often based on analogy with uranium while lanthanide values are used for the estimation of trivalent actinide complexes. With few exceptions, this is certainly the case for the important carbonate species. Such estimates may be satisfactory in some situations but probably not when mixed complexes are involved, or at high ionic strength. Thus thermochemical data for transuranium elements are still fragmentary. Despite their obvious importance, the state of knowledge on redox potentials of the actinides is not satisfactory.

Thermodynamic data for complexes with organic ligands including simple organic acids, several polyaminoacids, ISA (isosacharinic acid) etc. are scarce. As these data are important for modelling the interaction of radionuclides with the degradation products of wood, plants and other (anthropogenic) organics further work is required.

Fission products

The chemistry of the mono- and divalent fission products such as Cs^+ , I^- , Sr^{2+} , Ra^{2+} is relatively simple and therefore well known. Data on the aqueous chemistry of tetravalent technetium and on aqueous carbonates and phosphates of transition metals such as Ni, Co, Fe are lacking or poorly defined. A lack of data is also apparent for redox couples. For example, the aqueous chemistry of Se where data on aqueous complexes with selenide, selenite and selenate are virtually non-existent.

Table 3.1: State of knowledge of the aqueous chemistry of actinides and fission products at ambient temperatures.

Oxidation state	Elements	State of knowledge
+I	Cs	well known
+II	Sr, Ra, Ni, Co	well known except for phosphate and carbonate complexes
+III	Am, Cm, Pu, REE	simple inorganic complexes, except for phosphates, are known not known: - mixed (ternary) complexes - complexes with organics at high pH
+IV	Th, U, Pu, Np, Tc, Se	overall aqueous chemistry is not in a satisfactory state, formation and stability of colloids is not well known
+V	Pu, Np	aqueous chemistry, except for phosphate complexes, is known
+VI	U, Pu, Np, Se	known for U, extrapolation to Pu is possible not well know: - ternary complexes - aqueous chemistry at high pH - colloid formation - complexes with organics at high pH
+VII	Tc	known
-I	I	known
-II	Se	not well known

3.2.2 Activity coefficients

The information available for low ionic strength solutions is regarded as satisfactory. The application of semi-empirical approaches, such as extended DH or SIT for the evaluation of activity coefficients for aqueous ions and complexes is well established. Ion-interaction parameters are available for the most important species.

For high ionic strength systems, in particular for multicomponent brines, the situation is very different. It has been shown that, for these systems, only Pitzer's ion-interaction approach can be applied with confidence. The database of ion interaction (Pitzer) parameters is restricted to a few recently investigated systems of tri- and pentavalent actinides and of fission products such as TcO_4^- and Cs^+ (Fanghänel and Kim (1998), Fanghänel et al. (1995), Könnecke et al. (1997), Li, Nishikawa et al. (1998), Blumhagen et al. (1998)). However, the parameter base for the

main components of natural brines (Na-K-Mg-Ca-Cl-SO₄-CO₃) is well established at ambient temperature (Harvie et al. 1984). At higher temperatures activity coefficients of actinides and fission products are virtually non-existent.

3.3. SOLIDS

3.3.1. Homogeneous solids

Solubility studies have provided a great deal of information on solid species such as hydroxides, carbonates, phosphates, sulphates, etc. However, in many cases the solids are not well characterised (amorphous or of low crystallinity). Data on solid actinide phosphates and actinide silicates are less well known and tend to be contradictory. Missing is knowledge on ternary solid phases e.g. hydroxo, oxo carbonates etc. Solid phases of mono- and divalent fission products such as Cs⁺, I, Sr²⁺, Ra²⁺ are usually highly soluble and, therefore, less important for defining source terms in repository performance assessment. The state of knowledge is summarised in Table 3.2.

Table 3.2: State of knowledge on pure solid phases of actinides and fission products.

Oxidation state	Elements	State of knowledge
+I	Cs	satisfactory but less important for source term definitions
+II	Sr, Ra, Ni, Co	well known or less important except for Ni
+III	Am, Cm, Pu, REE	relatively well known, except for phosphates,
+IV	Th, U, Pu, Np, Tc, Se	relatively well known, except for silicates
+V	Pu, Np	state of knowledge is patchy
+VI	U, Pu, Np, Se	relatively well known
+VII	Tc	incomplete data set
-I	I	less important for source term definition
-II	Se	not well known

In most solubility studies, the hydration of a given compound is not determined experimentally. Such determinations are, of course, very difficult when the number of water molecules depends on the ionic strength of the medium, temperature, etc. Double carbonates with alkali metal or alkaline earth ions are, in this respect, noteworthy.

Determination of the enthalpy of solution leading to the molar enthalpy of formation of well

the above families (carbonates, hydroxides, sulphates, phosphates, mixed sources,...), in connection with solubility measurements would lead to a full thermochemical picture of the stability relation of the phases involved. It would also be important to have at hand directly determined entropy values for a few important compounds. Such data would help verify the consistency of ΔH° and ΔG° values. Thermochemical data on many important clay and diagenetic minerals are missing. It is necessary to identify and characterise the alteration products of the various types of host rocks by modern techniques and determine phase relations by experiments. We may cite as an example a phase, sudoite, which occurs in the Cigar Lake deposit. Little information is available on either the physical or thermochemical characters of this phase. This applies also to many other hydrous phyllosilicates. For example, studies of structural stability of chlorite are confined to the chlorite IIb form and information on other forms is lacking.

Solubility data (solubility products, chemical potentials) for secondary solid phases (weathering products) which are the most important phases when modelling rock - groundwater interactions are largely missing. As the solubility of trace elements in natural systems is largely governed by substitution in more common minerals, thermodynamic data for solid solutions are very important for the prediction of radionuclide concentrations. These data are, with very few exceptions, completely absent. At present, modelling of solid solutions is performed by assuming ideal mixing behaviour (ideal mixing entropy). Moreover, mechanisms and principles for the formation of solid solution in such systems are poorly understood. For clay minerals, the uptake of trace metals has been described successfully in terms of ion exchange models. However, the database available is still very restricted. We need to augment our information on clay minerals and other secondary minerals in many respects. Quantitative structural data on many naturally occurring solids such as the expandable and non-expandable mixed-layered clays is still quite unsatisfactory. Similarly, we need more information on minerals such as sepiolite, which forms due to a dissolution-precipitation mechanism incorporating components from pre-existing detritus. The sorptive properties of most clay minerals and diagenetic products are of great importance in all dynamic models. These properties can be properly evaluated only by complete surface characterisation which includes fibre dimensions (in chain-structures) and crystal imperfections.

3.3.2. Solid/Aqueous Interfaces

Sorption of trace elements on mineral surfaces is thought by many workers to be one of the key processes for predicting the migration behaviour of radionuclides or other contaminants. It is now common to describe sorption processes in terms of surface complexation. Although in recent years considerable progress has been achieved, surface complexation data are still fragmentary and the actual operating mechanisms are poorly understood. Therefore, surface complexes are often derived by fitting experimental sorption data without any confirmation of the species postulated. Modern speciation techniques such as EXAFS and laser spectroscopy (see Chap. 6) which allow the characterisation of surface complexes are promising tools which have considerable potential to overcome this shortcoming. Extensive experimental studies are needed in this field.

A large body of experimentally determined K_d values are available. However, the applicability of K_d 's for predictive geochemical modelling is very restricted. K_d 's are system

specific, and apart from idealised uptake of, for example Cs, do not account for the mechanisms occurring in rock-water systems.

3.4. THERMODYNAMICALLY ILL-DEFINED SYSTEMS

3.4.1. Mineral chemistry

There are many examples of solid phases, which frequently occur in sedimentary or in altered igneous rocks, for which no structural information is available. The reason is that these are metastable in nature but cannot be synthesised in the laboratory. Although we have an extensive file on those metastable products which have been characterised, each of these requires a separate experimental study to provide thermodynamic data on the stability of the solid and other physical properties for dynamic modelling. Methods of in-situ analysis using novel techniques are described briefly in Chapter 5.

3.4.2. Naturally occurring organics including humic/fulvic acids

A core body of data exists for the complexation of actinides with naturally occurring organics such as humic and fulvic acids. A major problem is the treatment of these data within the framework of thermodynamics. Extra-thermodynamic definitions are required. For highly charged ions, data are scarce and almost completely absent for tetravalent elements. The reaction mechanisms, in particular the reversibility of complexation reactions on long-timescales, are not well understood. Very little is known about the formation of mixed (ternary) "complexes". The state of the art is summarised in Table 3.3.

Table 3.3: State of knowledge on complex formation with naturally occurring organics.

Oxidation state	Elements	State of knowledge
+I	Cs	less important
+II	Sr, Ra, Ni, Co	less important
+III	Am, Cm, Pu, REE	data set incomplete
+IV	Th, U, Pu, Np, Tc, Se	not known
+V	Pu, Np	data set incomplete
+VI	U, Pu, Np, Se	data set incomplete
+VII	Tc	less important
-I	I	less important
-II	Se	less important

3.4.3. Colloids

Colloids (Eigencolloids) are considered by many authors to be important for the migration behaviour of actinides and fission products. Highly charged ions such as tetravalent, trivalent and hexavalent actinides have a strong tendency to form colloids. Indeed this is one of the reasons why reliable thermodynamic data on tetravalent actinides are scarce. The mechanisms are not well understood and hence a methodology for handling the formation and transport of colloids in geochemical models is not well established. The state of knowledge is summarised in Table 3.4.

Table 3.4: State of knowledge on colloid formation (Eigencolloids).

Oxidation state	Elements	State of knowledge
+I	Cs	less important
+II	Sr, Ra, Ni, Co	data set incomplete
+III	Am, Cm, Pu, REE	data set incomplete
+IV	Th, U, Pu, Np, Tc, Se	not known
+V	Pu, Np	less important
+VI	U, Pu, Np, Se	data set incomplete
+VII	Tc	not important
-I	I	not important
-II	Se	not important

3.4.4. Components of engineered systems

- Steel corrosion

Description of the chemical evolution of near field components in the post-operational phase is normally based on thermodynamic considerations. This is the case for assessing the evolution of the steel canister/groundwater system under anoxic conditions and the most probable consequences in terms of the amount and characteristics of the corrosion products generated (iron oxyhydroxides and hydrogen gas evolution).

There is a substantial body of literature on the corrosion of iron and the overall process is

oxygen. The anaerobic corrosion of iron has been less studied, although in recent years SKB has commissioned some dedicated research looking at the anoxic long term corrosion of carbon steel (Platts et al., 1994, Blackwood et al. 1994, Blackwood et al, 1995) and later on the comparative effects with iron (Smart et al. 1997).

- Spent fuel

The spent fuel/water interface is an intrinsically dynamic system. This is due to the alpha, beta and gamma radiolysis of water which generates oxidising species, mainly H_2O_2 and O_2 which tend to oxidise the UO_2 surface to dissolved U(VI) species.

However, even if the release of U(VI) species and the associated radionuclides is kinetically controlled by the radiolytic production of oxidants, the final concentrations of these radionuclides in solution is controlled by the thermodynamic solubility of secondary phases: oxyhydroxides in the first stage, silicates and phosphates in the longer term. These observations are backed up by a large experimental database relating to spent fuel dissolution experiments under various conditions. Consequently, thermodynamic models are currently used in most performance assessments related to spent fuel disposal systems to calculate **source term** concentrations of the various radionuclides in different groundwater conditions. In the context of spent fuel assessment, this constitutes the only situation in which a thermodynamically derived chemical parameter is put directly into PA calculations.

Generally, source term concentrations are calculated by using the solubilities of individual “pure” secondary phases of the different radioelements. This practice is, of course, unsatisfactory given our knowledge of the chemical behaviour of trace elements in nature and their association through co-precipitation and solid solution formation. More realistic thermodynamic models designed to provide source term concentrations take these phenomena into consideration and present developments are going in this direction (Berner 1994, Bruno et al 1997).

- Backfill systems

Existing thermodynamic databases are relatively weak with respect to critically evaluated data relevant to high pH environments, as may exist in chemical backfills such as cement, or as may occur in leachates from such backfills. Data accumulated in the course of experimental studies on cement supported by literature values have been corrected to zero ionic strength and put into a format consistent with the PHREEQE code. These data, together with supporting references have been merged with the more comprehensive CHEMVAL and HATCHES geochemical databases (Glasser and Paul 1999). The latter was released in November, 1998.

It should be noted, however, that though many of the data employed for cementitious systems are analogues to those used for groundwater speciation/solubility calculations, others utilise model constructs which are not entirely compatible.

3.4.5. Biological Systems

In the context of radiological assessment, chemical interactions in the biosphere have attracted far less attention than have aspects of vault and geosphere evolution. Current approaches make use of simplistic compartmental models by which the many and varied processes

applied with little further treatment in order to estimate exposure to pre-determined population groups.

However, outside the area of radioactive waste disposal, a number of speciation-based methods for calculating the mobility and toxicity of pollutants in the biosphere exist, as exemplified by the work of May and colleagues (eg May and Murray, 1991, 1993; Murray and May, 1995). Their JESS (Joint Expert Speciation System) is supported by a very comprehensive thermodynamic database, comprising around 50,000 entries for reactions involving more than almost 100 metal ions with 700 ligands. The majority of the data relate to biological systems and have been applied successfully to soil, plant and animal speciation problems. Novel approaches to the complex structural chemistry of soil organics and the use of surrogate functions in a manner akin to well-known 'shadow-modelling' techniques have been incorporated into the system.

Although there is no generally accepted methodology for modelling biological systems, possibilities exist using experience from several different fields:

- biocatalysis-models specific reactions using v_{\max} , K_m
- microbial physiology metabolic models whole organism with different levels of simplification, e.g. rate-limiting reaction with other reactions lumped, metabolic control theory,
- lumped models e.g. Monod equation
- black frame model of reaction embedded in lumped model

There is a body of literature data available in each area and although mostly empirical and, hence, strictly suitable only for studying similar systems, such data could be used for data estimation or initial guess purposes.

Thermodynamic data are also needed for species which sorb to, or are taken up by, microorganisms. These data are not known for several reasons. First, the difficulty of studying specific biochemical reactions in isolation from the rest of the microbiological metabolism. This is especially true for reactions which depend upon membrane-bound enzymes (as is the case for sorption and uptake of metal ions). The second is the difficulty of working with the types of mixed cultures which are found in natural groundwater systems.

There are several laboratories working in the area of microbial uptake of uranium (e.g. FZR). A collaboration between laboratories experienced in microbial biocatalysis and degradation of non-radioactive contaminants and those experienced in radiochemistry might prove the most effective means of generating new data.

Mobilisation and immobilisation of radionuclides and toxic metals by the activities of autotrophs, in the case of inorganic waste, and heterotrophs in mixed wastes containing organics, could be significant. The form in which the metal occurs (e.g. elemental, oxide, sulphide, ionic, inorganic complex, organic complex, or organometallic), the availability of electron donors and nutrients (carbon, nitrogen, phosphorus), the presence of alternative electron acceptors (Fe^{3+} , Mn^{4+} , NO_3^- , SO_4^{2-} , organic compounds), and environmental factors (pH, Eh, temperature, moisture) will affect the type, rate, and extent of microbial activity and microbial transformation of metals (West et al. 1982, West et al. 1985, Francis 1990, Francis et al. 1991).

Microorganisms play an important role in the dissolution of metal oxides by direct action or indirectly by production of metabolites, such as organic acids and chelating agents, and by lowering the pH of the medium. Direct action involves enzymatic reductive dissolution of the metal oxide, whereby the oxide is used as a terminal electron acceptor. For example, oxides of Mn(III, IV), Fe(III), Co(III), and Ni(III), when reduced to divalent ions under anoxic conditions, show an increase in solubility of several orders of magnitude (Stone 1986). In the case of U(VI) microbial reduction causes precipitation of insoluble U(IV). This microbial reaction plays an important role in the geochemical cycle of uranium and may be of interest for bioremediation processes. As known from the literature, several Fe(III)-reducing bacteria, e.g., *Shewanella putrefaciens* and *Geobacter metallireducens*, as well as sulphate-reducing bacteria, e.g., *Desulfovibrio desulfuricans* and *Desulfovibrio vulgaris* (Lovley & Phillips 1992, Gorby & Lovley 1992), are able to use U(VI) as a terminal electron acceptor. Characterization of the precipitate has shown that during this enzymatic reduction uraninite (UO₂) is formed. In deep geological formations a number of sulphate-reducing bacteria have been found. These heterophilic bacteria which use sulphate as an energy source live under anaerobic conditions and can have an important influence on the migration of radionuclides and heavy metals in radioactive waste repositories.

Additionally, uranium minerals are often associated with metal sulphides such as pyrites, pyrrhotite and chalcopyrite. Iron and sulphur oxidising bacteria are able to solubilise various metals by oxidation of their sulphide minerals. The rate of metal dissolution increases in the order CuS < PbS < CdS < ZnS < CoS (Torma & Sakaguchi 1978). For dissolution of uranium minerals, one representative of this group, *Thiobacillus ferrooxidans*, is of particular interest. *Thiobacillus ferrooxidans* is a gram-negative, acidophilic bacterium with an pH-optimum between 1 and 4. It is obligately chemolithotrophic, i.e. it obtains its carbon by fixing carbon dioxide from the atmosphere and derives its energy by oxidising ferrous iron and reduced or partly reduced sulphur compounds which results in the production of sulphuric acid and Fe(III). Consequently, this organism has been used industrially in metal leaching from ores and decontamination of industrial wastes. In the presence of uranium minerals, the Fe³⁺ oxidises U(IV) to U(VI). However, these bacteria can not only oxidise uranium, they can also accumulate U(VI) which may then be transported and released elsewhere by remineralization. The mechanism and the enzymatic and kinetic basis of the uranium oxidation has been studied extensively (Hutchins et al. 1986, Rawling et al. 1995), though relatively little information is available on the quantity, binding strength, reversibility and structure of the U(VI) complexes within the biomass (DiSpirito & Tuovinen 1982, Panak et al. 1998).

In comparison to processes involving only inorganic constituents, the main mechanisms responsible for microbiological processes are still poorly known. Numerous studies have been reported in the literature on metal binding including those on heavy metals such as copper, lead, uranium, cadmium, and mercury. Most of these studies either determined the accumulation capability of different strains at a fixed concentration of the metal ions (Horikoshi et al. 1981, Nakajima 1986) or used Langmuir and Freundlich isotherms (McLean et al. 1996) to obtain the maximum binding capacity for each strain. This, in turn, means that no information on the binding mechanism and the structure of the complexes formed is available. So far only some phenomenological parameter sets have been determined. The situation is similar with respect to kinetic data. Thus, there is an urgent need for new data, first to identify the underlying basic processes, and secondly to determine the appropriate parameter sets. One clue to the basic mechanisms is identification of the sorption sites on (or inside) the respective microorganisms in case of living material (Blackwell et al. 1995, Ono et

the sorption process (Huber & Seienska-Pobell, 1994, Seienska-Pobell et al., 1995) and may even lead to improved sorption characteristics through genetic engineering.

Techniques developed for predicting speciation in groundwaters are also appropriate in biological systems where the aqueous chemistry is generally more complex. Thus, in order to estimate the extent to which metal ions are accumulated in food chains and the subsequent bioavailability to man, data are required for both naturally occurring and synthetic chelating agents. For example, although plutonium is readily polymerised in groundwater solutions at $\text{pH} > 2$, the presence of citrate in digestive tracts suppresses this hydrolysis and retains the metal in solution. Similarly, the widespread industrial use of complexing agents such as NTA, EDTA and their derivatives will exert an influence on actinide uptake by agricultural products.

A great deal of work has been undertaken on the binding of actinides by natural organic (humic and fulvic) acids, notably by Kim and co-workers within the MIRAGE Project (Czerwinski et al., 1996). In peaty or loam soils, these polyelectrolytic ligands are thought to play a dominant role in the fixation of cations in the root zone. However, relatively little attention has been paid to these findings by workers engaged in performing radiological assessments, where reliance is still placed on empirical 'constants'. Much the same could be said of fundamental speciation research in the biological sciences. The fate of plutonium in man, for example, is well known and is highly speciation - dependent; colloidal particles are rapidly removed from the blood by phagocytosis and concentrated to a large extent in the liver; soluble Pu becomes rapidly associated with transferrin and is then cleared slowly to the liver and skeleton where it is bound in ferritin and haemosiderin, respectively. Very little of the Pu ingested is excreted but is ultimately stored as insoluble oxides, hydroxides and polymeric aggregates or 'hot spots', which may cause tumour growth.

4. DATA ESTIMATION METHODS

4.1. MODELLING REQUIREMENTS

The focal points of this Concerted Action are on chemical thermodynamics, thermodynamic data/databases and their applications. It is appropriate, therefore, to make some comments on the applicability of thermodynamics to the systems relevant for radiological and environmental assessment.

Thermodynamic data may be used to assess which chemical reactions are possible and their extent in a given system, provided that equilibrium is finally attained. In equilibrium systems where the total analytical concentrations of the dissolved components and the values of a small number of master variables, such as pH, redox potential etc. are known from measurements, one can calculate the *speciation*, *i.e.* the chemical states of each element in the solution, from known thermodynamic data. Information of this type is important because the chemical states of a given element will determine its solubility and transport characteristics and properties derived from these such as sorption, bio-availability and toxicity. There are two major questions to address before using thermodynamics to describe the properties of systems in nature. The first is to decide if the systems explored are at equilibrium, or not, the second to decide which are the main chemical factors affecting the properties. The quality of the thermodynamic data available to account for these processes then becomes of paramount importance.

Whether a system will attain equilibrium is determined by the rates of the reactions that may take place and, for open systems, of the rate of transport of chemical constituents to and from the reactive zone. The latter is often determined by the rates of mixing and diffusion. The possibility of using thermodynamic data is then related to the rate differences between the different processes taking place. A given system may be at dis-equilibrium as a result of slow physical processes, e.g. the slow mixing of water from two streams with different chemical composition. If the rate of the chemical reactions are fast, which is often the case for homogeneous reactions in solution, we can assume *local* chemical equilibrium, and calculate the extent of reaction and the speciation, at each stage of the mixing process. There are a number of different methods available to describe coupled transport, *i.e.* the combination of advection, diffusion and chemical reactions in a heterogeneous aquifer. These methods are well known but they lie outside the scope of this report.

Equilibrium modelling can also be used without complete information on the relative rates of the processes in a complex system, but will then only give information on the boundary conditions for the system. Nevertheless, this may also constitute important information and a thermodynamic analysis is often the first stage in modelling complex aquatic systems.

Transformations of solid phases are generally much slower than reactions in solution and can rarely be studied at ambient temperature. One may have to use “accelerated testing”, *i. e.* studies at higher temperature in order to achieve equilibrium, the rates of chemical reactions in general increase strongly at elevated temperature. This technique requires information on the thermodynamic characteristics of the possible solid phases in the system in order to ensure that the same reactions are being studied over the temperature range.

Determining which are the main chemical processes operating in a complex system is one of the major problems in performance and safety assessment. One is likely to be faced with a lack of quantitative information on several plausible chemical reactions. In order to decide whether these reactions are important or not, scoping calculations using estimated (thermodynamic) data are of practical importance. Such calculations are also useful when setting priorities for experimental work.

4.2. ESTIMATION OF THERMODYNAMIC DATA FOR SOLUTES IN MULTICOMPONENT SYSTEMS

Chemical systems encountered in nature contain many components, whereas most of the published thermodynamic data refer to systems containing one metal ion and one ligand (binary systems). The published data are more a reflection of the preferences of the laboratory chemists than of the relative importance of complexes containing several different ligands and metal ions, in the following termed, ternary or higher systems. This must be considered when performing thermodynamic modelling.

Calculations of chemical speciation are only useful if all of the major chemical reactions that are feasible in the system have been included. The aim within this Concerted Action is to “establish the mechanism by which a quality assessed thermodynamic database...may be built”, however, one must realise that no database will ever be complete. Future experimental efforts must be directed therefore towards the determination of thermodynamic quantities for the major reactions which, taken together, define the processes most relevant for the chemical description of the waste systems under scrutiny. In order to identify these it is practical to devise methods by which thermodynamic quantities may be estimated. Such methods are available and they are all based on well-established chemical theories. A more detailed description of these methods is given in Grenthe et al. (1997a). Some examples are listed below:

- Chemical elements of the same charge and the same configuration of valence electrons have similar chemical properties. *e.g.* actinides in a given oxidation state have similar chemical characteristics, with the exception of their oxidation-reduction properties. Hence, information on Th(IV), U(IV) and U(VI), for which much information is available may be used to estimate the properties of the corresponding transuranium elements. Information on actinide(III) compounds may often be inferred from the corresponding lanthanide(III) compounds etc.
- There are empirical rules that can be used to decide the relative affinities between different donor atoms (“ligands”) and metal ions, to provide a crude estimate of stability constants for different complexes.
- Structural information on the preferred coordination geometry of different metal ions and ligands may be used to assess the stoichiometry of complexes, both in binary and ternary systems.

It is important to state that a speciation model is much more robust if a major reaction is included with an estimated value of the relevant thermodynamic quantity than if it is not included at all. Consequently, for data estimation, the thermodynamic quantities of the

4.3. CORRECTION OF THERMODYNAMIC DATA TO THE CHOSEN STANDARD STATE

Thermodynamic data are always given for a specified standard state. They must be recalculated if they are to be used under other conditions, as is the general case when describing chemical systems in nature. Correction to standard state conditions is usually an integral part of an experimental determination of thermodynamic data. However, coherent aqueous chemical data determined in the presence of one ionic medium is an exception. Different investigators may have selected different ionic media/ ionic strength and it is necessary to recalculate the values to a common standard state in order to determine if they are consistent. Calculations of this kind require methods for the estimation of activity factors for reactants and products. Most chemical data in solution have been determined in ionic media of low to moderate ionic strength and at best there are experimental data from five to ten different ionic media. In the case of U, for example, data of this type have been recalculated to a common standard state using the specific ion interaction (SIT) method. This method is not suitable for the recalculation of standard state data to mixed electrolyte systems at high ionic strength. In these cases, one has to use the Pitzer equations with the necessary number of interaction parameters for the reactants/ products. Pitzer parameters have been determined for a number of ions but very few data for complexes are available. This is a serious drawback because such determinations require a very extensive experimental effort. A description of the SIT- and Pitzer-models, and the methods used to estimate interaction parameters is given by Grenthe et al. (1997b).

Descriptions of the use of the Pitzer formalism and the determination of Pitzer parameters for complex formation reactions in brine systems have been given by Fanghänel and Kim (1998), Fanghänel et al. (1995), Könnecke et al. (1997a,b), Neck et al. (1998) and Plyasunov et al. (1998).

Thermodynamic data vary with temperature and it is also necessary therefore to be able to recalculate them to any desired temperature. The thermodynamic laws provide the framework for such calculations but the thermodynamic quantities required often need to be estimated. A description of the thermodynamic framework and various estimation methods are given by Puigdomenech et al. (1997).

4.4. ESTIMATION AND EXTRAPOLATION OF THE THERMODYNAMIC PROPERTIES OF MINERALS AND SOLID SOLUTIONS

4.4.1 Mixing properties

Thermodynamic properties are ultimately macroscopic manifestations of interactions at the atomic scale. However, detailed calculations and integration of these interactions are formidable tasks, especially for complex ionic solid solutions. Consequently, most works on the theoretical calculation of the thermodynamic properties of minerals and mineral solid solutions are semi-empirical in nature. We present below a selected review of these works.

The mixing properties of a solution ultimately depend on the similarity or dissimilarity in the properties of the substituting atoms.

Quite often, the enthalpy of mixing of an isostructural solid solution is thought to have two components: (a) a strain energy term arising from the mismatch in size when one atom substitutes for another of different size, and (b) a chemical energy term arising from the interactions of the atoms with their surroundings in the crystal lattice. The chemical energy also depends on the difference in the size of the atoms substituting in the solid solution. To some extent, the elastic and chemical effects are, therefore, co-operative in nature

An interesting demonstration of the strain of a crystal lattice due to the substitution of an atom of different size can be found in Bragg and Nye's (1947) classic study of a bubble-raft analogue of a crystal. There is a widespread disruption of the symmetry of the raft, suggesting a similar widespread effect by the substitution of one atom for another of different size in a crystal lattice. Several observations imply that it is the mismatch of the molar volumes of the compounds, rather than that of the radii of the interchangeable atoms, that should be considered in estimating the ΔH^{mix} of solid solutions.

Greenwood (1979) reviewed the metallurgical literature on the elastic contributions to the excess Gibbs free energy of mixing and has combined the works of Lawson (1947) and Christian (1975) to derive an expression of ΔG^{XS} (elastic) for a binary solid solution in terms of the elastic parameters of the end-member components.

Christian (1975) emphasised that the strain energy is the elastic component of ΔG^{XS} (neglecting the negligible amount of P-V work against external forces), and not just the elastic component of the enthalpy of mixing, as sometimes implied. The elastic effect could contribute to positive excess entropy of mixing and tend to offset ΔS^{XS} due to the configurational effect (non-random distribution), which must be negative.

Greenwood (1979) has estimated the strain Margules parameters, W_{SB} and W_{SA} , terms for a number of solid solutions and compared the results with the experimentally determined values of the $^{\wedge}W^{\text{H}}$ Margules parameters in these systems.

Davies and Navrotsky (1983) found good linear correlation between the regular and subregular parameters of a wide variety of binary solid solutions and a volume mismatch term. The data set includes solid solutions in which cations are being mixed on four-, six-, and eight-coordinated sites. These authors have also calculated the solubility limits in a binary system as a function of volume-mismatch of the end-member components.

As discussed earlier, the elastic strain energy theory often predicts a positive enthalpy of mixing which is much less than the value measured calorimetrically, suggesting significant "chemical" contributions to the enthalpy of mixing. Thus, the fact that Davies and Navrotsky (1983) have still succeeded in finding a good linear correlation between the interaction parameters and volume mismatch terms of a wide variety of solid solutions seems to suggest an interrelationship between chemical and volume mismatch properties of the end-members in a solid solution series. We also note that Davies and Navrotsky did not seek correlation between interaction parameters and volume mismatch terms according to the forms suggested by elastic theory.

The "chemical effects" on the enthalpy of mixing may arise from the differences in electronegativity and electronic polarization of the atoms substituting for each other, their charges, and from specific electronic effects, such as the change of ligand field stabilisation energy of transition metal ions as a function of the composition of the solid solution. Darken and Gurry (1953) have explored the effect of electronegativity differences on the mutual solubility of two metals. The electronegativity difference contributes to positive enthalpy of mixing, thus limiting the mutual solubility. Calculation of the ligand field effect on the enthalpy of mixing is a very difficult problem. However, as a first approximation, we can consider the simpler and more tractable theory, namely the crystal field theory (CFT), to account for the effect of d orbital splitting of transition metal ions on the enthalpy of mixing of silicate and oxide solid solutions, which are largely ionic crystals. In general, the splitting between the t_{2g} and e_g orbitals, Δ , increases as the metal-ligand distance decreases and vice versa. The change of Δ as a function of composition in a solid solution leads to $\Delta CFSE^{mix}$, the sign of which depends on the nature of the transition metal ion and the geometry of the coordination polyhedron.

ΔH^{mix} of a solid solution involving a transition metal ion has to be estimated by combining the contributions from lattice strain and other chemical effects with $\Delta CFSE^{mix}$ (or, more appropriately, with the ligand field stabilisation energy of mixing).

4.4.2. Thermochemical Data on Pure Phases

Entropy.

Fyfe et al. (1958) proposed the calculation of entropy of a compound from oxide data by the summation method. For isostructural compounds of spherical cations (e.g., Be, Mg, and Ca), it was shown that a linear relationship exists between molar volume and entropy.

Many workers (e.g., Helgeson et al. 1978) have obtained good estimates of entropy of a compound by considering a reaction between the compound and an isostructural compound and component oxides for which S is known. Wood (1981) found that the entropy of fayalite calculated by using this method is much higher ($38.92 \text{ cal mol}^{-1} \text{ deg}^{-1}$) than the observed value of 35.50. Wood (1981) suggests that this difference represents the change in electronic entropy of $Fe^{2+}(d^6)$ in changing from the regular octahedral environment of FeO to the somewhat distorted octahedral environment in fayalite. In a regular octahedron, Fe^{2+} has three distinguishable electronic configurations, since the 6th d electron has an equal probability of occupying any one of the three energetically degenerate lower energy orbitals. Thus Fe^{2+} has an electronic entropy in a regular octahedron.

In a distorted octahedron, the orbital degeneracies are partly or completely removed. In the latter case, there is only one electron configuration of Fe^{2+} , the lowest orbital being occupied by two electrons, and consequently $S_{el} = 0$. It appears that the structural analogue method used by several workers and recommended by Helgeson et al. (1978), coupled with Wood's (1981) crystal field corrections, should enable reasonable entropy estimates for ferrous iron silicates at 298K. Blander and Stover (1991) have proposed a statistical-mechanical theory based method.

Heat Capacity

ROBINSON and HAAS (1985) assumed that silicates could be considered as comprising certain fictive components, e.g., MgO-4, MgO-6, Al₂O₃-4, Al₂O₃-6 etc.; MgO-4 signifies the Mg ion in four-fold co-ordination and so on. Because of the success of the oxide summation values for entropy, it was considered that the overall silicate lattice modes are largely a function of the modes of the individual cation-oxygen polyhedra. The heat capacity and calorimetric entropy contribution of each fictive component (cation-oxygen polyhedra) may be estimated from regression analysis of the available thermodynamic data. Such component coefficients have been presented by Robinson and Haas for a number of fictive components, from which the C_p of a component can be obtained. The authors consider that the uncertainty of the estimates using this technique is approximately 2% for heat capacity and 5% for calorimetric entropy.

There has been very impressive success in the detailed calculation of mixing energies of simple ionic solutions such as alkali halides from fundamental lattice theory (e.g., Dick and Das 1962 a, b; Fancher and Barsch, 1969). The interested reader is also referred to Prigogine (1957) for an authoritative treatment of the molecular theory of solutions and to the various papers in the volume edited by Kieffer and Navrotsky (1985) for in-depth discussions on the relationship between atomic environments and thermodynamic properties of minerals.

5. DESIGN OF AN EXPERIMENTAL PROGRAMME TO PROVIDE PRIORITY FUNDAMENTAL DATA

5.1. DATA REQUIREMENTS FOR THE NEAR FIELD

5.1.1. Fundamental aspects of actinide chemistry

Application of thermodynamic data is one way to develop and codify chemical theories and this is essential for *all* predictive work, whether in the area of nuclear waste management, nuclear fuel reprocessing, or others. A review of the present status of actinide chemistry, albeit a rather summary one, has recently been made by OECD/NEA (Grenthe et al. 1992, Silva et al. 1995). This study identifies the chemistry of the tetravalent actinides as a key area in which additional laboratory studies are required in order to improve and broaden our current chemical understanding. We share this opinion. In view of the importance of solubility limitations in safety assessments, the solubility of M(IV) phases and their redox reactions should be given high priority. Plutonium chemistry is an example of an area where additional basic research is needed, *e. g.* in order to reduce some of the large uncertainties in current performance assessment calculations. Fundamental research on transuranium chemistry requires a co-ordinated international effort as the laboratories which have the capability for this type of work are becoming scarce. An even more serious problem is that the number of qualified scientists with experience of this field is rapidly decreasing. As a result too few young scientists enter the area. Urgent measures are necessary to improve the situation, otherwise Europe may be faced with a serious shortage of expertise within the next decade. This issue can and should be addressed within the Fifth Framework Programme by establishing a scheme for the support of the research infrastructure within the area, and for training and mobility of young scientists from universities. In this way they can participate in, and learn from research programmes at the existing actinide laboratories. We envisage that the fundamental research areas proposed *e. g.* within the JETDEM activity will provide a range of suitable subjects for diploma and thesis projects.

5.1.2. The waste matrix and near field geochemistry

These are areas where to date little co-ordinated effort has been carried out at the European level. This is the part of the repository system where most of the key chemical gradients and interfaces will occur. It is a system that, from the engineering point of view, can be designed and optimised; hence, a research area with the possibility of large returns in terms of transnational research investments. Thermodynamic (and kinetic) data will be important for the validation of the models used to describe the near-field region. Some of the important research issues are described below:

- Radiolytic generation of oxidants, in terms of radicals, recombination of the radicals and generation of stable oxidants. The role of groundwater ions in these processes, particularly chloride, sulphate and bicarbonate. Understanding of the specific contribution of alpha, beta and gamma radiation to radiolytic generation of oxidants (and reductants). Here, a fundamental understanding of the processes and the determination of the rate constants for the key unknown processes is essential. There are a few European laboratories working in

- Study of the fundamental mechanisms for the radiolytic oxidation of the spent fuel matrix. This is closely related to the previous section, but much understanding can also be gained by using non-active materials, such as un-irradiated UO₂. The effort here should be directed towards understanding and quantifying the rates and mechanisms of **oxidation** (not oxidative dissolution) of the matrix by the critical oxidants, O₂ and H₂O₂, under conditions relevant to the repository system (anoxic environment). The role of the major ligands in groundwater (bicarbonate, sulphate and chloride) on the rate of oxidation should also be ascertained.

5.1.3. Chemical backfills and matrices for conditioning nuclear wastes

The EC has supported research on barrier, container and backfill materials for the immobilisation of radioactive wastes for more than 20 years. During this time perception of the problems has shifted. Feasibility studies, initially concentrating on *processing* and *demonstrations* have gradually been supplanted by studies of *intrinsic matrix properties*, of *waste-matrix interactions* and the *time dependence of these properties*. Also, alkaline cements have emerged as leading matrix contenders because they afford chemical as well as physical conditioning for the waste.

The case for additional engineered barriers has also been strengthened by perceived weaknesses in the containment afforded by purely geological barriers. Difficulties in proving beyond reasonable doubt the transmissive properties of several km³ of rock, coupled with potential intrusion, have led to a greater emphasis on chemical barriers. Thus, the design and future performance of chemical barrier systems assumes considerable importance in the overall performance assessment.

Work supported by the EC will have achieved by the end of the present R+D programme (in 1999):

Quantification of the properties of cementitious backfills including physical and chemical properties such as:

- Cracking and crack properties
- Aqueous chemistry and pH evolution
- Preliminary data on radionuclide sorption processes
- Internal properties: pH, Eh
- Longer term reactions with groundwater, canister materials, waste forms etc.
- Leach mechanisms and testing
- Metallic corrosion phenomena, and rates, at high pH
- Chemical thermodynamic models appropriate to represent cement performance.

And achieved limited progress on quantifying the following:

- Response of cement systems to prolonged elevated temperatures and the subsequent impact on performance.
- Characterisation of redox processes in cement systems.

- Nature of solubility limiting phases; isolation, characterisation and input data suitable for verification and inclusion in performance assessment.
- Impact of alkaline backfills on other man-made barriers (clay, zeolites etc.) and in minerals/rocks in the near/far field (the so-called alkaline plume).
- Quantification of backfill-organic interactions: reduction of potential organic complexant concentrations as a consequence of reaction with cement components.

A focused programme of research should be supported to address the five problem areas outlined above. A suggested task list is presented below.

- *Thermal Impacts on Cement Performance.* The chemically active gel phase undergoes irreversible crystallisation at temperatures $> 40-60$ °C. The products of crystallisation should be characterised, synthesised and their relative stabilities and solubilities measured. Their ion exchange capacities should be measured for selected waste species as well as for low molecular weight organic complexants. The objective is to define and quantify the performance of cement barriers at ages up to 100 years particularly when exposed to warm, humid conditions.
- *Redox Processes.* Cement systems typically have low poisoning capacities and near-neutral (*i.e.* neither strongly oxidising nor reducing properties). The problem is, therefore, to determine the impact of other constituents on cement properties and the coupling between processes. For example, cements absorb oxygen arising from radiolytic decomposition of water, presumably forming solid peroxides. The task is to quantify these oxidative processes as well as reductive processes (H_2 and CH_4 generation from waste, low-valent iron from corrosion). Their impact on cement - related waste species couples should be measured to determine waste species' oxidation states in the post-closure phase. The objective is to establish more clearly the evolution of redox conditions in the post-closure phase and determine their impact on radioelement solubility.
- *Quantification of Solubility-Limiting Processes in Cement Systems.* Using five key chemical components of cement; Ca, Al, Mg, Si and (OH, H_2O), the solubility limiting phases formed with selected radionuclides: Sr, Sn, Cr, I, Zr, Se, Th and U could be determined. A critical review of currently available data was released in November 1998 and will assist in experimental design. The review should systematically:
 - Identify the phase or phases that act as hosts.
 - Synthesise these phases and determine self generated solubilities.
 - Determine phase stability limits, at least approximately, in regimes of decreased pH.
 - Measure the ability of these phases to extend their range of stability by reaction with other geochemically abundant species, especially anionic species: CO_3^{2-} , SO_4^{2-} , Cl^- .

It is apparent that the quality and quantity of information presently available diminishes in the order (i) to (iv). Owing to the difficulty of working directly with actinides, it is proposed to approach selected actinides (Pu, Am, Np) by a two-stage process - initially by using actinide simulants, such as lanthanides, in order to define key experiments to be performed subsequently with actinides, themselves. The objective is the establishment of a robust database for the solubility limited systems, capable of independent verification.

to explain the mechanisms and confirm the solubility values used routinely in performance assessment.

- *Integration of Cement Performance Models with Complexation - Solubility Models.* Common low molecular weight organics/organometallics react with and solubilise radionuclides. However, not all potential organic complexants are stable in a cement environment: for example, citrate and oxalate. A list of priority complexants including EDTA, phosphates, carbonates, ISA and humic/fulvic acids should be studied. Reactions of these substances with cement should be quantified and the kinetic mechanisms and reversibility of reaction established. The objective is to set more realistic limits for performance assessment of the concentrations of complexants sustainable in the presence of cement barriers/backfills.

The tasks proposed above involve two strands: experimental determinations followed by database collation and integration with performance models. There are several laboratories in the EU that could contribute to both sets of tasks, though those with expertise in cementitious systems and possessing experimental facilities for handling/characterising actinide-containing solids are scarce.

5.2. DATA REQUIREMENTS FOR THE FAR FIELD

5.2.1. Sorption Data Bases

The goal of an experimental programme in this area should be to understand the processes controlling the uptake and release of safety relevant radionuclides on natural minerals in the far field and on materials important in radioactive waste management. The work should be directed towards understanding sorption mechanisms and the development of models which can be incorporated into computer codes to predict sorption in real systems.

Clay minerals such as illite and kaolinite are present at significant levels in many sedimentary and crystalline rock units that are currently under consideration for the disposal of radioactive waste. In addition, bentonite is of particular relevance in European high level radioactive waste management programmes since it has almost universally been chosen as the preferred backfill material in the near field. Clay minerals are likely to dominate the sorption characteristics of many radionuclides in the near and far fields. Because of their potential importance, the retention characteristics of clay minerals should be the subject of future fundamental investigations.

It has become evident that in order to increase our understanding of sorption/desorption processes and our confidence in the predictive capacity of sorption models, current wet chemistry techniques need to be extended to include, for example, surface analytical methods such as extended X-ray absorption fine structure spectroscopy (EXAFS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), various laser spectroscopic methods, etc.

A potential way forward for this work would be the development of a "thermodynamic sorption data base" for key minerals containing protolysis constants, site capacities, intrinsic surface complexation constants and selectivity coefficients (ion exchange) for safety relevant

radionuclides. These values, together with the appropriate models and codes, would potentially allow sorption to be calculated in natural systems under relevant conditions. Competitive effects for mixtures of radionuclides should be considered.

5.2.2. Microbiology

In order to improve the situation with respect to both the theoretical background and the determination of model parameters, several approaches are possible. Each of them must have in common a consistent record of the in-situ parameters of the microbes to ensure laboratory experiments under conditions that are as close as possible to natural environments. All physico-chemical processes relevant for metal-ion binding and their interrelationships should be investigated. This includes information on speciation from TRLFS, LPAS, UV/Vis and other methods. XPS, EXAFS and XANES experiments can reveal structural details of the complexes in addition to redox state information.

A promising strategy could include the following steps:

- Isolation of bacterial strains from the relevant sites, their characterisation by molecular genetic methods, and cultivation of the dominant strains (both from the site and from bacterial strain collections).
2. Simultaneously, determine all parameters that define the environmental conditions for these organisms, i.e., in-situ measurements of temperature, pH, redox potential, gas - phase composition, humidity, water analysis for ionic and colloidal components.
- Detailed quantitative determination of the uptake of the contaminants by the microbes from rocks, soils, ground and seepage waters. This would include possible changes of redox conditions to check whether the uptake is coupled to redox reactions.
- Determination of maximum loads (gram toxic component per gram dried biomass) and reaction constants for the binding between a bacterium and contaminant. Bioaccumulation has to be measured as a function of pH, ionic strength and competing complexing agents to account for the natural conditions at various sites.
- Determination of the selectivity of contaminant uptake by adding other metals or anions. The role of inhibitors should be ascertained.
- Determination of the effects of increased contaminant concentration on microbial growth.
- Selection of the most effective strains and performed tests on their mutagenesis.
- Identification of the cellular components that are responsible for contaminant uptake by means of electron spectroscopy, analysis of genetically modified microbes and biochemical methods.
9. Investigation of the reversibility of bioaccumulation and its kinetics. Determination of whether transport occurs on the cell wall or in the cell plasma and identification of the

6. DATA VERIFICATION

The set of data required in practical applications, such as evaluating the performance of natural or man made systems, is strongly dependent on the underlying model concepts. Therefore, data verification can not be dealt with separately from the associated modelling approach. In the context of JETDEM, the starting point is the choice of a set of species that is considered to be present and of relevance in the system under investigation.

Applying models to better understand fundamental processes in nature and to draw conclusions based on prognostic simulations are complex tasks. Models are necessarily simplifications of reality and even the most elaborate and complex models can only reflect some of the many aspects of natural processes. Thus, the choice of a model should be determined by the processes or phenomena to be investigated rather than the availability of data to parameterise any particular model. Models do not necessarily have to be realistic in order to be useful in certain circumstances (Grenthe and Puigdomenech, 1997). Provided they are based on sound physical, chemical and biological principles and their range of applicability is known, they can give valuable insight into complex problems. This, in turn, enables a better description of the system and assists in defining additional, specifically focussed investigations.

Model “validation”, especially in the field of geosphere transport of radionuclides and other solutes, has been the topic of much scientific effort in the past (e.g. OECD, 1997) and will be so in the future (e.g. OECD, 1998). Whereas the technical work performed under the title "model validation" is relatively clearly defined – when seen from a broad angle -, the term "validation" has given rise to an extensive and unresolved controversy as to its meaning (GEOVAL'94, 1994). The root of this controversy is, on the one hand, the impossibility of predicting events far into the future together with the inherent complexity of natural systems and, on the other hand, the need to judge data, tools and results of a performance assessment. Pragmatically, we understand “model validation” as model corroboration. Subsequent model testing entails the use of independent experiments, or, since this can seldom be achieved completely, extraction of model parameters from an experiment and comparison of these parameters with independent information. Whether a model passes a ‘validation test’ will depend on the level of rigour required as well as the intended application and is, to a large extent, subjective. Model validation requires, therefore, carefully planned and executed experiments and *a priori* acceptance criteria having the specific purpose of hypothesis testing in mind.

Generally, two types of model that need further ‘validation’ can be distinguished. The first class are those models describing microscopic processes at a molecular level and are most closely associated with the issue of data verification. Within the frame of JETDEM, these “microscopic models” are considered in more detail than the second class, here called “macroscopic models”. The latter are models describing processes in natural systems at larger scales and *de facto* encompass microscopic processes. Such models are the final goal for applications in nuclear safety assessment and, in a broader sense, environmental assessments, thus they will be referred to also in a separate section, even when they are not directly used for data verification purposes.

6.1 EXPERIMENTAL METHODS FOR DATA VERIFICATION

It is not trivial to determine a robust chemical model for a complex chemical equilibrium system, starting with the identification of all relevant species (aqueous, solid and gaseous) in the given system forming the set of chemical entities. Usually such sets are derived from experimental data without intrinsic identification of species, but are rather results of numerical solution of the pertinent thermodynamic equations and 'goodness of fit' procedures. Most are based on the least-squares method and may differ in the numerical strategy used. They may also contain a "species selector" that uses a statistical procedure, e.g., the Hamilton R-factor ratio (Hamilton, 1965), to decide whether or not a new species results in a significant improvement in the fit between the experimental data and the underlying model.

A key problem with all experimental methods is the presence of systematic errors (which in general are method dependent). In order to avoid that such errors influence the choice of chemical model it is advisable to use several methods in tandem. The key uncertainty is the validity of the assumption that activities and concentrations are proportional when the total concentrations of reactants and products are varied. To confirm a postulated set of species, independent evidence is required. This usually requires a spectroscopic method (or combinations thereof), such as:

- Conventional UV/Vis spectroscopy: This is a standard method. Data interpretation requires the determination not only of equilibrium constants but also of molar absorptivities. A general problem is the overlap of absorption bands of different species. Limitation is that absorption coefficients for many species of interest are too low. Usually this is overcome by using a competition method, where the complexing ligand forms strongly absorbing complexes. However, this means disturbance of the chemical system under investigation, the original speciation pattern may be lost.
- Infrared (IR) and Raman spectroscopy: IR is difficult to use because of the very strong background absorption of water which requires high total concentrations of the reactants, which are rarely found in environmentally relevant waters, as well as efficient methods of measuring spectral differences. Raman spectroscopy also requires rather high reactant concentrations, around 10^{-2} M. With the possible future use of free electron lasers this restriction may become obsolete. The advantage with these methods is that the spectra for the different species in equilibrium overlap much less than in UV/VIS spectroscopy. Hence, the molar absorptivities and the concentrations of the various species can be determined *directly*. It is difficult to obtain structural information from these data - however, one may be able to detect the mode of bonding of ambidentate ligands. One may also be able to detect if a carbonate complex contains coordinated bicarbonate, or not. IR and Raman spectra give information on the *symmetry* of the species. This can be used to eliminate some structural models and thereby give additional chemical insight.
- Time-resolved laser-induced fluorescence spectroscopy (TRLFS): This method is only applicable to species with fluorescent emissions, limiting it, in the case of actinides, to the uranyl ion, americium, and curium. However, the concentration limits required to obtain interpretable spectra are very low, down to 10^{-6} , 10^{-7} , and 10^{-9} mol/dm³, respectively, depending on the experimental equipment and the fluorescence yield of the species. Applications can be found in for example Wimmer et al. (1992), Fanghänel and Kim (1998), Bombard et al. (1996) and Geipel et al. (1997). In situ experiments are possible

with this method. Another advantage is the possibility of using the time resolution for deconvolution.

- Laser-induced photoacoustic spectroscopy (LPAS): This is a more advanced adsorption spectroscopic technique, but with the detection of an absolute value directly proportional to the concentration. Depending on the absorption coefficients the detection limit can be as low as 10^{-9} mol/ dm³. For a comprehensive guide see Kim et al. (1990). Again, in-situ experiments are possible. Details of the technique are given in Tam (1986), several applications can be found for example in Klenze and Kim (1989).
- Extended X-ray absorption fine structure (EXAFS): Like XANES based on synchrotron radiation, and with the same range of applicability, here the information obtained is the type and number of atoms in the various coordination shells of the atom investigated, together with the respective bond lengths. It should also be mentioned that the development of quantum chemical methods is now proceeding rapidly and a choice can be made between different structural models, which greatly facilitates the interpretation of EXAFS data, Wahlgren et al. (1998). Representative applications of EXAFS are given, e.g., in Denecke et al. (1997) or Moll et al. (1998). A good introduction is provided by Teo (1986).
- X-ray absorption near edge structure (XANES): This mainly provides information on the oxidation state of the element investigated, in some cases, together with information concerning the coordination sphere. The method is element specific and applicable to solids (crystalline and amorphous), to aqueous solutions and to surface sorbates. The degree of invasion of the sample is small in comparison to methods such as XPS. Presupposing strong light sources as provided by modern synchrotron radiation facilities, the concentration limit may be down to 10^{-4} mol/ dm³ as in the case of the uranyl cation. For details the reader is referred to Konigsberger and Prins (1988), who also cover EXAFS techniques.
- Nuclear magnetic resonance spectroscopy (NMR): It is extremely difficult to get NMR signals directly from radionuclides due to their very low gyromagnetic ratios. High concentrations and special equipment are required. Thus, the most realistic applications of NMR spectroscopy are for studying equilibria and dynamics in actinide systems containing NMR-active ligands such as ¹³C, ¹⁵N, ¹⁹F, ²⁹Si, ³¹P or ³³S. The method does not alter the sample, but requires rather high concentrations for many nuclides. NMR data may give separate peaks for each complex formed. Whether this is the case or not depends on the rate of exchange between the different species and their chemical shift differences. A number of NMR studies have been made on actinide systems which have given information both on equilibria, structure and dynamics, e.g., Szabo and Grenthe (1998). A good example of combining NMR, Raman, EXAFS and XRD can be found in Allen et al. (1995).
- X-Ray photo-electron spectroscopy (XPS): This yields information on redox speciation at surfaces. Concentrations need to be relatively high. For an introduction, see Veal et al. (1977). A speciation-related application can be found, e.g., in Teterin et al. (1994).
- Atomic force microscopy (AFM): This technique yields information on the morphology of surfaces. Quantification with respect to microscopic structure may be difficult however:

- Analytical electron microscopy and diffraction: Hren et al. (1979) give an introduction.
- ICP-MS as a sensitive tool for radionuclide analysis yields information on both elemental and isotopic composition. Concentration limits are generally in the ppt range and may go down to the ppq range with high resolution (Probst, 1996).

Some of the afore mentioned experimental techniques can also be used to verify thermodynamic data quantitatively. The basic principle in most cases is simply to determine a thermodynamic parameter via independent experimental approaches.

An overview of experimental techniques suitable for data verification is given in Table 6.1, which also outlines their areas of application.

Table 6.1: Application areas (marked with x) for experimental data verification techniques:

Method	Aqueous Solution	Solids	Gas	Quantitative Data	Structural Data
UV / Vis	x	x		x	(x)
IR / Raman	x	x			x
TRLFS	x	x		x	(x)
LPAS	x	x		x	(x)
EXAFS	x	x		x	(x)
XANES	x	x		x	(x)
NMR	x	x	x	x	x
XPS		x		x	(x)
Electron microscopy with analysis		x		(x)	
Electron diffraction		x			x
ICP/OES and /MS	x	x	(x)	x	
AFM	(x)	x			
XRD		x			x

Modelling simple reactions involving aqueous species is usually straightforward. Such reactions are generally fast within the accessible experimental time window and thermodynamics can be applied unequivocally. For certain cases, parameters may be missing which poses a serious problem (Section 3.2). The theoretical framework of thermodynamics in conjunction with appropriate combinations of experiments provide means to derive the required parameters. Thermodynamic data determined by independent methods in reproducible experiments can then be regarded as verified.

The situation is different for interactions of aqueous species with solid surfaces (or with naturally occurring organics). Describing sorption of trace elements on oxides and hydroxides in terms of surface complexation has a relatively long tradition (Stumm and Morgan, 1996). Main difficulty involved is the speciation of sorbed complexes, for which there are not so many direct methods available. However, surface complexation models have only been applied recently *in extenso* to sorption processes on complex minerals such as clays. For an overview of ongoing work the reader is referred to NEA (1998). The main questions remaining open include the nature of active surface sites (which can be studied by surface analytical methods such as EXAFS), the relevance of the electrostatic repulsion term in the surface complexation models (Bradbury and Baeyens, 1997), and the influence of kinetics.

Thermodynamic and kinetic experiments carried out to study the dissolution and alteration of solid samples (e.g. spent fuel, uranium secondary solid phases etc.) yield information that can be compared directly to independent modelling results. Such experiments can be used to study any system at the laboratory scale, making them useful model validation tools. Surface analysis of the solid samples allows interpretation of the dissolution process and, consequently, the behaviour of different variables studied (e.g. formation of secondary solid phases).

A reliable comparison between experiments and model calculations requires experiments which are tailored to the model structure and its data needs. These different data requirements mean that it is extremely difficult to use data from "historical" experiments for quantitative comparison with modelling results. To compare experiments and modelling results quantitatively, it is usually necessary to have significant interaction between experimental and modelling groups. However, there are some general criteria that experiments must meet if they are to be used for this purpose:

- As many data as possible with respect to experimental conditions (e.g. temperature, gas pressure, Eh, pH, ionic strength, metal concentrations, handling operations) should be recorded and any conditions not being deliberately varied should be kept as constant as possible.
- In general, it is best to change only one experimental condition at a time, but care has to be taken that the parameter space is adequately covered.
- It is essential to use experimental systems (e.g. buffers) for which thermodynamic data are available if they are to be modelled geochemically.
- Column (and field) experiments should show breakthrough curve data as well as recovery (specify the injected mass) and the results of subsequent column sectioning.

6.2. APPLICATION OF THERMODYNAMIC DATA FOR MACROSCOPIC MODEL VALIDATION

Thermodynamic models and data form a basis for macroscopic model concepts, especially when considering reactive tracer transport as a practical application in environmental assessments. Macroscopic models are usually tested quantitatively through laboratory and field experiments and validation through the use of natural and

Laboratory experiments range from small-scale column experiments (e.g. Trotignon et al., 1997) to experiments with large rock blocks (Vandergraaf et al., 1997). Their advantage is that they allow detailed system characterisation and, within certain bounds, for a controlled variation of system parameters. The last feature is important since it yields a test of whether the model correctly reproduces the parameter dependencies. Laboratory experiments should be performed with solids that remain as much as possible in their natural state. For instance, using crushed hard rock in a column experiment not only increases the surface area but also introduces “fresh” surfaces with possibly different properties.

Field experiments offer the advantage of simulating natural conditions. However, they are time consuming, costly and the boundary conditions are difficult to constrain. Carefully executed field experiments offer the possibility of testing consistency between static laboratory measurements (and the underlying microscopic models) and dynamic field values (e.g. Heer and Smith, 1998). Generally, however, field experiments can be described satisfactorily by a number of very different models. Solutions are not unique and thus complementary interpretations and choice of model depends upon laboratory experiments and independent investigations. Presently, a comprehensive international study to test transport models is in progress using dedicated migration experiments at the Äspö site, Sweden, (Äspö, 1998). Colloid migration experiments are being considered by institutions from several countries at the Grimsel Test Site, Switzerland (Kickmaier et al., 1999).

Up to now, almost all field experiments have been performed with simple reactive tracers such as the alkali, alkali earth or halide ions. There is a clear need for field experiments with more complex tracers and complementary laboratory programmes.

Another way to check the reliability and consistency of thermodynamic data is to review their application to modelling of natural analogues. These are usually characterised by detailed mineralogical information as well as groundwater compositions. However, uncertainties regarding initial and boundary conditions and associated time frames are often too large to be of quantitative use. Presently, such information from natural analogues is considered as important ‘soft’ data, contributing to confidence building rather than to quantitative model testing.

A potentially more promising approach may be the investigation of anthropogenic analogues, such as the abundant uranium mines, rock piles and tailings from milling processes available in the EU, the areas of former nuclear weapons testing, and even places contaminated by nuclear accidents. Timescales are not as great as for natural analogues and the initial conditions are better characterised. Moreover, these sites may more closely resemble the areas where the results from radiochemical experiments will finally be applied: *i.e.* nuclear waste repositories and radioactively contaminated areas. This research area is currently not sufficiently studied, despite its tremendous potential for generating new information.

“Validation” of macroscopic models poses several problems, the first arising from upscaling microscopic observations to macroscopic scales. This process generally introduces new terms into the constitutive equations. The impact of chemical heterogeneity in natural media remains an intractable problem. For instance, if the availability of sorbing surfaces along a flow path is not known, the impact of sorption on tracer migration cannot be described reliably. In this context, it is very important to test the extent to which microscopic surface complexation

chemical parameters, such as Eh, pH, water constituents) for rocks be synthesised from those of the constituent minerals? What are the limitations?

A second important problem arises from the fact that natural systems may be in a steady state but sometimes not in thermodynamic equilibrium. This is especially pertinent in the case of a nuclear waste repository as this introduces significant thermodynamic instability into the ambient geologic environment. Often thermodynamic descriptions (or a sequence of thermodynamic equilibria) are useful approximations. The range of applicability of the equilibrium models, however, must be shown (Note: The broad field of kinetics is outside the scope of JETDEM).

6.3. A PLEA FOR ERROR ESTIMATES

For “model validation” it is essential to include error estimates for input parameters. Without these, alternative models cannot be compared on a scientific basis and there is no measure for the extent to which they can be considered reliable or robust. Ignoring measurement errors in modelling can lead to very misleading conclusions (e.g. Parkhurst, 1997) and there is no way of ascertaining the overall uncertainty in the final model predictions.

This is not only true for macroscopic models. Thermodynamic databases must also contain error estimates. A first step in the direction of taking into account uncertainties of stability constants in speciation calculations is shown in Silva et al., (1995). It is not easy to consider such uncertainties in standard speciation and reactive transport codes and there is an urgent need for the development of new concepts and codes in this area.

The assignment of uncertainties to experimental parameters requires comprehensive knowledge of the accuracy and internal limits of an experimental set-up. However, it is not always possible to use statistical criteria because the distribution functions of the various sources of uncertainty and the presence of system errors may not be known. Therefore, one has to rely on “expert judgement”. When comparing results obtained using different experimental methods one often finds that the differences between the constants are larger than expected from the precision of the individual determinations. This is a clear indication of systematic errors which are larger than the stated precision, determined by repetition of experiments. When numerical evaluation is attempted, computed uncertainties may differ from one least-squares method to the other depending on the statistical weights assigned to the data and on the quantity minimised in the least-squares refinement. Most investigators prefer to ascribe unit weight to each experimental determination. However, because the number of experimental points will give an indirect weighting of the data, one should ensure that there is a comparable number of experimental data in the concentration ranges where the different complexes are predominant. When a particular species is formed only in a narrow concentration range, usually only a few experimental data in this range are available to derive complex formation constants. This results in their being assigned a greater uncertainty in comparison to species which form in large amounts, over a broad concentration range, and for which many experimental determinations are presented. Hence, minor species, i.e. those present in at most a few percent in the test solutions, should be looked at carefully. Additional information, e.g., for similar complexes, or “chemical plausibility”, that might support their formation should be sought. Sensitivity analysis on sets of experimental data may both reveal the data most critical to the modelling of a complex system and also those data that do not

When publishing thermodynamic data, it is essential to state clearly how the estimated uncertainty has been obtained, e.g. if it represents a 95% confidence interval, a "maximum" error, or some other estimate. Unfortunately, one often finds only a value +/- some deviation, without any explanation of the nature of this uncertainty. Sometimes the standard deviation of a single measurement is mistaken for the standard deviation of the respective mean. A special problem is encountered with deterministic thermodynamic models, which cannot incorporate uncertainty in the same way as stochastic models (by using probability distributions with parameters derived from the experimental data). The data uncertainties are taken into account only in a semi-qualitative way. It is good practice to publish the complete original set of primary experimental data, which will enable later re-calculation of derived parameters, using different weights for data points, new model assumptions, other sets of species etc.

7. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH ACTIVITIES.

In the Final Report from the Concerted Action “Joint European Thermodynamic Database for Environmental Modelling - JETDEM” we have described the rationale for, and the mechanism by which such a database may be established and managed, and how it could fit into the envisaged Euratom programme for 1998 - 2002. The focus of JETDEM is on nuclear waste management issues, a field where organizations and scientists in Europe play an internationally leading role. In this Chapter we will outline strategies and suggest research areas which need to be sustained in order to preserve this lead and ensure environmentally sound waste management practices. Existing nuclear waste will have to be managed whatever future energy sources become available. It is reasonable that the societies that have received the benefits of nuclear energy also ensure that future generations are provided with a technical/scientific basis for the construction, management and safety/performance assessment of nuclear waste repositories. The three most important messages from the JETDEM group are:

- Establish a central facility with responsibility for the management of a joint thermodynamic database for the nuclear waste, reprocessing and partitioning fields. This facility should act as the hub in a network organisation and could be based on the already existing Institut für Nukleare Entsorgungstechnik in cooperation with the Transuranium Institute at Karlsruhe. In order to ensure efficient cooperation with the scientists producing, evaluating and using thermodynamic data, the centre should establish an electronic network with an electronic discussion forum where information on ongoing data activities are presented and where questions can be asked, discussed and answered. An essential element is the availability and efficient dissemination of primary experimental information. In those cases where such data are not published, the centre should establish a system encouraging experimentalists to submit their data so that they are readily available to the scientific community. This should be a forum for scientific discussion and consensus building. The NEA Data Bank is an alternative site for the database management activities, but it is felt that the ongoing evaluations and discussions of experimental data are best handled by an organisation involving active scientists.
- Goal-oriented research is necessary to find socially, economically and technically acceptable solutions for the handling of radioactive wastes of different types. This requires multi-disciplinary team-building, both in the form of networks and by concentrating some of the research resources to those few European research institutions that possess the necessary facilities for handling radioactive material. Funding within the Fifth Framework Programme is essential to encourage continued cooperation within already existing research organisations and to add new contributors.
- Considerable effort is required to make the research challenges within the nuclear waste management area attractive to new generations of scientists. There is need both for nuclear systems-oriented scientists, and for scientists from related fields, including non-nuclear sectors. A programme for training of young scientists and mobility is necessary to ensure efficient use of existing research resources and to ensure that the European capability which already exists is maintained and enhanced.

in the JETDEM report we have identified several important areas for future research. In the following section these are specified in some detail. This section is also an attempt to translate the general statements above into operational goals.

Research areas:

- Initiate a cooperation between “computational” and experimental chemists, in order to ascertain whether the recent developments in quantum chemistry can be utilized to place semi-empirical estimation methods on a better theoretical footing. The rationale for this is provided in Chapter 4 of the JETDEM report. Theoretical methods may be particularly useful for the estimation of chemical properties of transuranium elements, where the models can often be calibrated against experimental data on thorium, uranium, and in some cases lanthanide elements. By using theory one may avoid the restrictions set by the availability of laboratory facilities and cost. European scientists are leading theoretical developments, with strong research groups in Cambridge, Stockholm, Munich and Toulouse. These groups should form the nodes in a future network, with funding mainly for training and mobility.
- Redox transformations. The engineered barriers form an important part of the safety system in nuclear repositories. This is also the only part of the system where one has some control of the system parameters, including chemical processes and gradients. An understanding of how local chemistry affects the stability of these barriers is essential. The integrity of spent nuclear fuel and metallic containers is strongly affected by redox processes of various kinds (“corrosion”). In the same way the solubility of many important radionuclides, notably uranium, neptunium, plutonium and technetium is strongly dependent on their oxidation state. The EC has an ongoing project on spent fuel dissolution which falls within this area, which has taken redox interfaces as one of the key future activities. Similar problems are being treated in the Palmottu Natural Analogue project.

Some redox transformations are slow and it is necessary, therefore, to obtain information on the rates and mechanisms of these processes. Uranium can be used to establish initial models. However, at some stage they must also be tested with transuranium elements. In order to accelerate the sometimes slow reactions it may be practical to work at elevated temperatures, up to 200 °C. Facilities of this type, together with state of the art equipment for spectroscopic analysis of solutions and solid phases are available at Uppsala, and Karlsruhe. Fundamental studies of redox transformations of uranium are being made in Stockholm and Barcelona, while spent fuel investigations are being undertaken by SKB and FZK/INE.

- Transformations of container and buffer material (cement and clays) may result both in a change of their functions as barriers (mechanical integrity and as barriers for water flow) and as sorbents for released radionuclides. Transformations are governed by the thermodynamic characteristics of the initial materials and the products. Such data are, therefore, important, but also in this case it is necessary to determine how rapid the transformations are. Many of these processes are known to be slow and a practical method to study them seems to be to accelerate the rates of transformation by using elevated temperatures. Studies of the properties of cement and clays are financed by the EC, and we

envisage that these studies will go on also within the next framework programme, at for example Univ. Aberdeen, PSI, UPC and Univ. Uppsala.

- Most radionuclides will be present in trace quantities once they have left the repository. Thermodynamic data for pure phases are only required for those present in the repository, whereas modelling of radionuclide behaviour in the far-field region requires data for “mixed” phases. The initial stage of the retention of radionuclides may be sorption of radionuclides onto solid phases of various types, such as backfill material and their transformation products and fracture minerals. Sorption can be described using “surface complexation” models and the related thermodynamic quantities. This process may be succeeded by incorporation of the trace elements into the solid lattice, for example, in the form of a “solid solution”. Solubility will then be determined by the thermodynamic properties of the solid solutions and this will determine the long-term retention of the radionuclides and their maximum concentration in the ground or surface water system. However, very few data of this type are available. They are often difficult to determine experimentally, and it is essential therefore to develop a theoretical basis for the estimation of thermodynamic data for such phases. Ongoing experimental and modelling effort in this area is being performed within the ENRESA programme. PSI also has an active programme in this field.
- Thermodynamic data and other chemical information are obtained in the laboratory under carefully controlled conditions. When these data are used to describe the more complex situation in a nuclear waste repository, or other complex systems in nature, it is necessary to test if the predictions are compatible with the field observations. This requires the development of new analytical techniques. An array of such methods has been developed and is used routinely by the participants in JETDEM. They are described briefly in Chapter 6. Existing methods must be upgraded continuously, and new methods developed in order to meet the requirements of safety and performance assessment.

In situ experiments to simulate the formation of meta-stable products and their evolution to equilibrium can be done in cells equipped with diamond windows and graphite heaters. The diamond windows permit the use of many modern techniques for studying the physical and chemical properties of the matter undergoing transformation. These techniques are x-ray diffraction (generally CCD based with rotating anode or third generation synchrotron at Grenoble), x-ray fluorescence and Micro-Raman and infra-red spectroscopy. Where necessary heating to temperatures of 50 to 100°C can be used to speed the approach to equilibrium for constructing experimental phase diagrams and determining thermodynamic data. X-ray methods can be used to study solid solutions, surface characters and structural defects. Mössbauer techniques can similarly be used to determine redox conditions in situ as the experimental reactions progress to equilibrium.

- Actinide chemistry is a key area for reprocessing of spent nuclear fuel, for partitioning and for understanding the behaviour of these elements in nature. There is a large body of chemical information available but gaps are apparent in some areas of fundamental importance for nuclear waste repository systems. For example, there is a general lack of data for highly alkaline systems, such as those encountered in contact with cementitious material. Experimental data for complexes of organic material of various types and of ternary complexes are also scarce. In order to avoid excessive experimental work one should initially concentrate efforts on the development of theoretically based methods for

Targeted research on fundamental Pu chemistry should be launched at the European level. The data concerning this critical element is flawed and relevant complexation and redox processes are still not fully understood and quantified. This is of paramount importance when dealing with any strategy for nuclear waste management (normal cycle operation) and mismanagement (accidents, clean up strategies in the former Soviet Union).

The above examples illustrate the need for a holistic approach to the environmental speciation of radioactive elements. Such an approach will require the application of thermodynamic models and data in a consistent manner throughout the barrier system.

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APPENDIX

A1. ANSWERS TO THE QUESTIONNAIRES

The answers provided by each group are summarised below in different sub-sections. In this sense, a short description of the geochemical codes and databases used by these groups is given. This description includes the main considerations remarked on by the different groups about their limitations and their capabilities taking into consideration the kind of work performed by the different partners.

From the answers we can see that the geochemical codes as well as the databases used by each group depend mainly on the needs of the different groups. Therefore an extensive compilation of geochemical codes and databases has been achieved.

A1.1. FZK-INE

A1.1.1. Geochemical codes

The FZK/INE group uses six different geochemical codes:

- EQ3/6 Rel.7.2a and SALT, the main outputs that these codes give are pH, Eh, activity of water, ionic strength, electrical balance, activity ratios of ions, gas fugacities, distribution of aqueous species: concentrations, $\log \gamma$, activities, mineral saturation states (saturation indexes and affinities), aqueous redox reactions, solid phases (reactant and precipitates).
- PHREEQE Rel.2.4 and PHREEQC Rel.1.5 give the same outputs as EQ3/6, in addition they have surface complexation and ion exchange.
- FITEQL Rel.3.1: This code is used to fit equilibrium and surface complexation constants to experimental data.
- MINEQL+ Rel.3.0: It provides equilibrium calculations in a similar manner than HALTAFALL.

One limitation found by FZK-INE in all the geochemical codes used is the temperature range of application. It depends mainly on the available thermodynamic data. In addition, PHREEQC and FITEQL also have the limitation of being restricted to $I < 0.5$ M, due to the lack of activity corrections.

With regard to user-friendliness, this group considers the PHREEQC code user-friendly, and easier to use than EQ3/6. The user-friendliness of SALT and FITEQL depends on the experience of the users, and it is not considered very user-friendly for beginners.

A1.1.2. Databases

The main databases used in FZK/INE are:

- With EQ3/6 Rel.7.2a, the databases included in the code release. These databases are:

- .com (from Gembochs database), .hmv, .pit (from Gembochs database), .nea (from NEA database) and .chv (from Chemval database).
- These databases give the master species, reacting species, equilibrium constants at different temperatures and in the case of .hmv and .pit the Pitzer interaction coefficients. The data source is also included.
- PHREEQE and PHREEQC are used with three databases:
 - Chemval database Ver.6, and own databases of WATEQ4f and MINTEQA2:
 - These databases also give the master species, reacting species, equilibrium constants at several temperatures, and ΔH . However, in the last two databases the data source is not included.
- SALT is used with its own database: It gives the same output as EQ3/6. The data source is also included.

This group consider that the databases format of EQ3/6 and PHREEQC codes are user-friendly, while PHREEQE and SALT contains a database format that is not user-friendly. The large number of geochemical codes and databases used by this group is partially due to the different kind of calculations that they perform. The EQ3/6 and SALT databases are used by this group because they contain Pitzer data necessary to perform calculations in highly concentrated solutions (i.e. in brines). An extended Pitzer database for e.g. Si, U and Np is included. The type of work carried out by this group in considering highly concentrated media lead them to use geochemical codes which perform calculations by using the Pitzer approximation for the ionic strength correction (EQ3/6 and SALT) and consequently the databases containing Pitzer data need to be available. To perform surface complexation and ion exchange calculations they usually use PHREEQE and PHREEQC codes. Major modifications have been made to the databases. In the EQ3/6 databases, the modifications comprise the addition of solids, aqueous species and Pitzer coefficients (ion-ion interactions and mixing terms) and their temperature dependence. In the databases used with PHREEQC the modifications consist of additional surface complexation and ion exchange reactions.

A1.2. FZR

A1.2.1. Geochemical codes

FZR uses three geochemical codes:

- EQ3/6 Ver.7.2b: The output given by this code is the same as the one given by Rel.7.2a, and it has been detailed in the previous sub-section.
In addition, this group remarked on the fact that usually this output has to be post-processed. The main limitations of this geochemical code are regarded as mainly due to data availability, in principle concentrations up to the limits of the Pitzer model and temperatures from 0 to 300°C are possible. Another limitation is that surface complexation models are not implemented, and finally it is not possible to compute scans over pH, Eh or a component concentration.
- MINTEQA2 Ver.3.11: The information given by this code is very similar to the one given

This group also remarked that this code produces large ASCII files but in a more tabular structure than EQ3/6. However, they consider that data must also be post-processed to a certain degree. MINTEQ also has several limitations: No implicit charge balancing is implemented, solid solutions cannot be included. There is no limit for temperatures if the coefficients for an empirical equation are provided, otherwise, the Van't Hoff equation can be used restricting the temperature to $T < 100^{\circ}\text{C}$, Pressure can't be specified, and ionic strength must not exceed the validity range of the Davies equation for activity coefficients. Surface complexation models are available.

- FITEQL Ver.3.2: This code produces several ASCII tables; for speciation plots there is a separate table. This table, however, only contains a limited number of species, so it's necessary to make several of these files to create all the necessary graphs. There is also an on-screen graph display in B/W with very limited features. This geochemical code has the same limitations as MINTEQA2, but temperature is not limited.

With regard to user-friendliness of the different geochemical codes used by this group, they consider that the EQ3/6 code is user-friendly, but requires some training by experienced users. For MINTEQA2 there is a separate input program that makes its use much easier, but the structure is worse than EQ3/6. The FITEQL code also has a cumbersome input, and they consider and agree with FZK-INE that it is not really user-friendly.

A1.2.2. Databases

FZR uses seven databases:

- MINTEQA2 own database
- NIST Standard Reference Database 46, Ver.2.0 (Critical Stability Constants)

The EQ3/6 code package is used with the following databases:

- .nea (from NEA-TDB)
- .com (from LLNL database)
- .alt (like .com, but with alternative data sets for Pu and Np)
- .chv (from Chemval database)
- .sup (from SUPCRT database)

The information included in these databases is the stability constant of aqueous complexes and the solubility product of solid phases, the EQ3/6 version also contains their temperature dependence. All these databases have the data source included. FZR has chosen these databases because they cover the species of interest for their work, and mainly because all of them, except NIST, can be used in the respective modelling software. The EQ3/6 databases have a unified and well-documented format, whereas the NIST database has not mechanism for adding or modifying data. All these databases are being restructured at present, adding experimental results for known species and introducing new species.

A1.3. KTH

A1.3.1. Geochemical codes

KTH uses three geochemical codes: PHREEQE, MINEQL and HALTAFALL/SOLGASWATER. The outputs obtained from PHREEQE and MINEQL have been given previously. HALTAFALL/SOLGASWATER give equilibrium compositions, aqueous speciation and solubilities. This group do not specify any limitation for the codes and in general they consider that such codes are not especially user-friendly.

A1.3.2. Databases

The databases used by KTH are mainly three:

- IUPAC (Stability Constants).
- NIST (Critical Stability Constants).
- USGS (U.S. Geological Survey) DataBase.

These databases give equilibrium constants and surface complexation data, and not all data are referenced to source. No modifications have been made. KTH uses these databases because of their availability or free cost, and for their apparent quality.

A1.4. PSI SWITZERLAND

A1.4.1. Geochemical codes

The most frequently used codes are:

- MINEQL and MINSORB, an extended version of MINEQL, which includes surface complexation and ion exchange: MINSORB give the results of series of computations in tabular format.
- PHREEQE (and its family of codes PHREEQM, PHRQPITZ and PHREEQC).

The less frequently used codes are:

- C-HALTAFALL (E. Östhols), this code is used occasionally if SIT coefficients are necessary for ionic strength corrections.
- PREDOM (I. Puigdomènech): they use this code to calculate predominance diagrams.
- BACKDOOR (W. Hummel): This code is used for *ad hoc* calculations. This code produces files suitable for commercial visualisation software (2D and 3D plots).

In general, this group is limited to near surface geochemistry (i.e. $T < 100^\circ\text{C}$ and $P = 1\text{atm}$). All codes used are limited to ionic strength effects of $IS < 0.3\text{ M}$ due to the use of Davies or extended Debye-Huckel equations. The exceptions are PHRQPITZ and C-HALTAFALL, which are suitable for high salinity systems. In such case, Pitzer or SIT coefficients

A1.4.2. Databases

PSI Switzerland uses the Nagra Thermochemical DataBase (Pearson and Berner, 1991; Pearson et al., 1992), which gives them all the information they require for their geochemical calculations except volume data, SIT and Pitzer coefficients. $\log K$ and ΔG are available for all entries. All data sources are included. PSI Switzerland uses the Nagra Database because it is the standardised database, which all Nagra contractors must use for consistency and traceability of results. They consider this database to be user-friendly.

The major advantage of the Nagra Thermochemical DataBase is its concept of distinguishing between Core Data and Supplemental Data. The Core Data comprise well-established data which most probably will not change in the near future. The Supplemental Data comprise less well established data which may change due to new experimental results and/or new data reviews. Some modifications have been included in the database. New elements (Bi, Pa, Pb, Ra, Sb, Sn) and additional aqueous species and solids have been included (Berner, 1995). Solubility products for hydrogarnet and ettringite were derived from experimental data and added to the database (Neall, 1994). Experimental data of some aqueous complexes of Co, Ni, U(VI) and Eu with carbonate and the organic ligands oxalate, IDA, NTA, HEDTA and EDTA have been critically re-evaluated (Glaus et al., 1997).

A1.5. QUANTISCI

A1.5.1. Geochemical codes

The geochemical codes more frequently used by QuantiSci are:

- EQ3/6 Ver.7.0
- HARPHRQ
- PHREEQC Ver.1.0
- HALTAFALL (SED,PREDOM and EC)

The main outputs that these codes give are aqueous speciation, saturation indexes for minerals, solid solutions, surface complexation and ion exchange. These codes have two main limitations. The temperature range, that will depend mainly on the thermodynamic data available; however, the area of work of this group is in general limited to near surface geochemistry, this stands on $T < 100^\circ\text{C}$. The other principal limitation is the ionic strength corrections. These codes use rudimentary Davies, and extended Debye-Huckel corrections, therefore ionic strength effects are limited to $I < 0.3 \text{ mol dm}^{-3}$. This group considers that these geochemical codes are user-friendly, but it depends on the experience of the users.

A1.5.2. Databases

QuantiSci uses mainly the NAGRA database associated to the EQ3/6 and PHREEQC code packages, however, occasionally, when the HARPHRO code is used, the database is the

HATCHES_NEA 7.0. To run the HALIFALL code package, the information extracted from the NAGRA database is also used.

- NAGRA Database: It comprises one database file with aqueous species, solid phases and gases. For each specie it gives: stoichiometry of the dissociation reaction, logarithm of the dissociation constant, logarithm of the solubility constant for aqueous and solid phases respectively at different temperatures, and the enthalpy and Gibbs energy of formation.
- HATCHES-NEA 7.0 (associated to the HARPHRQ code package): It comprises two databases files, one for the aqueous species, and one for the solid phases and gases. For each record it gives: stoichiometry of the formation reaction, logarithm of the formation constant and logarithm of the solubility constant for aqueous and solid phases respectively, the enthalpy of formation for the aqueous species and the enthalpy of dissociation for the solid phases.

These databases have been chosen since they are well documented and tested and also because of their user-friendliness. It is also important that they have the data source included. However, some modifications have been made after a review exercise of the thermodynamic databases available and according to a review of the relevant literature.

A1.6. RMC AND UNIV. MANCHESTER

A1.6.1. Geochemical codes

RMC and the Univ. of Manchester use three geochemical codes all of them belong to the same family of codes:

- PHREEQE
- PHREEQC.
- PHREEQE96 Ver.1.0 and new versions (1.1, 1.2)

These geochemical codes give essentially ASCII text, although PHREEQE can produce graphical representations. The outputs obtained by these codes have been previously given. These groups consider that only PHREEQC code is user-friendly; not the other ones. The main limitation of these codes is the temperature correction via Van't Hoff and via analytical equation. The temperature range depends on the correction of the reaction and on the availability of equilibrium constants at different temperature and enthalpy measurements. All codes allow Davies and Debye-Hückel corrections. Besides, PHREEQE96 can also use SIT coefficients.

A1.6.2. Databases

RMC and the Univ. of Manchester use five databases:

- "Old" NIREX Database Ver.B and NEA Database. They use these databases because they consider that data is very reliable.

- CHEMVAL: This database is used because it contains the right data for the sort of systems that RMC needs to model, but on the other hand it has a significant number of incorrect entries. They remark that it has the most useful data for Eu/PO₄ system.
- Stability Constants of Metal-Ion Complexes: They use this database because it is very useful to model reaction solutions, particularly for synthetic chemistry.
- Critical Stability Constants (vols. 1-5): As the previous one, it is used because it is very useful to model reaction solutions. It is also used because the book contains very useful enthalpy and entropy data.

All these databases give log K values for complex formation of mainly inorganic species. In addition Stability Constants and Critical Stability Constants give also thermodynamic data of organic species. This group considers that none of these databases are user-friendly, and neither have the data source. About their compatibility with codes, the "Old" NIREX, NEA and CHEMVAL can be used directly with PHREEQE.

They have also made some modifications at databases: First of all, the own database included in the PHREEQE code package has been extended and modified with data from NIREX, CHEMVAL and NEA, and besides, extra data has been taken from Stability Constants, Critical Stability Constants, and from journal papers. However, additional modifications have been also made by this group:

- The NIREX database has been modified to decouple the redox of the nitrate/ammonia system to model nitrate solutions.
- Introduction of "dummy" inert species in order to perform calculations on a completely inert electrolyte.
- To simulate high ionic strength solutions they take stability constants determined under the same high ionic strength conditions as the solution, and then, they use the Davies equation to produce an intermediate zero ionic strength value, which is inserted into the database. When the calculation is running, the Davies equation is specified as the method of ionic strength correction, with the result that, during the calculations, the original and valid experimental stability constant is regenerated within the computer.

A1.7. UNIV. ABERDEEN-READING

A1.7.1. Geochemical codes

The geochemical codes used by the Universities of Aberdeen and Reading are PHREEQE96, PHREEQC and PHRQPITZ. The main limitations that this group consider agree with the rest of the groups involved, these are mainly the rudimentary temperature corrections, limited to T<75°C, and the use of the Davies equation for ionic strength corrections, except for PHREEQ96 (SIT) and PHRQPITZ. They consider the PHREEQE codes to be user-friendly, though data handling could be improved in the Fortran versions. An extensive verification of the PHREEQE family of codes has been carried out at Reading.

A1.7.2. Databases

Univ. Aberdeen and Reading routinely use two databases:

- Modified CHEMVAL6.0: It gives equilibrium constants for aqueous species and solids, and includes the data source. They have chosen this database because it is extensive, well documented and in the case of earlier versions tested within international programmes.
- CEMENTS gives equilibrium constants for aqueous species and solids specific to high pH cementitious systems. It also includes the data source. The main problems are the use of fictive solids for gel phases and complex-hydrous formulae. Instability of codes such as PHREEQE caused by Gibbs rule violation can also be a problem.

A database has been compiled by this group from information extracted from experiments, and geochemical and mineralogical data from natural systems studies. They consider that CEMENTS database is probably as good as anything else available, though this area of research needs some degree of consistency. At low ionic strength, they use the PHREEQE code, and with more concentrated solutions they use the PHREEQPITZ code.

A1.8. UNIV. UPPSALA

A1.8.1. Geochemical codes

Univ. of Uppsala uses five geochemical codes:

- Thermo-Calc: Its main limitation is the applicable temperature range, which is 0-6000°C for Solid/Fluid, and 0-1000°C for the aqueous phase.
- DICTRA: Its main limitation is the applicable pressure range, which is 1-100000 bar for Solid/Fluid, and 0-5000 bar for the aqueous phase.
- ChemGeo: Its main limitation is the aqueous ionic strength (up to 6 molal).
- EQCALC
- SUPERFLUID

The limitations of the geochemical codes given before are in accordance with the type of studies and research that this group carry out. They work in a very specific area, by modelling different systems at very high temperatures and pressures. Consequently, the geochemical codes are very specific as well as the databases used.

These geochemical codes give different kinds of output to the conventional codes used routinely in radioactive waste applications: Heterogeneous phase equilibria, phase diagrams of multicomponent systems, thermodynamic properties of various substances, speciations in complex aqueous solution and fluid mixtures, composition-activity properties of complex solid solutions, diffusion-controlled phase transformation, material property variation in complex processes, origin and evolution of natural geochemical systems, and stability and variation of nuclear waste repositories. This group considers that all of them are user-friendly, especially the Thermo-Calc code.

A1.8.2. Databases

The Univ. of Uppsala uses eight different databases:

- GEOCHEM. Geochemical database
- AQUEOUS. Aqueous solution database
- SSUB/SSOL. Pure substances and solution database
- SUPCRT92. Aqueous solution database
- NEA-TDB. Nuclear material database
- FE-DATA. Metallurgical database
- MOB. Mobility database

These databases include thermodynamics and thermophysical properties, and mobility and other kinetic properties of steel-alloy systems. All the information has its data source included. They are compatible with software codes such as Chemsage and MTDATA. These databases have been chosen because they are good on modelling and simulation of material properties, phase transformation, origin and evolution of geochemical systems, and stability and variation of industrial waste repositories. Their user-friendliness is also an asset, but more kinetic data are needed. Some modifications have been made to meet the needs of geochemical and environmental research projects.

A1.9. SUMMARY

A summary of the information compiled previously is available in Table 1. In an attempt to order and clarify the different information provided by the various JETDEM groups about the geochemical codes most used a short description with the main characteristics and limitations of each code is given in the next sub-sections:

A1.9.1. PHREEQE family

The main information (outputs) given by these codes are pH, Eh, activity of water, ionic strength, electrical balance, gas fugacities, distribution of aqueous species: concentrations, activities of aqueous species including those involved in redox reactions, mineral saturation states and solubilities, aqueous redox reactions, solid phases (reactant and precipitates). In addition, the later versions, PHREEQC and PHREEQE96 include also solid solutions, surface complexation and ion exchange reactions. The outputs given by these codes are essentially ASCII text, although post-processors are available.

Limitations of these codes:

- One of the main limitations of these codes is the rudimentary temperature correction via Van't Hoff and via an analytical equation, limited to $T < 100^\circ\text{C}$. Consequently, the temperature range will depend mainly on the thermodynamic data available, i.e., on the availability of equilibrium constants at different temperatures and enthalpy measurements. However, temperature in the geochemical code can vary between -5°C and 300°C .
- The other main limitation is the method of ionic strength correction. These codes use rudimentary Davies, and extended Debye-Huckel corrections, therefore ionic strength effects are limited to $I < 0.3 \text{ mole dm}^{-3}$. PHREEQE96 can also use SIT coefficients, valid for $I > 1 \text{ mol-dm}^{-3}$.

Another exception is the `PHKQP11Z` code, which is suitable for high salinity systems, in such case, Pitzer coefficients are necessary.

A1.9.2. MINEQL family

The information obtained from this family of codes is very similar to that given by the PHREEQE family. pH, Eh, activity of water, ionic strength, electrical balance, gas fugacities, distribution of aqueous species and mineral saturation states and solubility. Some versions of MINEQL, like MINTEQA2, MINEQL+ or MINSORB now include surface complexation and ion exchange reactions. These codes produce large ASCII files but in a tabular structure. However, data must be post-processed to a certain degree. The FITEQL Ver.3.2 gives several ASCII tables; for speciation plots it provides a separate table.

Limitations of these codes:

- These codes have also several limitations. In principal, there is no limit for temperatures if the coefficients for an empirical equation are delivered, otherwise, the Van't Hoff equation can be used restricting the temperature to $T < 100^{\circ}\text{C}$.
- These codes are also limited to ionic strength effects of $I < 0.3 \text{ mol dm}^{-3}$ due to the use of Davies or extended Debye-Hückel equations.
- No implicit charge balancing is implemented and pressure can not be specified.
- In the MINTEQA2 code the solid solutions can not be included.

These codes are considered user-friendly. In particular, for MINTEQA2 there is a separate input program. The FITEQL code, however, has a cumbersome input, and several groups remarked on its lack of user friendliness.

A1.9.3. EQ3/6

The information obtained from these codes is very similar to that given by the PHREEQE family but a major advantage is that this code has implicit reaction path tracking facilities. Usually this output has to be post-processed.

Limitations of the code:

- These codes have in general the same limitations as the PHREEQE codes. A temperature range, in principle from 0 to 300°C provided thermodynamic data are available.
- The other limitation is the ionic strength correction: they also use rudimentary Davies, and extended Debye-Hückel corrections, therefore ionic strength effects are limited to $I < 0.3 \text{ mole dm}^{-3}$. However, concentrations up to the limits of the Pitzer model can be also introduced depending on data availability.
- Another limitation is that surface complexation and ion exchange models are not implemented in the present versions.
- Finally, it is not possible with this code to compute scans over pH, Eh or a component concentration.
- The different users think that this geochemical code is user-friendly, but requires some

Table A1: Summary information of the usage of geochemical code packages among the JETDEM groups. The number of participants that use every geochemical code are given in brackets and bold letters.

GEOCHEMICAL CODES USED	MAIN OUTPUTS	LIMITATIONS	USER-FRIENDLINESS
<ul style="list-style-type: none"> - PHREEQE (6) - PHREEQC - PHREEQM - PHRQPITZ - HARPHRQ - MINEQL (4) - MINSORB - MINTEQA2 - FITEQL - EQ3/6 (3) - HALTAFALL/ SOLGASWATER(3) - C-HALTAFALL - PREDOM - Thermo-Calc (1) - Dictra (1) - ChemGeo (1) - EQCALC (1) - SUPERFLUID(1) - BACKDOOR (1) - SALT (1) 	<ul style="list-style-type: none"> -Aqueous speciation (concentration & activities). -Saturation indices for minerals. -Eh (pe), pH, ionic strength and gas fugacities. -Aqueous redox reactions. -Non equilibrium reactions. -Solid solutions. -Surface complexation and ion exchange. -Phase diagrams of multicomponent systems. 	<ul style="list-style-type: none"> - The main limitations are Temperature and Pressure. - In general, Ionic strength below range of Davies and Debye-Hückel corrections for activity coefficients; $IS < 0.3 \text{ M}$ - These codes are in general limited to near surface geochemistry, and in some cases the limitations are given by data availability. 	<p>In general, they are user-friendly.</p> <p>However, most of the groups agree that it depends on the experience of the users.</p>

A summary of the information compiled previously is available in Table A2.

Table A2: Summary information of the Thermodynamic Databases used by the JETDEM groups. The number of participants that use every thermodynamic database are given in brackets and bold letters.

DATABASES	INFORMATION INCLUDED IN	DATA SOURCE INCLUDED ?	WHY THESE DATABASES?	ARE THEY USER-FRIENDLY?	COMPATIBILITIES WITH CODES	MODIFICATIONS INCLUDED IN TDB
EA-TDB (5) HEMVAL 6.0 (4) AGRA TDB (3) IST (3) SGS (2) EMBOCHS (2) JPAC (2) EMENTS (1) EOPHYS (1) EOCHEM (1) QUEOUS (1) SUB/SSOL (1) UPCRT92 (1) E-DATA (1) IOB (1) IINTEQA2 (1) ALT (1) IREX (1)	<ul style="list-style-type: none"> - Stoichiometries of the formation and dissociation reactions. - Equilibrium constants for aqueous species and solids, including in some databases temperature dependence (i.e. NAGRA). - Enthalpies and Gibbs energies of formation or dissociation. - Pitzer interaction coefficients (in some databases available: EQ3/6, TDB-pit). - Surface complexation. - Kinetic properties of steel-alloy systems. 	<p>Yes, at least almost all of them. i.e. CEMENTS hasn't been updated.</p>	<ul style="list-style-type: none"> - Well documented and tested within international programmes. - Cover the species of interest. - Pitzer data available. - The database information is easily available. - Flexible to be modified and updated. 	<p>In general they are considered user-friendly.</p> <p>However, some of them are considered user-unfriendly:</p> <ul style="list-style-type: none"> - CEMENTS. - USGS. - MINTEQA2. - SALT. 	<ul style="list-style-type: none"> - CHEMVAL 6.0, NIREX, CEMENTS, USGS & PMATCH → PHREEQE. - NAGRA TDB (PMATCH) → PHREEQE, MINEQL and EQ3/6. - NEA 7.0 (HATCHES) → EQ3/6, PHREEQE AND HARPHRQ. - GEOPHYS, GEOCHEM, AQUEOUS, SSUB/SSOL, SUPCRT92, NEA-TDB, FE-DATA and MOB → Chemsage and MTDATA. <p>In some cases there is the software necessary to translate it to other format; i.e. NEA (HATCHES) into the EQ3/6 format.</p>	<p>Everybody asked has made modifications on their databases, except KTH.</p> <p>Modifications made by:</p> <p>Univ.Aberdeen / Reading:</p> <ul style="list-style-type: none"> - Corrected errors in the Cu enters. - Added Zn & Cr data. <p>PSI Switzerland:</p> <p>Solubility products for hydrogarnet & ettringite were added.</p> <p>QuantisSci:</p> <p>Updated data: Fe, Sr, Zr, Nb, Tc, Sn, Th, U, Np, Pu and Am.</p> <p>Added data: Ag, Sm, Ho, Ra and Cm.</p>

A1.10. COMPATIBILITIES OF GEOCHEMICAL CODES WITH THERMODYNAMIC DATABASES

One of the main problems which has arisen in the last decades due to the spread in the use of geochemical codes and consequently in the compilation of very different databases is the compatibility between the codes and the databases available. In general, all codes supply their own database with a very specific format. It means that as a general rule only specific databases can be used with the corresponding geochemical codes or, alternatively, an extensive conversion has to be carried out. However, more software programmes are becoming available with the capacity to convert a database with a pre-determined format to another one in order for it to be used with a different geochemical code. Despite progress, there are still problems in the use of geochemical codes and thermodynamic databases due to incompatibilities and the lack of the software necessary for conversion.

From the answers to the questionnaires, we have obtained the following information about this subject.

The PHREEQE family of codes (particularly PHREEQE and HARPHRQ) is the one that is compatible with more databases than the others, including: CHEMVAL, CEMENTS, USGS, NAGRA TDB and NEA 7.0.

The PMATCH thermochemical management program has its own internal database format, but produces data files compatibles with geochemical codes like PHREEQE. There is also available software to translate these formatted data into MINEQL and EQ3/6 format. The NAGRA database has been developed and maintained by using the PMATCH program.

Consequently, the NAGRA thermodynamic database is also compatible, in addition to the PHREEQE family of codes, with MINEQL and EQ3/6 geochemical codes.

The NEA 7.0 is also compatible with the EQ3/6 geochemical code.

So, as seen above, the PHREEQE family of codes and the EQ3/6 geochemical code are the ones compatibles with a greater number of thermodynamic databases. Consequently, they are the geochemical codes most used by the JETDEM groups.

PHREEQE96 has been released as FORTRAN code which can be compiled on UNIX or PC. PHREEQC is the way forward but, at present, it doesn't possess all the functions of PHREEQE96 and is not accompanied by a sufficiently extensive database for the majority of radioactive waste applications.

Another incompatibility found related to the EQ3/6 code package is that the databases for EQ3/6 Rel.7.2 are incompatible with Rel.8. However, tools are available for transferring the pre 7 versions of EQ3/6 database to Rel.7.2.

The University of Uppsala works on very specific projects, which consist of calculations at very high temperatures and pressures, and that force them to work with a constrained suite of geochemical codes and thermodynamic databases. The databases that they use are in general compatibles with other software codes, ChemSage and MTDATA, and they are easy to convert from one format into another format.

The NIST and IUPAC databases are stand-alone and it is not possible to achieve an on line connection to a geochemical code.