Andra thermodynamic database for performance assessment: ThermoChimie

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ABSTRACT

Thermodynamic data are an essential input for relevance of geochemical modeling and more particularly to assess the behavior of radionuclides and other pollutants in the performance assessment of a radioactive waste repository. ThermoChimie (http://www.thermochimie-tdb.com/), the thermodynamic database developed by Andra, meets the requirements of completeness, accuracy and consistency for numerous radionuclides and chemotoxic elements and various major components of a geological repository: solid phases constitutive of the host-rock, bentonites, concretes, and corresponding secondary minerals with respect to their long term evolution. ThermoChimie developments are also dedicated to evaluating specific conditions of the near field of radioactive waste, in particular regarding temperature increase and release of organic ligands or soluble salts. ThermoChimie database is extracted into compatible formats with different geochemical codes, allowing an overall consistency between different models using it in support.

1. Introduction

Thermodynamic modelling constitutes a critical tool for evaluating the nature and extent of chemical processes likely to affect the migration of polluting elements in complex, evolving geochemical environments. The accuracy and credibility of thermodynamic modelling output depends heavily on the quality and completeness of the thermodynamic database (TDB) which is used. An universally applicable TDB containing quality-assured mass action laws and thermodynamic constants for all possible equilibria involving the complete periodic table of elements does not exist. TDB do however exist, and are continually being developed and improved, with the objective of supporting the thermodynamic modelling requirements for more or less broad-ranging environmental and/or industrial situations.

This manuscript aims at describing the main characteristics and applicability of the ThermoChimie TDB (http://www.thermochimie-tdb.com/). This database is the result of a broad and deep work undertaken over the last decade, aimed at modelling the wide range of geochemical contexts encountered in the safety and performance assessment of disposal facilities for radioactive wastes (radwaste) generated in France.

Safety assessment of a radwaste disposal facility (existing or projected) is based on the ability to predict the migration of radionuclides (as well as certain stable but toxic elements) released from the waste packages along all pathways leading to potential future exposure of humans. This requires the coupling of a thermodynamic (or kinetic) model of radionuclide chemistry with a mass transport model. Since the main migration vector is transport of dissolved radionuclide species in water-saturated engineered materials (concrete, bentonite, etc.) or natural environments (host-rock, aquifers, etc.), the credibility of the extreme time–space extrapolations made by modelling is directly linked to the capacity to demonstrate that the model is highly likely to provide correct representations of (i) the pertinent chemical characteristics of each geochemical system as a function of time and (ii) the solubility and speciation of each radionuclide for each state of the system being considered. The same type of information is also needed for assessing the safety-related performance of different design and operation options during the development phase of a disposal facility project. These types of models are used at all phases of the French project for a deep geological disposal facility for high and medium activity, long half-life radioactive waste in eastern France (the Cigéo project, www.cigeo.com). One example is the evaluation of

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the consequences of mixing wastes containing organic complexing compounds with other, non-organic wastes in order to optimize waste cell geometry and disposal zone architecture.

One of the major challenges of thermodynamic modeling of waste repository situations is to properly describe the main geochemical evolutions, which will take place in each of the compartments comprising a potential migration pathway. This concerns especially the evolution occurring in transition zones between materials characterized by steep geochemical gradients and highly evolving solid and dissolved phase composition. This information is needed in order to prioritize phenomena in terms of chronology and to identify significant reactions and sensitive parameters, with an end goal of estimating safety margins with respect to the conceptualization adopted in the performance assessment. All links leading to the final results must be justified in terms of a consistent and robust knowledge base and provide an understandable support for external review and public acceptance. These links can cover all scales of data acquisition and analysis, from the fine interpretation of results obtained in small scale, well-controlled laboratory experiments to the coupled modeling of data generated by larger scale, more 'realistic' but less controlled in situ experimentations. The quality and completeness of the TDB which is used constitutes a critical element in this demonstration, and the use of a single TDB is very important in order to ensure a consistent and ubiquitous link between all models.

A variety of TDB have been developed in support of the modeling required for safety and performance assessment of national radwaste management programs. Examples are the TDB developed by the Swiss radwaste management agency (NAGRA Hummel et al., 2002), the Japanese JNC TDB (Yui et al., 1999), the British HATCHES developed since 1987 (Cross and Ewart, 1991) or the Lawrence Livermore National Laboratory TDB (Wolery, 1992; Wolery and Sutton, 2011). The Thermodynamic Reference Database (THEREDA) focused on transuranic elements is being developed by various German institutions since 2006. The French A significant source of high quality data for all radioactive waste-related TDB is the Nuclear Energy Agency Thermochemical Database project, published in several books within the *chemical thermodynamics* series (Grenthe et al., 1992; Silva et al., 1995; Lemire et al., 1999; Guillaumont et al., 2003; Gamsjäger et al., 2005, 2012; Hummel et al. 2005; Olin et al., 2005; Brown et al., 2005; Rand et al. 2009). Thermoddem TDB (BRGM, Blanc et al. 2012) is an example of thermodynamic data sets with application to problems others than nuclear wastes, such as mining and chemical pollution issues.

As presented later in more detail, the guiding principles of a TDB used for a variety of applications within the radioactive waste management system must be accuracy, completeness and traceability. In the following subsections, the strategy followed to develop ThermoChimie is briefly presented.

2. ThermoChimie: the Andra TDB

ThermoChimie is the thermodynamic database initially created by the French National Agency for radioactive waste management (Andra) in 1996, especially designed and qualified for systems of interest for the French repository concepts. It is supported by an experimental program on clay minerals, cementitious phases, actinides and fission products, and it has been continuously updated to undertake geochemical calculations related to the performance assessment of different waste packages, backfill/buffer materials and/or geological formations considered in nuclear waste disposal facilities.

The ThermoChimie project especially deals with different tasks, in consistency with PA requirements and with specific geochemical conditions in the Callovo-Oxfordian host-rock formation or inside the waste disposal cells:

- determination of radioelement and chemotoxic element aqueous speciation and solubility,
- study of geochemical evolution of both the near- and the far-field of the disposal system, covering the stability of the constituents of clay minerals and secondary minerals of the aluminosilicate systems,
- assessment of the process of cement degradation to account for the stability of cementitious phases including a broad composition range with respect to concrete formulae,
- assessment of the evolution of metallic/steel components present in the containers, liners, reinforced waste packages, etc. with special emphasis to of iron/steel corrosion processes and secondary phases formed,
- assessment of the role of complexing agents derived from the degradation of Natural Organic Matter (NOM) present in the Callovo-Oxfordian clay stone (about 1% mass) as well as the impact of the degradation products of organic compounds from technologic wastes on the mobilization of radionuclides,
- tools and applications of the ThermoChimie database under different disposal scenarios.

Development priorities of the ThermoChimie database were set regarding the chemical reaction paths defining the long term evolution of disposal components. The reaction paths are identified from field/experimental observations and from modelling exercises, and applied to all waste categories (High Level radwastes, Intermediate Level radwastes, Low Level radwastes of short and long life, Radium bearing wastes, etc.). In the framework of the Cigéo project, the TDB requirements for modeling water–mineral interactions and the evolution over time of the host-rock and engineered barrier system components are focused on three main types of material:

- the clayrock of the Callovo-Oxfordian geological formation, composed mainly of phyllosilicates (essentially interstratified illite/smectite), carbonates and quartz, with smaller amounts of other minerals (pyrite, celestite, etc.),
- swelling clay-based materials, mostly composed of smectite and accessory minerals similar to those from clayrock,
- cement-based materials containing, in addition to aggregates, a set of hydrates: calcium silicate hydrate (C–S–H), portlandite, sulfates, hydrogarnet, hydrotalcite.

In addition, an effort has been devoted to the stability of the compounds resulting from the corrosion of steel components (HLW packages, liners, concrete reinforcement) especially for ferrous and ferric solid such as oxy-hydroxides, carbonates, sulfurs or secondary clay minerals.

Due to the long-term assessment needed in any study of nuclear waste management repository, it is important to develop thermodynamic data not only for the materials initially present in the system, but also for those likely to form from chemical transformations of the initial constituents including theoretical end members for the clay minerals, for example. Geochemical pathways are defined iteratively based on on-going experimental results or field observations. This leads to gradually complete and improve the TDB. Temperature is also expected to evolve in the repository system due to the waste materials, thus temperature effects on the stability and/or transformations of the initial materials must also be considered. The temperature elevation is a criteria applied to disposal design. In the Cigéo project, the temperature domain is limited to 90 °C on the short term and 60 °C when dissolved radionuclides are released. These two temperature

limitations are considered for the ThermoChimie validity domain, respectively for mineral stability and radionuclide behavior.

Furthermore, some of the wastes to deposit present complex matrices, with very high salinity (multi-molar concentrations of nitrate and sulfate dissolved salts on the short term in contact with the waste packages) and/or with large amount of organics materials prone to degrade and form shorter chain organic ligands.

Modeling the migration of radionuclides and toxic elements in these varying geochemical systems requires data allowing consistent treatment of each element's solubility and speciation over a wide range of physical–chemical conditions.

ThermoChimie uses a coherent and stringent data selection framework to satisfy these needs for reaction pathways and behavior of numerous radionuclides and toxic elements. In addition to typical major elements such as C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe and Ba, data have been reviewed and introduced into ThermoChimie for a large list of radionuclides and chemiotoxics, including (i) long life radionuclides ($T_{1/2} > 1000$ years) and actinide daughters: C, Al, Cl, K, Ca, Mn, Fe, Ni, Se, Rb, Zr, Nb, Mo, Tc, Pd, Sn, I, Cs, Ba, Sm, Ho, Hf, Pb, Ra, Th, Pa, U, Np, Pu, Am and Cm (Be, La, Bi and Ac foreseen in the near future); (ii) short life radionuclides such as Co, Sr, Ag and Eu; (iii) chemically toxic elements: B, Cr, As, Cd and Sb. The database is including currently around 2300 secondary species in consistency with these chemical elements. A summary of the elements studied and included in the ThermoChimie database is shown in Fig. 1.

The guiding principles for ThermoChimie development are completeness, accuracy and consistency. The TDB must contain all data needed to represent the expected behavior of radionuclides under the ranges of conditions likely to occur in the different disposal situations. It is considered preferable to acknowledge the existence of a complex known to be important rather than neglecting its formation because it has a large uncertainty. This means that in some cases data not selected in other TDB due to high level of associated uncertainty are selected in ThermoChimie in order to ensure *completeness*. The *accuracy* of ThermoChimie is continuously tested by confronting its predictions with independent data through modelling exercises (cf. examples in following sections). The general process of data selection ensures internal *consistency*. The selected data and their uncertainties in ThermoChimie are formation constants (ΔG_f°, ΔH_f°), reaction constants (log K°, ΔG_r°, ΔH_r°, ΔS_r°, ΔCp_r°) and absolute entropy data (S°) and heat capacity (Cp°). Related to solid compounds, the molar volumes are provided to model the coupling effects between dissolution/precipitation processes and transfer characteristics (porosity). All data included in ThermoChimie must maintain the basic thermodynamic relationships given in Table 1.

The identification of the original data selected from the literature, whether it is the stability constant, the reaction enthalpy and entropy or the magnitudes of formation of the individual species and compounds is crucial for a proper TDB maintenance. This avoids future unwanted inconsistent changes. For example, one cannot change log K_r° without modifying ΔG_r° in the database. One cannot change ΔH_f° of a species intervening in a reaction without revising the ΔH_r° of the reaction, etc.

Specific interaction coefficients are provided for Na, Cl, NO_3 and ClO_4 for ionic strength corrections using the SIT (Specific Ion Interaction Theory) approach, optionally with other laws of extended Debye–Huckel equations (see below regarding application on activity corrections). A dedicated ThermoChimie version excluding weak complexes has been developed for the specific SIT use.

The modelling of kinetically-controlled reactive transfer is a current challenge in order to correctly model geochemical transient and non-equilibrated redox systems. The ThermoChimie TDB contains kinetic models based on the transition state theory (see Section 4.4) and in consistency with the Gibbs free energies of the equilibrium data sets for treating phase dissolution and/or precipitation in terms of kinetics for a variety of reactive mineral phases: ubiquitous minerals (quartz, feldspars, gibbsite, calcite, dolomite, siderite, celestite); clay minerals (kaolinite, illite, smectite, chlorite, biotite); cement minerals (C–S–H).

The ThermoChimie TDB can be extracted into data formats compatible with the input needs for several numerical codes commonly used for geochemical applications (PhreeqC (Parkhurst and Appelo, 2013), Chess (Van der Lee and De Windt, 2002), Crunch (Steefel, 2009), Toughreact (Xu et al., 2011)). These extraction capabilities will be extended to other codes depending on identified needs (e.g. Medusa (Puigdomenech, 2012), Geochemist's workbench (Bethke and Yeakel, 2014), etc.).

3. Data selection and validation for radionuclide elements

Each individual datum introduced in ThermoChimie is the result of an exhaustive work of literature research, comparison and/or estimation of thermodynamic data values. The following sections describe the essential aspects of the data selection procedure for inorganic and organic (low molecular weight) complexes with radionuclide and major elements, and provide an illustration of how data is applied and validated.

3.1. Inorganic complexes

The main sources of thermodynamic data used for radionuclides in ThermoChimie are:

Fig. 1. Periodic table summarizing elements included in the ThermoChimie database.

Table 1
Set of equations governing the relation between data in ThermoChimie that must be always fulfilled.

For a given reaction $v_1R_1 + v_2R_2 + \ldots + v_nR_n = P$	
Hess' law and extensions:	$\Delta H_r^o = (\Sigma_i v_i \, \Delta H_f^o(R)) + \Delta H_f^o(P)$
	$\Delta G_r^o = (\Sigma_i v_i \, \Delta G_f^o(R)) + \Delta G_f^o(P)$
	$\Delta S_r^o = (\Sigma_i v_i \, \Delta S_f^o(R)) + \Delta S_f^o(P)$
Thermodynamic equilibrium:	$\Delta G_r^o = -RT \ln K_r^o$
Gibbs free energy:	$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o$ for constant T

- Previous TDB compilations: The selection process includes a compilation of the thermodynamic data reported in previous databases such as SUPCRT92 (Johnson et al., 1992), NBS (Wagman et al., 1982), USGS Database (Robie and Hemingway, 1995) for major elements and the IAEA (Fuger and Oetting, 1976) or the NEA-TDB's for radionuclides (Grenthe et al., 1992; Silva et al., 1995; Lemire et al., 1999; Guillaumont et al. 2003; Gamsjäger et al., 2005, 2012; Hummel et al. 2005; Olin et al., 2005; Brown et al., 2005; Rand et al. 2009).
- Open scientific literature: Active databases are generally continuously updated to reflect the most recent knowledge. However, some databases have not been updated for a long period of time or they lack information on certain elements of interest. In these cases the open scientific literature has been reviewed to fill in the gaps.
- Data obtained by means of specific experimental programs on actinides and fission products carried out under the auspices of the Andra or other reputable experimental programs endorsed by Nuclear Waste Management organizations and research institutions.
- Estimations: In some cases, data gaps exist and good quality data are not available in previous compilations or in the open literature. When this is the case, estimations have been carried out to address this problem. More detailed information about some of the methodologies used for data estimation can be found in the following sections.

Radionuclide data included in ThermoChimie can be classified into three different types according to the data selection process:

1. Selection of **thermodynamic stability**, i.e., aqueous stability constants and solubility equilibria are selected as main data, when possible. In some cases these data allow the calculation of Gibbs free energy of formation of the species as far as the free energy of formation of the basic components is available. $\log K^o$ and ΔG_r° are the therefore first parameters selected and ΔG_f° are calculated accordingly.
2. Assessment of **temperature effects**, i.e., enthalpies and entropies. In some cases Gibbs free energies are calculated from ΔH_f° and S_f° data although this is not always possible. There are not many sources for enthalpy data in the literature and in some cases enthalpy must be calculated from Gibbs free energy and entropy data when available. The selection of ΔH_r° and ΔS_r° allows the calculation of ΔH_f° and S_f° when enthalpy and entropy data for the basic components are available.
3. Assessment of **electrolyte effects**. ThermoChimie primes the Specific Interaction Theory (SIT) to correct to infinite dilution and provides interaction coefficients for anion and cations. Data for these coefficients are either taken from the published literature or estimated based on chemical analogies.

The procedure used when necessary for **estimating** thermodynamic parameter values depends on many factors, among them: the type of data, the original values available, the element studied.

Estimations can be based on different principles, such as chemical analogies among elements or among ligands, correlations that take into account the charge and the ionic radii of different elements, or empirical algorithms. The estimation procedures can be used to obtain different thermodynamic data, such as $\log K^\circ$, or S_m°. The validity and the accuracy of the estimations depend on each particular case and must be individually evaluated.

Due to the inherent difficulties associated with the experimental determination of stability data at temperatures other than 25 °C there is a lack of enthalpy data for radionuclides in the literature. This makes proper assessment of the effect of temperature variations on radionuclide behavior difficult. A special effort has been done to fill in this gap in ThermoChimie. Data in the literature have been revisited and existing or newly developed estimation procedures have been applied for this purpose (Langmuir, 1978, 1979; Baes and Mesmer, 1981; Shock et al., 1997; Sverjensky et al., 1997).

Available experimental formation entropies for lanthanide and actinide aqueous complexes follow a defined parabolic trend relative to the charge of the complex, as previously proposed by Langmuir and Herman (1980) (see Fig. 2). Standard molal enthalpies of formation at 25 °C and 1 bar for several radionuclide-bearing aqueous species have been estimated by this method. The estimated entropies have been used to calculate reaction entropies and these to obtain reaction enthalpies and the subsequent stability constants by applying the Van't Hoff equation.

For solid compounds, estimations have been mainly based on the Latimer approach, that is, the apparent entropy contribution of a given anion is related to the charge of the cation in the salt (Latimer, 1952). In Fig. 3 the comparison between the application of the Latimer approach to oxide hydrates and available experimental data is shown. The level of coincidence is very high, obtaining an average deviation between predictions and experimental data of 14 kJ mol^{-1} and a maximum deviation of 40 kJ mol^{-1}. This test was taken as an indication of the reliability of the application of Latimer approach to amorphous compounds presenting different hydration waters.

Several types of radioactive wastes can contain significant amounts of soluble salts (e.g. nitrates, sulfates, etc.). The evaluation of the behavior of these wastes entails carrying out calculations at high ionic strength values. A significant effort has been done to test and improve the performance of the database for high ionic strength calculations by both modelling of experimental data obtained at high salinity (Duro and Grivé, 2012) and benchmarking exercises (comparisons with other databases).
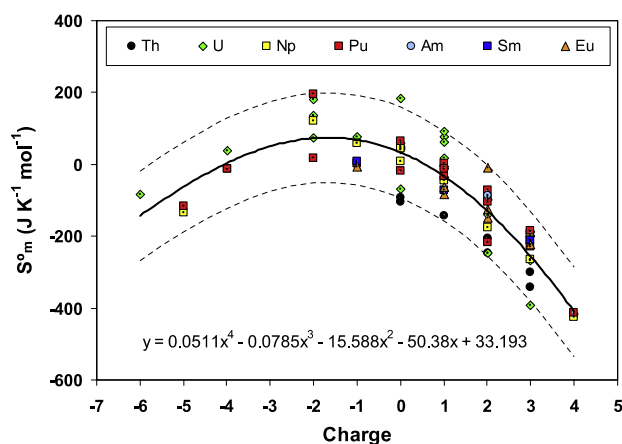

Fig. 2. Experimental data available for some actinide and lanthanide aqueous complexes (symbols) and fitting of the available experimental data to a 4th degree polynomial (curve).
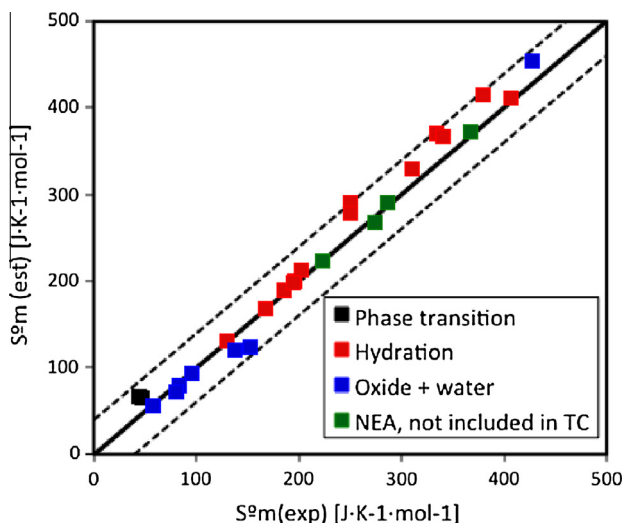
Fig. 3. Comparison between experimental entropy of formation (symbols) of water containing solids and entropy of formation calculated by applying the Latimer approach. (TC stands for ThermoChimie).

ThermoChimie relies principally on the SIT Theory to obtain activity coefficients of aqueous species and correction to infinite dilution (Grenthe et al., 1997). The use of SIT can provide adequate ionic strength corrections of data up to ionic strength in the range 6–10 mol/kg, depending on the particular system and the ionic media considered. The SIT ion interaction coefficient depends on the species, the ionic medium and the counter-ion(s) in solution. The ions present in higher concentrations in the solutions of interest are Na^+ and Cl^-, therefore the SIT activity coefficients for $\varepsilon(Na^+,$ anion) and $\varepsilon(cation, Cl^-)$ are included in ThermoChimie database. The interaction coefficients for cations with ClO_4^- and NO_3^- are also included when available.

If individual coefficients are available in the literature, it is possible to calculate $\log K°$ values accordingly. If the individual interaction coefficients are not reported, it is possible to calculate $\log K°$ values if stability constants at different ionic strengths ($\log K$) are available, by interpolating $\log K°$ and $\Delta\varepsilon$ from a linear regression. In some cases individual interaction coefficients are estimated based on well-founded correlations. If activity coefficients are not available and the estimation of interaction coefficients is not possible, the extended Debye-Hückel equation is used to obtain infinite dilution values in ThermoChimie.

3.2. Low molecular weight organic complexes

Organic materials in the French medium level long-lived waste include bitumen (embedding matrix for some low and intermediate level radioactive waste), polymers such as PVC or polyoleofins and many other organic containing substances (papers, ion exchange resins tensioactives, flocculants, cement adjuvants). These organic materials can undergo different types of degradation (radiolysis, hydrolysis, biodegradation, etc.) that release a variety of short-chain organic ligands (e.g. acetic, adipic, phthalic and other acids from polymers such as PVC; oxalate from radiolytic degradation of bitumen and ion exchange resins; isosaccharinic acid from cellulose degradation under alkaline conditions; gluconic acid as a simple molecule representative of breakdown of complex superplasticizers under cement conditions). Multidentate chelating decontaminant agents such as citrate, NTA or EDTA, are widely used in the nuclear industry and consequently these organic compounds are also in the waste inventory. All these different species are considered in the ThermoChimie database, due to their ability

to form stable, water-soluble complexes with a wide range of metal ions.

The ability of organic compounds to form stable complexes with metallic cations is widely recognized (Hummel et al., 2005). A significant increase on thorium solubility in the alkaline pH range can be expected in the presence of isosaccharinate or gluconate. Fig. 4 shows the agreement between ThermoChimie calculated solubility and experimental results.

The presence of calcium significantly modifies the impact that these substances have on the behavior of radionuclides, especially under cement environments, as this major ion competes with radionuclides for the available organic ligand. This is why special attention has been devoted to the selection of thermodynamic data for calcium complexation with organic ligands in the ThermoChimie database. Fig. 5 shows an example of such an application.

An exhaustive literature review allowed identification of several knowledge gaps regarding the stability of radionuclide-organic complexes. A special attention has also been paid to organic iron species due to their high stability and considering the competitive effects between dissolved iron and radionuclides *versus* the organic complexation.

Existing correlations between the stability constants of the complexes and certain properties of the metal ion or the organic ligands such as charge or radii were used to test the adequacy of the thermodynamic data selection performed (see Gaona et al., 2008 for some examples). These correlations have been applied for predictive purposes to estimate thermodynamic data not available in the literature. Given the deficient state of knowledge regarding the stability of the complexes formed between gluconate and isosaccharinate and radionuclides of interest, a specific experimental program on this issue was setup early in 2009 (Colàs et al., 2011, 2013a, 2013b).

3.3. Application and validation

The consistency and reliability of a thermodynamic database is often judged by its capability to reproduce independent experimental data gathered from either laboratory experiments or field observations. Testing and validation have been essential in the building process of ThermoChimie. It is important to ensure not only that all the aqueous species and solid phases that may have a role under the conditions of the applicability of the database
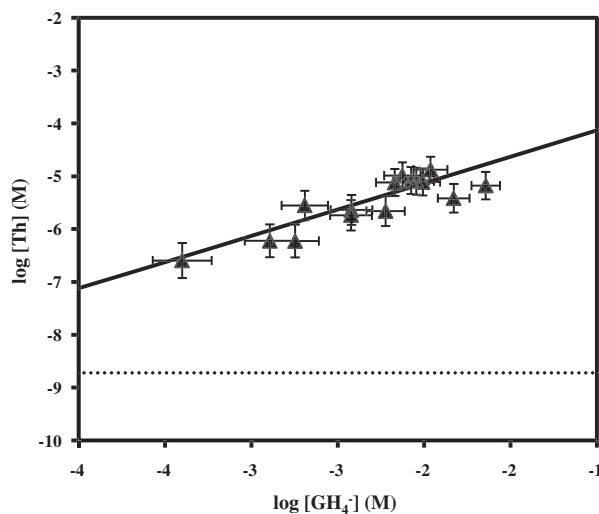

Fig. 4. Solubility of thorium hydroxide (from undersaturation or oversaturation direction) as a function of gluconate concentration at fixed pH = 12 (I = 0.5 M). Solid line represents calculated solubility in the presence of gluconate; dotted line stands for thorium hydroxide solubility in the absence of organic ligands. Data from (Colàs et al., 2013a).
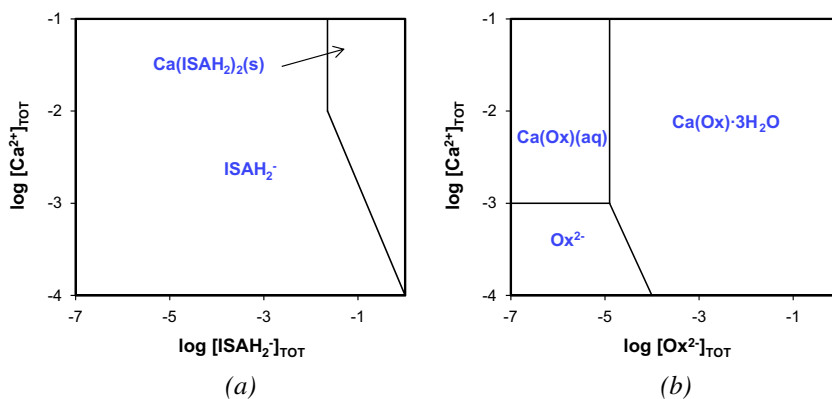
Fig. 5. Predominance diagram of log $[Ca]_{TOT}$ vs log $[L]_{TOT}$, for (a) isosaccharinate and (b) oxalate complexes. pH = 12.5, $I = 0$.

are included in ThermoChimie, but also that their selected thermodynamic data are accurate and consistent. Validation exercises are continuously undertaken to cover the whole range of aqueous species and solid phases relevant for the different scenarios of interest. Different types of exercises can be distinguished:

1. *Direct comparison exercises.* Some examples are the direct comparison of the data included in ThermoChimie with data included in other thermodynamic databases, such as LLNL (Wolery, 1992; Wolery and Sutton, 2011), JNC (Yui et al., 1999) or Nagra-PSI TDB (Hummel et al., 2002). Similarities and discrepancies between databases help to identify additional sources of information and to check the exhaustivity and completeness of the database.
2. *Benchmarking exercises.* A geochemical model relevant to conditions of interest for Andra is identified in the open literature. The model is run several times by using the same geochemical calculation code with different thermodynamic databases, one of them being ThermoChimie. The comparison of the results provides an additional test for the performance of ThermoChimie.
3. *Modelling of experimental data.* Literature is reviewed to identify experimental data not previously considered in ThermoChimie. The performance of ThermoChimie in the interpretation of the new data is tested. Results are interpreted and conclusions extracted.
4. *Modelling of natural analogue data.* Natural analogue studies have become excellent occasions to test the conceptual geochemical models, the associated thermodynamic databases and the required numerical codes to describe radionuclides migration under repository conditions. Poços de Caldas (Brazil), Cigar Lake (Canada), Maqarin (Jordan), El Berrocal (Spain), Oklo (Gabon) or Palmottu (Finland) are some of the natural analogues used to test different aspects of the thermodynamic databases (Bruno et al., 2002). Fig. 6 shows the comparison between the solubility of UO$_2$ calculated by ThermoChimie and the concentrations of uranium measured in groundwaters from different natural analogue sites, such as Cigar Lake, Okélobondo or Palmottu.

4. Data acquisition/selection for major elements: host-rock and EBS applications

Data on major elements are selected following the same principles set forth above. Data related to the stability of ubiquitous natural solids such as quartz, feldspars, calcite, dolomite have been extensively reviewed. Data set for more than 350 minerals are available in ThermoChimie. With regard to their particular interest in the context of repository, a special effort has been devoted to
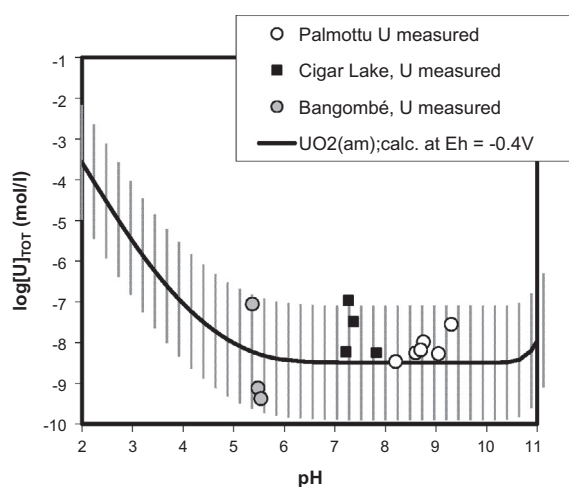

Fig. 6. Symbols: measured concentrations of uranium in reducing samples of Cigar Lake, Palmottu and Bangombé (Oklo). Line: UO$_2$ solubility calculated with ThermoChimie.

phyllosilicate phases (around 100 clay minerals are considered), cement constituent phases (30 solid compounds) and zeolites (20 solid compounds).

4.1. Phyllosilicate (clay) phases

- Critical review for phyllosilicates is based on measured calorimetric data (for ΔH_f^0, S^0 or $Cp(T)$) or on high temperature experiments (Blanc et al., 2013a). The Gibbs energy is then deduced from S^0 values. Furthermore, comprehensive data from literature are relevant formicas, kaolinite and talc, from calorimetric measurements.
- Chlorites, from equilibrium experiments carried out at high temperatures.

However, for smectites, vermiculite, illites and their interstratified forms, the thermodynamic parameters available in literature are only defined from estimation models (Wolery, 1992; Gaucher et al. 2004). Solubility measurements were not considered for these phases because of the questionable conditions for reaching equilibrium in solution (see Essene and Peacor, 1995).

Because of the lack of qualified data for several phyllosilicates, a specific experimental program has been carried out concerning illites, smectites and vermiculites. Clay minerals selected for this program are chosen with respect to the main transformation pathways identified in disposal scenarios (Fig. 7):

- T1 corresponds to illitization of smectite which is the main transformation resulting from cement/clay interaction (Gaucher and Blanc, 2006).
- T2 (Chloritisation) refers to a transformation of smectite resulting from the iron/clay interaction (Mosser-Ruck et al., 2010).
- T3 (Toward saponite/vermiculite) may also correspond to a transformation pathway of smectite within the framework of iron/clay interactions (Mosser-Ruck et al., 2010).
- T4 (Beidellitisation) may be observed in some experiments related to cement/Clay interactions (Gaucher and Blanc, 2006).

Data acquisitions include (i) calorimetric measurements; (ii) estimation models able to predict the thermodynamic properties of clay minerals for the most common compositions (Blanc et al., 2013b); (iii) verification based on solubility experiments and on data from the literature.

Experimental results obtained from calorimetric measurements have been used to define thermodynamic data sets for chlorite, illite, montmorillonite, beidellite, vermiculite, saponite, nontronite and berthierine (Gailhanou et al., 2007, 2009, 2012, 2013; Blanc et al., 2013c).

For consistency and reliability, solubility measurements are also carried out (Gailhanou, 2005) on samples which had already undergone calorimetric measurements. Such a different experimental approach confirmed former results for illite, smectite and vermiculite.

In order to extend this data set to other compositions of clay minerals, estimation models are applied at first for the thermodynamic properties of anhydrous clay minerals. Enthalpy of formation are deduced from the electronegativity difference for for n_s cations $M_i^{z_i^+}$ bounded to the same oxygen atom (Vieillard, 1994a,1994b) according to a fictive reaction between a multi-oxide $M_{k_1} M_{k_2} .. M_{k_i} .. M_{k_s} O_N$ broken down into a sum of n_s oxides $M_i O_{x_i}$.

$$\Delta H_f^0(M_{k_1}, M_{k_i}, M_{k_s}O_N) = \sum_{i=1}^{i=n_s} * \left(k_i * \frac{z_i}{2}\right) * \Delta H_f^0(M_i O_{xi})_{(c)}$$
$$- N\left[\sum_{k=1}^{k=n_s-1} \sum_{l=k+1}^{l=n_s} X_k X_l (\chi_{\text{site } k} - \chi_{\text{site } l})\right] \quad (1)$$

The last term accounts for the contribution arising from the electronegativity difference between cations occupying sites k and l having a same oxygen atom. Entropy and heat capacities are derived from polyhedral decomposition of the mineral into a sum of oxides and/or hydroxides of fictive solid–solid reactions between oxides and the mineral of interest (Chermak and Rimstidt, 1989).

Both electronegativity and polyhedral decomposition estimation models are parameterized with experimental calorimetric measurements and checked using independent data. Fig. 8 illustrates the results obtained when predicting the Gibbs energy of formation of anhydrous clay minerals from ΔH_f^0 and S^0 obtained with the model based on the electronegativity scale and the polyhedral decomposition approach, respectively. Discrepancies with measured values decrease significantly when compared to the Chermak and Rimstidt (1989) model only. The models developed for anhydrous clay phases can be extended to include elements outside of the parameterization set. Application to recent measurements realized on Li-bearing minerals provided representative results with respect to the experimental uncertainty (Blanc et al., 2013b).

For the hydration properties, the model is based on an asymmetric sub-regular binary solid solutions developed for Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} smectites. In addition, it takes into account the effect of temperature (Vieillard et al., 2011). Hydrated clay properties are deduced by means of the reaction:

$$(\text{dehydrated clay mineral}) + n \cdot H_2O$$
$$\rightarrow (\text{hydrated clay mineral}), nH_2O \quad (2)$$
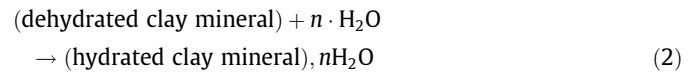
The models applied for hydration (Vieillard et al., 2011) and for anhydrous clay minerals (Blanc et al., 2013b) allows obtaining the thermodynamic properties of a large number of theoretical clay end members included in ThermoChimie.

4.2. Cement-related phases

Solution equilibrium is an efficient means of retrieving thermodynamic properties of cementitious phases (Matschei et al., 2007), which explains the numerous data available in the literature. A
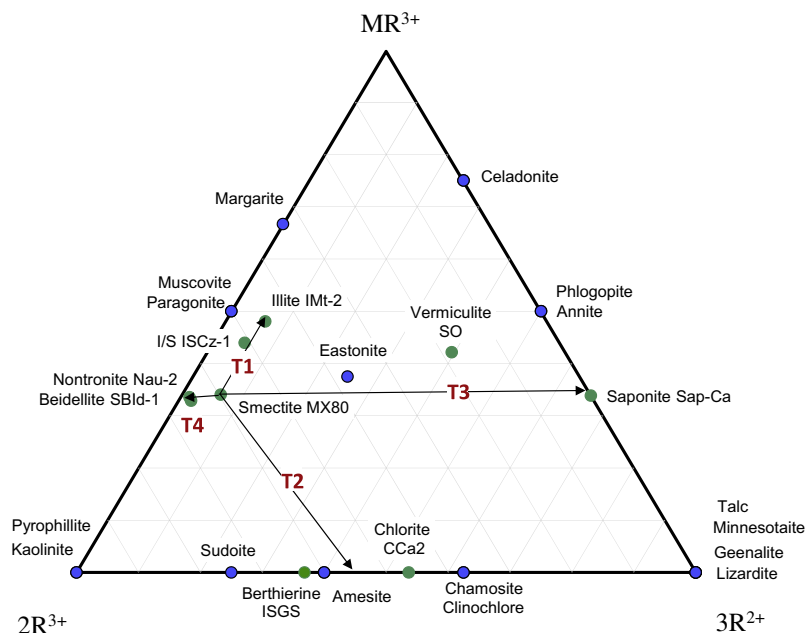

Fig. 7. Composition of phyllosilicates, projected on a MR3–2R3–3R2 triangle. In blue: thermodynamic properties selected by Blanc et al. (2013b) from the literature. In green: thermodynamic properties acquired by calorimetry for the database.
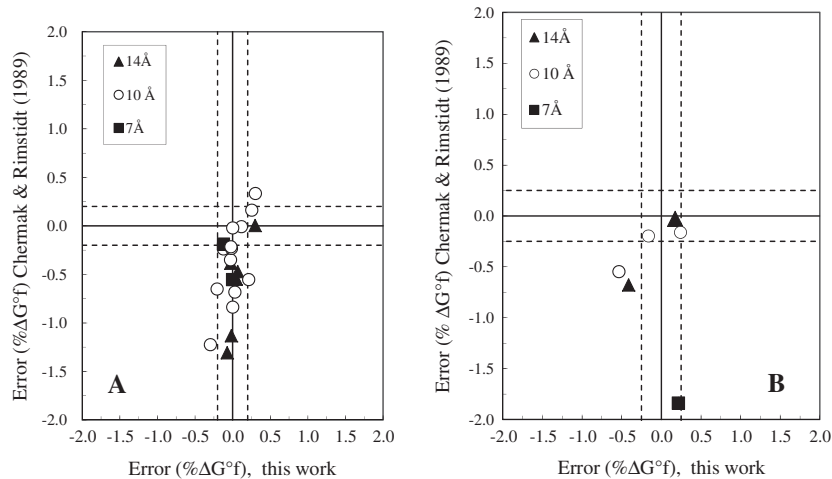
Fig. 8. Predicted ΔG_f^0 for phyllosilicates: comparison of the discrepancy between experimental measurements and values calculated either with the present model or with the method of Chermak and Rimstidt (1989). (A) Phases for parameterization; (B) verification phases.

recent example is given in Lothenbach and Winnefeld (2006) and Matschei et al. (2007).

In ThermoChimie, a global reassessment of the phase diagram of crystalline C-S-H was realized as a function of temperature based on previous literature (Blanc et al., 2010a). A general polyhedral decomposition model similar to that of Chermak and Rimstidt (1989) was used. For phases other than C–S–H (Blanc et al., 2010b), a critical review has been conducted accordingly to the guidelines previously explained for the data selection. The missing parameters (heat capacities) were assessed by using a versatile estimation model proposed by Helgeson et al. (1978).

An activity diagram resulting of the ThermoChimie data selection is shown in Fig. 9 for the chemical system CaO–SiO$_2$–Al$_2$O$_3$–H$_2$O at 25 °C, showing a succession of the stability fields of nano-crystalline C-S-H with a decreasing CaO/SiO$_2$ ratio as the activity of dissolved silica increases.

4.3. Zeolites

The thermodynamic properties of zeolites have been the subject of numerous experimental studies either using calorimetry or solution equilibrium, which have been reviewed by Blanc et al. (2013b). A data set has been selected in consistency with Thermo-Chimie. Lacking heat capacities were estimating using the model developed by Vieillard (2010). The verification was achieved by drawing activity diagrams and assessing the stability domains calculated with respect to observations from the literature. Fig. 9, which applies both to cement-related minerals and to zeolite stability, provides an example of consistency: the increase in silica content of zeolites as dissolved silica increases (see Savage et al., 2007) is well represented in the figure, since the Al/Si ratios are close to 1.0 and 0.2 for zeolite CaP and mordenite respectively.

4.4. Near-field perturbations and kinetic modeling

Several studies have illustrated that modeling must take into consideration reaction rates in order to represent geochemical phenomena observed in laboratory or natural environments (e.g. Hellevang et al., 2013; Marty et al., 2010). Even if many kinetic parameters are available in the literature (see for instance Palandri and Kharaka, 2004), a dedicated selection focusing on the most sensitive mineralogical systems is carried out for improvement and consistency purposes in ThermoChimie. A selection of 13 minerals is defined with respect to the modeling of the
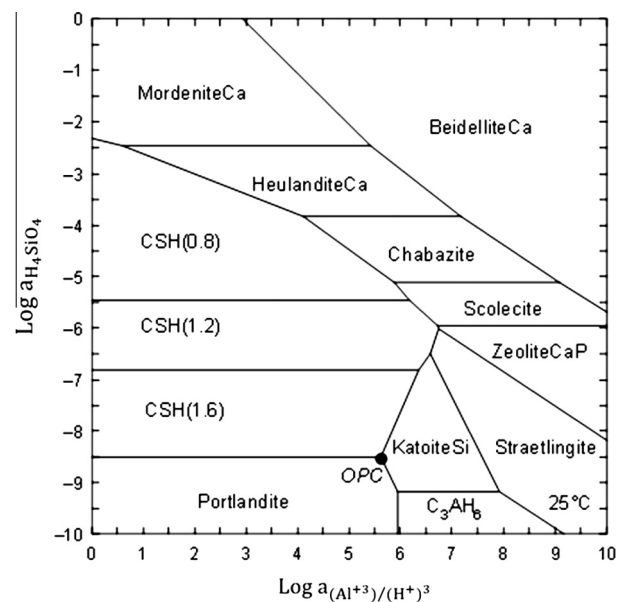

Fig. 9. Predominance diagram for the chemical system CaO–SiO$_2$–Al$_2$O$_3$–H$_2$O at 25 °C.

long-term evolution of the clay-rocks and clayey engineered barrier system (EBS) (Marty et al., 2013a,b). This selection includes the most recent references and additional kinetic parameters such as those necessary to describe deviations close to equilibrium, in consistency with corresponding Gibbs energies in ThermoChimie.

Among several kinetic models (Lüttge et al., 2013), the transition state theory (Lasaga, 1981) has been applied because of its adequation to geochemical codes, following a general expression (Lasaga et al., 1994) that corresponds, for a given mineral n, to:

$$r_n = \pm k(T, pH, a_i)_n A_n |1 - \Omega_n^\theta|^\eta \tag{3}$$

where the positive values of r_n (in mol s^{-1} kg w^{-1}) denote dissolution reactions and negative values denote precipitation (by convention), k_n is the kinetic dissolution or precipitation constant (in mol m^{-2} s^{-1}) that may depend on pH, temperature (T) and the activity of given species (a_i), A_n is the reactive surface area (m^2 kg w^{-1}) and Ω_n is the saturation index (dimensionless). The two parameters θ and η empirically describe the dependence of reaction rate on the saturation index and K_n corresponds to the

equilibrium constant of the mineral, which depends on temperature.

The equilibrium constant (K_n) in the above expression is given by ThermoChimie, including its temperature dependence. When corresponding solution compositions are given, the saturation indexes are re-calculated using ThermoChimie. In addition to the general guidelines for selecting data in ThermoChimie, the collection is processed by considering three main rate law dependences: pH, temperature and the saturation index. Only congruent dissolution is considered, in order to ensure that the experimental rate laws do not depend on the element studied. This question may be critical for low temperature experiments (Marty et al., 2011).

As an example, the kinetic rate law selection is illustrated for smectite (Marty et al., 2013a,b). Fitted linear regressions are shown in Fig. 10 for both acidic and basic conditions, where the smectite dissolution rate law is represented as a function of pH. Experimental data obtained at 25 °C are discarded because of the uncongruent dissolution discussed above (Golubev et al., 2006; Marty et al., 2011).

Most geochemical codes use two types of kinetic models to account for the variation of the dissolution rate as a function of pH, a linear-regression model or a regression-curve model. In Fig. 10 both models are implemented and the constants extracted by least squares minimization. The fitted rate laws are systematically compared to experimental datasets other than those selected for the parameterization of the rate laws.

5. Example of general application

A first example of application of ThermoChimie is applied to the interactions between a cement material (CEM I OPC-based concrete) and a clayey rock (Callovo-Oxfordian formation) for a 100,000 years period of time using PhreeqC code (Marty et al., 2013a,b). The aim of the model is to assess stability of the materials and extension of a geochemical disturbance through the host-rock.

Cement material is composed of portlandite, C–S–H with Ca/Si = 1.6, ettringite, hydrotalcite, monocarboaluminate and calcite for the aggregates. The detailed mineralogy of the Callovo-Oxfordian clay-rock is set according to Gaucher et al. (2004) and Claret et al. (2004). The primary clay minerals are selected according to the model proposed by Gaucher et al. (2009). Zeolites are considered as potential transformation products.

The results of the model are shown on Fig. 11 in terms of volume fraction of minerals as a function of distance. The amount of carbonates produced in contact with the concrete leads to a
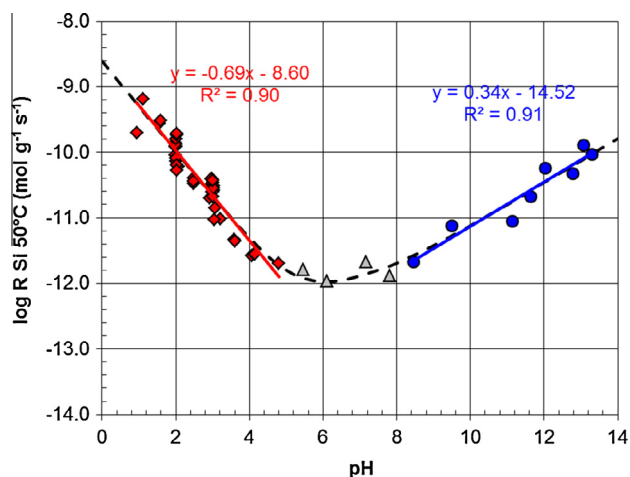
volume fraction higher than 1, which indicates a porosity clogging phenomena that has been observed in some field experiments (Gaboreau et al., 2012). Marty et al. (2013a,b) have considered different transformation indicators, as the extension of the portlandite dissolution front (0.825 m) and the pH plume in the clay barrier (pH > 9, 0.075 m).

ThermoChimie has also been applied to the evaluation of radionuclide solubility's in the assessment of the long-term performance of a nuclear waste disposal facility. This type of assessment aims at providing the maximum concentration of a given radionuclide that can be found in case that groundwater contacts the waste. This type of solubility evaluation has been done for disposal of high, intermediate and low activity wastes, and considers the composition of the water that is most likely to interact with the waste. The water composition varies depending on the materials it contacts before reaching the wastes and, therefore, cement-affected waters as well as groundwater from the host formation are considered. As previously shown, the release of organic materials present in the wastes can also modify radionuclide solubility's. For this purpose, the solubility assessment must cover a relatively wide range of water compositions, temperatures and ionic strengths, and the capacity of the thermodynamic database (ThermoChimie in this case) to cover these conditions is of high relevance. Some examples of solubility evaluations are shown below:

- Calculation of radionuclide (e.g. selenium, uranium, etc.) solubility under the conditions of interest (Callovo-Oxfordian and cement-affected groundwater). The selection of the solubility controlling solid phase is an important part of the assessment.
- Comparison of the calculated results with available experimental data and/or measured concentrations in natural analogue environments. This step allows evaluation of the real significance of the calculated solubility values, and other solubility controlling processes (such as formation of solid solutions) can be suggested.

In the case of selenium, the calculations performed by using ThermoChimie database indicate that Se solubility under Callovo-Oxfordian conditions is low (10^{-7} to 10^{-11} M), being controlled by precipitation of the solid phases $FeSe_2(s)$, $Fe_{1.04}Se(s)$ or $Se(c)$. This can be compared to measured selenium concentrations in clay waters from Cigar Lake which are below the detection limit ($4 \cdot 10^{-7}$ M) (Bruno et al., 2002).

For oxidizing cement-affected porewater, the solubility of selenium is not considered to be limited by any pure solid phase given the high solubility of the common alkali and alkali earth salts of the higher redox states of selenium. In the Maqarin and Oman alkaline porewaters Se concentrations are in the range of 10^{-5} to 10^{-6} M and below $3 \cdot 10^{-9}$ M, respectively (Bruno et al., 2002). All the aqueous Se was observed to be in anionic form in the Maqarin waters, in agreement with the calculations performed with ThermoChimie.

The solid exerting a solubility control of uranium under the conditions of the Callovo-Oxfordian porewater is $UO_2 \cdot 2H_2O(am)$. The calculated U solubility under those conditions is in the order of 10^{-8} M. The underlying U aqueous speciation is mainly dominated by U(VI)-carbonate and Ca(II)–U(VI)-carbonate species with some contributions of $U(OH)_4(aq)$. The calculated concentrations are in agreement with uranium concentrations measured under reducing conditions in sampled porewaters from the Oklo natural analogue site and with porewaters sampled at the clayey reducing waters of the Cigar Lake uranium deposit (Bruno et al., 2002).

Under the prevailing conditions of the cement-affected porewater, becquerelite ($Ca(UO_2)_6O_4(OH)_6 \cdot 8H_2O$) and Ca uranates ($CaU_2O_7 \cdot 3H_2O$ (s)) have been identified to exert a solubility control

Fig. 10. Retrieving of the rate law constants for the dissolution of smectite, at 50 °C.
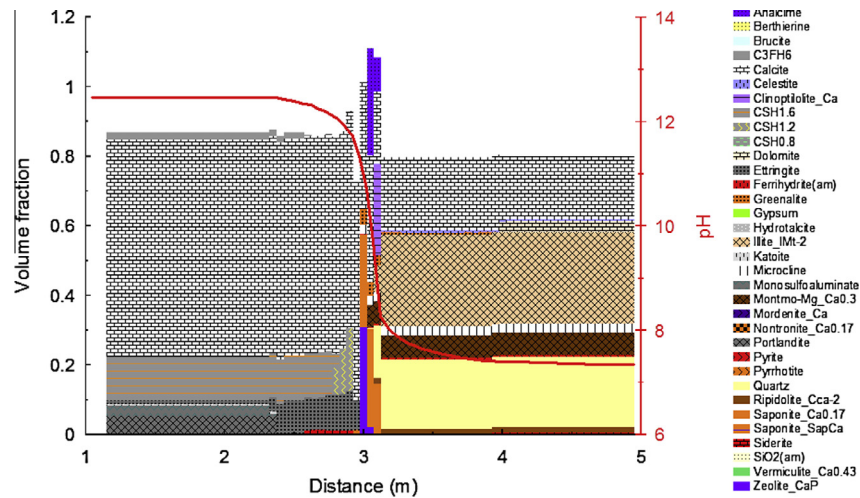
Fig. 11. Mineralogical and pH changes in concrete and claystone after 50,000 years. More details in Marty et al. (2013).
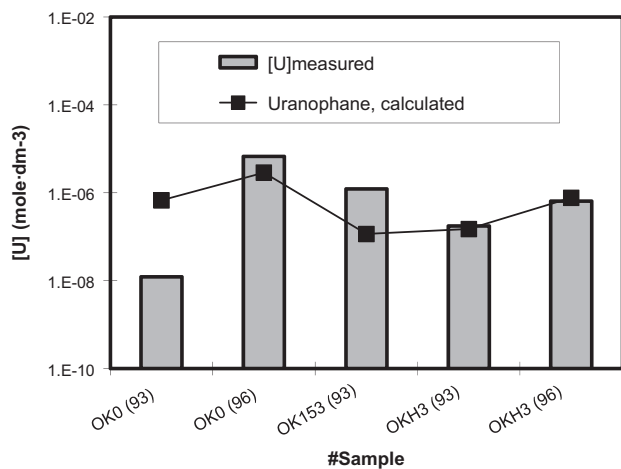

Fig. 12. Comparison between uranium aqueous concentrations measured in the groundwaters of the Okélobondo mineralization of Oklo and the calculation assuming that the solubility of Uranium is given by equilibrium with Uranophane, a Calcium-Uranyl silicate identified in the area.

(Altmaier et al., 2005). The wide variation of pH and water compositions developed due to cement degradation results in a range from 10^{-11} to 10^{-6} M for uranium solubility under such conditions. The presence of silicon in groundwater increases the stability of uranium silicates. Phases such as uranophane, $(Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O)$ have been reported to form as secondary phases in the vicinity of massive uranium ores (Bruno et al., 2002) and, therefore, its precipitation can be possible under the flow regimes and water composition expected in the surroundings of the repository (see Fig. 12).

6. Conclusion

6.1. Summary and conclusions

The ThermoChimie database is developed by Andra since 1996 to support the performance assessment of radwaste disposal exercises. Development priorities are intended to reflect the relevant reaction paths under disposal situations. The main applications are water/rock interactions in natural systems, specific geochemical conditions and materials in the near field of the disposal, and chemical behavior of radionuclides and chemotoxic elements in these contexts.

For this purpose, a wide range of conditions and geochemical systems is considered, including the pristine mineralogical composition of the host-rocks or cementitious materials and secondary phases from iron steel corrosion and interactions between components of the disposal. Most long life radionuclides (actinides and fission products and activation) are studied in consistency, as well as elements known for their chemical toxicity. Specific conditions are also considered regarding saline wastes (especially nitrate salts) and exothermic waste.

The ThermoChimie database provides thermodynamic functions for reaction and formation of species and relevant compounds identified through characterization and interaction informations coming for instance from experiments carried out in the LSMHM Underground Research Laboratory sited at Bure. These data are consistent, selected with their uncertainties, and as complete as possible with respect to central features (species, solids, pollutants and overall interactions). ThermoChimie also includes kinetic models of dissolution/precipitation for solid phases involved in strong geochemical interactions occurring in the near field of the disposal. The first development priority was given to the conditions to be applied to the French project of deep disposal of high level and intermediate radwaste in the Callovo-Oxfordian geological formation. However, the needs regarding other disposals in operation or in project are also considered.

Data selection is based on comprehensive and critical reviews of the literature, estimation models and a dedicated experimental program applied to most sensitive and ill-defined systems. Recommended data from the NEA-TDB project are a reference and associated guidelines for selection procedure, uncertainty assessment or ionic activity corrections are applied.

ThermoChimie is a useful database to meet a set of modeling requirements for performance assessment. The database is compatible and available in various formats of usual geochemical codes. The ThermoChimie database is available and open to the public community (http://www.thermochimie-tdb.com/), presenting an interface to view data by element and reaction, and providing data files directly usable for most of the different geochemical codes used in the scientific community.

6.2. Future of TDB development

ThermoChimie aims at aggregating knowledge to identify and report on reaction pathways and behavior of radionuclides to a

set of disposal configurations. Since the last decade, considerable progress has been made in the context of numerical modeling. Reactive transfer modeling currently integrates geochemical models that account for reaction schemes aimed completeness of field or experimental observations. Priorities of the database implementation will aim to complete reaction paths given in terms of stability constants and kinetic models.

For natural systems, a wide range of primary and secondary minerals corresponding to water–rock characteristics and interfaces with disposal components is already available in the database. Improvement of the clay data set will focus on hydration properties, mixed-layer solid compounds and on the inclusion of cationic exchange parameters.

The engineered materials consist mainly of iron steel and concrete. For carbon and alloyed steel, the corresponding corrosion products data set will be improved regarding temperature elevation up to 90 °C. On the other hand, remaining issues to improve the field of applicability of ThermoChimie are related to fill in the gap for some cement phases such as C–A–S–H, which are relevant in blended cements. A dedicated experimental program is on-going under the ThermoChimie project to face this data gap. Chemical models of cementitious materials must meet the different formulations proposed for disposal structures and waste packages.

Depending on the nature of the waste and the scenarios defined in the safety analysis, the list of radioelements introduced in ThermoChimie will be extended: Be, La, Bi, Ac for which long-lived isotopes are present in the inventories of some radioactive wastes. Priorities related to the specific conditions for high level waste will aim to better reflect the conditions of temperature up to 80 °C applied to the radionuclide behavior in order to assess the potential for optimization in terms of waste package density.

Stoichiometry and stability of organic complexes of radionuclide, especially under cementitious conditions, is a strong focus and need of the program under development. Thus, expanding the list of organic ligands incorporated in ThermoChimie following the characterization of degradation products of waste packages and as soluble molecules identified in the interstitial waters of the host-rocks is foreseen. A further effort and development will be also made regarding the ionic strength corrections for concentrated nitrate aqueous solutions.

A broader ThermoChimie project definition and development is envisaged and open to future opportunities of collaboration, especially among waste management agencies, in order to join common efforts for future integration of different needs, increasing the applicability range of the database.

Acknowledgements

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