FUELBASE, TAF-ID Databases and OC Software Advanced Computational Tools to Perform Thermodynamic Calculations on Nuclear Fuel Materials

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FUELBASE, TAF-ID Databases and OC Software: Advanced Computational Tools to Perform Thermodynamic Calculations on Nuclear Fuel Materials

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Summary

In case of a severe accident, the phase equilibria and thermodynamic properties of the corium which designates the complex mixture formed by chemical interaction at high temperature between different fuel and structural materials in the reactor have to be predicted. CALPHAD is a suitable method to develop a thermodynamic database to investigate such complex materials containing a large number of elements. New advanced computational tools will be presented in this work: (i) the Open Calphad Software (www.opencalphad.com) developed by B. Sundman, which is an open source code to perform thermodynamic calculations by Gibbs energy minimization; (ii) the FUELBASE database, developed at the CEA since 2005, which allows calculations on complex corium compositions to be performed; and (iii) the TAF-ID (Thermodynamics of Advanced Fuels – International Database) database, which is an OECD/NEA project (www.oecd-nea.org/science/taf-id) launched in 2013 to develop a thermodynamic database on nuclear fuel materials in the framework of an international collaboration between Canada, France, Japan, the Netherlands, Korea and the United States of America.

A. INTRODUCTION

During a severe accident in a Light Water Reactor (LWR), the chemical interaction between fuel and structural materials at very high temperature (up to 3000°C) is possible. In such case, a complex mixture could form, designated as corium, that is constituted of partially or fully molten core materials.

The U-Pu-Zr-Fe-Cr-Ni-O chemical system is representative of the in-vessel corium, which is formed by chemical interaction between UO_2 or MOX fuel, partially or totally oxidized Zr alloy cladding (Zr-ZrO_2) and steel structural materials (Fe-Cr-Ni). The presence of non-volatilized fission products as well as neutron absorber materials (e.g., B_4C) in the in-vessel corium has to be accounted for as well. During a severe accident, a pool of molten material can form in the reactor vessel. To investigate the physic-chemical properties of the pool, it is important that compositions and the relative fractions of the liquid and solid phases be well predicted.

In the ex-vessel scenario, corium could eventually melt through the reactor vessel wall and relocate in the reactor cavity [1]. The cavity can be wet or dry when the corium arrives. In such a case, the concrete cavity could be dissolved by the corium leading to basemat penetration. If the heat removal is not sufficient, the melt temperature will increase until melting or dissolution of adjacent structures. Also, the release of steam and concrete decomposition gases increases the containment pressure. To avoid this phenomenon, sacrificial refractory materials are added. Once the corium interacts with concrete, the melt will be continuously enriched in concrete decomposition products (mainly CaO and SiO_2). To investigate Molten Core-Concrete Interaction (MCCI), the corium chemical system becomes: UO_2-ZrO_2-CaO-SiO_2-Al_2O_3-MgO-Fe_2O_3.

Another key issue is fission product release. Thus, fission products have to be introduced in the corium chemical system as well.

Thermodynamic calculations are required to predict the compositions, the relative fractions and the temperatures of the phase transitions in the corium during the different steps of a severe accident. Moreover, calculation of partial pressures of the different gaseous species is useful to estimate the fission gas release.

To predict thermodynamics of such a complex chemical system, CALPHAD (CALculation of PHAse Diagrams) is the most suitable method [2,3,4]. The basic principle is to calculate the thermodynamic equilibrium for given conditions (mole fraction of *i* constituent x_i^α, or site fraction of constituent *k* on sublattice *l* in a given phase α, $y_k^{(l,\alpha)}$, temperature *T* and pressure *p*) by minimization of the total Gibbs energy of the system G:

$$\min(G) = \min\left(\sum_\alpha m^\alpha G_m^\alpha (T, p, x_i^\alpha \, or \, y_k^{(l,\alpha)})\right)$$

where m^α is molar fraction of phase α, G_m^α is the molar Gibbs energy of phase α.

The total Gibbs energy of the system is a function of the Gibbs energies of all stable phases α of the system:

$$G = \sum_\alpha m^\alpha . G_m^\alpha$$

To perform such calculations, databases containing the mathematical description of the Gibbs energies of the phases (solid, liquid, and gas) as functions of temperature and composition have to be developed.

NUCLEA is a thermodynamic database for severe accident calculations. It contains 18 elements: (Al–Si–Mg–Ca–U–Zr–O–Fe–Ni–Cr–Ag–In–B–C–Sr–Ru–La–Ba)+ (H, Ar) [5]. The associated GEMINI2 code is a Gibbs energy minimization software. Both computational tools are commercial. At present, there is no high quality open source software for calculations of multicomponent systems using CALPHAD type models.

In this paper, advanced computational tools, the Open Calphad free software and the thermodynamic databases FUELBASE and TAF-ID are described.

B. OPEN CALPHAD

In the thermodynamic databases, the values are obtained by using all available experimental data (phase diagram, enthalpy, heat capacity, chemical potential data ….) as well as theoretical data (ab-initio) for different systems to obtain the model parameters for the Gibbs energy functions for the solid, liquid and gas phases, as functions of temperature (T), composition (x_i) and pressure (P). Binary and ternary sub-systems are modelled in a consistent manner. By extrapolation, this makes it possible to predict and calculate phase equilibria and thermodynamic properties of multicomponent real materials (e.g. corium) where little or no experimental data are available. This assessment technique is described in the book by Lukas et al [4].

There is a strong coupling between software and databases as the databases can only use models that are implemented in the software. Until recently, all thermodynamic software have been proprietary, which has limited the scientific development of new models and databases. The Open Calphad (OC) initiative [6,7] provides a free thermodynamic software, which makes it possible to implement thermodynamic calculations in applications for materials science without becoming limited to a specific vendor. It also makes it possible to implement new sophisticated thermodynamic models to take better advantage of the computer hardware for the development of databases.

The source code for OC software, which can be downloaded from Refs. [8,9], applies a well-established global minimization technique [10,11,12] for equilibrium calculations. It is capable of calculating multi-component equilibria for various models based on the Compound Energy Formalism (CEF) [12] as described in [4] with sublattices and ions as well as liquids with strong short-range order. Also, the OC software has capabilities to calculate properties and construct phase diagrams. A software interface for application programs is available. Thus it is possible to couple the OC software with other codes, that requires a thermochemical calculation module on multi-component systems.

The current version of OC can handle standard multi-component Compound Ebergy Formalism (CEF) models with multiple sublattices, and is capable of including magnetism, regular solutions, and gas. Composition-dependent binary and ternary parameters are implemented. Models and model parameters can be read from a standard, unencrypted thermodynamic database (compatible with Thermo-Calc format). The equilibrium can be calculated in multi-component systems for: (i) given conditions in *T, P*; (ii) amounts; or (iii) fractions of components, chemical potentials, or stable phases. The global minimization method allows calculating miscibility gaps. The current version of the code allows for binary phase diagrams calculations. Also, the ionic liquid model for liquid with short-range order as

well as CEF models with ionic species can be handled with OC. An extensive documentation is available.

The ongoing development of this software includes a module for thermodynamic assessments and as the software is free, it is expected that interested users will provide many different capabilities.

C. FUELBASE DATABASE

From 2005 to 2012, the FUELBASE database was developed in CEA to perform thermodynamic calculations on fuel materials for Generation IV reactors; mainly Gas cooled Fast Reactor (GFR) and sodium cooled Fast Reactor (SFR) systems. This project was completed in collaboration with Calcul Thermo, ITU, NRG in the framework of European projects (ACTINET-6, ACTINET-I3, F-BRIDGE). The aim was to build a thermodynamic database by merging published models in the literature (when available) and our own models (when no satisfactory description existed) to progressively describe complex nuclear fuel materials.

As an example, thermodynamic models of both mixed carbide $(U,Pu)C_{1\pm x}$ and oxide $(U,Pu)O_{2\pm x}$ fuels were described. This required a complete model of the U-Pu-O-C system [13] based on experimental data from the literature as well as recent experimental data on solidus/liquidus temperatures measured at ITU using an advanced laser heating device [14,15]. Calculated phase diagrams of U-Pu-O (at 2500 K) and U-Pu-C (at 1773 K) systems are presented in Figure 1(a) and (b). Also, models for (U,Pu)N nitride and (U,Pu,Zr) metal fuels were introduced.

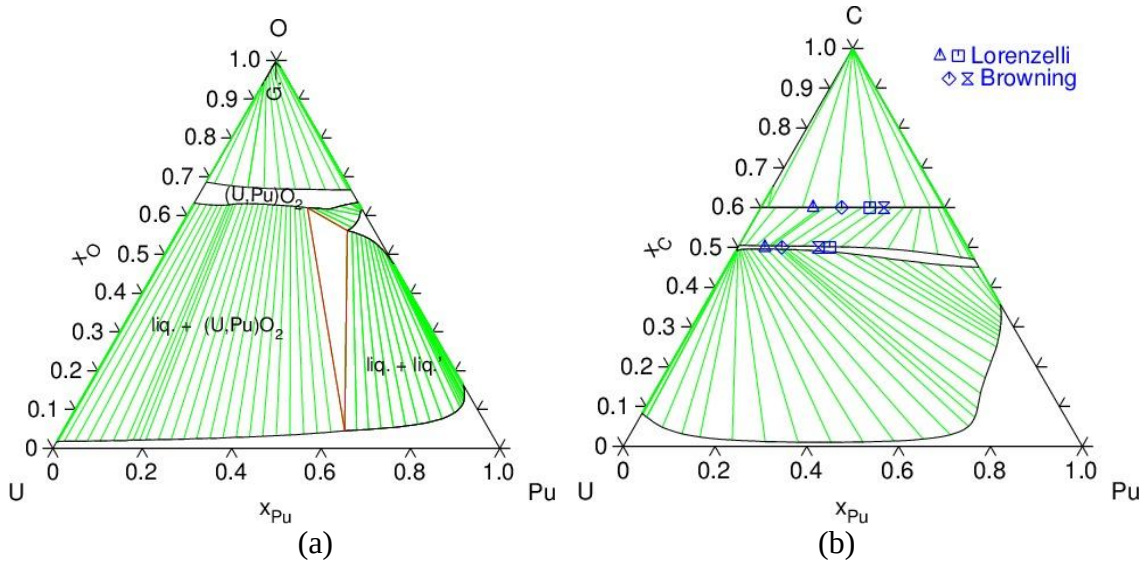


Figure 1: Calculated phase diagrams using the FUELBASE database: (a) U-Pu-O at 2500 K (b) U-Pu-C at 1773 K [13]

For GFR applications, elements representative for SiC/SiC composite cladding and metallic liners (W,Mo,Re,Ta,Nb-Zr) were incorporated into FUELBASE to investigate the chemical interaction between the carbide fuels and candidates cladding material.

For SFR applications, the minor actinides (Am,Np) were incorporated to study the influence of these elements on thermodynamics of MOX fuels. Also, the fission products (Ba, Cs, Te, I, La, Mo, Nb,Nd,Pd,Rh,Ru,Sr) were introduced to create a preliminary model that was capable of predicting the behavior of the chemistry of irradiated fuels. At the end of the FUELBASE project, an oxide database for concrete (Al-Ca-Fe-Si-Mg-O) was added as CEA initiative to assist severe accident projects.

As several international laboratories showed their interest in joining the FUELBASE project, an international database, the TAF-ID project, was launched.

D. TAF-ID DATABASE

The TAF-ID project [16] started in January 2013 within the OECD/NEA (www.oecd-nea.org/science/taf-id). This project is focused on the development of an international thermodynamic database, and is a collaboration between several countries: Canada (CNL, AECL, RMCC, UOIT), Korea (KAERI), France (CEA), Japan (JAEA, CRIEPI), the Netherlands (NRG) and the United States of America (ORNL, INL, LLNL, Univ. of South Carolina).

Following the Fukushima accident, the scope of the fuel materials was extended to Generation II and III systems in order to cover severe accident topics for LWR and BWR reactors. Generation IV fuel materials are still considered MOX $(U,Pu)O_2$ with Am and Np, carbide (U,Pu)C, metallic (U,Pu,Zr), and nitride fuels (U,Pu)N.

Among the topics of interest, the evolution of irradiated fuel chemistry as function of burn-up is investigated. As such, different families of fission products are taken into account (Lanthanides: Ce, La, Gd, Nd, Alkaline earth and transition metals: Ba, Sr, Mo, Zr, Metals: Pd, Ru, Rh, Te, Volatiles: Cs, Te, I, Ru).

To study the chemical compatibility at high temperature between the fuel and structural materials, elements representative for steels (Fe-Cr-Ni), Zirconium alloys, SiC, B_4C (neutron absorber) and concrete (SiO_2-CaO-Fe_xO_y-MgO-Al_2O_3) were introduced.

The TAF-ID is developed from existing databases:

France:

FUELBASE (Calphad) developed at CEA
Fuels $(U, Pu)O_2$ + Am, Np + (U, Pu)C + (U, Pu, Zr) + Fission products (Ba, Cs, Te, I, La, Mo, Nb, Nd, Pd, Rh, Ru, Sr) + Materials (Fe-Cr-Ni, Zr, SiC, W, Ta, Nb, V, B_4C, concrete SiO_2-CaO-FexOy-MgO-Al_2O_3).

The Netherlands:

TBASE (mainly compounds) developed at NRG Petten: MOX + Fission products.

Japan:

Database on metallic fuels (CALPHAD) developed at CRIEPI (U-Pu-Zr-Fe-Am-Np-Cd-Ce-Gd-La-Nd-Pr-Y); and database on corium for BWR (CALPHAD) developed at JAEA (Fe-B-C-O, Pu-Zr-O).

United States of America:

Database on MOX containing Ce, Gd, La (oxide solution) developed at ORNL; and database on metallic fuels (U-Pu-Zr-Fe-Am-Np …) (CALPHAD) developed at LLNL.

Canada:

Database on UO_2 containing fission products (mainly compounds and a few solutions) developed at RMC (Ba, Ce, Cs, H, I, La, Mo, Nd, Np, O, Pd, Pr, Pu, Rb, Rh, Ru, Sr, Tc, Te, Y, Zr).

It was decided to adopt the models available in the FUELBASE database, which were considered to be the most versatile ones to describe both phase diagrams and thermodynamics, especially on metal-oxide systems. In the TAF-ID database:

- the liquid phase is described using a single ionic two-sublattice model with the following species:

  $(Ag^{+}, Al^{3+}, Am^{3+}, Ba^{2+}, Ca^{2+}, Ce^{3+}, Cr^{2+}, Cs^{+}, Cs_2Te, Fe^{2+}, La^{3+}, Mg^{2+}, Mo^{4+}, Nb^{2+}, Nd^{3+}, Ni^{2+}, Np^{4+}, Pd^{2+}, Pu^{3+}, Re^{4+}, Rh^{3+}, Ru^{4+}, Si^{4+}, Sr^{2+}, Ta^{2+}, Th^{4+}, Ti^{2+}, Ti^{4+}, U^{4+}, V^{2+}, W^{4+}, Zr^{4+})_P$ $(AlO_2^{-}, I^{-}, O^{2-}, SiO_4^{4-}, \emptyset, B, BO_{1.5}, C, CeO_2, CrO_{3/2}, Cs_2O_2, Cs_2Te, FeO_{3/2}, I_2, MoO_3, NbO_2, NbO_{5/2}, N, O, Te, PuO_2, SiN_{4/3}, SiO_2, Si_2Te_3, TeO_2, UN)_{Q.}$

- mixed oxides with a fluorite structure described using three sublattice model with the following species:

  $(Al^{3+}, Am^{3+}, Am^{4+}, Ca^{2+}, Ce^{3+}, Ce^{4+}, Gd^{3+}, La^{3+}, Mg^{2+}, Nd^{3+}, Np^{3+}, Np^{4+}, Pu^{3+}, Pu^{4+}, Th^{4+}, U^{3+}, U^{4+}, U^{5+}, Zr^{2+}, Zr^{4+})$ $(O^{2-}, \emptyset)_2$ $(O^{2-}, \emptyset)$.

The lists of binary and ternary systems that are modelled in TAF-ID (December 2014 Version) are presented in Figure 2 and 3, respectively.

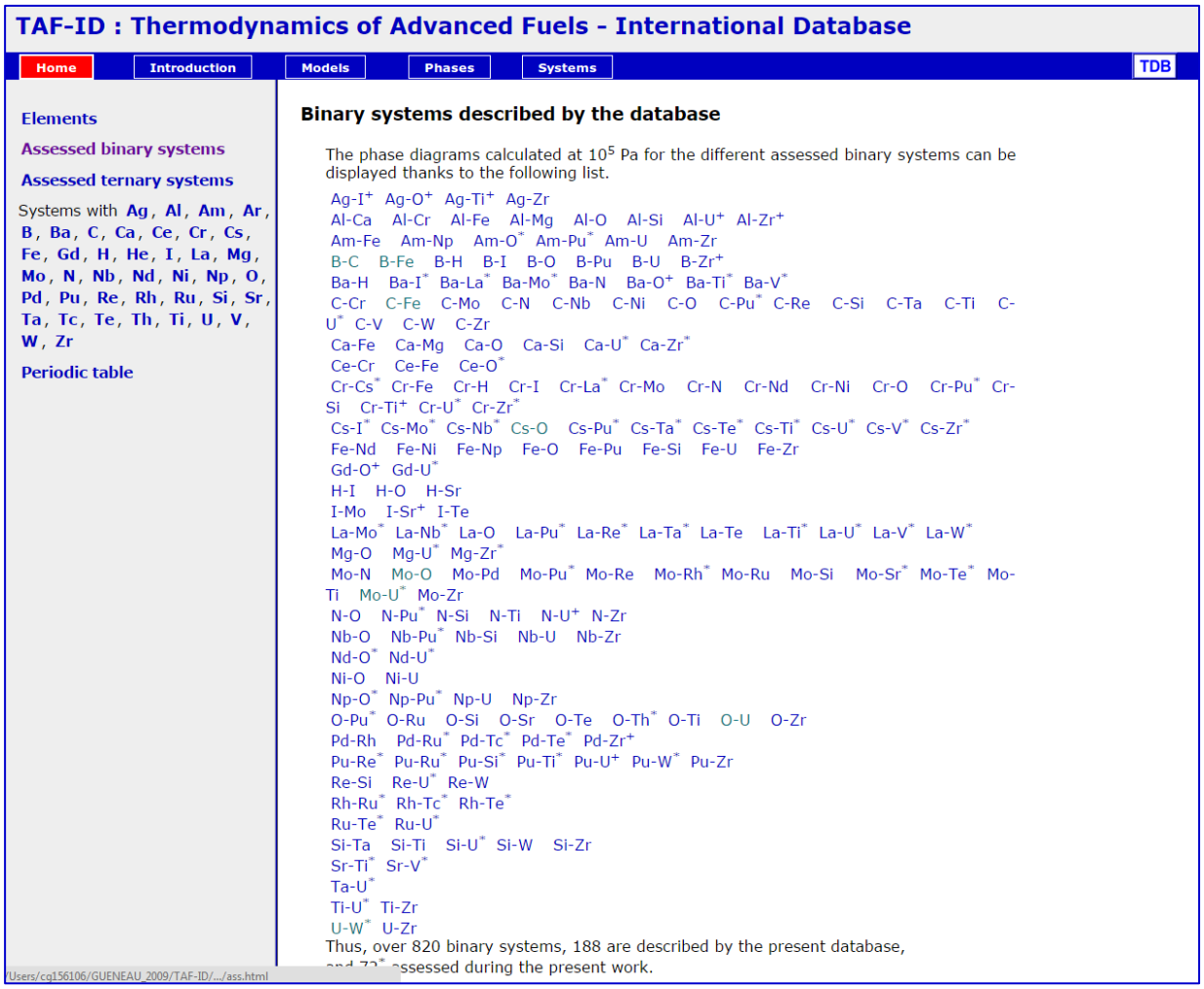


Figure 2: Binary systems modelled in TAF-ID (Dec. 2014 Version)

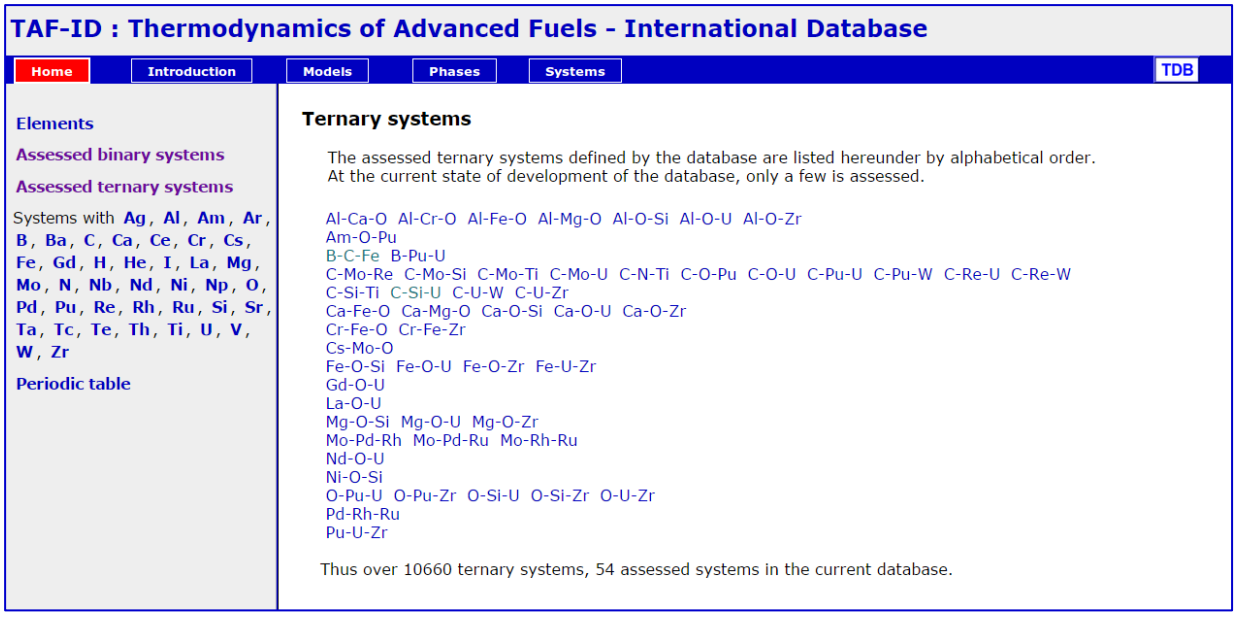
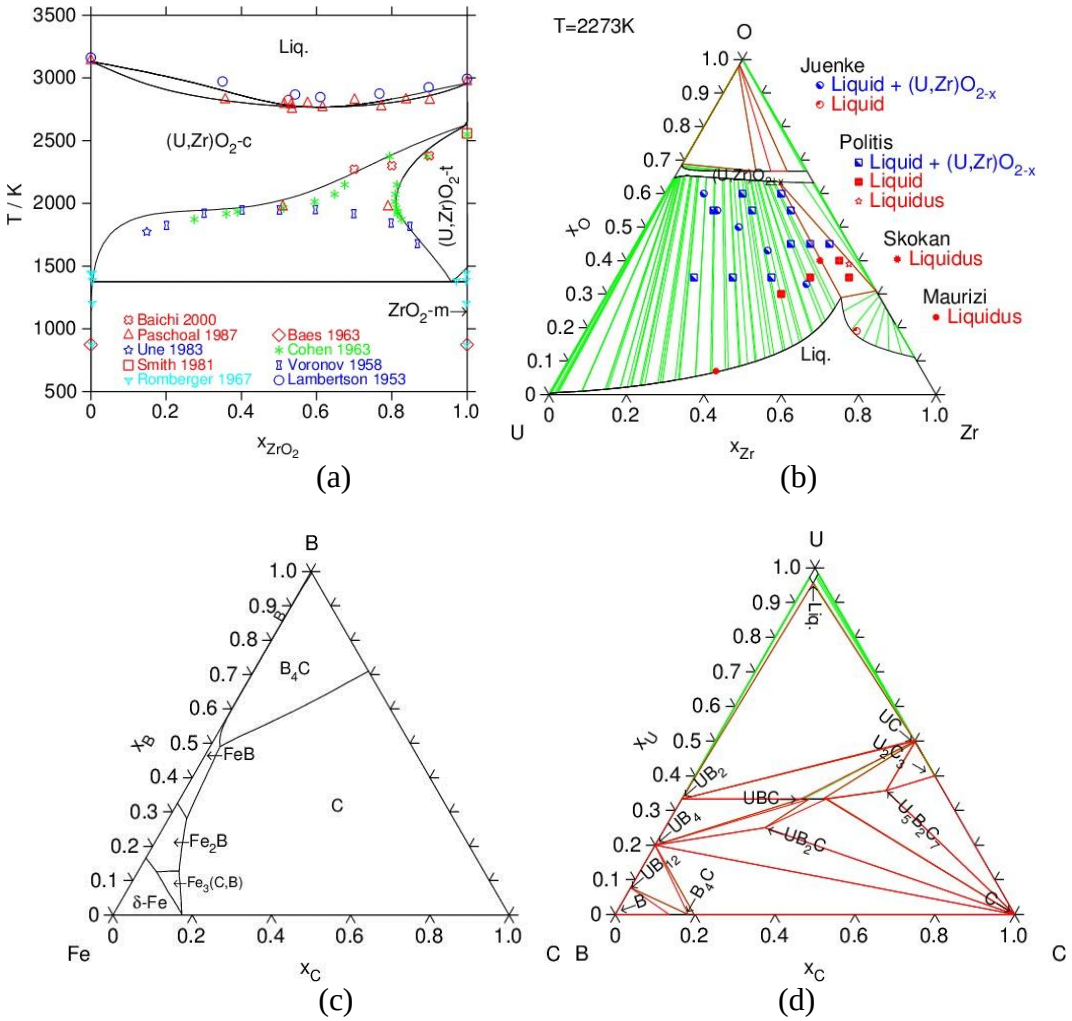
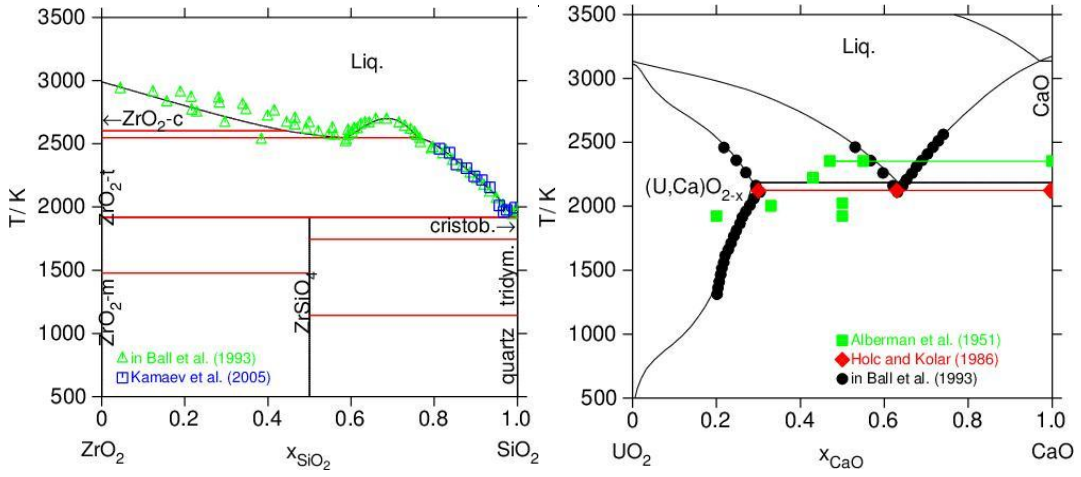


Figure 3: Ternary systems modelled in TAF-ID (Dec. 2014 Version)

In some cases, for binaries and/or ternaries, the models come from published work. For other systems, the assessment was performed within the framework of the TAF-ID project.

Documentation is available in *.html* format (www.oecd-nea.org/science/taf-id). For each binary or ternary system, the description source is given and figures with a comparison of calculated and experimental data are presented for all binary and ternary assessed systems. Examples are given in Figure 4 for systems that enter corium compositions.





(e) (f)

Figure 4: Calculated phase diagrams using the TAF-ID: (a) UO_2-ZrO_2 section assessed by A. Quaini (b) U-O-Zr at 2273 K section assessed by A. Quaini (c) C-B-Fe liquidus projection from M. Kurata (d) U-B-C at 1500 K assessed by N. Dupin (e) ZrO_2-SiO_2 assessed by N. Dupin (f) UO_2-CaO assessed by N. Dupin. A comparison with experimental data is reported when data are available.

The database is available in Thermo-Calc format and software is being developed to convert the database into FactSage format.

The full working version is only available for the signatories of the OECD/NEA agreement. A restricted public version on U-Pu-O-C, U-Pu-Zr and U-C-N systems is now accessible on the OECD/NEA website (www.oecd-nea.org/science/taf-id).

E. CONCLUSIONS

Advanced computational tools to perform thermodynamic calculations on corium are available. These include: (i) the Open Calphad code, which is a Gibbs energy minimization open source software; (ii) the FUELBASE database; and (iii) the "Thermodynamics of Advanced Fuels – International Database" (TAF-ID) on nuclear fuel materials, which is an international project under the OECD/NEA framework.

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