

DE LA RECHERCHE À L'INDUSTRIE

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THE TAF-ID DATABASE – APPLICATION CALCULATIONS TO SEVERE ACCIDENTS AND IRRADIATED FUEL

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Context

TAF-ID database

- Objectives
- Structure of the OECD project
- Current status

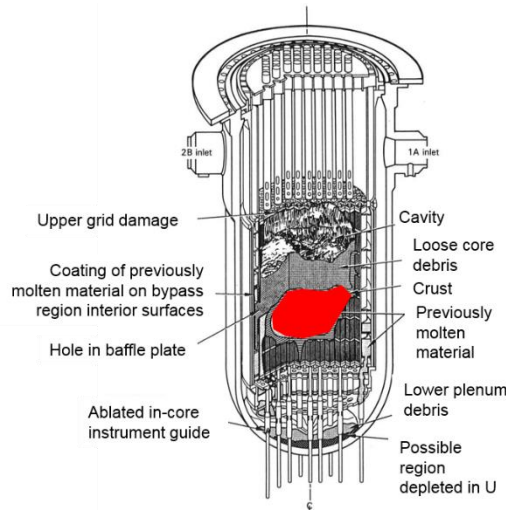
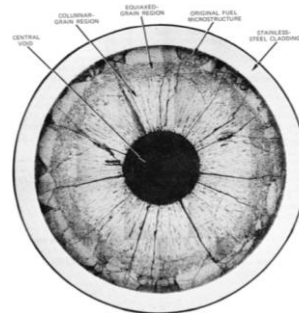
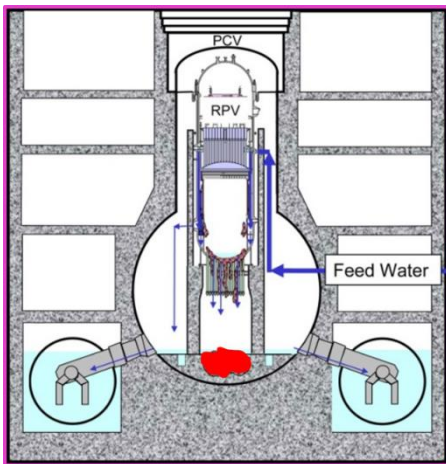
Calculations

- Severe accidents in LWR
- SIMFUELS

Conclusions & Perspectives

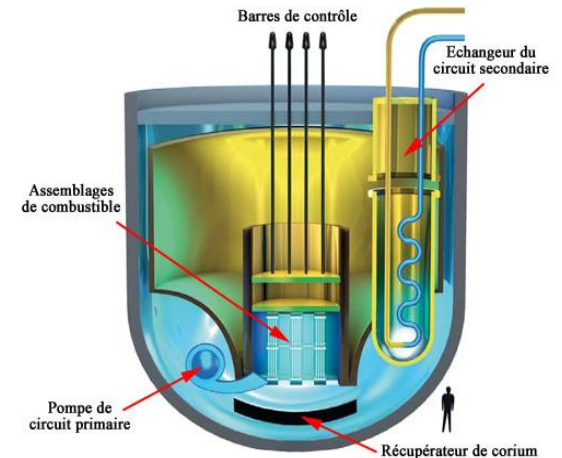
Gen II-III reactors

- Support of safety improvement
- Severe accidents
- Life extension



Gen IV

- Support design
- Severe accidents



Scheme of the ASTRID reactor

• Objectives

→ To develop a **thermodynamic database** as a **computational tool** for advanced fuel materials using the Calphad method

Phase diagrams + Thermodynamic properties of the phases → Multicomponents

→ To exchange on the models, review of experimental data, software, assessments,

...

• System of interest: Reactor materials for Gen II, III and IV

→ **Fuel**

➤ UO_2 , $(\text{U,Pu,Am,Np})\text{O}_2$, $(\text{U,Th})\text{O}_2$, (U,Pu,Zr,Am,Np) , UN, $(\text{U,Pu})\text{C}$

→ **Fission products**

➤ Ba, Sr, Mo, Zr, Lanthanides (Ce, La, Nd, Gd), metallic FPs (Pd, Rh, Ru), volatile FPs (Cs, I, Te)

→ **Structural materials**

➤ Fe-Ni-Cr, Zr alloys, Fe-Cr-Al-Y, Concrete ($\text{SiO}_2\text{-CaO-Fe}_x\text{O}_y\text{-Al}_2\text{O}_3\text{-MgO}$), SiC, B_4C

• Applications

→ **Fuel behavior at high temperature under normal and off-normal conditions**

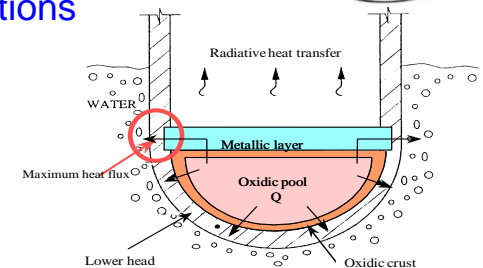
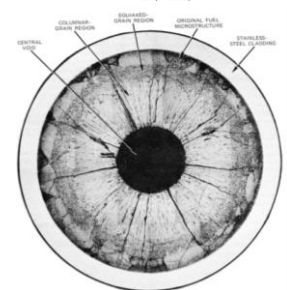
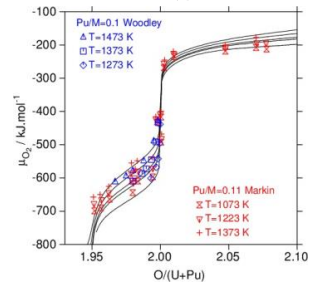
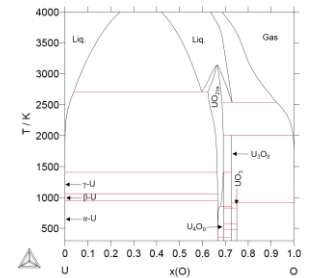
➤ Influence of minor actinides

➤ FPs “chemistry”

➤ Solid/liquid transitions and vaporization

→ **Fuel-cladding chemical interaction at high temperature**

→ **Fuel fabrication**



The Calphad method

Minimisation of the Gibbs energy of the system

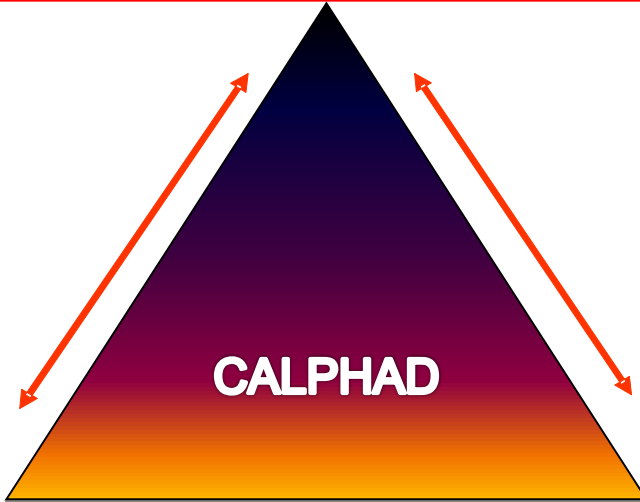
$$\min(G) = \min\left(\sum_{\alpha} n^{\alpha} G_m^{\alpha}(T, p, x_i^{\alpha} \text{ or } y_k^{(l,\alpha)})\right)$$

n=number of mole of phase α
 x=molar fraction of i in α
 y=site fraction

Critical analysis of experimental data

Prediction of higher order systems behaviour by extrapolation from lower order systems

Only phases described in the thermodynamic model can be calculated



Synergic approach
 Experiments ↔ Calculations

Experimental data acquisition
 Thermodynamic data ⇒ Calorimetry, D.S.C.
 Phase diagrams ⇒ Heat treatments, D.T.A.

Thermodynamic modelling

↓ Optimization
 (Code Thermo-Calc)

Thermodynamic database
 $G(\text{phases}) = f(T, x) @ P=1 \text{ atm}$

Minimization of $G(\text{system})$
 (Code Thermo-Calc)

→ Thermodynamic properties
 Phase diagrams
 Application calculations

Roadmap

- Proposed by CEA in 2011
- Project started in 2013 for 3-years duration : OECD-NEA
- **Canada, France, Japan, Republic of Korea, The Netherlands, UK, USA**
- Extension of the project until the end of 2017
- Phase 2 of the project: 2018

www.oecd-nea.org/science/taf-id/

41 elements

TAF-ID : Thermodynamics of Advanced Fuels - International Database

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Assessed binary systems

Assessed ternary systems

Systems with **Ag, Al, Am, Ar, B, Ba, C, Ca, Ce, Cr, Cs, Fe, Gd, H, He, I, La, Mg, Mo, N, Nb, Nd, Ni, Np, O, Pd, Pu, Re, Rh, Ru, Si, Sr, Ta, Tc, Te, Th, Ti, U, V, W, Zr**

[Periodic table](#)

1 H																	2 He	
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba	57-71 Ln	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra	89-103 An	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn			114 Fl			116 Lv	118 Og
		57-71 Ln	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
		89-103 An	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

TAF-ID working version V7 (January 2017)

204 assessed binary systems

TAF-ID : Thermodynamics of Advanced Fuels - International Database

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Assessed binary systems

Assessed ternary systems

Systems with **Ag, Al, Am, Ar, B, Ba, C, Ca, Ce, Cr, Cs, Fe, Gd, H, He, I, La, Mg, Mo, N, Nb, Nd, Ni, Np, O, Pd, Pu, Re, Rh, Ru, Si, Sr, Ta, Tc, Te, Th, Ti, U, V, W, Zr**

Periodic table

The phase diagrams calculated at 10⁵ Pa for the different assessed binary systems can be displayed thanks to the following list.

Ag-I⁺ Ag-O⁺ Ag-Ti⁺ Ag-Zr
 Al-Ca Al-Cr Al-Fe Al-Mg Al-O Al-Si Al-U⁺ Al-Zr⁺
 Am-Fe Am-Np Am-O⁺ Am-Pu⁺ Am-U Am-Zr
 B-C B-Cr B-Fe B-H B-I B-Ni B-O⁺ B-Pu B-U B-Zr⁺
 Ba-H Ba-I⁺ Ba-La⁺ Ba-Mo⁺ Ba-N Ba-O⁺ Ba-Pu⁺ Ba-Sr⁺ Ba-Ti⁺ Ba-U⁺ Ba-V⁺ Ba-Zr⁺
 C-Cr C-Fe C-Mo C-N C-Nb C-Ni C-O C-Pu⁺ C-Re C-Si C-Ta C-Ti C-U⁺ C-V C-W C-Zr
 Ca-Fe Ca-Mg Ca-O Ca-Si Ca-U⁺ Ca-Zr⁺
 Ce-Cr Ce-Fe Ce-Nd⁺ Ce-O⁺
 Cr-Cs⁺ Cr-Fe Cr-H Cr-I Cr-La⁺ Cr-Mo Cr-N Cr-Nd Cr-Ni Cr-O Cr-Pd Cr-Pu⁺ Cr-Si Cr-Ti⁺ Cr-U⁺ Cr-Zr⁺
 Cs-I⁺ Cs-Mo⁺ Cs-Nb⁺ Cs-O Cs-Pu⁺ Cs-Ta⁺ Cs-Te⁺ Cs-Ti⁺ Cs-U⁺ Cs-V⁺ Cs-Zr⁺
 Fe-Nd Fe-Ni Fe-Np Fe-O Fe-Pd⁺ Fe-Pu Fe-Si Fe-U Fe-Zr
 Gd-O⁺ Gd-U⁺
 H-I H-O H-Sr
 I-Mo I-Sr⁺ I-Te
 La-Mo⁺ La-Nb⁺ La-O La-Pu⁺ La-Re⁺ La-Ta⁺ La-Te La-Ti⁺ La-U⁺ La-V⁺ La-W⁺
 Mg-O Mg-U⁺ Mg-Zr⁺
 Mo-N Mo-O Mo-Pd⁺ Mo-Pu⁺ Mo-Re Mo-Rh⁺ Mo-Ru Mo-Si Mo-Sr⁺ Mo-Te⁺ Mo-Ti Mo-U⁺ Mo-Zr
 N-O N-Pu⁺ N-Si N-Ti N-U⁺ N-Zr
 Nb-O Nb-Pu⁺ Nb-Si Nb-U Nb-Zr
 Nd-O⁺ Nd-Pd⁺ Nd-Pu⁺ Nd-U⁺ Nd-Zr⁺
 Ni-O Ni-U
 Np-O⁺ Np-Pu⁺ Np-U Np-Zr
 O-Pu⁺ O-Ru O-Si O-Sr O-Te O-Th⁺ O-Ti O-U O-Zr
 Pd-Rh Pd-Ru⁺ Pd-Tc⁺ Pd-Te⁺ Pd-U⁺ Pd-Zr⁺
 Pu-Re⁺ Pu-Ru⁺ Pu-Si⁺ Pu-Sr⁺ Pu-Ti⁺ Pu-U⁺ Pu-W⁺ Pu-Zr
 Re-Si Re-U⁺ Re-W
 Rh-Ru⁺ Rh-Tc⁺ Rh-Te⁺
 Ru-Te⁺ Ru-U⁺
 Si-Ta Si-Ti Si-U⁺ Si-W Si-Zr
 Sr-Ti⁺ Sr-U⁺ Sr-V⁺ Sr-Zr⁺
 Ta-U⁺
 Ti-U⁺ Ti-Zr
 U-W⁺ U-Zr

Thus, over 820 binary systems, 204 are described by the present database, and 84⁺ assessed during the present work.

TAF-ID working version V7 (January 2017)

66 assessed ternary systems

TAF-ID : Thermodynamics of Advanced Fuels - International Database

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Assessed binary systems

Assessed ternary systems

Systems with **Ag, Al, Am, Ar, B, Ba, C, Ca, Ce, Cr, Cs, Fe, Gd, H, He, I, La, Mg, Mo, N, Nb, Nd, Ni, Np, O, Pd, Pu, Re, Rh, Ru, Si, Sr, Ta, Tc, Te, Th, Ti, U, V, W, Zr**

Periodic table

Ternary systems

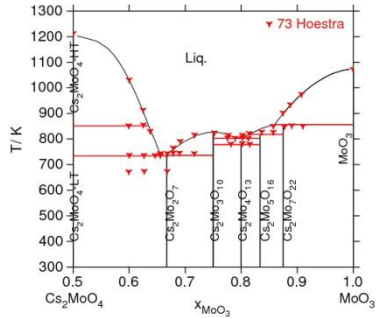
The assessed ternary systems defined by the database are listed hereunder by alphabetical order. At the current state of development of the database, only a few is assessed.

Al-Ca-O Al-Cr-O Al-Fe-O Al-Mg-O Al-O-Si Al-O-U Al-O-Zr
Am-O-Pu
B-C-Fe B-C-U B-C-Zr B-Fe-Zr B-Pu-U
Ba-O-U Ba-O-Zr
C-Mo-Re C-Mo-Si C-Mo-Ti C-Mo-U C-N-Ti C-N-U C-O-Pu C-O-U C-Pu-U C-Pu-W C-Re-U
C-Re-W C-Si-Ti C-Si-U C-U-W C-U-Zr
Ca-Fe-O Ca-Mg-O Ca-O-Si Ca-O-U Ca-O-Zr
Ce-Fe-Nd
Cr-Fe-O Cr-Fe-Zr
Cs-Mo-O Cs-O-U Cs-O-Zr
Fe-O-Si Fe-O-U Fe-O-Zr Fe-U-Zr
Gd-O-U
La-O-U
Mg-O-Si Mg-O-U Mg-O-Zr
Mo-O-U Mo-Pd-Rh Mo-Pd-Ru Mo-Rh-Ru
Nb-O-U
Nd-O-U
Ni-O-Si
O-Pu-U O-Pu-Zr O-Si-U O-Si-Zr O-Sr-Zr O-U-Zr
Pd-Rh-Ru
Pu-U-Zr

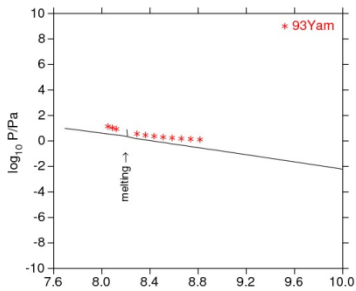
Thus over 10660 ternary systems, 66 systems are assessed in the current database.

Example : Cs-Mo-O system

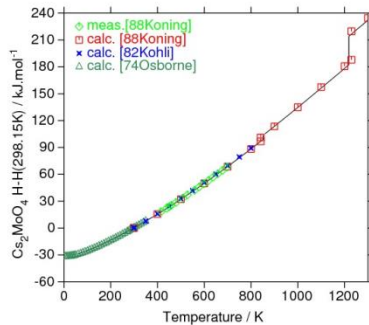
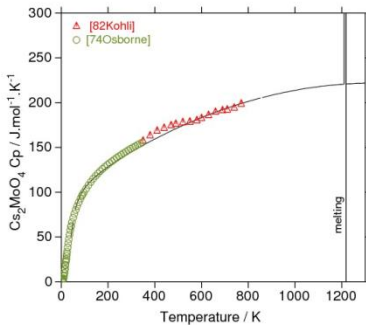
Phase diagram



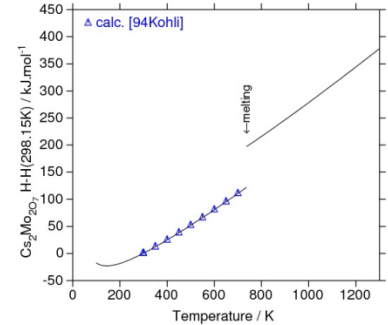
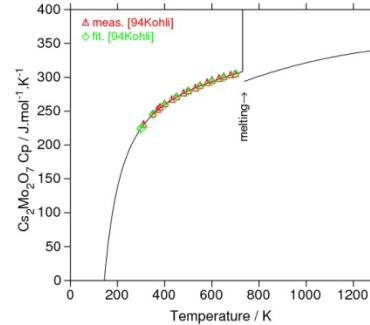
Vapor pressure over Cs₂MoO₄



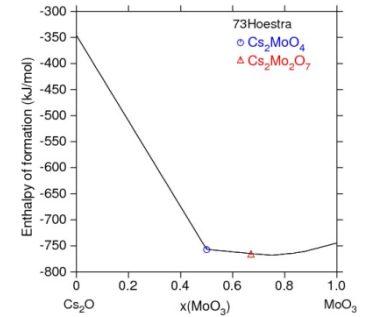
Cp and heat increment for Cs₂MoO₄



Cp and heat increment for Cs₂Mo₂O₇



Enthalpy of formation



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Ternary system Cs-Mo-O TDB Cs-Mo Cs-O Mo-O Cs Mo O Binary systems Ternary systems Periodic table

Section Cs₂MoO₄-MoO₃

Isothermal section at 730 K

Source of the description

N. Dupin and Tam Ngoc PHAM THI, 2014 november based on Tam Ngoc PHAM THI, Thesis, AIX MARSEILLE UNIVERSITE, 2014.

Revision by N. Dupin in october 2016 during the TAF-ID project due to modification of the Mo-O description.

Calculations – Severe accident in LWR

Application to a simplified in-vessel corium : $UO_2-ZrO_2+steel$

Miscibility gap in liquid in-vessel corium:

$$\rho_{metallic} < \rho_{oxide}$$

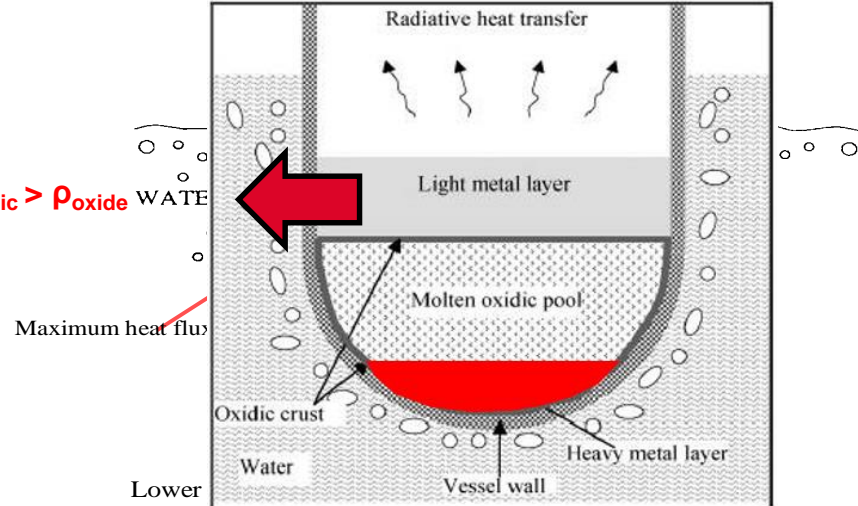


Degree of oxidation of zirconium
U/Zr ratio
Amount of molten steel



$$\rho_{heavy\ metallic} > \rho_{oxide}$$

Thickness of upper metallic layer ↓
→ Enhanced focusing effect
→ Failure of the reactor vessel



Calculations – Severe accident in LWR

Application to a simplified in-vessel corium : UO_2 -Zry+steel

Miscibility gap in in-vessel corium:

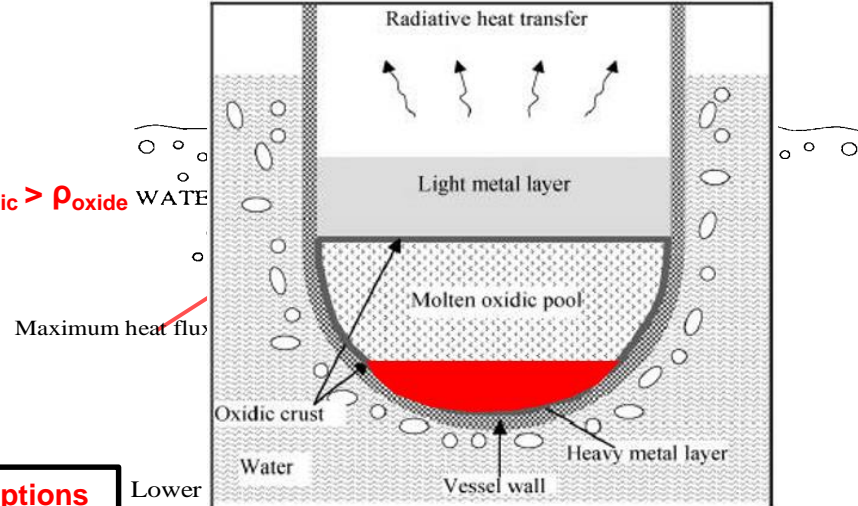
$$P_{\text{metallic}} < P_{\text{oxide}}$$

Degree of oxidation of zirconium
U/Zr ratio
Amount of molten steel

$$P_{\text{heavy metallic}} > P_{\text{oxide}}$$

Thickness of upper metallic layer ↓
→ Enhanced focusing effect
→ Failure of the reactor vessel

Calculations obtained by extrapolation (15) binary and (20) ternary descriptions



Corium E2	Oxide liquid		Metallic liquid		
	Overall	Exp.	TAF-ID	Exp.	TAF-ID
Weight %		50	49.4	50	50.6
U	30.0	61.0	60.7	<0.6	0.03
Zr	9.3	19.8	18.8	<0.4	0.005
Fe	37.9	1.2	2.8	70.0	72.2
Ni	5.4	<0.2	0.0006	12.0	10.7
Cr	9.3	2.2	1.6	16.2	16.8
O	8.1	15.1	16.1	0.5	0.3

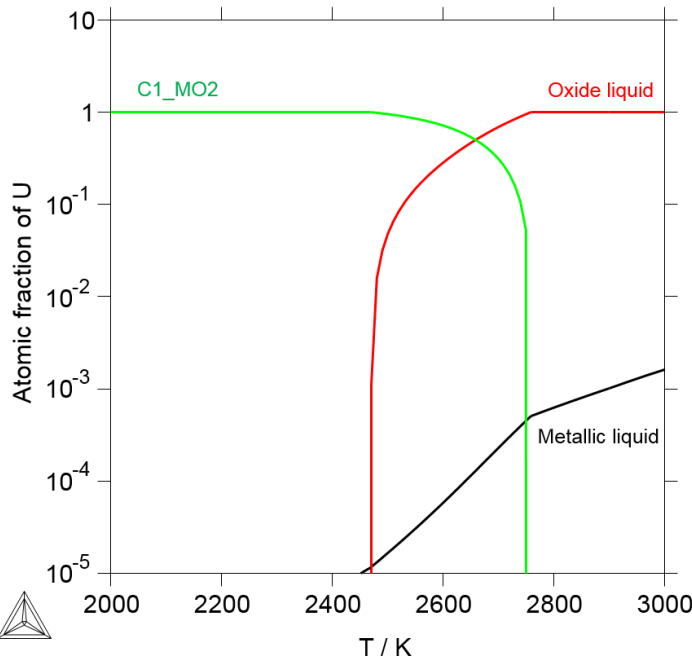
Corium A1	Oxide liquid		Metallic liquid		
	Overall	Exp.	TAF-ID	Exp.	TAF-ID
Weight %		68	69.7	32	30.3
U	60.4	67.3	66.3	45.6	46.9
Zr	17.3	17.8	20.7	16.4	9.5
Fe	9.7	1.8	0.20	26.6	31.5
Ni	1.5	0.3	0.0001	4.1	4.9
Cr	2.2	0.5	0.09	5.9	7.1
O	8.9	12.3	12.8	1.4	0.05

Calculations – Severe accident in LWR

Application to a simplified in-vessel corium : UO_2 -Zry+steel

Corium E2	Oxide liquid			Metallic liquid	
	Overall	Exp.	TAF-ID	Exp.	TAF-ID
Weight %		50	49.4	50	50.6
U	30.0	61.0	60.7	<0.6	0.03
Zr	9.3	19.8	18.8	<0.4	0.005
Fe	37.9	1.2	2.8	70.0	72.2
Ni	5.4	<0.2	0.0006	12.0	10.7
Cr	9.3	2.2	1.6	16.2	16.8
O	8.1	15.1	16.1	0.5	0.3

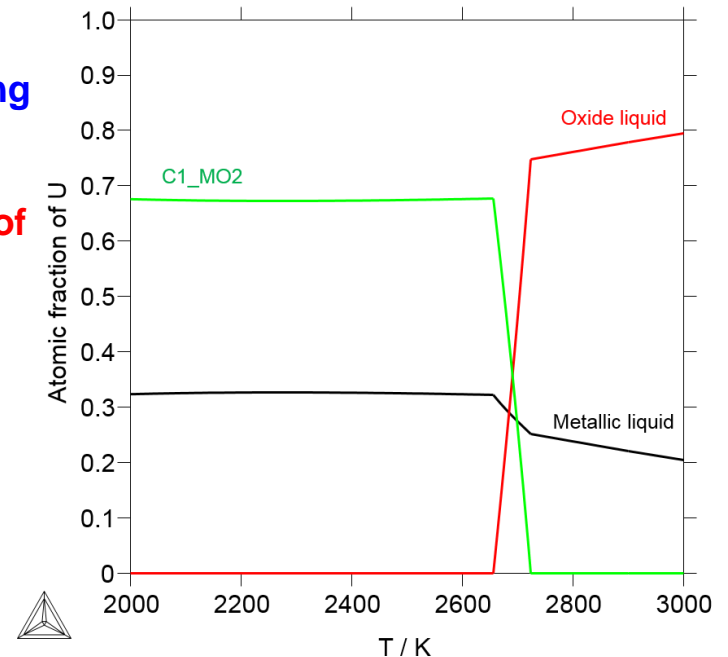
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Zr	17.3	17.8	20.7	16.4	9.5
Fe	9.7	1.8	0.20	26.6	31.5
Ni	1.5	0.3	0.0001	4.1	4.9
Cr	2.2	0.5	0.09	5.9	7.1
O	8.9	12.3	12.8	1.4	0.05



Different behaviour during stratification

Concentration of U (and minor actinides) in liquid phases

Re-criticality

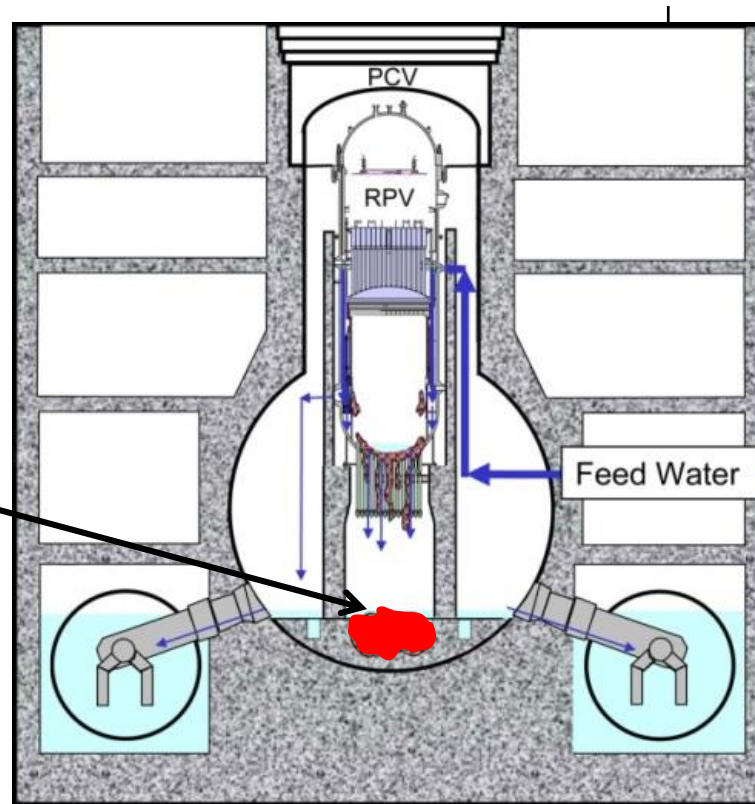


Ex-vessel scenario: Application to the interaction in-vessel corium/concrete

→ Reactor steel vessel failure

Fukushima Unit 1

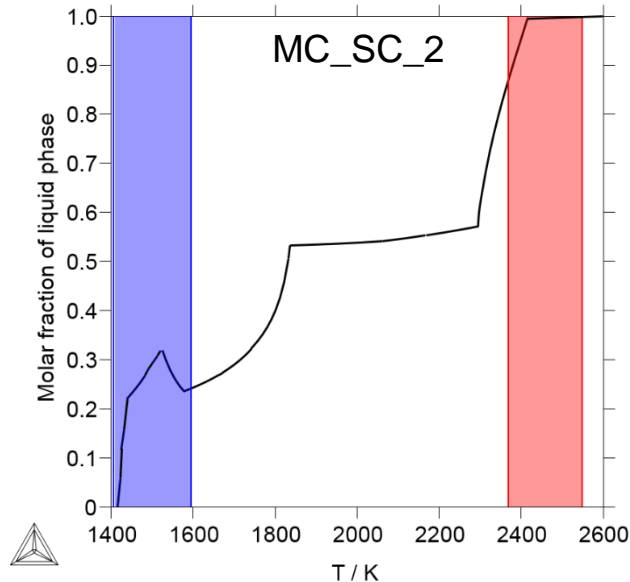
Corium/concrete interaction



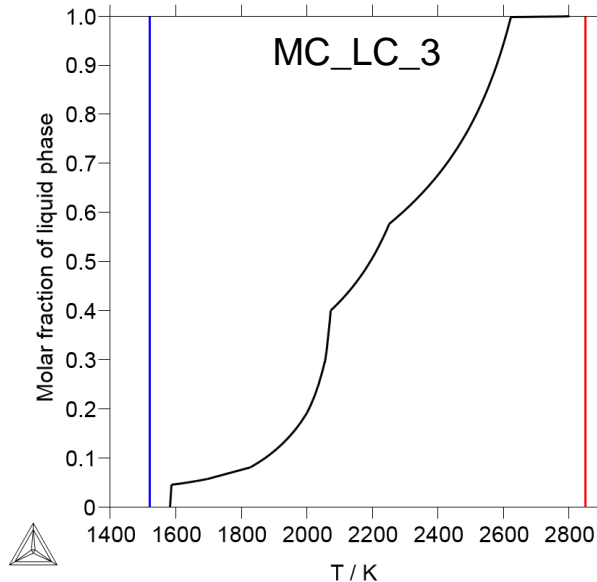
Ex-vessel scenario: Application to the interaction in-vessel corium/concrete

Calculations obtained by extrapolation from (28) binary, (56) ternary, 7 quaternary and 1 quinary descriptions

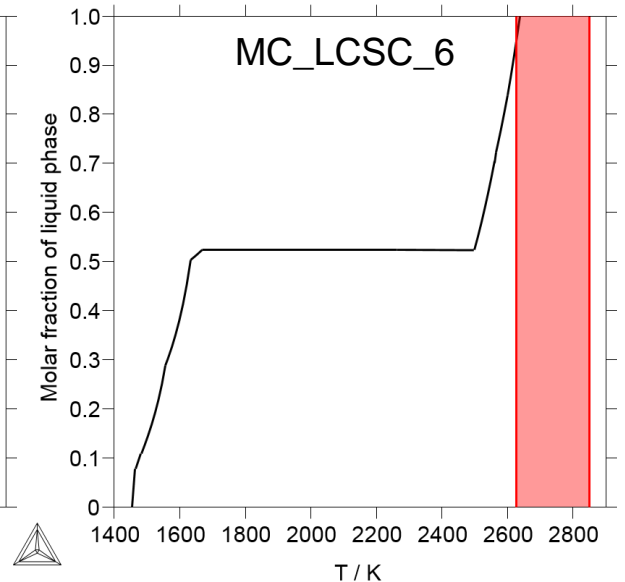
	Concrete type	Weight %							Solidus / K		Liquidus / K	
		UO ₂	ZrO ₂	CaO	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	Exp.	TAF-ID	Exp.	TAF-ID
MC_SC_2	Siliceous	56.5	16	4.1	21.5	1.4	0.275	0.275	1407-1595	1422	2369-2549	2418
MC_LC_3	Limestone	56.6	15.9	19.5	3.3	0.8	3.6	0.3	1520	1584	>2850	2801
MC_LCSC_6	Mix	56.6	16	10.4	11.3	1.4	3.9	0.5	1360	1456	2628-2850	2642



Last melting phase: C1_MO2



Last melting phase: CaUO₄



Last melting phase: C1_MO2

SIMFUELS: representative of irradiated fuel (but without radioactivity)

Sample composition (at%) / complement to UO_2

Ba	Ce	La	Mo	Sr	Y	Zr	Rh	Pd	Ru	Nd
0.26	0.61	0.20	0.51	0.13	0.06	0.60	0.03	0.42	0.64	0.91

PWR irradiated fuel: 76 GWd.t⁻¹

C1_MO2 (U,Nd,Ce,La, ϵ Zr)O₂

Perovskite (Ba,Sr)ZrO₃

Metallic precipitates (Mo,Ru,Pd,Rh)

Agreement with experimental observation on irradiated fuel

Heat treatment at 1973 K under flowing Ar+4% H₂ to reproduce the behavior of irradiated fuel during a severe accident

Mechanisms of degradation at an intermediate state of a severe accident

SIMFUELS: representative of irradiated fuel (but without radioactivity)

Sample composition (at%) / complement to UO ₂										
Ba	Ce	La	Mo	Sr	Y	Zr	Rh	Pd	Ru	Nd
0.26	0.61	0.20	0.51	0.13	0.06	0.60	0.03	0.42	0.64	0.91

Heat treatment

Ar + 4% H₂

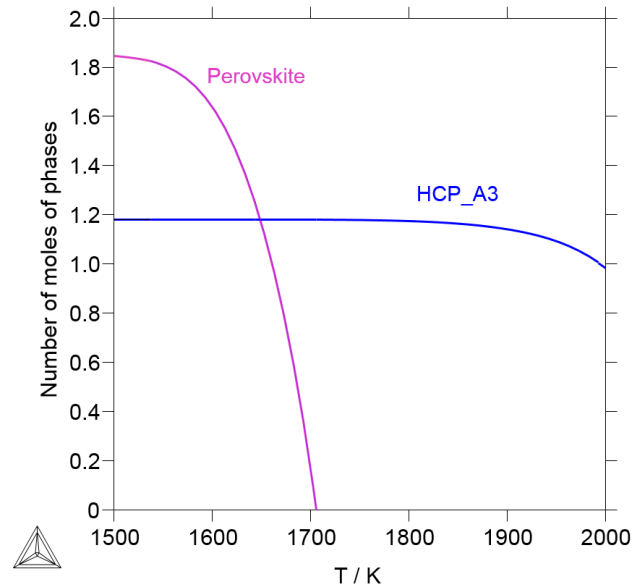
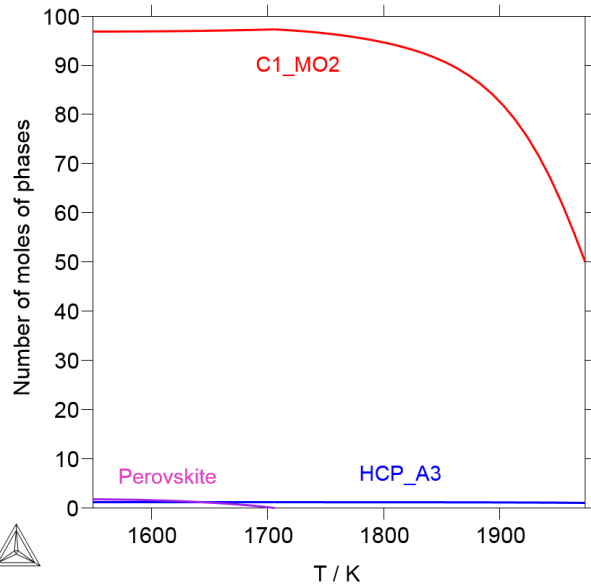
1973 K



Experimental observation

C1_MO2 (U,Nd,Ce,La,εZr)O₂
Perovskite (Ba,Sr)ZrO₃
Metallic precipitates (Mo,Ru,Pd,Rh)

C1_MO2 (U,Nd,Ce,La,εZr)O₂
Metallic precipitates



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Heat treatment

Ar + 4% H₂

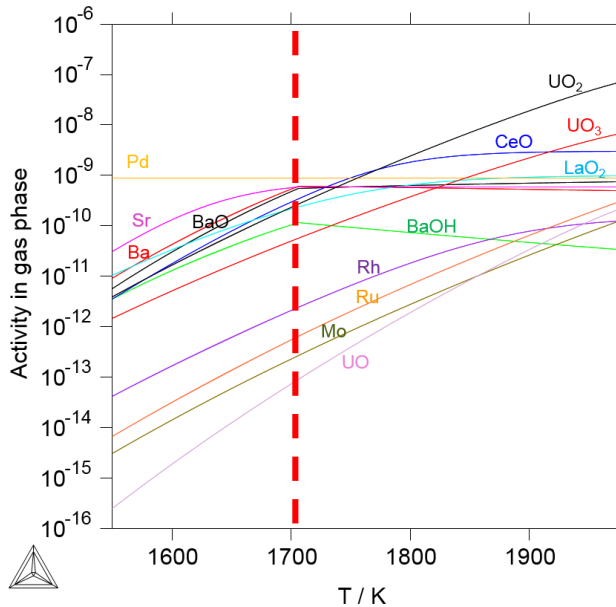
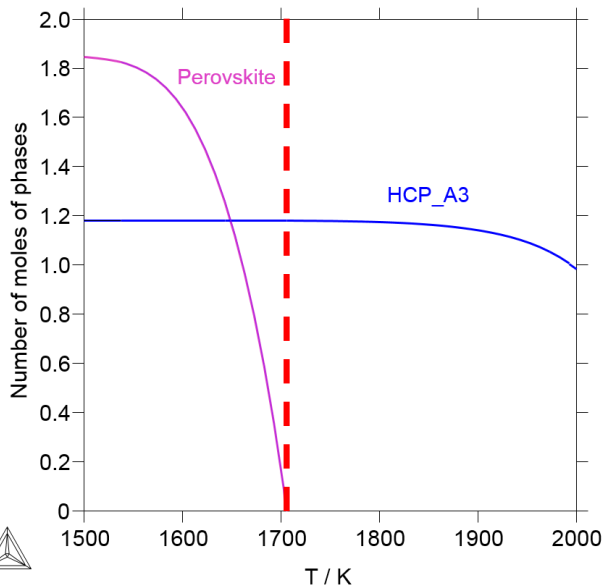
1973 K

Experimental observation

C1_MO2 (U,Nd,Ce,La,εZr)O₂
Perovskite (Ba,Sr)ZrO₃
Metallic precipitates (Mo,Ru,Pd,Rh)



C1_MO2 (U,Nd,Ce,La,εZr)O₂
Metallic precipitates



↓

Destruction of Perovskite
Ba and Sr relocate in the gas phase

- ➔ The current status of development of the TAF-ID database allows to perform thermodynamic calculations on complex multi-components compositions (oxides and metallic) containing fuel, cladding and structural materials.
 - ❑ **Severe accidents studies** : stratification behaviour, MCCI
 - ❑ **FPs are also described** in the database allowing calculations on SIMFUELS compositions → irradiated fuel
 - ❑ **Application to Gen IV related systems**: on going

- ➔ The **Phase 2** of the OECD-NEA TAF-ID project is foreseen to start in 2018. In this frame, the database will be further extended and a new task of the project will be dedicated to the validation of this tool.
 - ❑ **Coupling with other codes**:
 - ➔ DICTRA (diffusion)
 - ➔ Fuel performance codes
 - ➔ Multi-physics
 - ➔ Severe accident codes (thermal-hydraulics)
 - ❑ **Application calculations**: JOG, Gen IV, ...

Thanks for your attention

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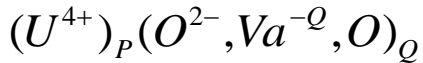
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Liquid phase

Two ionic sublattice model

Adapted to describe both metallic and oxide liquids



$$G_m^{Liq} = {}^{ref}G_m^{Liq} + {}^{ideal}G_m^{Liq} + {}^{excess}G_m^{Liq}$$

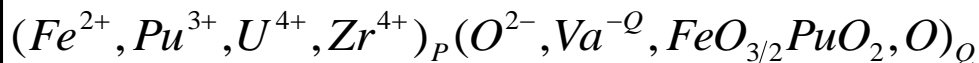
$${}^{ref}G_m^{Liq} = y_{U^{4+}} y_{Va} G_{(U^{4+})_1(Va)_4}^0 + y_{U^{4+}} y_{O^{2-}} G_{(U^{4+})_2(O^{2-})_4}^0 + y_{U^{4+}} y_O G_O^0$$

$${}^{ideal}G_m^{Liq} = QRT(y_{O^{2-}} \ln y_{O^{2-}} + y_{Va} \ln y_{Va} + y_O \ln y_O)$$

$${}^{excess}G_m^{Liq}$$

In-vessel corium liquid

Endmembers



Interaction parameters

