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DE LA RECHERCHE A L'INDUSTRIE

cea den

# Influence of plutonium on the thermodynamic properties and phase equilibria in corium

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**Context and aim**

**Calphad method**

**Experimental results on the  $\text{UO}_2$ - $\text{PuO}_2$ - $\text{ZrO}_2$  ternary system**

**Thermodynamic calculations on corium containing MOX fuel, comparison with corium containing  $\text{UO}_2$  fuel**

- **Phase distribution in the solidified corium**
- **Distribution of Pu in the liquid phases**
- **Distribution of Pu in the solid phases**

**Conclusions & Perspectives**

Out of nominal functioning may lead to a nuclear accident



**Severe accident (SA):** the normal functioning of the nuclear power plant is not re-established

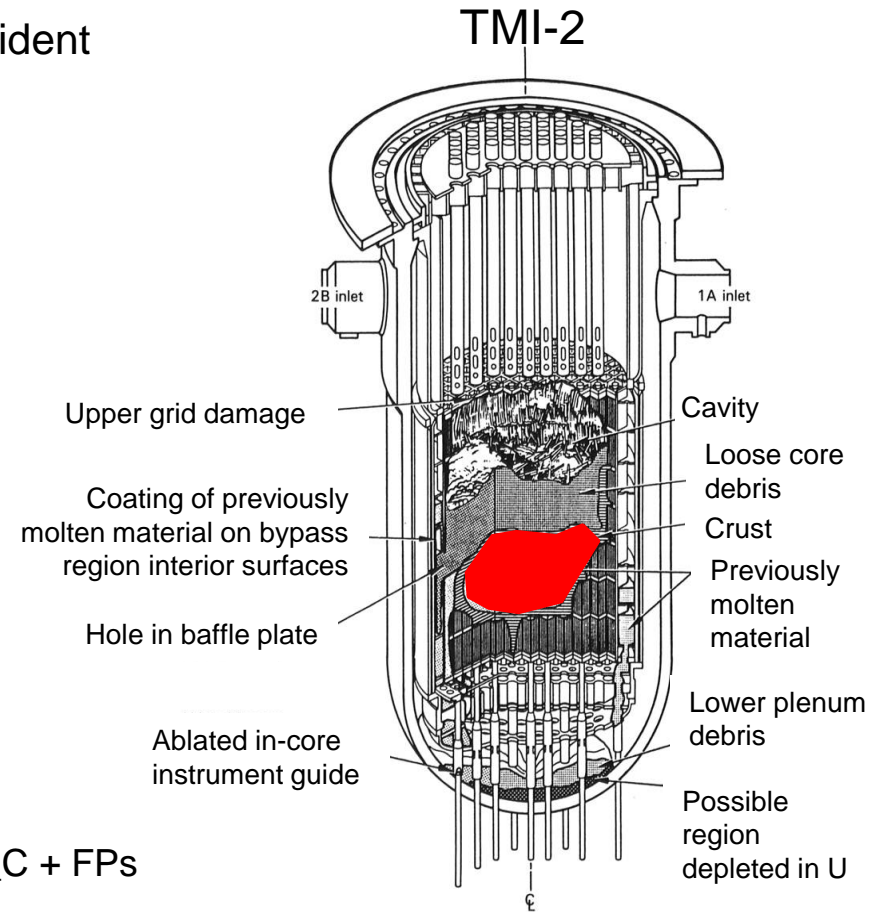


Fusion of the core and internal structure

→ Interactions MOx + Zircaloy + stainless steel + Inconel + B<sub>4</sub>C + FPs

(U,Pu)-Zr-O-Fe-Cr-Ni-Ag-Cd-In-B-C-FPs → In vessel corium

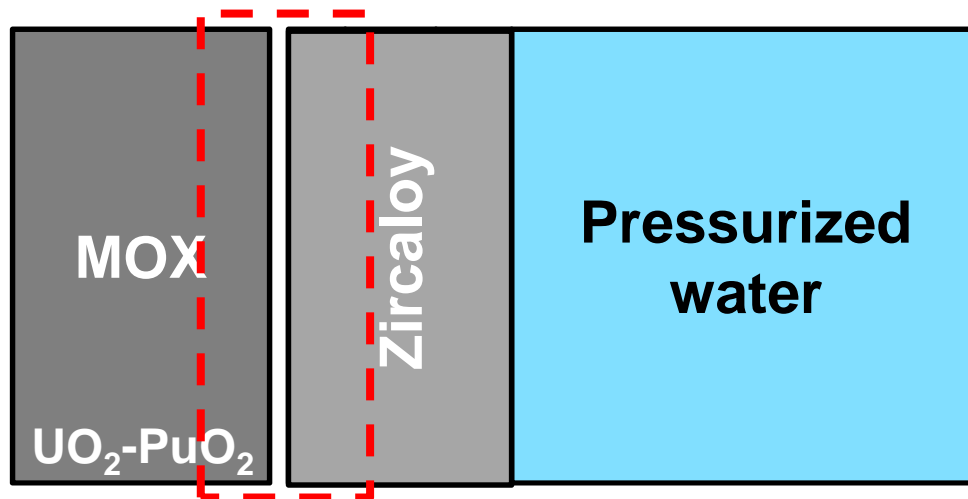
→ **U-Pu-Zr-Fe-O** system is selected as the “prototypic” in-vessel corium



PWR cross section

During **normal functioning** of a PWR → ZrO<sub>2</sub> forms at the inner and at the outer surface of the Zircaloy cladding

**Accidental scenario: MO<sub>x</sub> fuel + oxidized cladding** will interact with the metallic structures and the reactor vessel



MO<sub>x</sub> fuels → **What is the effect of PuO<sub>2</sub>?**  
**Melting behaviour of the U-Pu-Zr-O system**

- **UO<sub>2</sub> - PuO<sub>2</sub> - ZrO<sub>2</sub>**
- Experimental data are very rare
  - Development of the TAF-ID NEA-OECD database

Experimental data on Pu-containing systems → Thermodynamics of the U-Pu-Zr-Fe-O prototypic in-vessel corium

Key point: miscibility gap in the in-vessel corium system liquid phase

$\rho$  = density

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



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

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

Decrease of the thickness of the upper metallic layer

- Enhanced focusing effect due to high radiative fluxes
- Failure of the reactor vessel

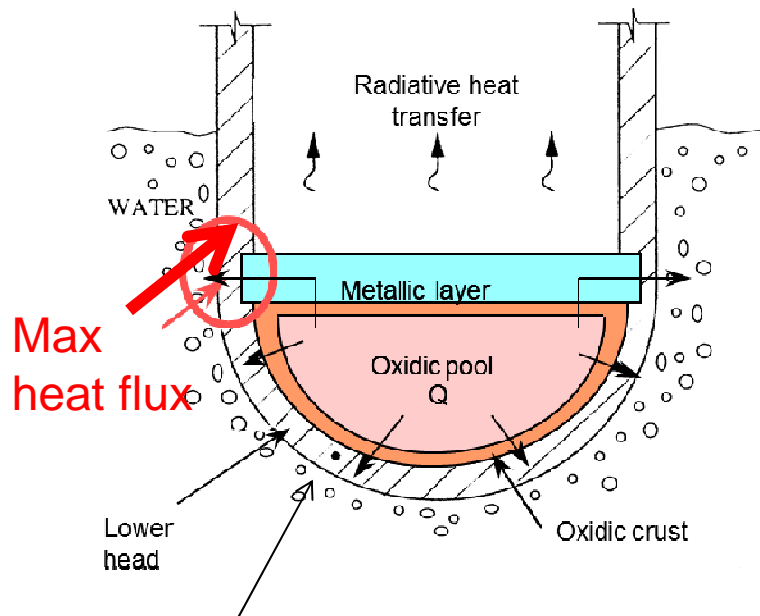


New experimental results are needed in the miscibility gap (U-Zr-O, U-Zr-O-Fe)

Knowledge of the chemical composition of liquids  
 $T_{\text{solidus}}$  and  $T_{\text{liquidus}}$  are paramount for density calculations  
Risk of recriticality by local concentration of fissile material

Thermodynamic calculations are needed to evaluate phases compositions and distribution in severe accident codes

Heavy metal layer below the oxidic pool (Input data for kinetic calculation of the stratification)



# **DEVELOPMENT OF THERMODYNAMIC DATABASES**

## **THE CALPHAD METHOD**

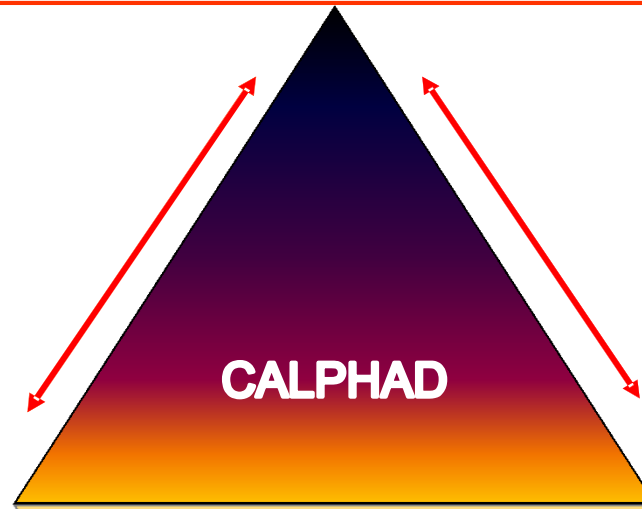
**Minimisation of the Gibbs energy of the system**

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

n=number of mole of phase  $\alpha$   
 x=molar fraction of i in  $\alpha$   
 y=site fraction

**Critical analysis of experimental data**

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



Synergic approach

Experiments  $\longleftrightarrow$  Calculations

**Experimental data acquisition**

Thermodynamic data  $\Rightarrow$  Calorimetry, D.S.C.  
 Phase diagrams  $\Rightarrow$  Heat treatments, D.T.A.

**Thermodynamic modelling**

*Optimization*  
 (Module **PARROT** of Thermo-Calc)

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

*Minimization of G(system)*  
 (Thermo-Calc)

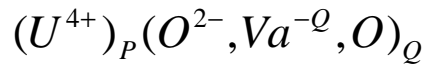
Thermodynamic properties  
 Phase diagrams  
 Application calculations



Liquid phase

Two ionic sublattice model

Adapted to describe both metallic and oxide liquids



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

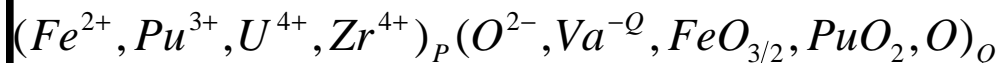
$${}^{ref}G_m^{Liq} = y_{U^{4+}} y_{Va} G_{(U^{4+})_1(Va)_4}^0 + y_{U^{4+}} y_{O^{2-}} G_{(U^{4+})_2(O^{2-})_4}^0 + y_{U^{4+}} y_O G_O^0$$

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

$${}^{excess}G_m$$

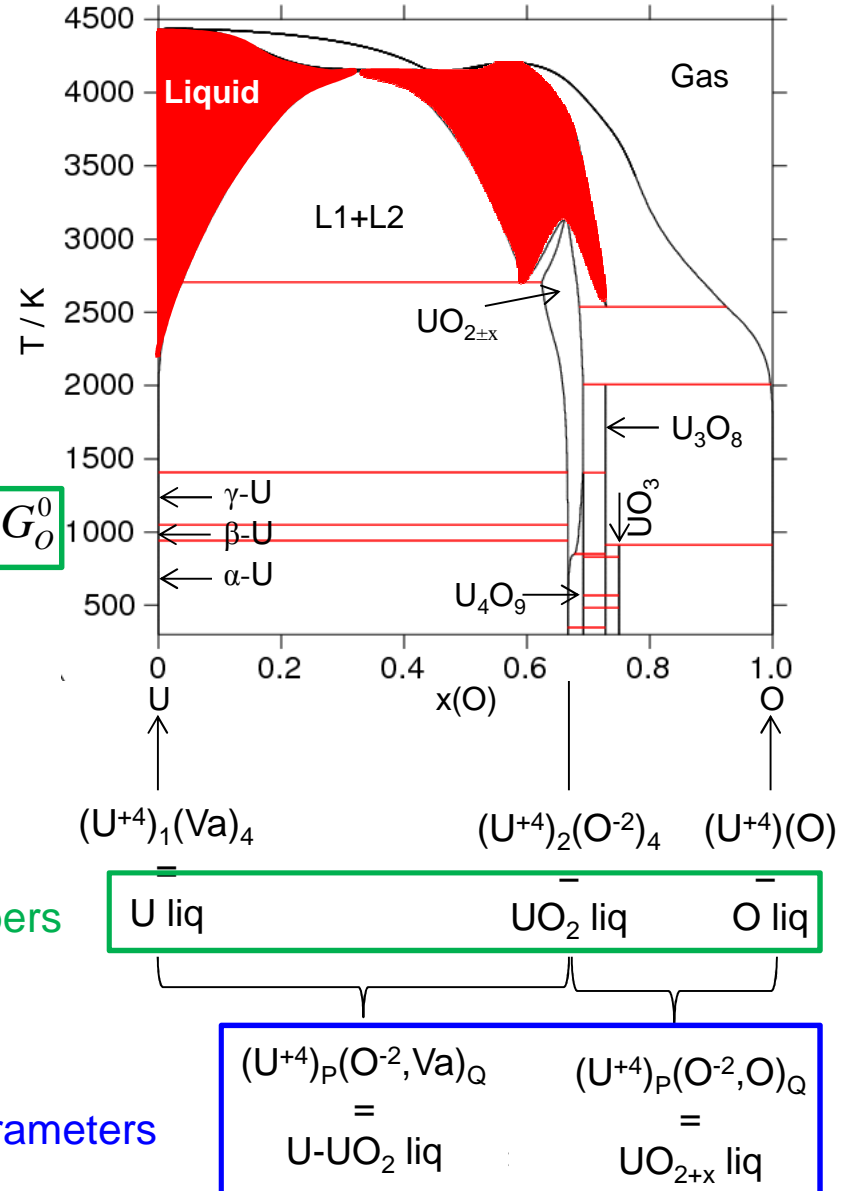
In-vessel liquid core melt

Endmembers



Interaction parameters

[Guéneau et al., JNM 419 (2011) 145]



**EXPERIMENTAL WORK**

**THE  $\text{UO}_2$ - $\text{PuO}_2$ - $\text{ZrO}_2$  SYSTEM**

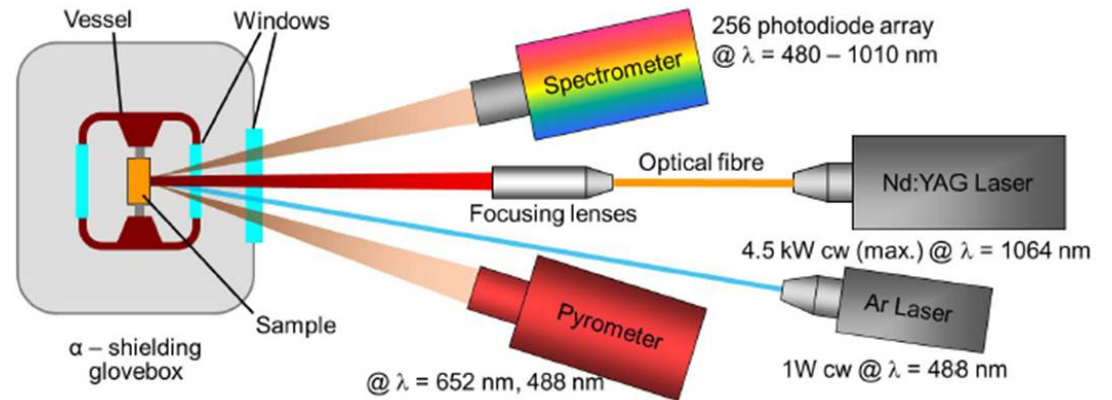
# cea den UO<sub>2</sub>-PuO<sub>2</sub>-ZrO<sub>2</sub> – LASER HEATING SETUP

Measurements of transition temperatures ( $T_{liquidus}$ ,  $T_{solidus}$ ,  $T_{eutectic}$ )

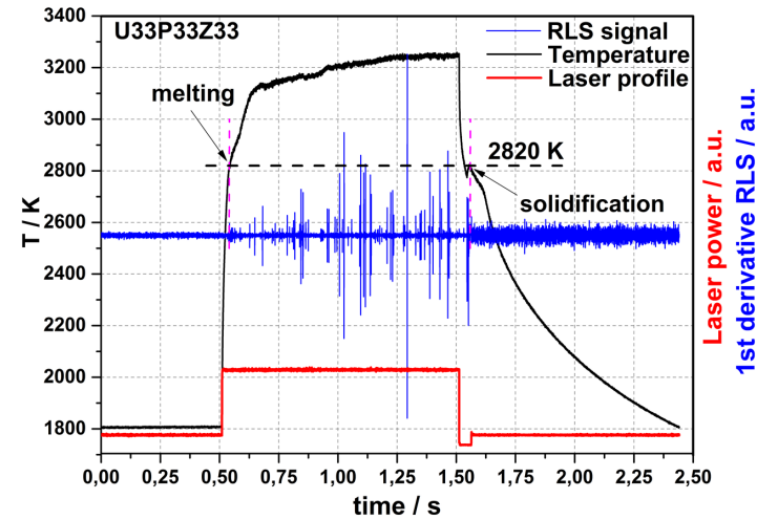
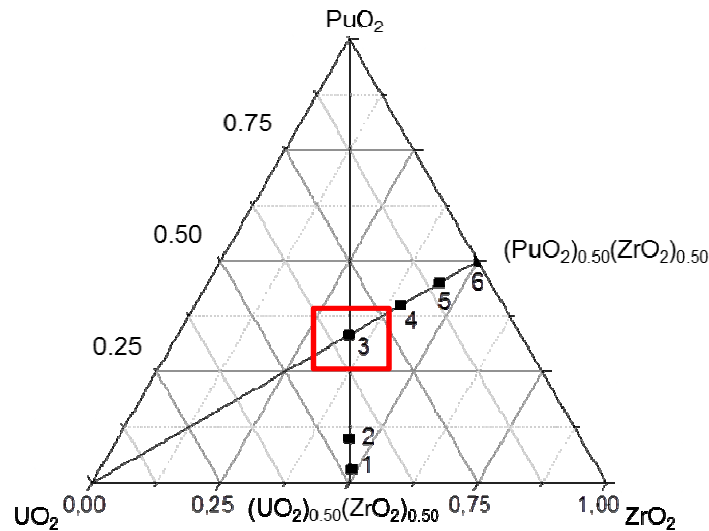
ITU's Laser heating setup  
Manara et al., *Rev. Sci. Instrum.* 2008

Laser heating setup at ITU Karlsruhe

- Rapid measurements
- High power & High temperature
- Containerless
- Control of Red/Ox atmosphere
- Actinide containing systems

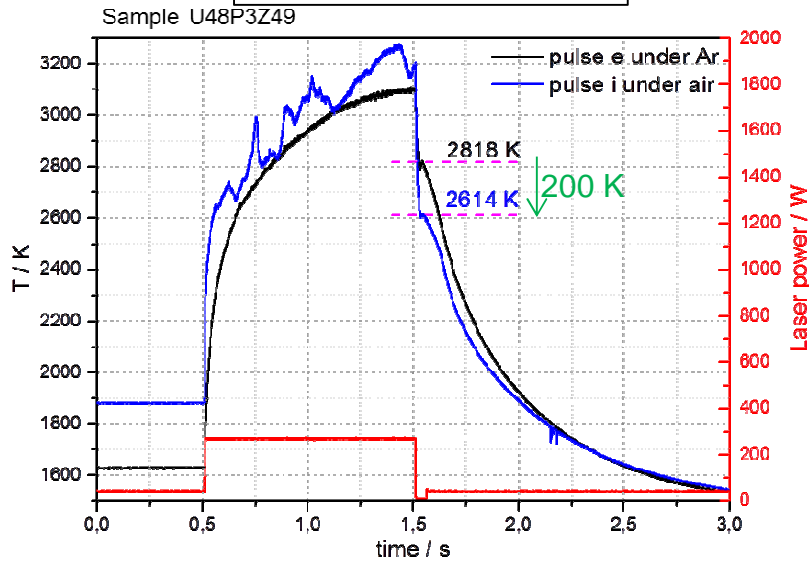


**But oxygen potential is not controllable**

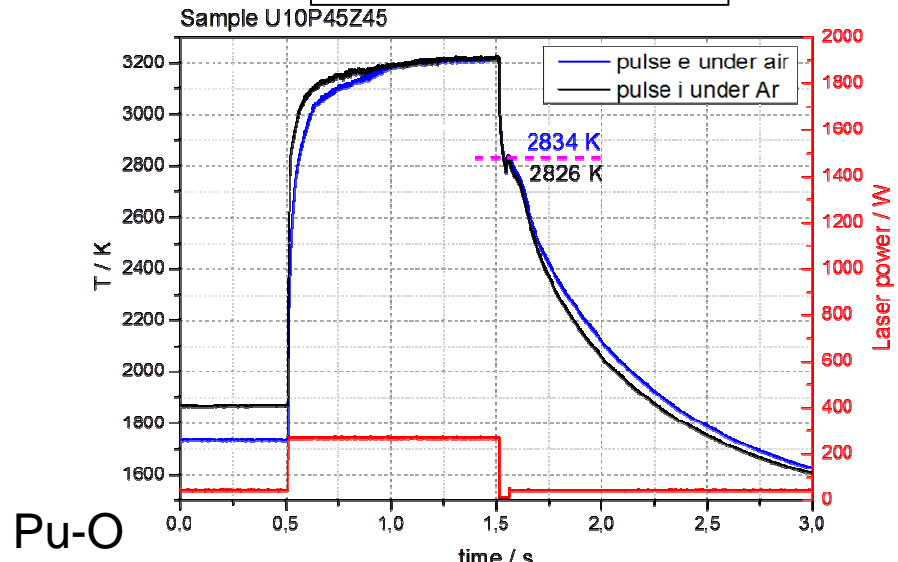


# cea den UO<sub>2</sub>-PuO<sub>2</sub>-ZrO<sub>2</sub> – EXPERIMENTAL RESULTS

UO<sub>2</sub>-rich sample



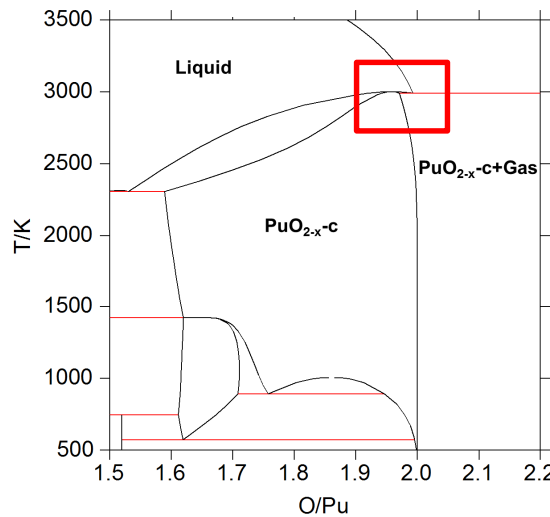
PuO<sub>2</sub>-rich sample



$T_{air} < T_{Ar}$   
large spread under air

Composition of the molten pool  
moved towards O/M > 2

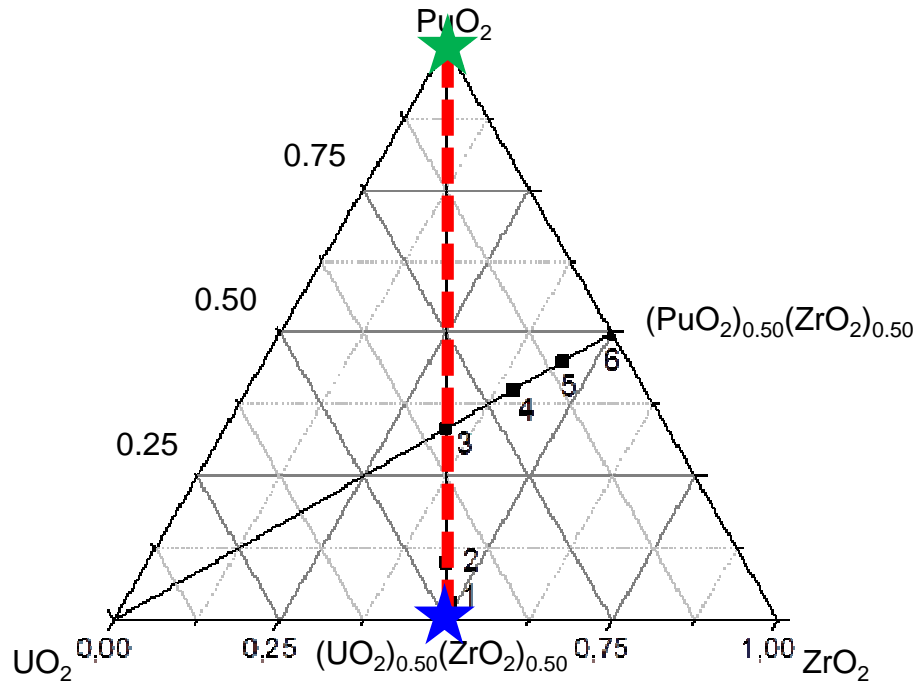
Experimental atmosphere  
has a significant influence



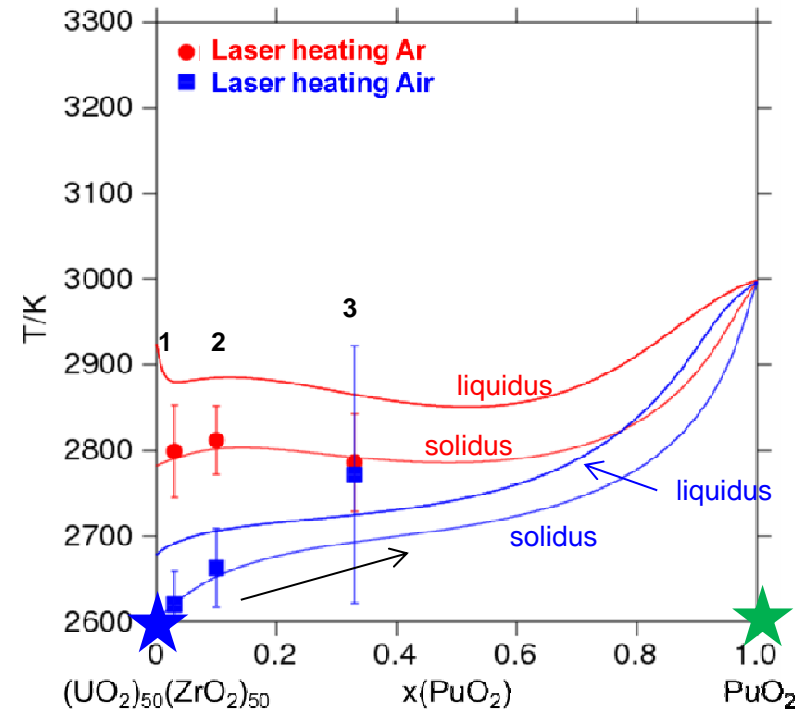
$T_{air} \approx T_{Ar}$

Experimental atmosphere  
has a weaker effect

Calculations by extrapolation from the quaternary U-Pu-Zr-O system



Solidus and liquidus temperatures



Oxidising and Reducing conditions → Excellent agreement with samples 1 and 2

Oxidising conditions →  $T_{\text{solidus}} \uparrow$  adding PuO<sub>2</sub>

From PhD thesis of Andrea Quaini, Université de Grenoble, France 2015  
(J. Nuc. Mater. 467 (2015) 660-676)

**PWR SEVERE ACCIDENT**

**APPLICATION CALCULATIONS**

**INTERACTION  $\text{MO}_x + \text{Zr(O)} + \text{Fe,Cr,Ni}$   
(30% oxidized Zr)**

All the thermodynamic calculations were performed using the estimated composition of a PWR corium. The prototypic composition is a representative mixture of UO<sub>2</sub> + Zr + ZrO<sub>2</sub> + Fe in-vessel core melt.

See:

W. Steinwarz and M. Sappok,

*Large-scale experiments on ex-vessel core melt behavior*

Nucl. Technol. 125 (1999) 363–370

In the present thermodynamic calculations:

- UO<sub>2</sub> fuel has been replaced by (U<sub>0.9</sub>,Pu<sub>0.1</sub>)O<sub>2</sub> MOx Fuel
- The oxidation rate of Zr has been slightly increased (30% vs. 20%)
- Fe has been replaced by a simplified Fe<sub>0.71</sub>Cr<sub>0.18</sub>Ni<sub>0.11</sub> Stainless Steel

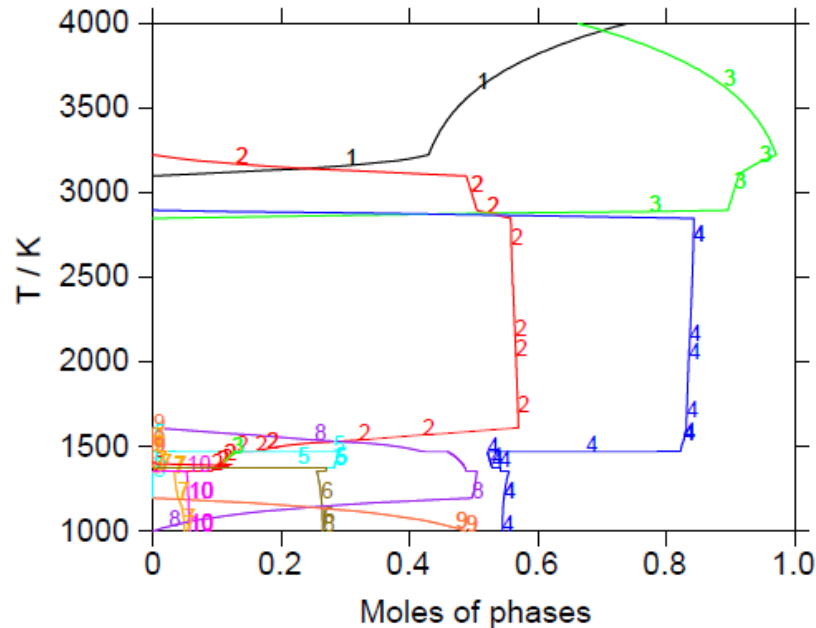
Conditions for the calculations (in grams):

Fuel + cladding: m(PuO<sub>2</sub>)=5.25, m(UO<sub>2</sub>)=47.25, m(Zr)=15.988, m(ZrO<sub>2</sub>)=9.2595

Stainless steel: m(Fe)=16.401 m(Ni)=2.541 m(Cr)=4.158

# UO<sub>2</sub> vs. U<sub>0.9</sub>Pu<sub>0.1</sub>O<sub>2</sub> + Zr + Fe,Cr,Ni Stainless Steel (30% oxidized Zr)

Calculations of solidification paths for PWR severe accidental compositions  
Comparison of molten core and corium compositions for UO<sub>2</sub> and (U<sub>0.9</sub>Pu<sub>0.1</sub>)O<sub>2</sub> fuels



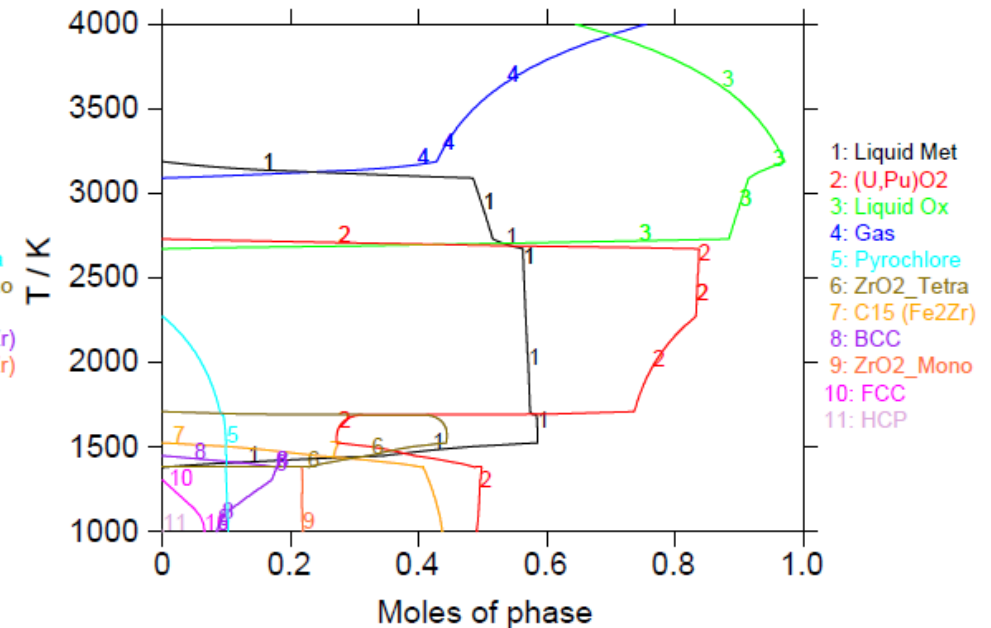
## UO<sub>2</sub> + Zr(O) + Fe,Cr,Ni Stainless Steel

Formation of oxidized liquid: T=2850 K

Formation of metallic liquid: T=1354 K

Major low T condensed phases:

- Metallic δ-Ni<sub>77</sub>U<sub>23</sub>, C14-(Fe,Cr)<sub>2</sub>Zr, BCC (Cr,Fe)
- Oxide ZrO<sub>2</sub>-Mono, UO<sub>2</sub>



## (U<sub>0.9</sub>Pu<sub>0.1</sub>)O<sub>2</sub> + Zr(O) + Fe,Cr,Ni Stainless Steel

Formation of oxidized liquid: T=2673 K

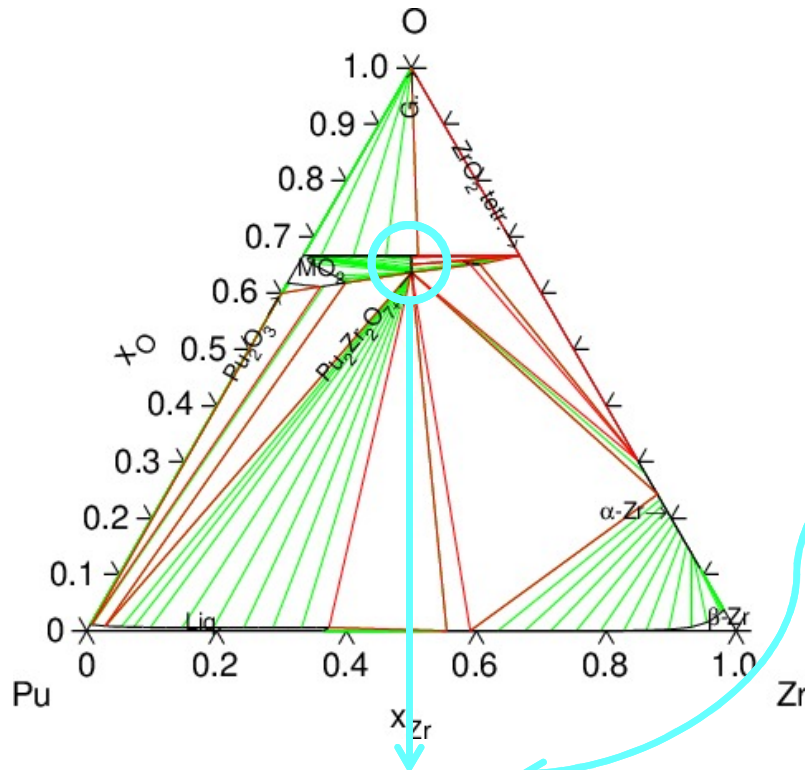
Formation of metallic liquid: T=1381 K

Major low T condensed phases:

- Metallic C15-Fe<sub>2</sub>Zr, BCC (Cr,Ni), FCC (Ni,Fe)
- Oxide ZrO<sub>2</sub>-Mono, (U,Pu)O<sub>2</sub>, Pu<sub>2</sub>Zr<sub>2</sub>O<sub>7+x</sub>

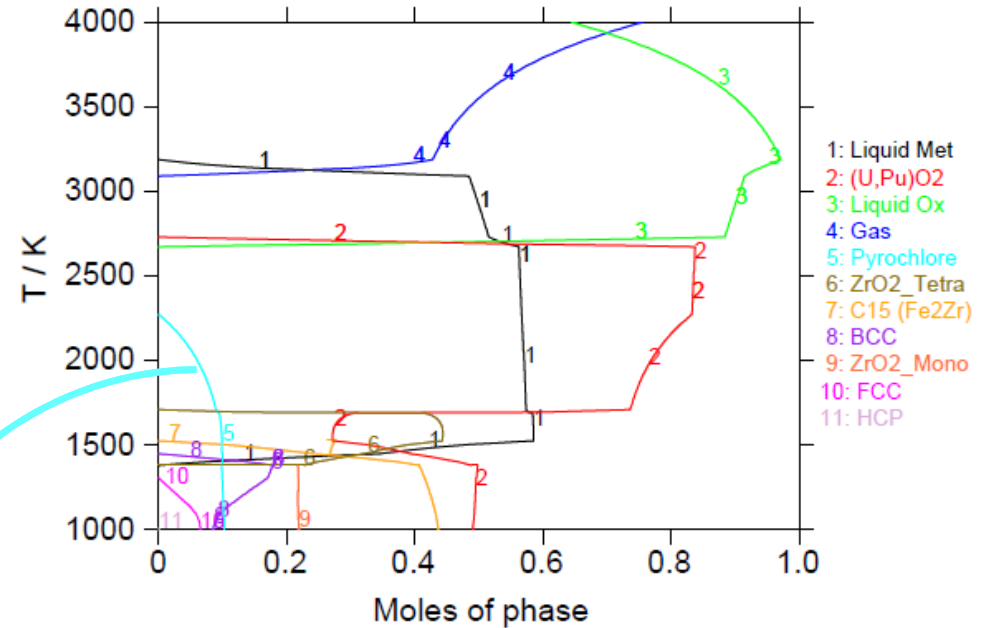


Pu-Zr-O system at 1500 K  
(Ref: M. Kurata, JAEA, Japan in TAFID database)



Calculation of a Pyrochlore phase: Pu<sub>2</sub>Zr<sub>2</sub>O<sub>7+x</sub>

From the calculated solidification path:



In the case of (U<sub>0.9</sub>Pu<sub>0.1</sub>)O<sub>2</sub> MOx fuel:

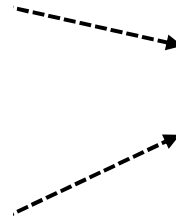
Almost no Pu in the metallic phases  
The exact composition of fuel at 1273 K is:



**The MOx fuel composition is depleted in Pu due to the formation of Pu<sub>2</sub>Zr<sub>2</sub>O<sub>7+x</sub>**

The Pyrochlore phase (Pu<sub>2</sub>Zr<sub>2</sub>O<sub>7+x</sub>) does not exist in U-Zr-O. Under accidental conditions, the high temperature **solid phases** formed by MOx vs. UO<sub>2</sub> fuels will mainly differ due to the formation of this ternary oxide phase.

**What about the liquid phases ?**



**Two liquids (Metal + Oxide) coexist in the temperature range 2673 K < T < 3188 K**

**What is the U,Pu,Zr composition of these liquids as a function of temperature?**

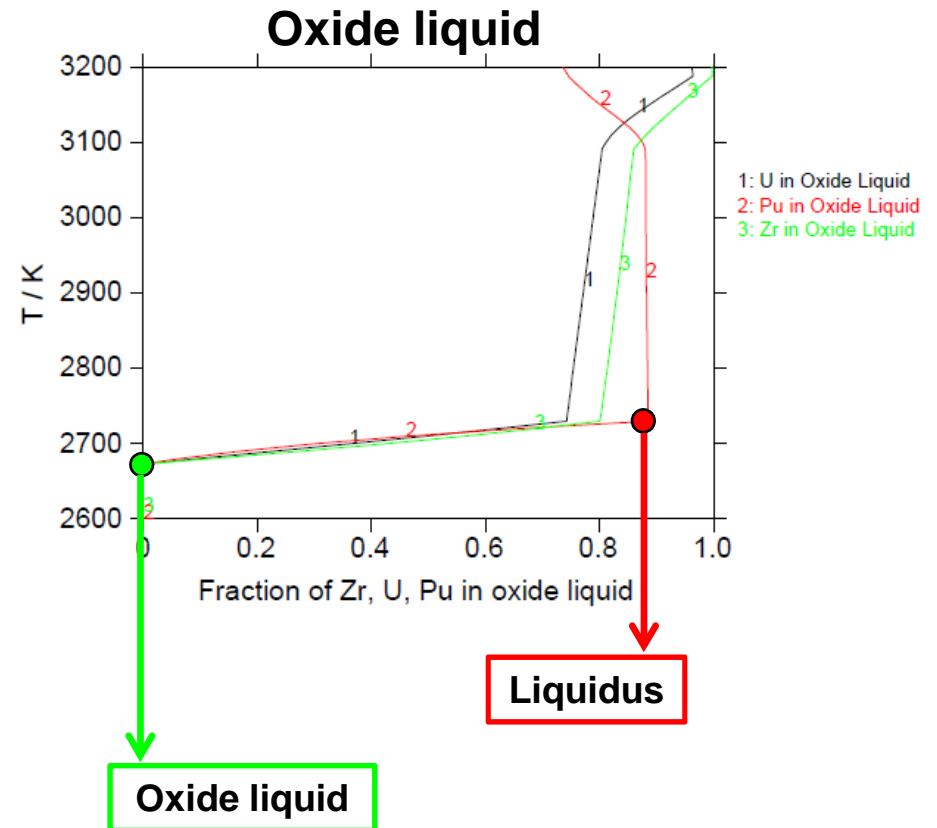
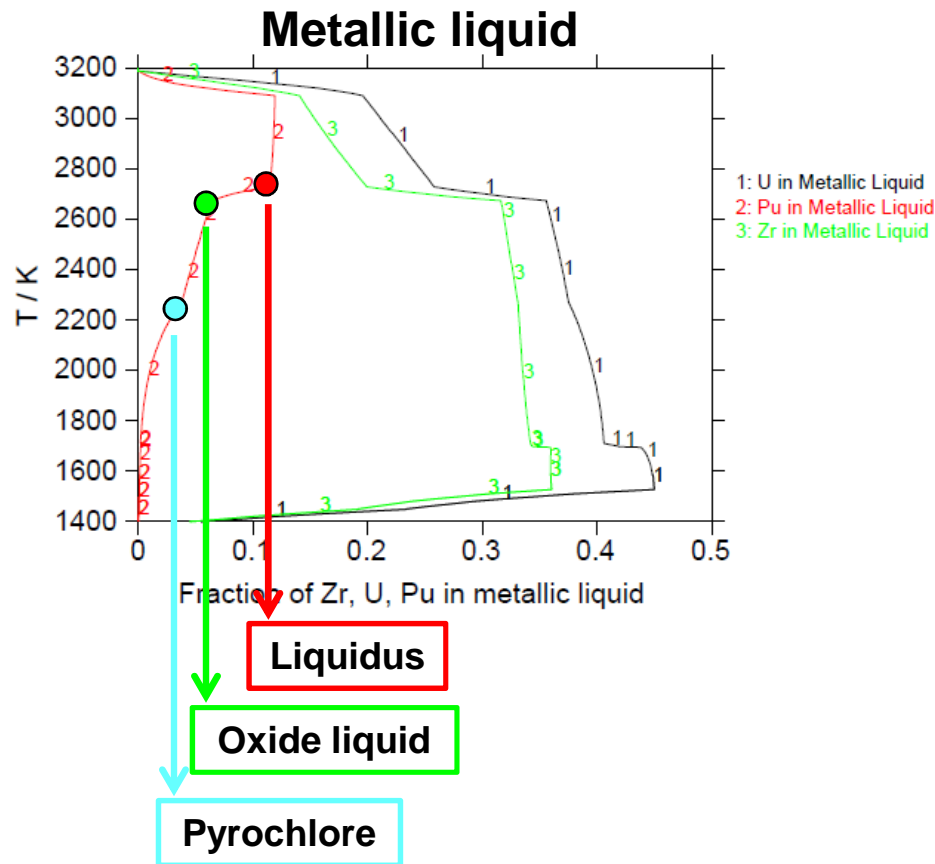
# UPuO<sub>2</sub> + Zr + Fe,Cr,Ni Stainless Steel (30% oxidized Zr) – Pu distribution in liquids

## Distribution of the overall Zr, U, Pu in metallic and oxide liquids

Where  $n$  is a number of mole and  $x$  is a molar fraction in the phase

$$\frac{(x_{Zr,U,Pu}^{Liquid\ met} \times n^{Liquid\ met})}{n_{Zr,U,Pu}}$$

$$\frac{(x_{Zr,U,Pu}^{Liquid\ ox} \times n^{Liquid\ ox})}{n_{Zr,U,Pu}}$$

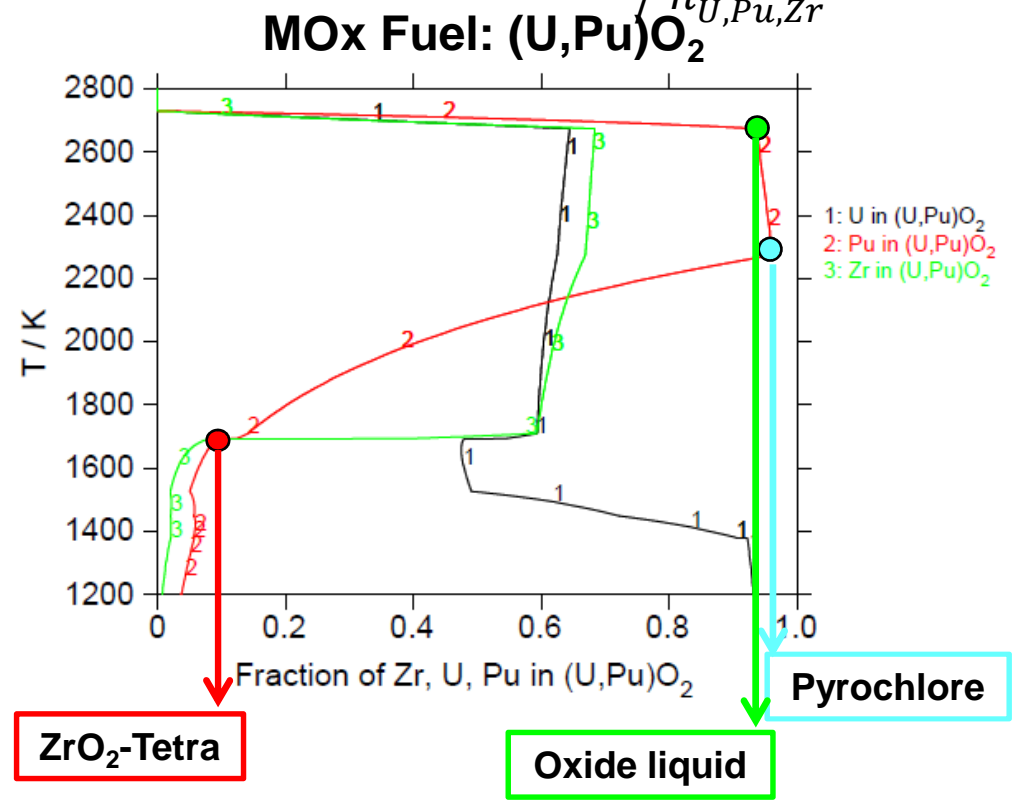
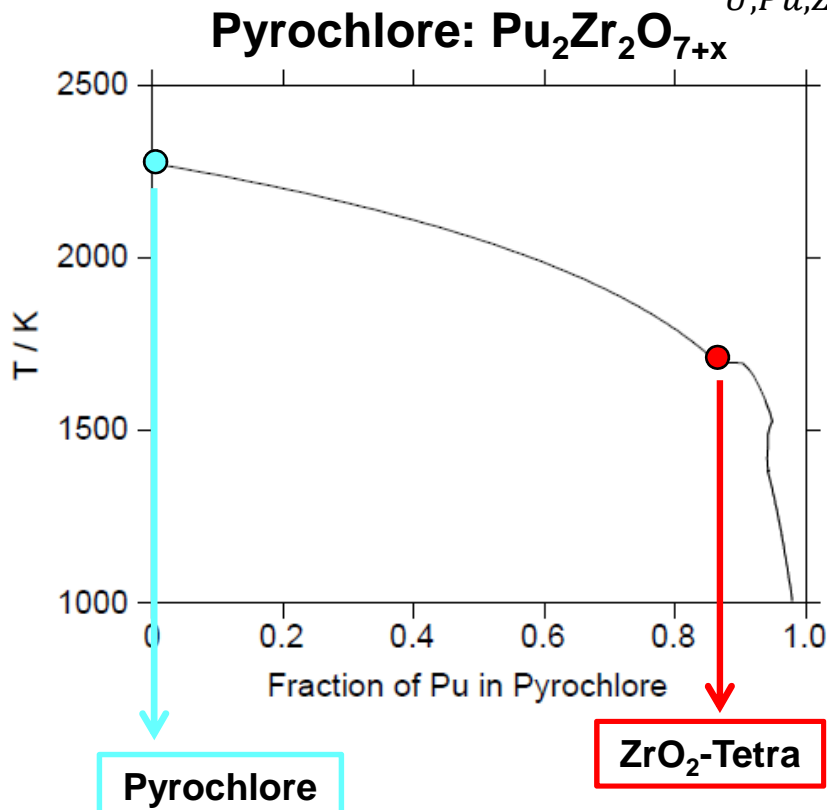


# UPuO<sub>2</sub> + Zr + Fe,Cr,Ni Stainless Steel (30% oxidized Zr) – Pu distribution in solids

Distribution of the solid Pu in Pyrochlore: Pu<sub>2</sub>Zr<sub>2</sub>O<sub>7+x</sub> and in MOx Fuel: (U,Pu)O<sub>2</sub>  
Where *n* is a number of mole and *x* is a molar fraction in the phase

$$\frac{(x_{U,Pu,Zr}^{Pyrochlore} \times n^{Pyrochlore})}{n_{U,Pu,Zr}}$$

$$\frac{(x_{U,Pu,Zr}^{(U,Pu)O_2} \times n^{(U,Pu)O_2})}{n_{U,Pu,Zr}}$$



**Relocation of Pu from (U,Pu)O<sub>2</sub> into Pu<sub>2</sub>Zr<sub>2</sub>O<sub>7+x</sub> during the severe accidental events**

Motivation: Need of exp. data on Pu-containing systems for MOx/oxidised cladding interactions

## PuO<sub>2</sub>-ZrO<sub>2</sub> system

### Experimental

Melting behaviour of the UO<sub>2</sub>-PuO<sub>2</sub>-ZrO<sub>2</sub> system

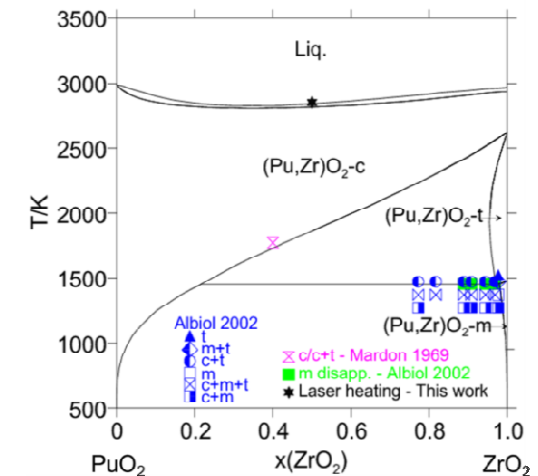
### Calculations

Thermodynamic assessment of the PuO<sub>2</sub>-ZrO<sub>2</sub> phase diagram

## UO<sub>2</sub>-PuO<sub>2</sub>-ZrO<sub>2</sub> system

### Experimental

**First systematic investigation** of the influence of the atmosphere on the high temperature behavior of the UO<sub>2</sub>-PuO<sub>2</sub>-ZrO<sub>2</sub> system



Main observations:

- Oxygen potential drives the high temperature behaviour of (Pu,U,Zr)O<sub>2+x</sub> phase
- Oxidising atmosphere →  $T_{\text{solidus}} \uparrow$  adding PuO<sub>2</sub>; no sensitive effect under reducing conditions



**Contribution to the understanding of the high temperature thermodynamics in U-Pu-Zr-O**

## UO<sub>2</sub> and (U,Pu)O<sub>2</sub> MOx fuel behavior under accidental behavior

Development of a thermodynamic database dedicated to the in-vessel corium of PWR  
(also ex-vessel corium/concrete interactions in PhD thesis of A. Quaini, Université de Grenoble, France 2015)

From the application calculations:

Different behavior of U and Pu in the corium containing UO<sub>2</sub> or MOx (U<sub>0.9</sub>,Pu<sub>0.1</sub>)O<sub>2</sub>

- U forms both metallic and oxide phases
- Segregation of Pu in the oxide phases (see table): Oxide liquid, (U,Pu)O<sub>2</sub>, Pyrochlore

	(U,Pu)O <sub>2</sub>	Oxide liq	Metallic liq	Pyrochlore	Gas
Pu @ 1500 K	5.58%	---	ε	94.36%	---
Pu @ 2500 K	94.79%	---	5.21%	---	---
Pu @ 3000 K	---	88.10%	11.90%	---	---
Pu @ 3500 K	---	---	45.30%	---	54.70%

### Questions:

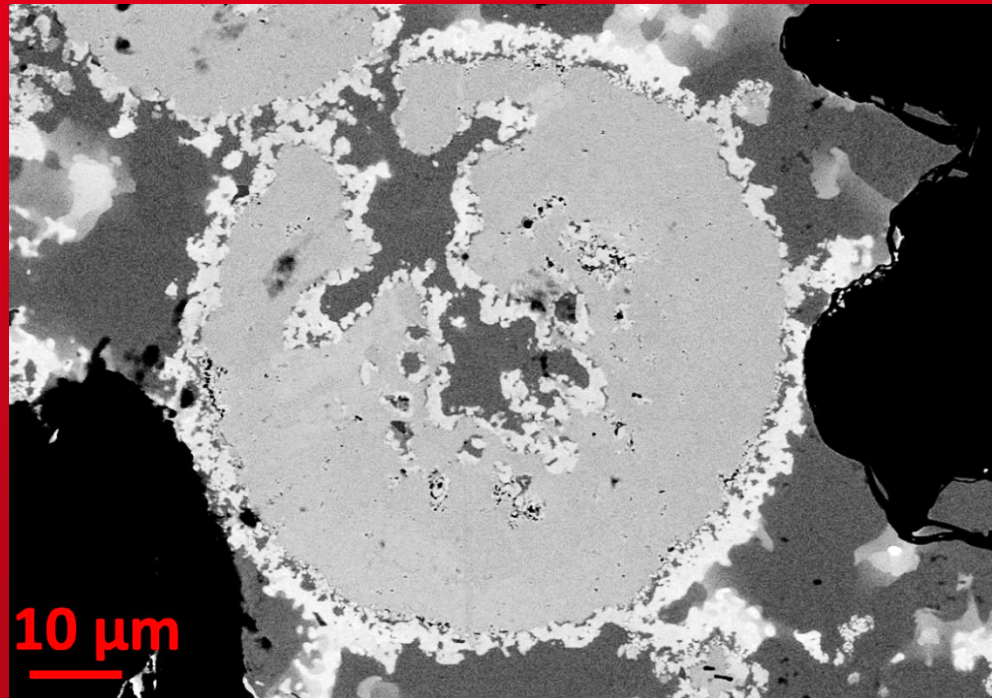
Is there any risk of recriticality due to the compaction of the core and Pu relocation?

What about the high rate of evaporation of Pu (Pu<sub>(g)</sub>, PuO<sub>(g)</sub>) above 3200 K ?

### Perspectives:

Performing high temperature heat treatments on Pu containing prototypic corium to check the reliability of these calculations

# THANK YOU FOR YOUR ATTENTION



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Thermodynamique et Thermochimie  
CEA de Saclay

# UO<sub>2</sub>-PuO<sub>2</sub>-ZrO<sub>2</sub> – CALCULATIONS

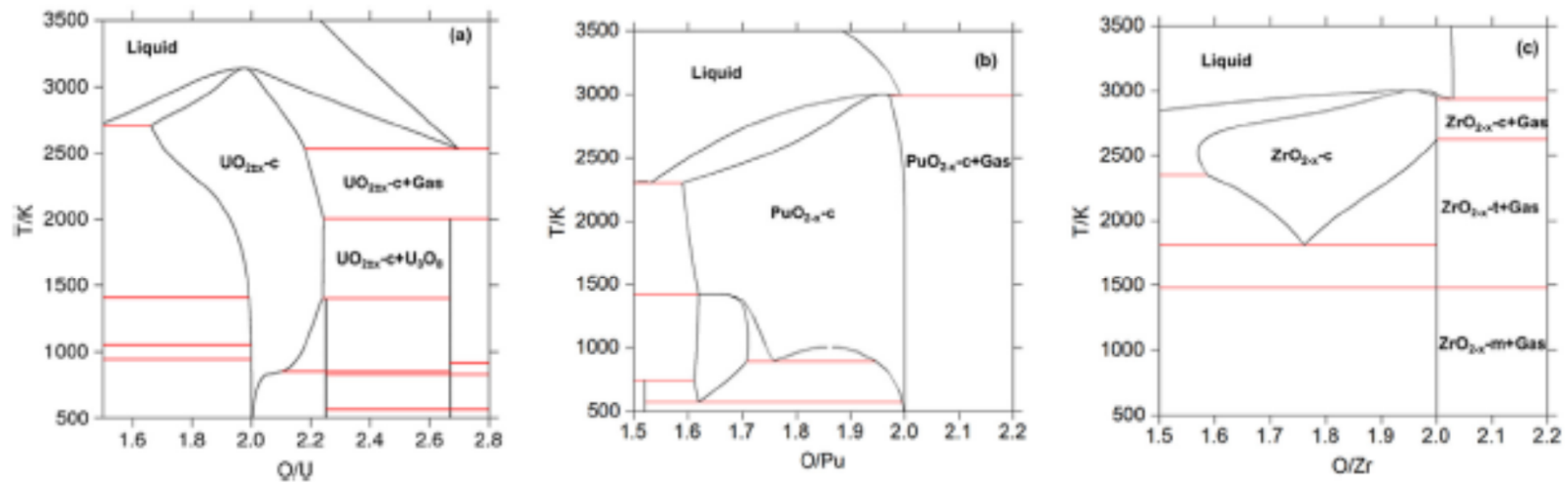
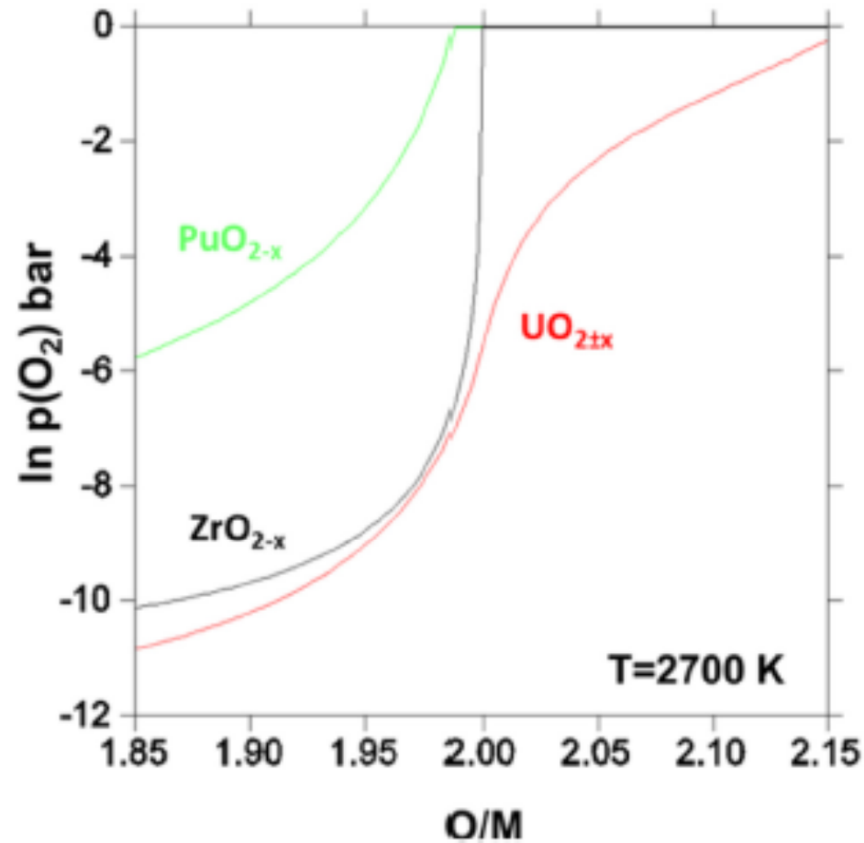


Fig 5. Calculated phase diagrams of: (a) U–O system [7]; (b) Pu–O system [7]; (c) Zr–O system (this work). The reported diagrams are a magnification of the high oxygen content regions of the respective systems.





**Fig 6.** Calculated oxygen partial pressure in the cubic UO<sub>2+x</sub> (red line), ZrO<sub>2-x</sub> (black line) and PuO<sub>2-x</sub> (green line) oxide phases at  $T = 2700 \text{ K}$  and  $p = 0.1 \text{ MPa}$ . As for PuO<sub>2</sub> and ZrO<sub>2</sub> beyond  $\text{O/M} = 2$ , it must be pointed out that the solid + gas equilibrium imposes a constant oxygen potential equal to zero, that is an oxygen partial pressure equal to  $0.1 \text{ MPa}$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

## ■ AIM

- To develop a **thermodynamic database** as a **computational tool** to perform thermodynamic calculations on advanced fuel materials using the Calphad method
  - ➔ **Phase diagrams + Thermodynamic properties of the phases**
- To facilitate the **exchange** on the models, review of experimental data, softwares, assessments
  - ....

## ■ CONTEXT ➔ Fuel materials for Generation 2,3 & 4 reactors

### ■ Fuels

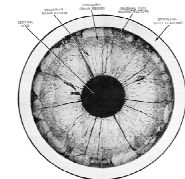
- $UO_2$ ,  $(U,Pu,Am,Np)O_2$ ,  $(U,Th)O_2$ ,  $(U,Pu,Zr,Am,Np)$ , UN,  $(U,Pu)C$

### ■ Fission products

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

### ■ Structural materials

- Fe-Cr-Ni, Zr alloys, Fe-Cr-Al-Y, Concrete ( $SiO_2$ -CaO- $Fe_xO_y$ - $Al_2O_3$ -MgO), SiC,  $B_4C$



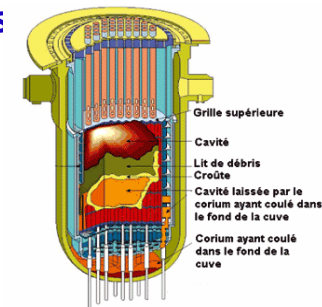
## ■ APPLICATIONS

### ■ Fuel behaviour at high temperature under normal and off-normal conditions

- Influence of the **Minor Actinides** on the fuel thermodynamic properties
- **Fission product** « chemistry »
- **Solid/liquid** phase transition
- **Vaporization**

### ■ Fuel / cladding chemical interaction at high temperature

### ■ Fuel fabrication



## ■ 2013-2016: Thermodynamics of Advanced Fuels – International Database

➔ The aim is to make available a comprehensive, internationally recognised and quality-assured thermodynamic database for advanced fuels

		Programme Review Group	
Country	Signatory	Representative	Alternate Member
Canada	CNL, RMCC, UOIT	M. Piro	E.C. Corcoran
France	CEA	C. Guéneau (Chair)	J.-C. Dumas
Japan	JAEA, CRIEPI	M. Kurata	T. Ogata
The Netherlands	NRG	R. Hania	G.-J. de Haas
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- The TAF-ID database is being built by **merging existing databases**
- N. Dupin (consultant) is responsible for maintenance and documentation
- Coordinated by S. Massara from OECD/NEA ➔ <http://www.oecd-nea.org/science/taf-id>