# Uncertainties on Thermodynamic and Physical Property DataBases for Severe Accidents and their Consequences on Safety Calculations.

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# Outline

- Introduction
- Uncertainties on phase diagrams
- Uncertainties on Physical Properties
- Application to Severe Accident Calculations
  - Example : Spreading calculations

# General procedure for calculation

- Composition and Temperature of corium
- Thermodynamic Modelling
  - Repartition of phases (liquids, solids, vapours)
  - Composition of Each Phase
- Physical Properties estimation
  - Database
  - Mixing Law
- Calculation of corium behaviour using calculated properties
- Determination of new temperature/composition

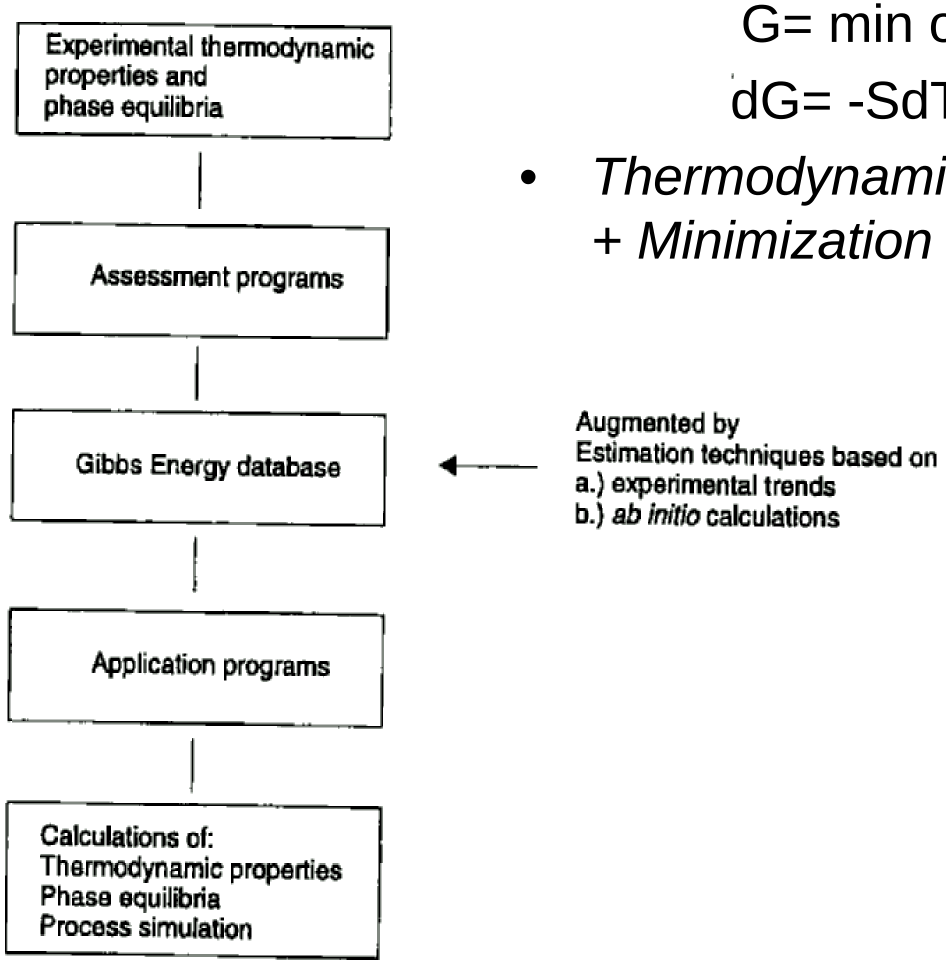
# Some aspects of thermodynamic modelling

- Research of the phases composition and proportions minimizing the system Integral Gibbs Energy

$$G = \min \text{ or } dG = 0 \text{ and } d^2G \geq 0$$

$$dG = -SdT + VdP + \Sigma \mu_i dn_i + \ldots$$

- *Thermodynamic database* + *Minimization software*



# Data in Thermodynamic Databases

- Thermodynamic data for pure elements
  (compiled by SGTE)
- Thermodynamic data for stoichiometric substances
  - H formation at 298.15K (from pure elements)
  - Entropy at 298.15K
  - Cp(T) from 298.15K to gaseous state
- Thermodynamic data for solutions
  - Mixing laws ( excess Gibbs energy)

$$G = G^{\text{reference}} + G^{\text{ideal mixing}} + G^{\text{excess}}$$

# How is the data produced ?

- Assessment of experimental work.
  - Some data (H,Cp) may be directly available
  - Usually, indirect validation on phase diagrams, partial pressures,….
  - Weighing of different works. *Expert judgement.*
- Choice of modelling (1 or n sub-lattices, order of excess terms, nonstoichiometries….)
- Use of an optimizer to determine the dataset which reproduces the best the experimental data.
  - This operation is done for binary interaction terms first, then on ternaries,….
  - The database is incremented gradually, no global reoptimization.
- NUCLEA, European Database
  - 18 elements
  - >300 binary and ternary diagrams

# Causes of Uncertainties

- Experimental errors (esp. at high temperatures)
- Exhaustivity of assessed experiments
- Modelling errors
- Optimization errors

- Errors due to the execution of Gibbs Minimizer

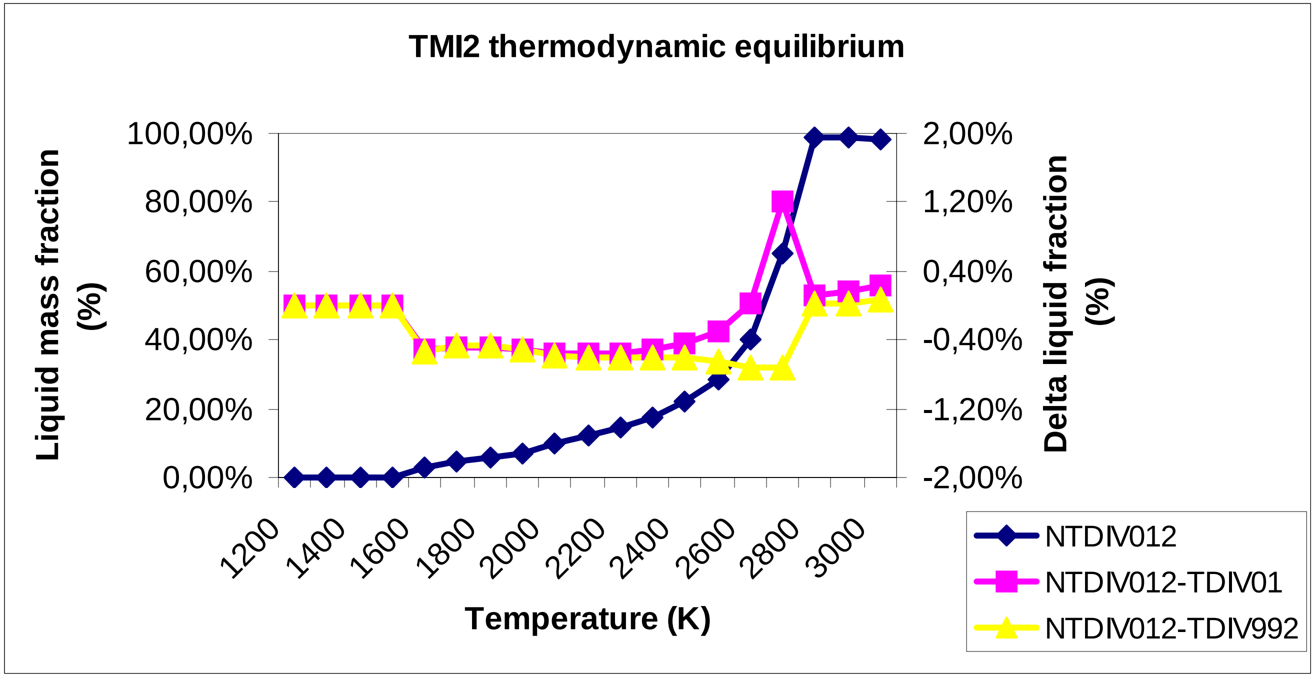
  + *Poor convergence/ divergence problems ! (metastability zones or numerical analysis ?)*

# How can we assess the uncertainties?
# (from an end-user standpoint)

- The database has been optimized as a whole.
  - ⇒ It is impossible to study independantly the effect of one term in the DB.
- Expert judgement provided ratings to subsystems (*,**,***,****)

Study of the evolution of database results with successive versions
=> order of magnitude of uncertainties at version n-1.

# TMI2 corium liquid fraction

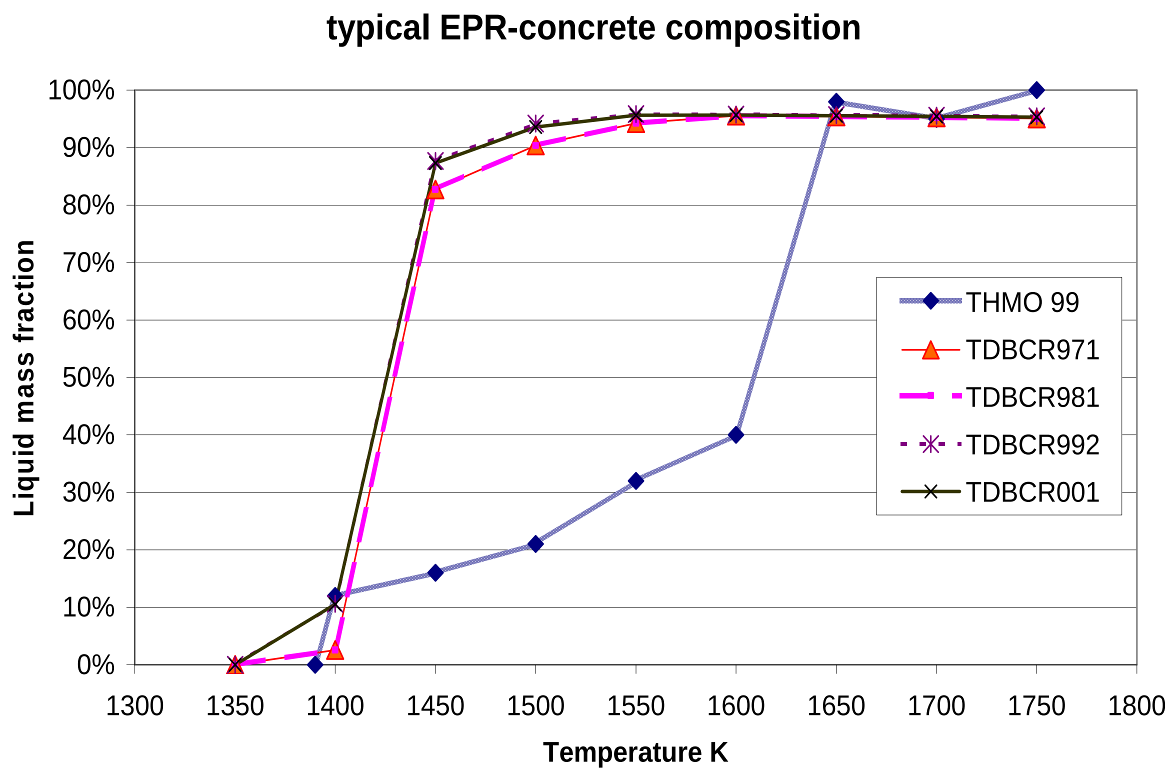



- Differences < 1.2%w => very consistent output.

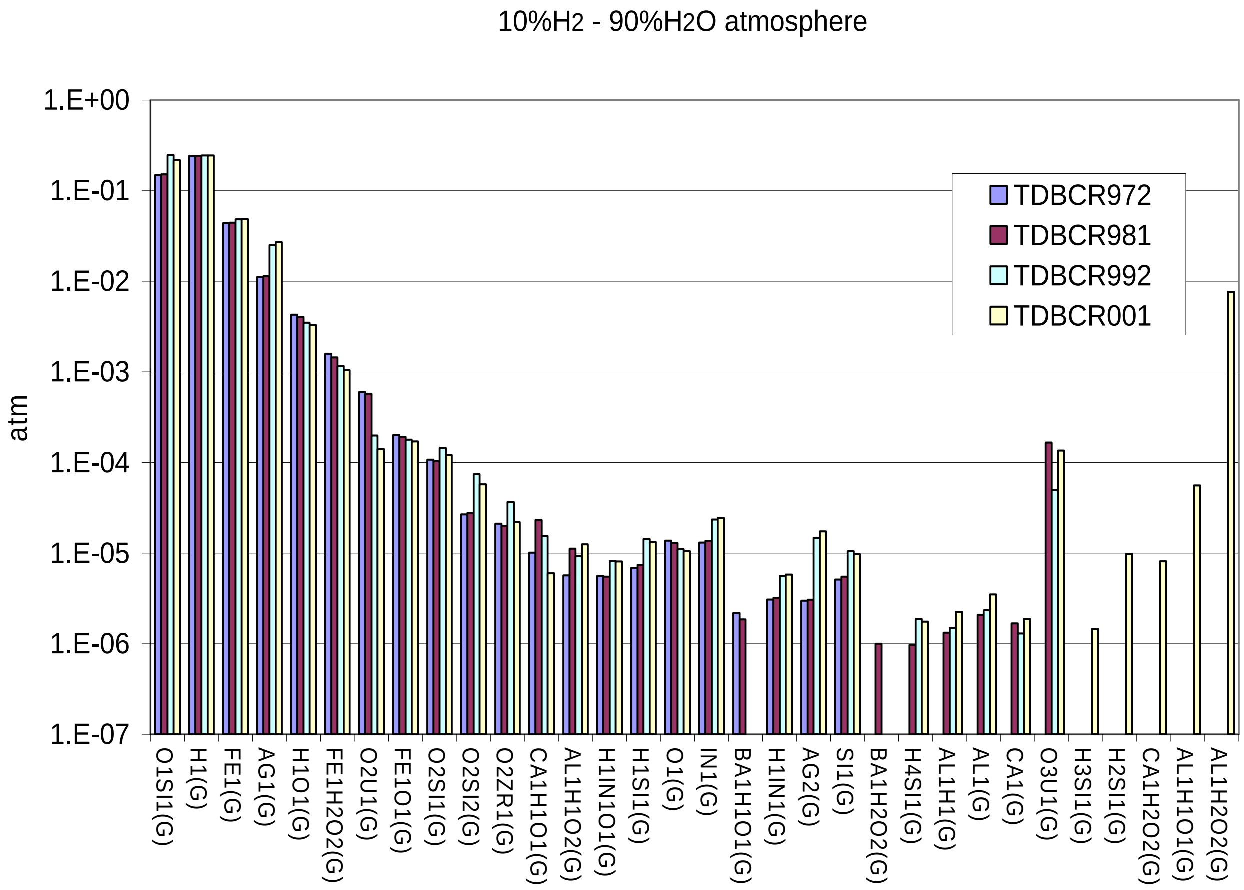
# Typical EPR Concrete

36%$_w$ $SiO_2$, 49%$_w$ $Fe_2O_3$, 5%$_w$ CaO, 6%$_w$ $Al_2O_3$, 4% $H_2O$

- Large discrepencies (100-200K) between THMO and TDBCR
- Consistency of TDBCR versions.
- $SiO_2$-$Fe_2O_3$ system rated *

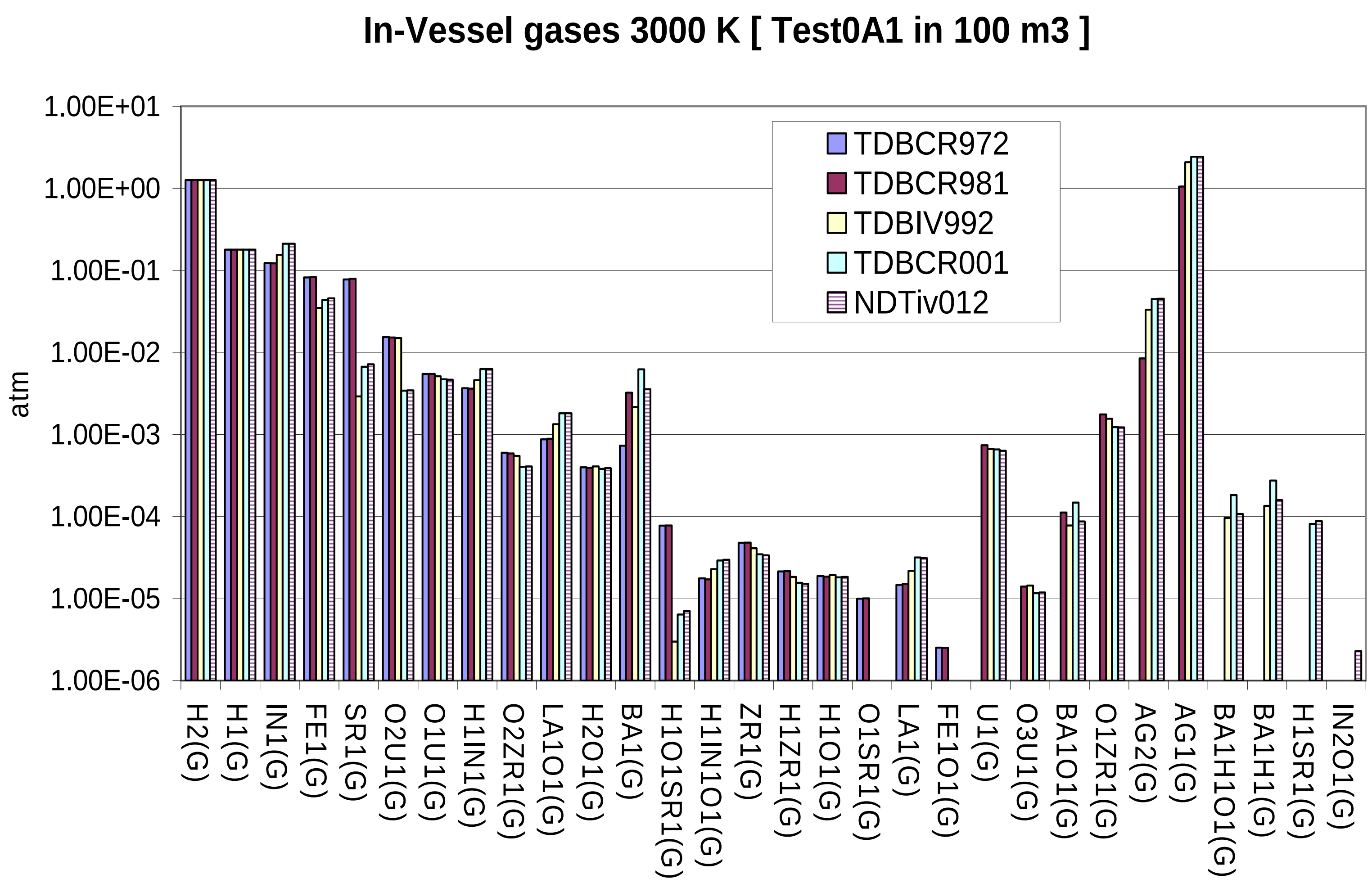


# Gaseous species over corium-concrete mixture at 2573 K




No large evolutions except appearances of new phases: $UO_3$, $Al(OH)_2$,
Disapearance of baryum hydroxides.

# Gases over In-vessel corium at 3000K




- Variations can reach factors of 3-10
- New gaseous species appeared in newer versions (ex. BaH, BaOH, HSr, …)

# Conclusions on Thermodynamic Uncertainties

- the thermodynamic outputs uncertainties are decreasing with the latest versions of the databases. All the thermodynamic outputs don't have the same uncertainties,
- for the liquidus and solidus temperatures and for the enthalpy, the uncertainties are getting lower for the successive databases,
- for the liquid, the uncertainties of the compositions are low,
- between solidus and liquidus temperatures, the uncertainties are may be important, especially for less validated systems,

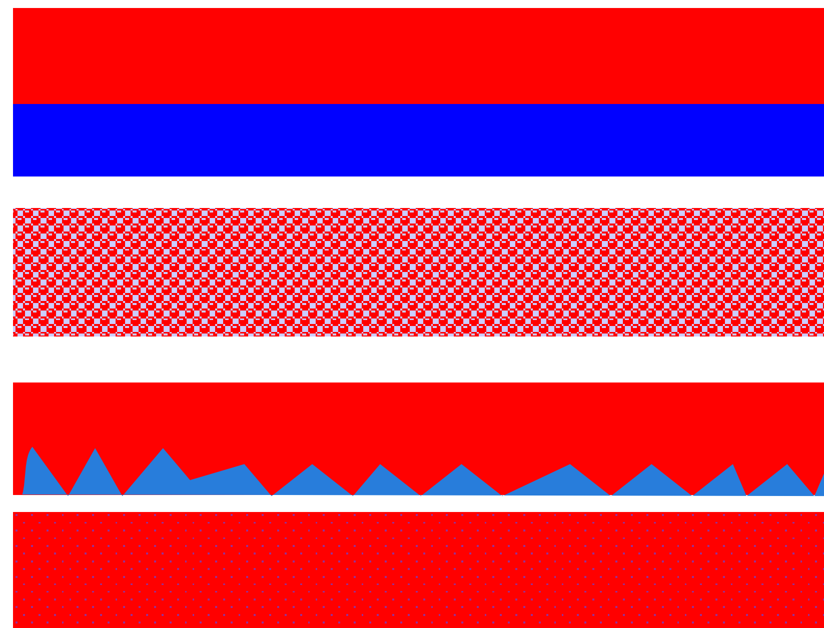
- for the gaseous substances, the uncertainties are mainly due to the absence of some vapours from the bases

- if all the pseudo-binary systems that constitute the corium composition have been well assessed, it's possible to have a good confidence that uncertainties on temperature will be less than 50K ;
- if one or more pseudo-binary systems that constitute the corium composition have a low assessment quality, at least an uncertainty on the temperature of $\pm$ 100 K could be expected.

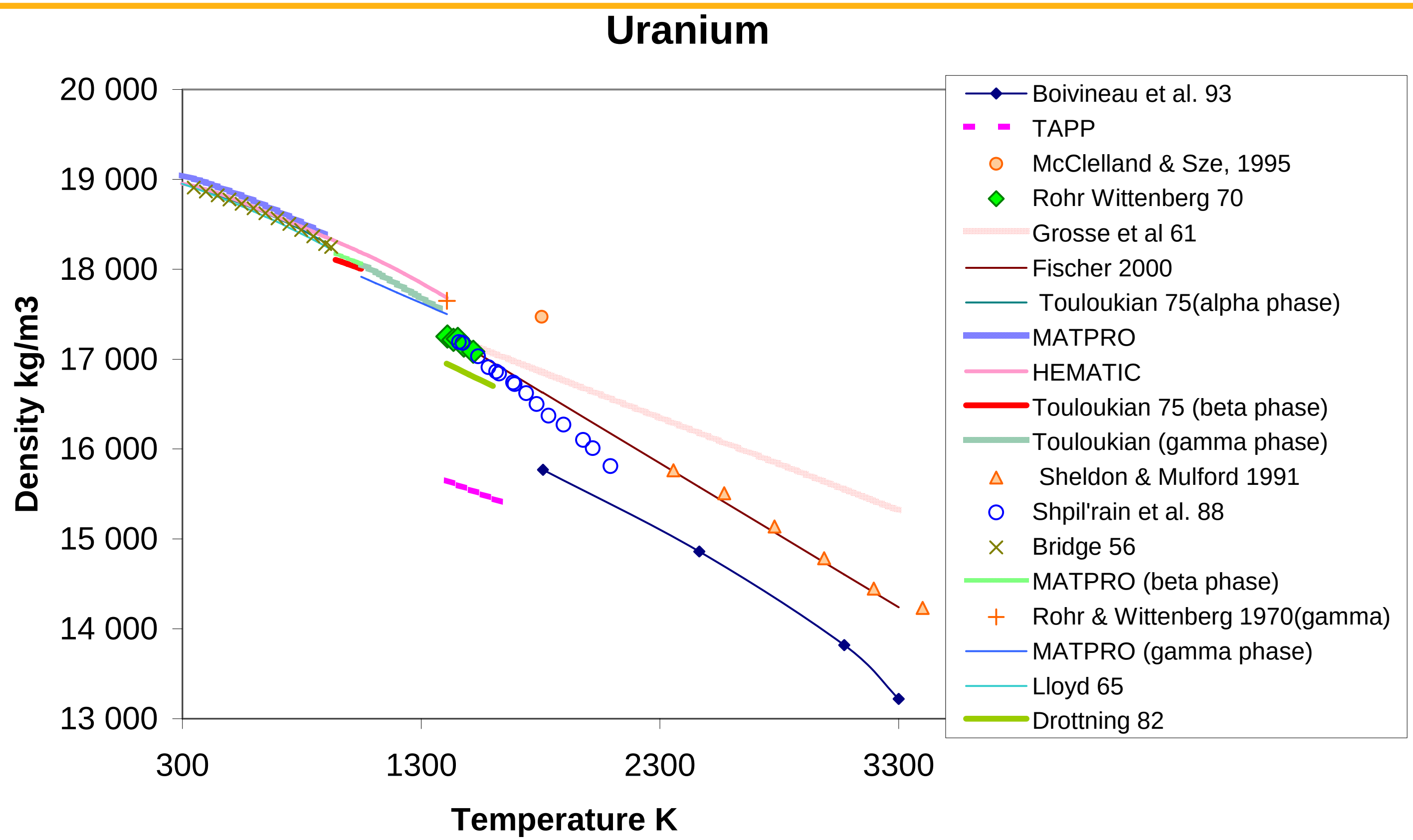
# Properties of Multiphasic Corium Mixtures

- Database of Pure-Substance Physical properties
- Mixture Physical properties depend on the spatial repartition of phases
  - Thermalhydraulic steady state => phase segregation
  - Rapid cooling => dendrites
  - Bubbling + shear => emulsions/ suspensions

- Only one phase
- 2 liquids (Sedimented)
- 2 liquids (Emulsioned)
- Dendritic mushy zone (percolation)
- Semi-solid suspension



# Density of Metallic Uranium




- Solid phase data quite consistent
- Large dispersion of liquid phase data
- Critical review by Fischer (FZK) 2000

$\rho_{liq}$ = **17270 –1.6010(T-1408)** *(brown curve)*

# Mixing laws for solutions (1)

$$V = \sum_i y_i \cdot V_i + V_{excess}$$

**Hypothesis: Ideal mixing – No excess volume**

**Applicable to solid and liquid solutions**

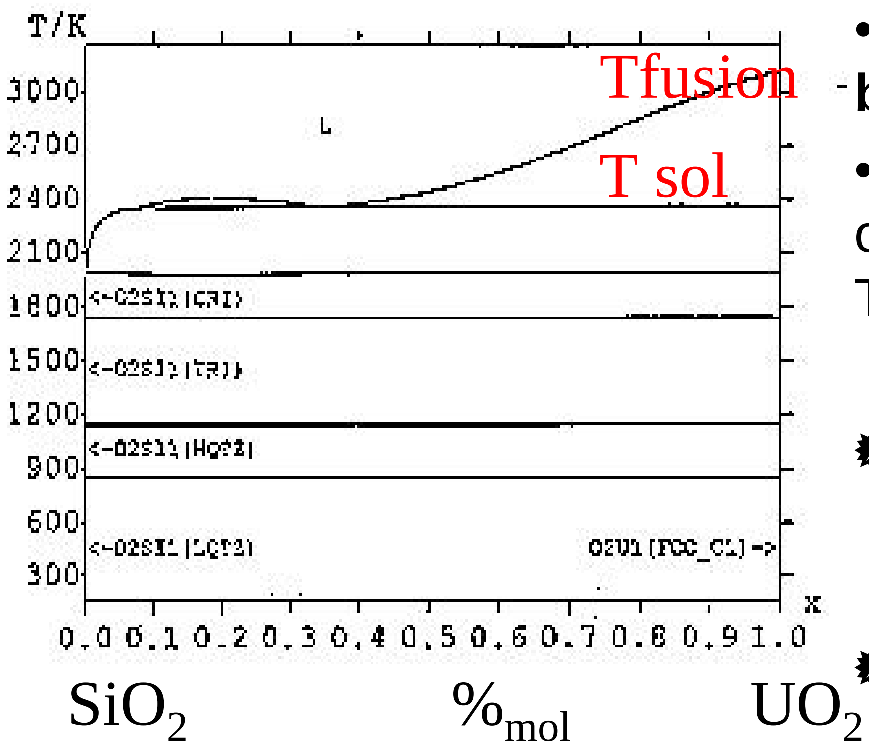
– Molecules of similar molar volumes (at ±30 %)

| | | | |
|---|---|---|---|
| $UO_2$ | 30.5 $cm^3$/mol | U | 13.8 |
| $ZrO_2$ | 22.3 | Zr | 14.6 |
| $SiO_2$ | 27 | ***Fe*** | ***7.9*** |
| $(FeO)_2$ | 26 | ***Cr*** | ***8.2*** |

– Excess volumes for metallic alloys (Crawley 74)
  - Maximum : -20 % for Na-In - 15 % for Fe-Si (at 50-50%$_{at}$)
  - Generally < ± 3 %

– For oxides (slags, natural silicates), Excess volume generally < 1% (Nelson & Carmichael 1974)

# Which density for liquids below Tfusion ?




- Between $T_{fusion}$ and $T_{sol}$, the refractory component is still present in the liquid phase
- **Which density to be used below $T_{fusion}$ ?**
- $UO_2$ present in corium-concrete oxidic phase for 1000 K below $T_{fusion}$ !!

Hypothesis #1

Constant volume

$V_{molar}(T<T_{fusion}) = V_{molar}(T_{fusion})$

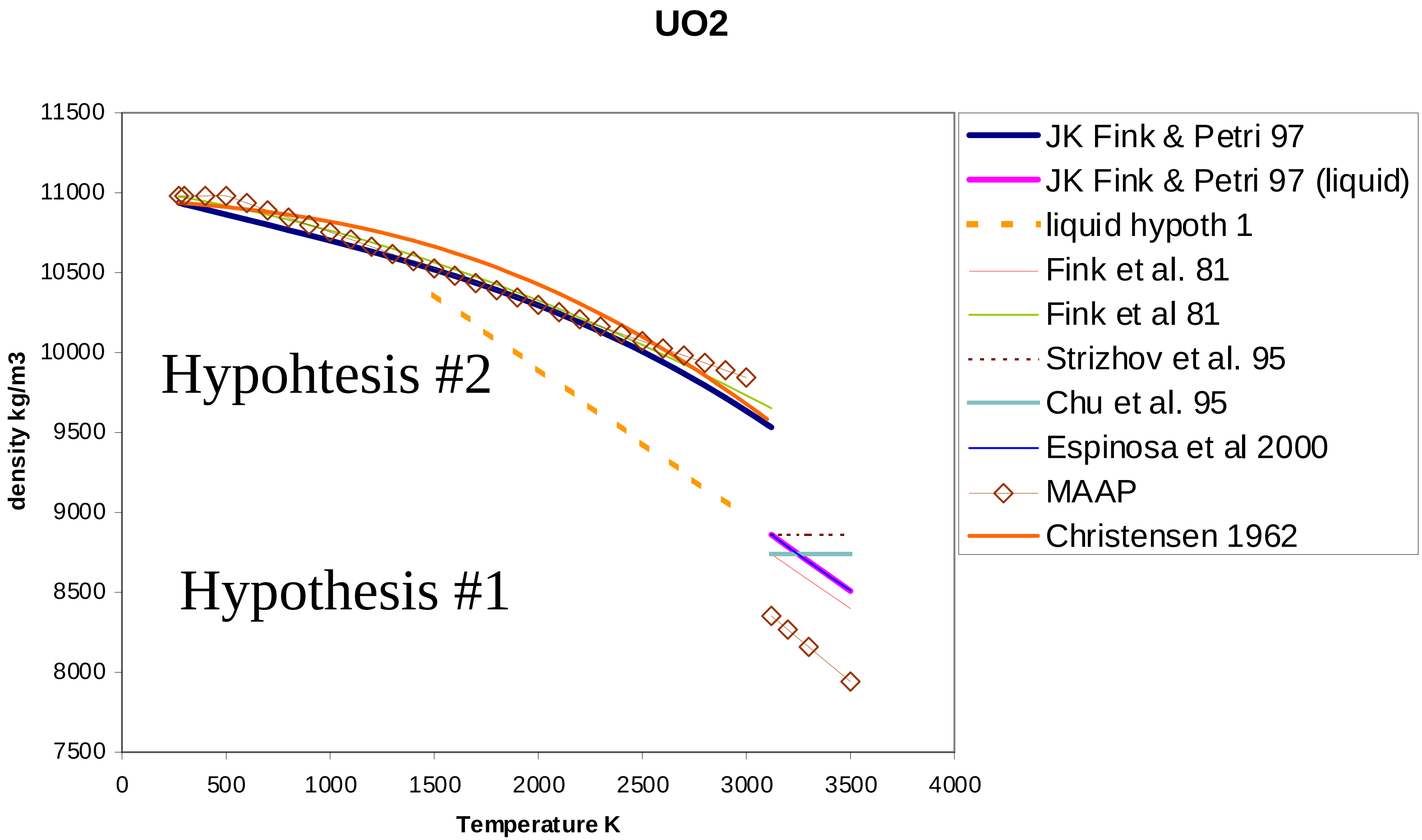
Hypothesis #2

Constant expansion coefficient

$V_{molar}(T) =$

$V_{molar}(T_{fusion})\,[1 + \alpha(T_{fusion})\,(T-T_{fusion})]$

# The 2 hypotheses below Tfusion



# Influence of these uncertainties to global calculation

Different types of uncertainties are present when calculating a SA experiment or a reactor case.

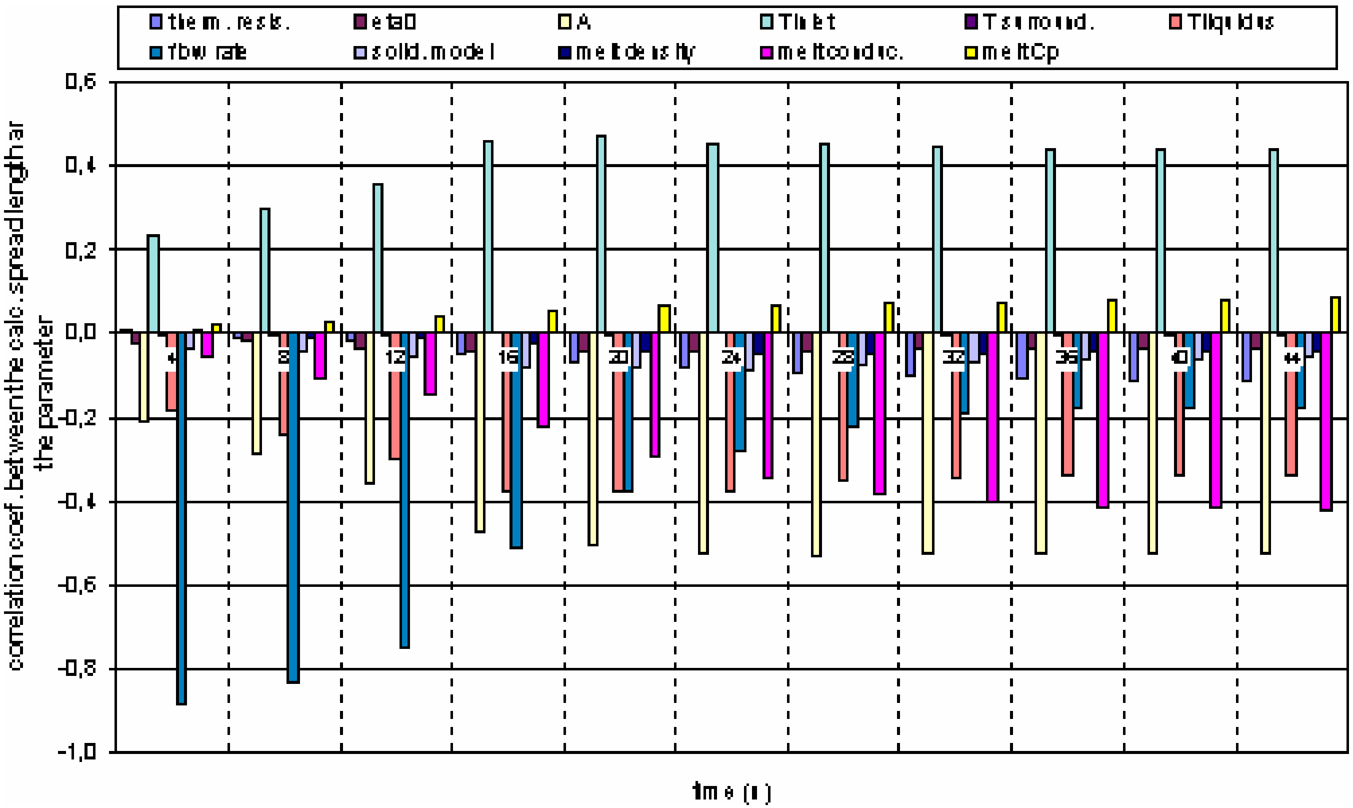
1. Uncertainties on initial/boundary conditions
2. Uncertainties on physical properties
3. Uncertainties due to modelling approximations

- Development of a methodology
  - n-Parameter analysis
  - 2 values for each parameter => $2^n$ calculations
  - Reduced map
- Example of Application
  - VE-U1 Spreading test
  - Post test calculations with THEMA (CEA Spreading code)
  - 11 parameters 2048 calculations !!
  - 128 calculation performed. Wilk’s quality level > 96%

# Parameters used in the exercises

| parameter | values of the studied parameters<br>low value | <br>high value | parameter used if not studied<br>V2.2mod 1c | <br>V2.3mod6 |
|---|---|---|---|---|
| $\eta_0$ Shaw correlation coefficient | 0.021 | 0.034 | studied | studied |
| A Shaw correlation coefficient | 0.01 | 0.024 | studied | studied |
| melt liquidus temperature, (K) | 2175 | 2325 | studied | 2250 |
| initial melt temperature (K) | 2015 | 2185 | studied | studied |
| assumption for the inlet flow rate | high flow rate | low flow rate | studied | studied |
| surrounding temperature (K) | 300 | 700 | studied | 300 |
| melt emissivity | 0.6 | 1 | 0.8 | studied |
| solidification model | bulk freezing | crust and bulk | studied | crust and bulk |
| solidification temperature (K) | 1300 | 2000 | 1300 | studied |
| transport of the upper crust | no | yes | no | studied |
| melt density (kg/m3) | std. values ±250 or ±500 (depend. on T) | | studied | std. values |
| melt therm. conduct. (W/m/K) | 1 | 5 | studied | studied |
| melt heat capacity | std. values ±10 % | | studied | studied |
| therm. resist. with substratum ($K.m^2/W$) | 0 | 0.006 | studied | studied |
| substratum thermal conduct. (W/m/K) | 0.8 | 1.4 | 1.1 | studied |

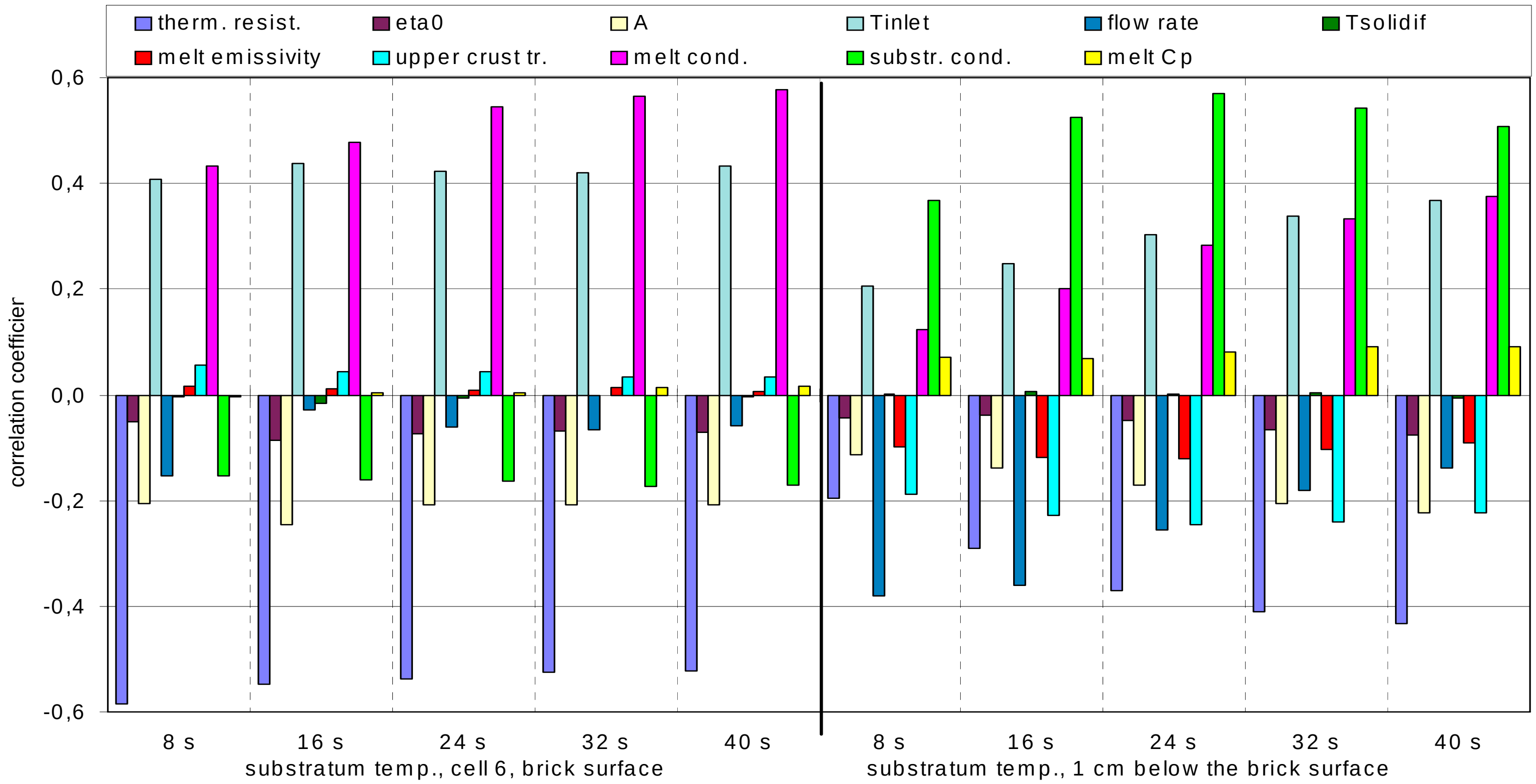
# Correlations between parameters and Spreading length




<u>Most correlated parameters</u>

1. Flow rate. Especially at initial instants of spreading
2. Viscosity Law exponent $\mu=\mu° e^{A(T-Tliq)}$
3. Liquidus Temperature
4. Inlet Temperature

# Correlations between parameters and substrate temperature




<u>Most correlated parameters</u>

1. Substrate conductivity
2. Thermal contact resistance
3. Melt conductivity
4. Flow rate and Inlet Temperature

# Conclusions

- Uncertainties due to uncertainties on Physical Properties and through those to thermodynamic modeling remain important.
- Sensitivity analyses are useful to determine which properties should be prioritized.
- R&D on corium viscosity has been performed for the validation of the EPR spreading concept, reducing these uncertainties.
- Several physical properties are still poorly known, esp. mixing laws
- Phase diagrams (thermodynamic database) must be improved e.g. in the corium-concrete diagram to reduce remaining uncertainties.

# Acknowledgement

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