Modelling and simulation of nuclear glass synthesis

Numerical simulation of the chemical reactions thermal effect during the vitrification process

K. Paraiso [1*] , E. Sauvage [1], E. Burov [2], V. Lemaitre [1], S. Schuller [1]

[1] CEA, DES, ISEC, DE2D, Univ Montpellier, Marcoule, France

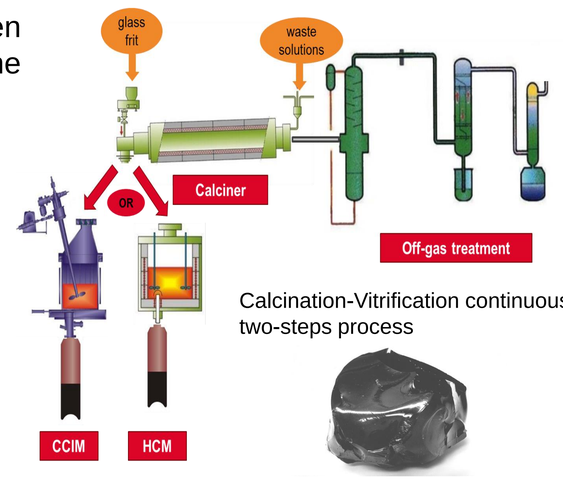
[2] CNRS/Saint-Gobain Recherche, Surface du Verre et interfaces UMR 125, 93300 Aubervilliers, France

*Corresponding author : kolani.paraiso@cea.fr

Context & objectives

- Calcination-vitrification process has been used in France for over 30 years for the high-level nuclear waste containment
  - Atomic scale confinement
  - Secure and sustainable containment
- Cold crucible technology used since 2010 at La Hague plant

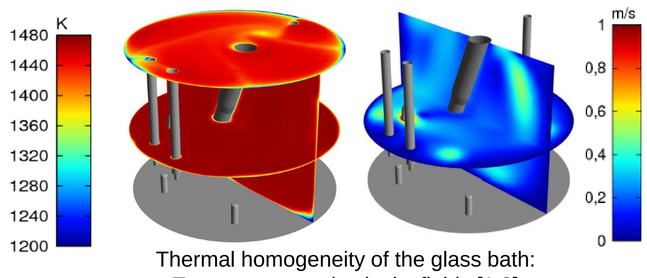
Hot cell for vitrification: La Hague



Calcination-Vitrification continuous two-steps process

Nuclear glass fragment

- Multiphysical modelling of cold crucible
  - Understanding of the different physical phenomena involved
  - Reducing the number of full scale experimental runs
  - Optimization of operating conditions



Thermal homogeneity of the glass bath: Temperature and velocity fields [1,2]

- The aim of this study is to add to existing simulations, a modelling of chemical aspects taking place during the nuclear glass synthesis in order to be able to predict:
  - The behavior of the reaction layer and its impact on thermal aspects in furnace
  - The optimization parameters of the elaboration capacity

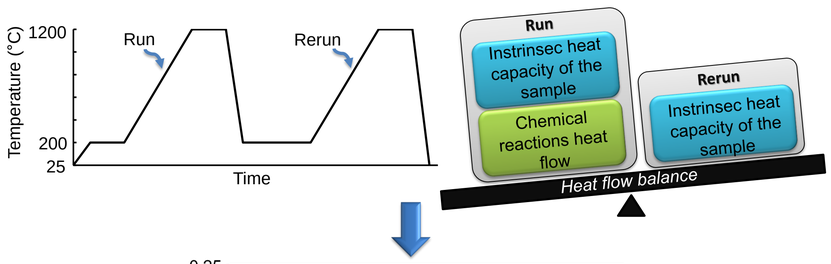
Methodology: Thermal approach

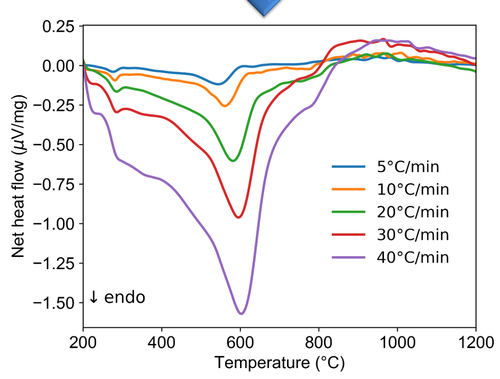
Reaction mechanism characterization

- Sample studied: Mixture of UOx glass precursors (more than thirty chemical elements)

Calcine + Glass frit

- Non-isothermal analysis (TGA-TDA) based on «run/rerun» method [3] at different constant heating rates

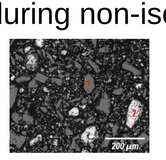




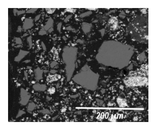
- Overall reaction enthalpy (ΔH) estimated through DSC/TGA analysis

Identification of chemical reactions

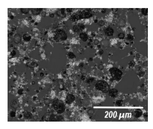
- SEM analysis at different steps of reaction mechanism during non-isothermal heating process at 10°C/min



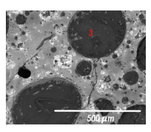
T_1= 300 °C



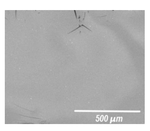
T_2= 450 °C



T_3= 650 °C



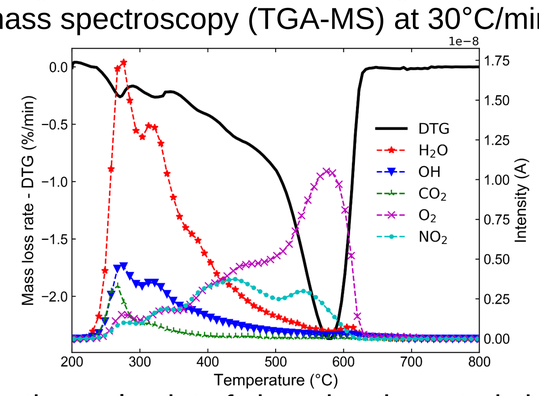
T_4= 800 °C



T_5= 1200 °C

1- Glass frit
2 - Calcine
3 - Marks due to the bubbles

- Evolved gaz analysis based thermogravimetric coupled with mass spectroscopy (TGA-MS) at 30°C/min



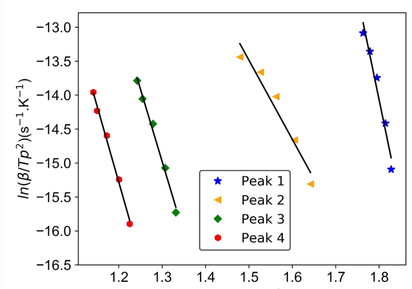
- From a thermal point of view, the characteristic events of the reaction mechanism are mainly associated with decomposition reactions (denitration, dehydration, etc.)

Modelling and coupling approach

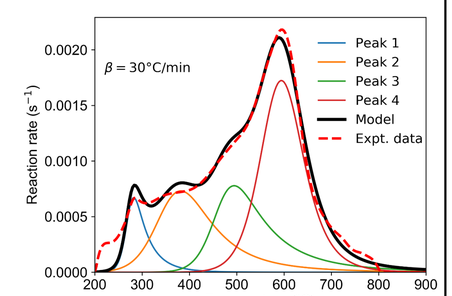
- Focus on endothermic events
- Overall reaction mechanism defined as a weighted sum of four nth order reactions:

$$\frac{d\alpha}{dt} = \sum_{i=1}^{4} w_i A_i (1-\alpha_i)^{n_i} \, exp\left(-\frac{E_i}{RT}\right); \quad \sum_{i=1}^{4} w_i = 1$$

- Apparent kinetic parameters (E_i, A_i, n_i, w_i) are identified using a combination of Kissinger and least squares methods.



Kissinger plots



Fit illustration at 30°C/min

- Coupling with electromagnetic-thermal-hydraulic 3D model
  - Generalization of 0D model with the integration of transport terms (advection and diffusion)
  - Coupling with MTH 3D model via the temperature

Full 3D simulation of vitrification process at mock-up scale
Coupling of chemical reactions modelling with thermal-hydraulic model

Experimental study

Measurements of the temperature variation induced by the chemical reactions endothermic effects coupled with the intrinsec heat capacity of the glass precursors

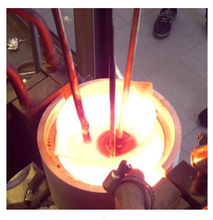
Procedure

- Remelting of UOx glass under mechanical stirring at 600 rpm
- Stabilization of the temperature
- Adding of 10 g of glass precursors
- Monitoring of the temperature evolution

Device overview: Platinum crucible heated by Joule effect - Stirrer -Two thermocouples

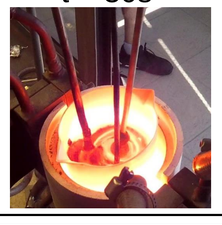
Reactive surface and temperature evolution

Initial conf.

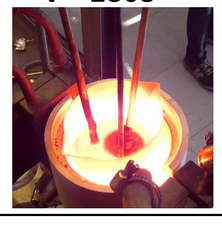


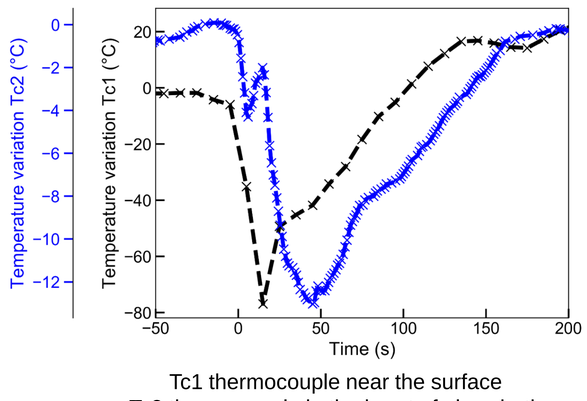
t = 0s

t = 30s



t = 180s





Tc1 thermocouple near the surface
Tc2 thermocouple in the heart of glass bath

Numerical simulation

Governing equations

- **Electrical**
  Joule effect heating
  $P_j = j.j/\sigma(T)$

- **Chemical**
  - Transport equation for each reaction (*i=1 to 4*) :

$$\frac{\partial \rho \alpha_i}{\partial t} + \frac{\partial}{\partial x_k}\left(\rho u_k \alpha_i - \Gamma_i \frac{\partial \alpha_i}{\partial x_k}\right) = \rho A_i (1-\alpha_i)^{n_i} \, exp\left(\frac{-E_i}{RT}\right)$$

  - Thermal retroaction through the overall reaction enthalpy (ΔH)

α_i, ΔH ⇄ T

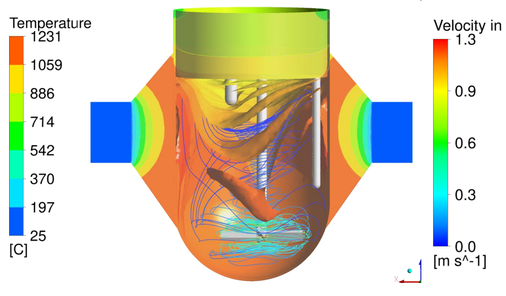
- **hydraulic**
  Navier Stokes equations

- **Thermal**

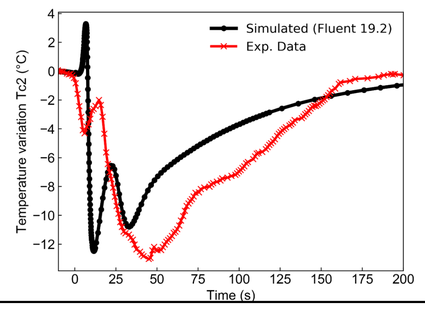
$$\frac{\partial \rho C_p T}{\partial t} + \frac{\partial}{\partial x_k}\left(\rho u_k C_p T - \lambda \frac{\partial T}{\partial x_k}\right) = \frac{j.j}{\sigma(T)} + \Delta H \sum_{i=1}^{4} w_i A_i (1-\alpha_i)^{n_i} \, exp\left(-\frac{E_i}{RT}\right)$$

Temperature evolution (Ansys Fluent 19.2)

- Steady state before adding glass precursors



- Temperature evolution after adding glass precursors (Simulation vs experiment)



Conclusion and perspectives

- The approach implemented in this work allows to satisfactorily predict the temperature variation induced by the chemical reactions endothermic effects coupled with the intrinsec heat capacity of the glass precursors
  - Next step: Full scale simulation

References

1. G. Barba Rossa, Modélisation multiphysique de l'élaboration de verre en creuset froid, Thèse de doctorat, Université de Grenoble Alpes, 2017.
2. E. Sauvage, Modélisation numérique thermo-hydrodynamique et inductive d'une fonte verrière élaborée en creuset froid inductif, Thèse de doctorat, Grenoble INP, 2009.
3. J. Chun, D.A. Pierce, R. Pokorný, P. Hrma, Cold-cap reactions in vitrification of nuclear waste glass: Experiments and modelling, Thermochimica Acta, 559, p.32– 39. 2013