Cold crucible for HLW vitrification : advances in the feed and PGM behavior modelling

Emilien Sauvage[1*], Patrice Brun[1], Zineb Nabil[1] and Régis Didierlaurent[2]

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

[2]Orano

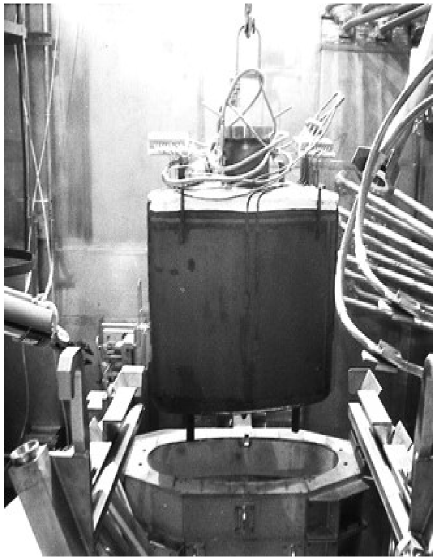
28/02/2023

*corresponding author : emilien.sauvage@cea.fr

Summary

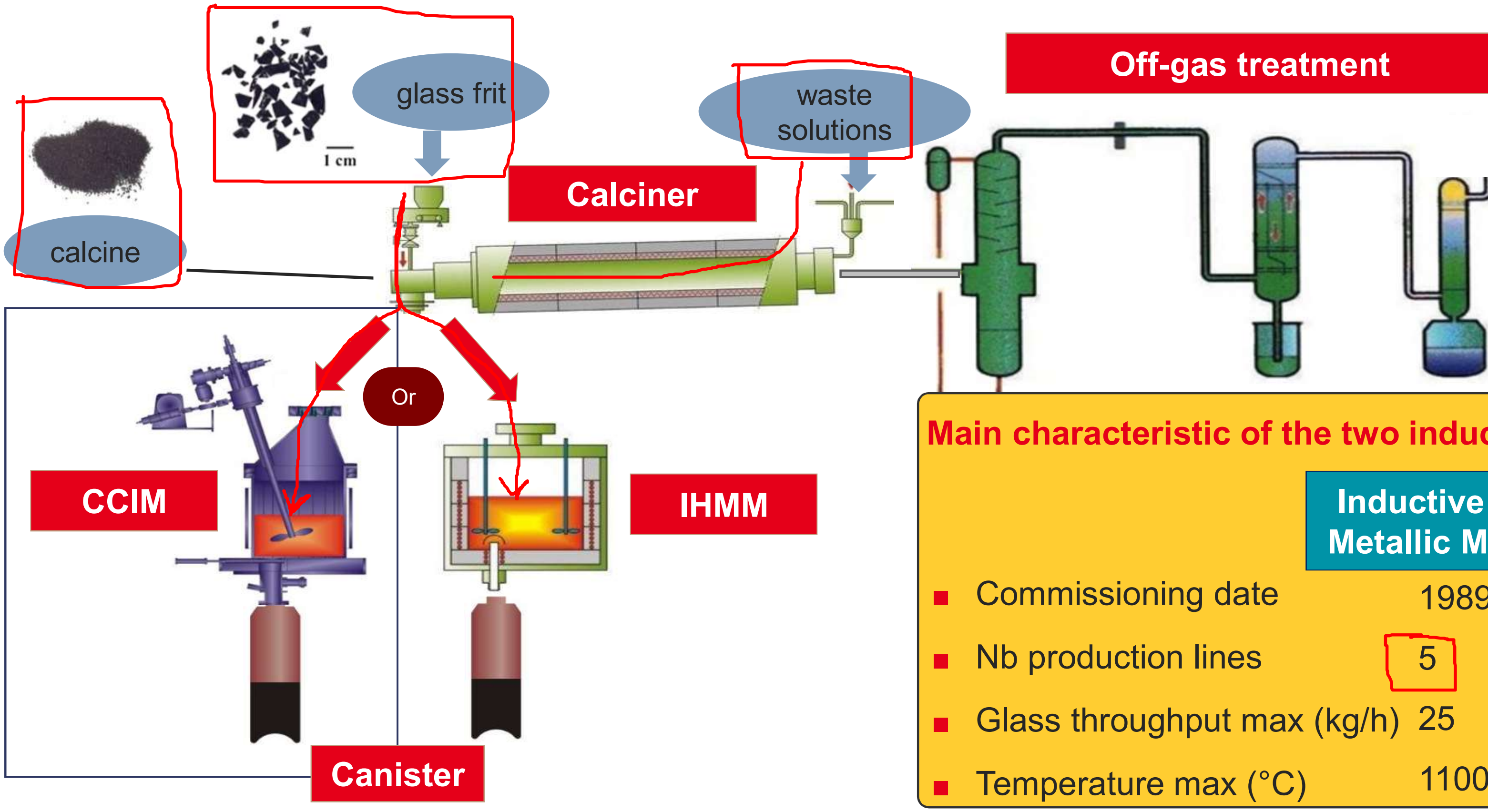
1. **French radioactive waste vitrification technology presentation**
2. **Platinum group metals particles in numerical simulation**
3. **Feeding modelling**
4. **Conclusion**

Cold Crucible Inductive Melter



Inductive Hot Metallic Melter

Calcination – vitrification continuous process



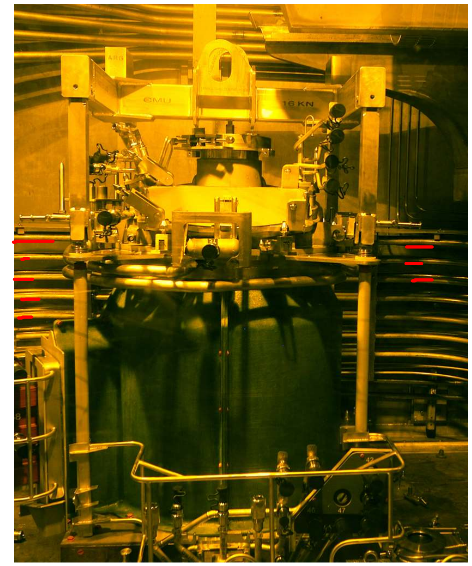
Main characteristic of the two induction furnace technology

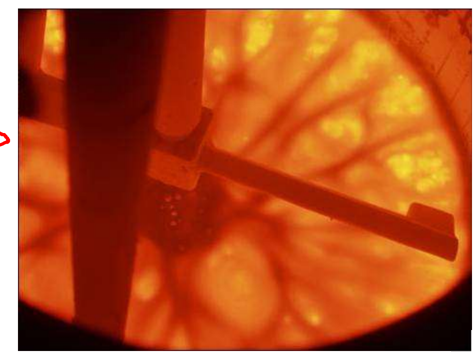
	Inductive Hot Metallic Melter	Cold Crucible Inductive Melter
Commissioning date	1989	2010
Nb production lines	5	1
Glass throughput max (kg/h)	25	45
Temperature max (°C)	1100°C	1300°C

- IHMM in operation in Orano plants of La Hague (Normandie) since 1989
- Higher temperature in CCIM leads to a higher production capacity

Melting with cold crucibles

- Main principles
  - Calcined HLW and glass frit are heated by direct electromagnetic induction
  - The crucible is cooled by an internal water-cooling system
  - The glass melt is mechanically stirred with a rotating agitator
  - Further homogenization is achieved with air bubbling in the glass
- The cold crucible technology has been developed by the CEA Marcoule and is working at the Orano La Hague reprocessing plant (France) since 2010
- Mission of CEA
  - Back industrial support
  - R&D and design of more efficient crucibles for future nuclear waste
  - Modelling and simulating the full vitrification process (hence diminishing new development costs)





Glass surface in the cold crucible

Production glass type with CCIM

CCIM implemented in the R7 facility for the production of 3 different types of vitrified waste canisters :

➲ CSD-B canisters

Intermediate level waste borosilicate glass for the vitrification of corrosive solutions from decommissioning and dismantling operations. (**Low** PGM content)

➲ CSD-U canisters

High level waste glass-ceramic for the vitrification of legacy highly-corrosive UMo fission products from reprocessing U-Mo-Sn-Al spent fuel. (**Low** PGM content)

➔ Production completed (see RGN N° 5 Sept-Oct 2020 p. 50-53)

➲ CSD-V canisters (R7T7 glass)

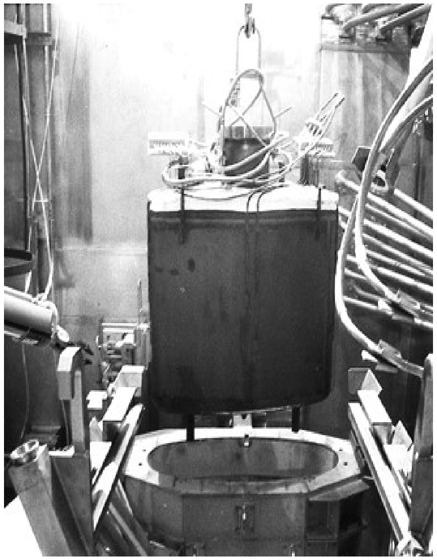
High level waste borosilicate glass for the vitrification of UOx fission products (ongoing PWR reprocessing activities) (**High** PGM content)

➔ In total, about 1100 canisters produced with the CCIM.

Summary

1. French radioactive waste vitrification technology presentation
2. **Platinum group metals particles in numerical simulation**
3. Feeding modelling
4. Conclusion

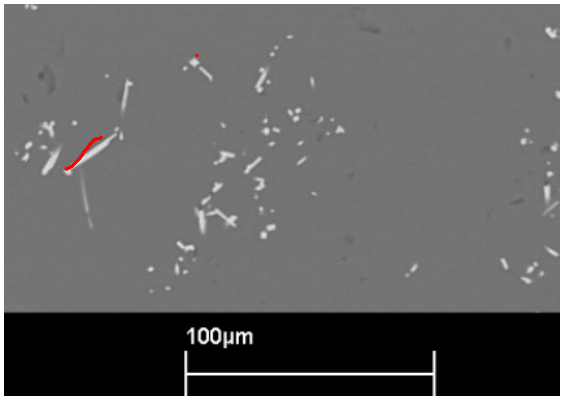
Cold Crucible Inductive Melter



Inductive Hot Metallic Melter

2 - Noble metal particles (1/5)

SEM picture of inactive nuclear glass



Platinum Group Metal particle (PGM)

- In the nuclear glass, noble metal particles are present
  - Concentration depending on the waste type (0.1 to 3 %w)
  - Ruthenium dioxide (RuO_2) needles
  - Palladium Rhodium ($Pd\ Rh$) spheres

- Strong impact on the vitrification process via the physical properties of the glass :

i. **Viscosity** → impact on the mixing quality of the glass

ii. **Density** → impact on the sedimentation / settling risk

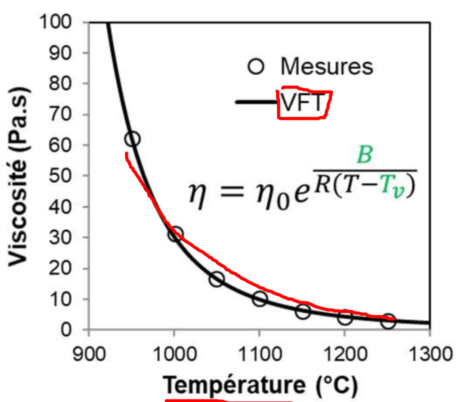
iii. **Electrical conductivity** → impact on the induction heating

2 - Noble metal particles (1/5)

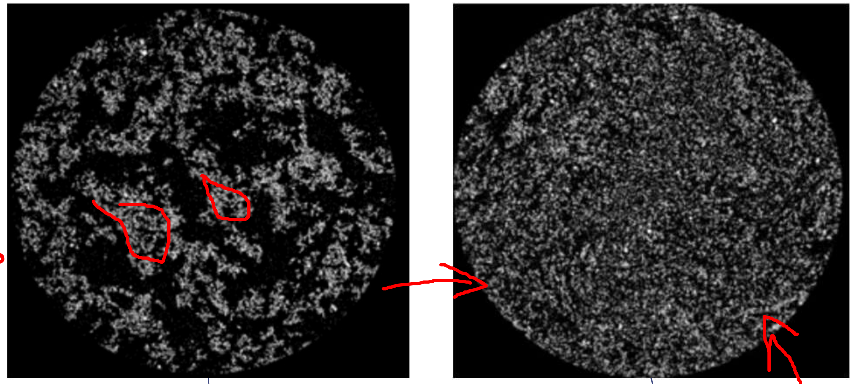
Noble Metal particles effect on the viscosity

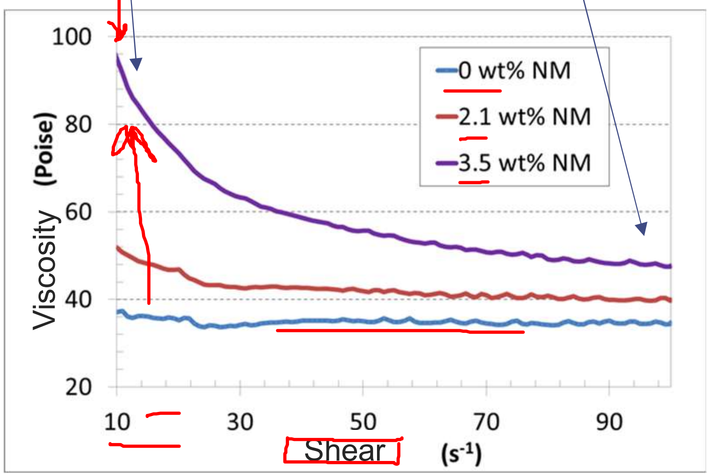
- The temperature dependence of the glass viscosity is well modeled with an VFT law
- A non Newtonian behavior of the viscosity is observed with NM particles
- Particles tend to aggregate under low shear conditions leading to an increase in apparent viscosity
- The phenomenon is reversible

Loi de Vogel-Fulcher-Tammann (VFT)



SEM picture of inactive nuclear glass





Caroline Hanotin, *et al.* (**2016**), Platinum group metal particles aggregation in nuclear glass melts under the effect of temperature, **Journal of Nuclear Materials**, 477.

2 - Noble metal particles (1/5)

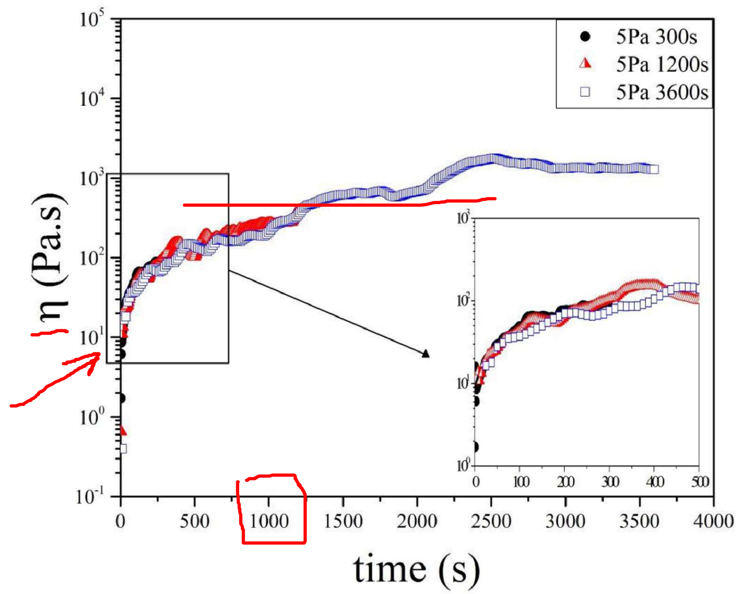
Noble Metal particles effect on the viscosity

- The apparent viscosity can be modelled with Cross law

$$\eta_{Cross}(T,\varphi,\dot{\gamma}) = \eta_{\infty}(T,\varphi) + \frac{\eta_0(T,\varphi) - \eta_{\infty}(T,\varphi)}{1 + \frac{\dot{\gamma}}{\dot{\gamma}_C(\varphi)}}$$

- But this lead to very high viscosity in the process simulation
- In fact, the structuration of the particles is quite a slow phenomenon (several hundred seconds)
- A time dependent viscosity model is required to predict the real glass flow at the process scale.
  - Ongoing work

Temporal evolution of viscosity after a sudden drop in shear rate



Machado, Norma Maria *et al.* (**2022**). Influence of Platinum Group Metal particle aggregation on the rheological behavior of a glass melt. **Journal of Nuclear Materials**. 563.

2 - Noble metal particles (2/5)

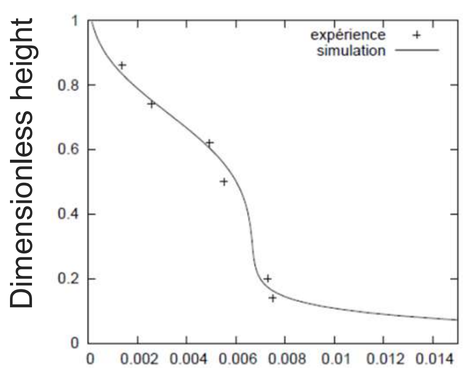
Sedimentation modelling of noble metal particles in the glass during vitrification

- A one phase model has been developed for individual settling
- Cloud settling in take into account via the density of glass
- Those models are able to simulate any concentration of PGM into the furnace

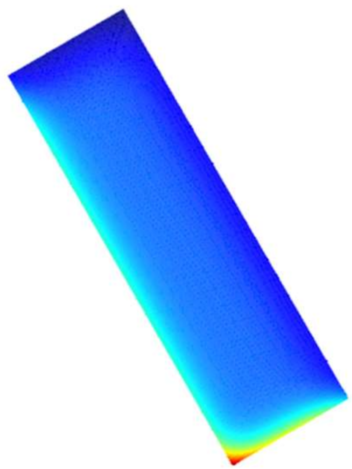
Individual settling (Eulerian model)

$$\frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C + \nabla \cdot \left(\tau \hat{\mathbf{g}} C \left(1 - \frac{C}{C_a} \right)^{\alpha} \right) = \nabla \cdot (\kappa \nabla C)$$

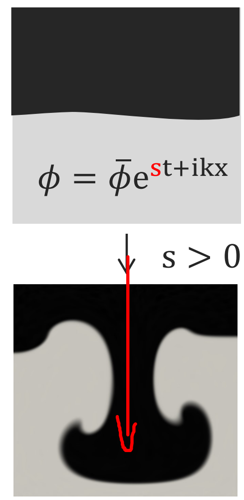
τ : Stokes terminal velocity ~ 1µm/s
$\alpha = 4{,}65$: hindering exposure
C_a : maximum concentration
κ : hydrodynamic diffusivity



Particle concentration %



Cloud settling through density of glass depending of particle concentration :



$$s_{max}^{-1} \propto \eta^{\frac{1}{3}} (\beta_p \Delta C)^{-\frac{2}{3}} \sim 1 \text{ s}$$

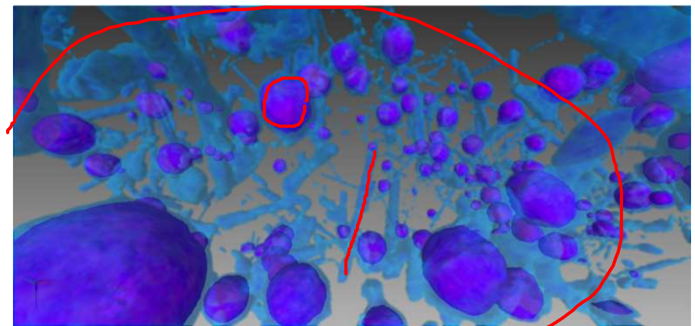
$$\rho(C) = \rho_f (1 + \beta_p C)$$

$$\beta_p = \frac{\rho_p}{\rho_f} - 1 \approx 2{,}1$$

Rayleigh-Taylor instabilities

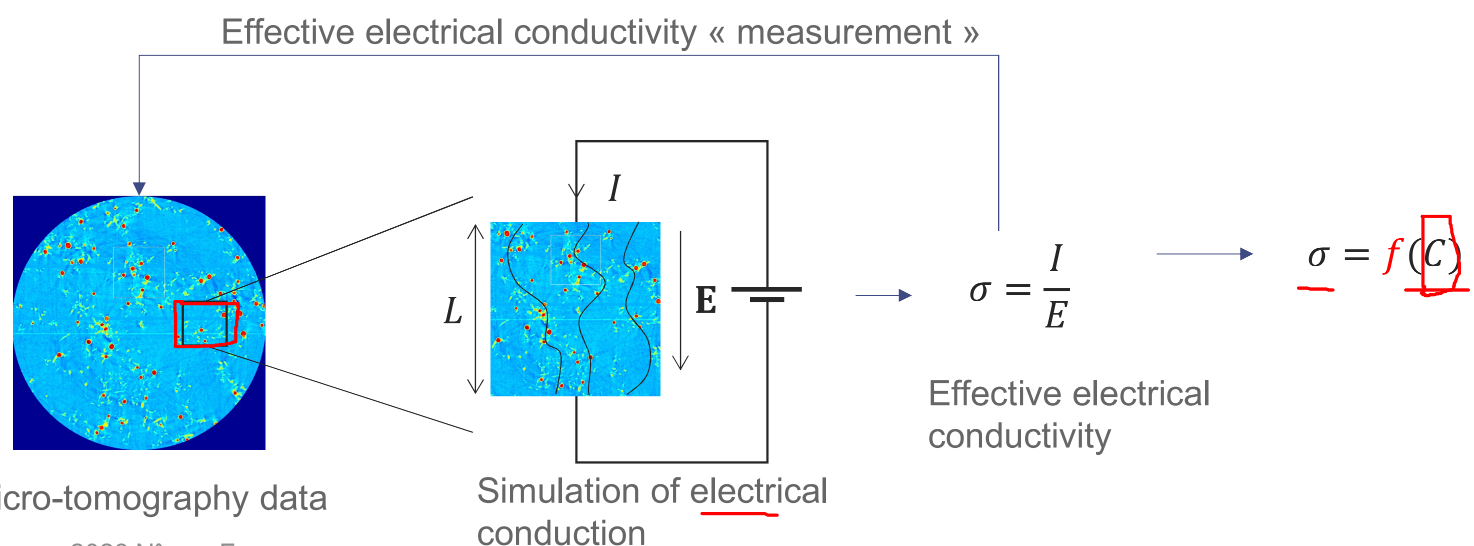
Klouzek et al.

2 - Noble metal particles (3/5)



Noble metal particles effect on electrical conductivity of the glass

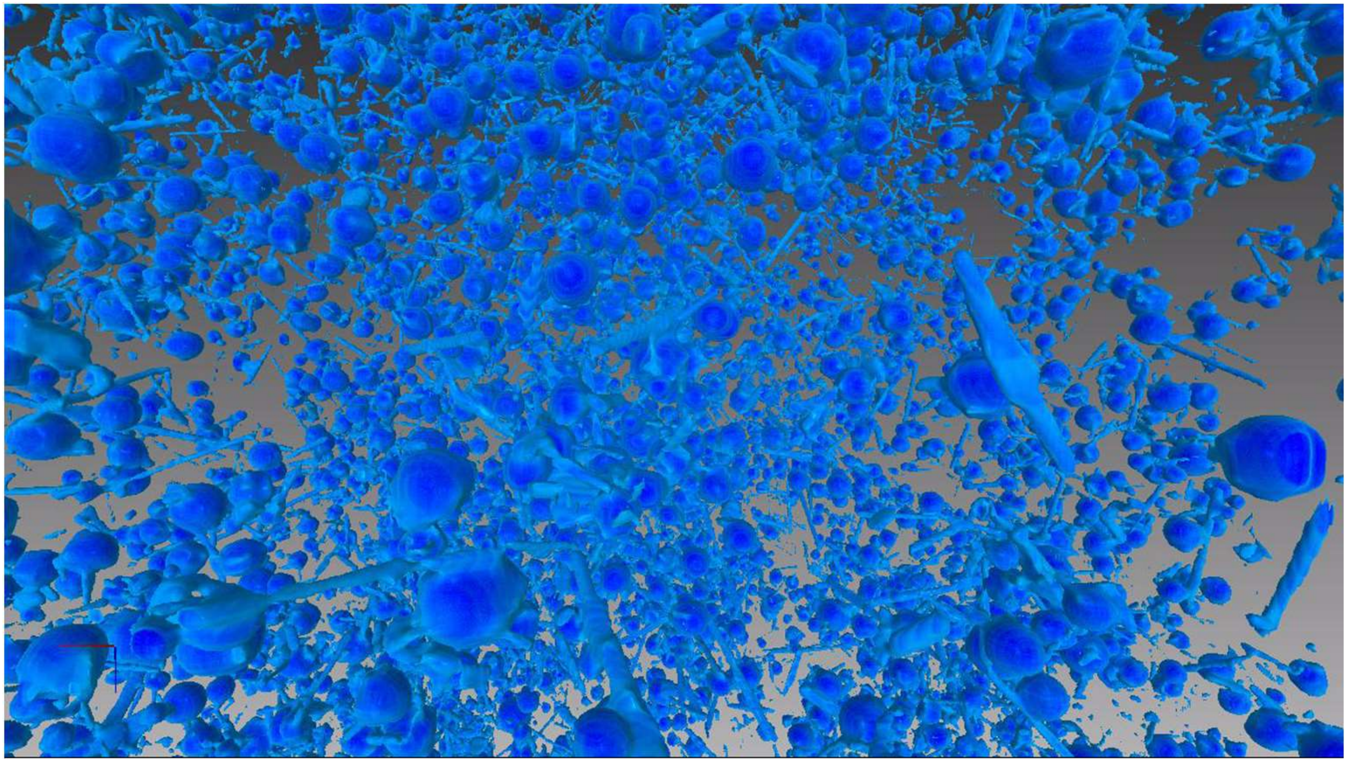
- Micro-tomography X of inactive glass sample
- Simulation of electrical conduction in small parts of the sample
  - Low conductivity for the glass : $10^{0}\ \Omega^{-1}m^{-1}$
  - High conductivity for the particles : $10^{6}\ \Omega^{-1}m^{-1}$
- Law of effective electrical conductivity function of the concentration



2 - Noble metal particles (4/5)

X Micro-tomography

- Samples of inactive glass send to the European Synchrotron Radiation Facility (ESRF, ID19)
- Voxel size of $0,16^3$ µm^3



Description

Needles : Ruthenium dioxide (RuO_2)

Spheres : Palladium (Pd)

- Diameter of one sphere : ~ 5 µm

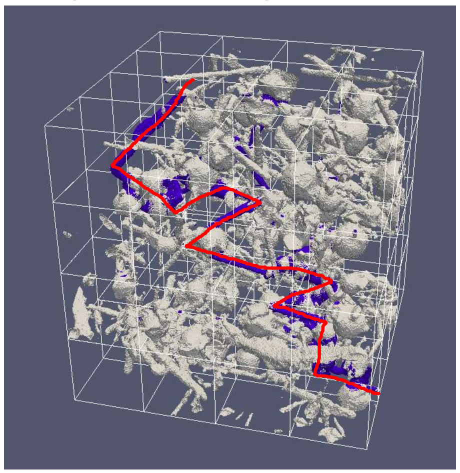
Volume fraction of particules in this sample : 3,5 %v (~10%w PGM)

2 - Noble metal particles (5/5)

Noble metal particle effect on electrical conductivity of the glass

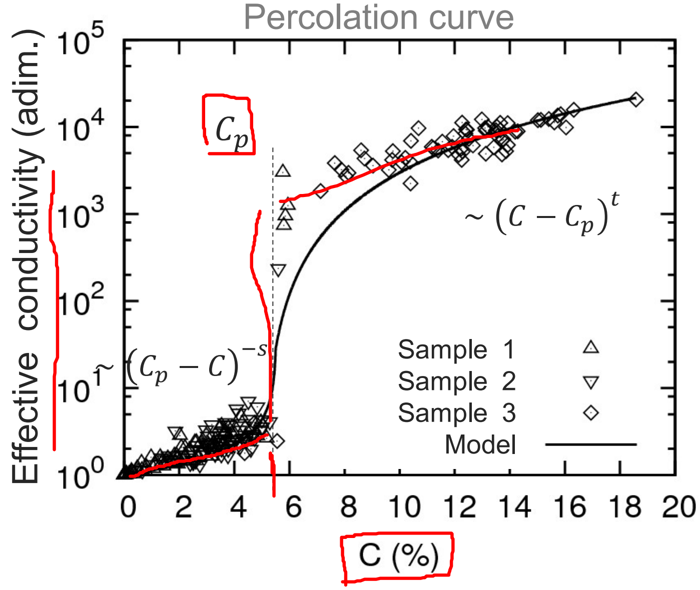
- More than 200 computation boxes on real 3D particles
- Range of concentration between 0 to 20 %v
- Law of effective electrical conductivity obtained shows a percolation threshold concentration : Cp

Example of a computation box



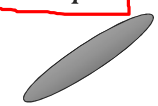
Barba Rossa G, Grenoble University, PhD 2018

Percolation curve



Garboczi *et al.* 1995

$$C_p \approx \frac{0.6}{\Psi}$$



aspect ratio $\Psi \approx 10$

$$\sigma = f(C, C_p, s, t)$$

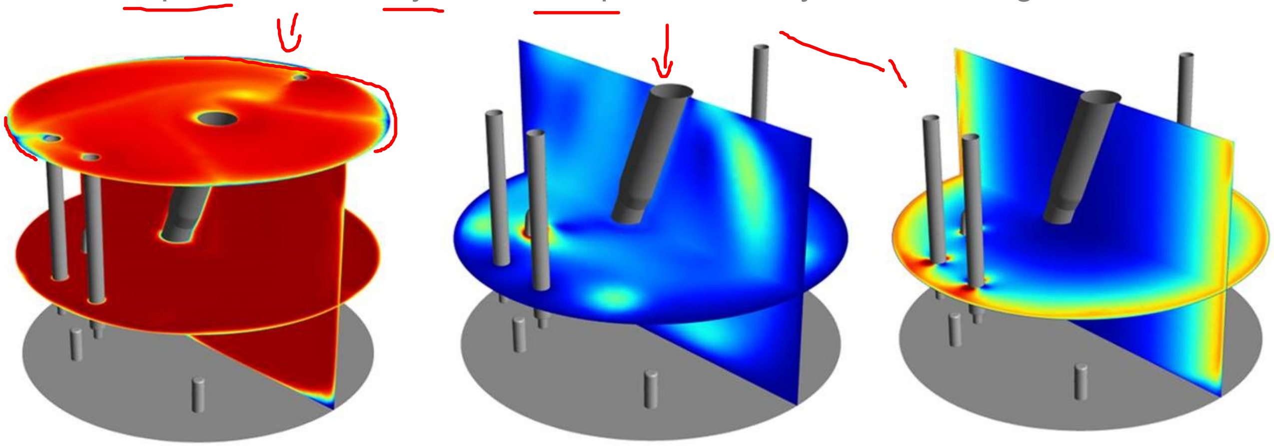
➢ This law is used in the induction heating simulation at the industrial scale

2 - Noble metal particles

Coupled simulation of direct induction heating with PGM sedimentation

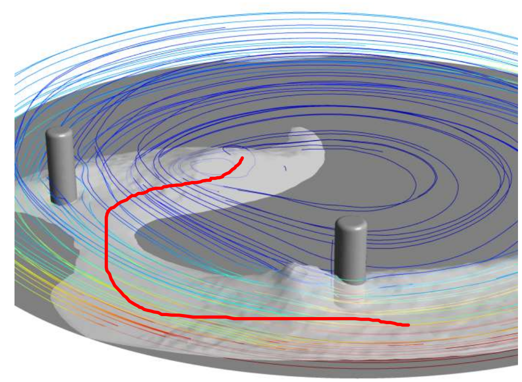
- Simulation of 400kg of glass. Total Joule power 180kW
- Artificially enhanced sedimentation for demonstration

Temperature, velocity and Joule power density fields in the glass

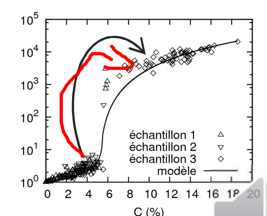


$T \in [1200; 1480]$ K $\quad U \in [0; 1]$ m/s $\quad p_J \in [0; 4]$ MW/m^3

Iso-contour of PGM concentration and Induced electric current in the glass



Iso-contour $C = 5{,}3$ %v



➢ Useful tool to predict sedimentation areas and their consequences on the heating process

Summary

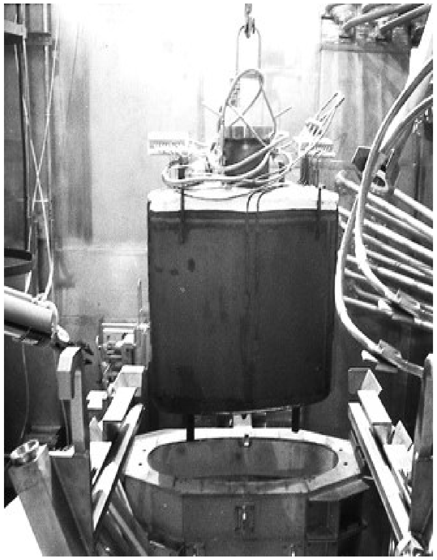
1. **French radioactive waste vitrification technology presentation**

2. **Platinum group metals particles in numerical simulation**

3. **Feeding modelling**

4. **Conclusion**

Cold Crucible Inductive Melter



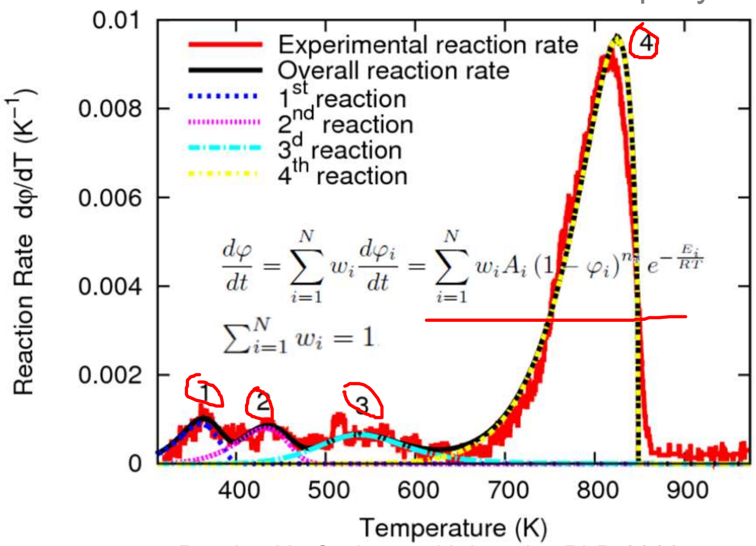
Inductive Hot Metallic Melter

3 – Feed modelisation (1/3)

Simulation of chemical reactions during vitrification process

- Idea : adapt the work of Hrma – Pokorny – Dixon et al.* (PNNL DOE) on the cold-cap reaction modelisation
- TGA DSC measurements & Identification of chemical reaction at various heating rates : 10 to 40°C/min

Chemical reactions in the cold cap layer



Paraiso K., Sorbonne University, PhD 2020

Generalization : advection term

$$\rho\frac{\partial\varphi}{\partial t} + \frac{\partial}{\partial x_i}\left(\rho u_i \varphi - \Gamma\frac{\partial\varphi}{\partial x_i}\right) = \rho A(1-\varphi)^n e^{-\frac{E}{RT}}$$

Coupling with temperature

$$\rho\frac{C_p\partial T}{\partial t} + \frac{\partial}{\partial x_i}\left(\rho u_i C_p T - \lambda\frac{\partial T}{\partial x_i}\right) = -\Delta H \rho A(1-\varphi)^n e^{-\frac{E}{RT}}$$

Solving in CFD software

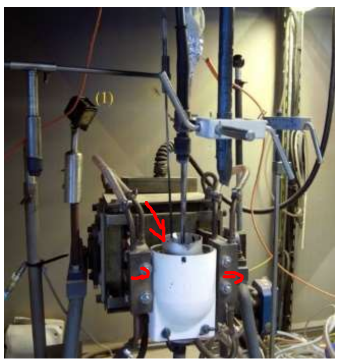
* J. Chun, D. Pierce, R. Pokorny and P. Hrma : Cold-cap reactions in vitrification of nuclear waste glass, Thermochimica Acta, 559 (2013) 32-39

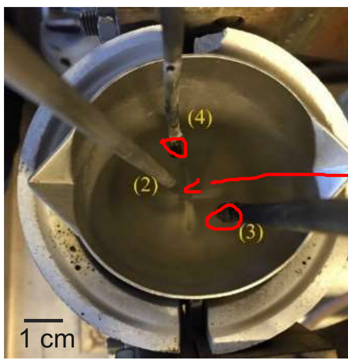
3 – Feed modelisation (2/3)

Example of the feed modelisation at small scale

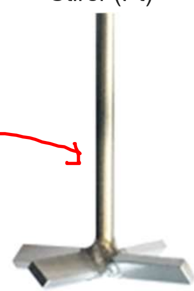
- Small furnace experiment

Platinum crucible (~ 1 Liter) heated by Joule effect

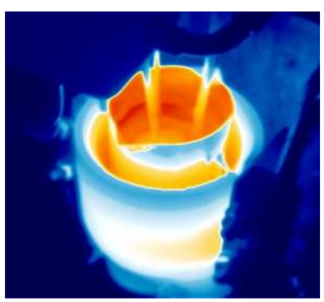




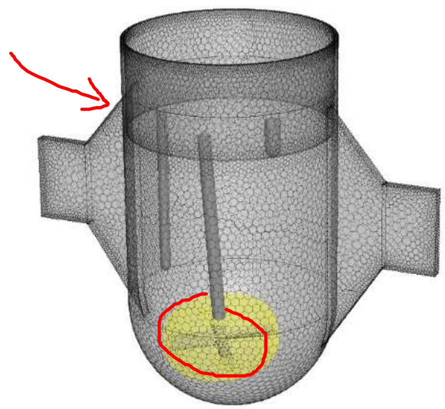
Stirer (Pt)



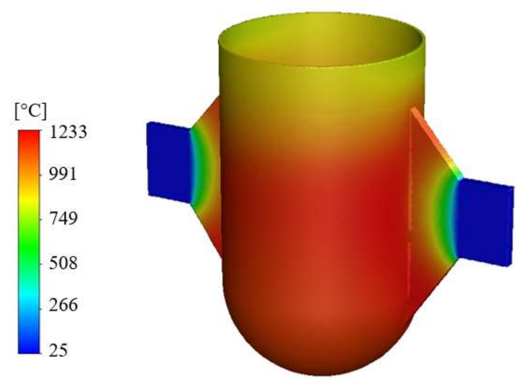
(1) Camera ; (2) Stirer; (3)Thermocouple (Tc1); (4) Thermocouple (Tc2)



- Modelisation (ANSYS Design Modeler/ Meshing)



Mesh

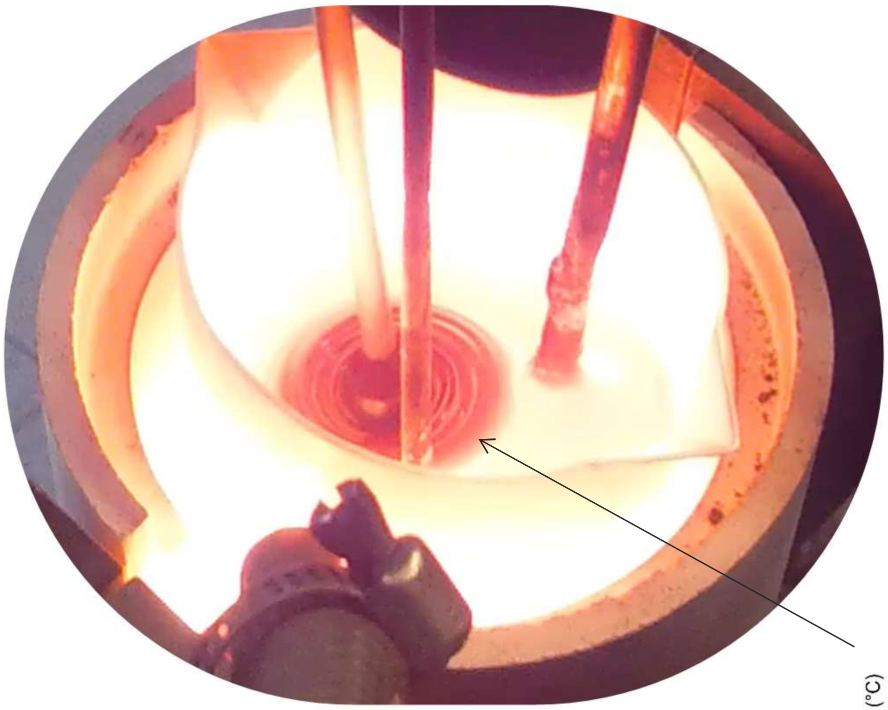


Crucible temperature

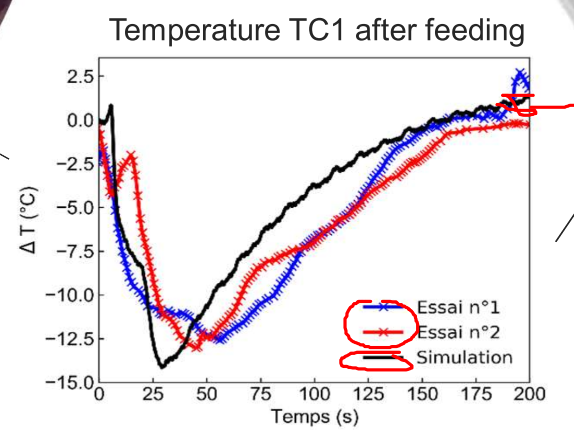
- Phenomena taken into account :
  - Glass flow
  - Joule effect in the crucible
  - Mechanical stirring
  - Radiation heat losses

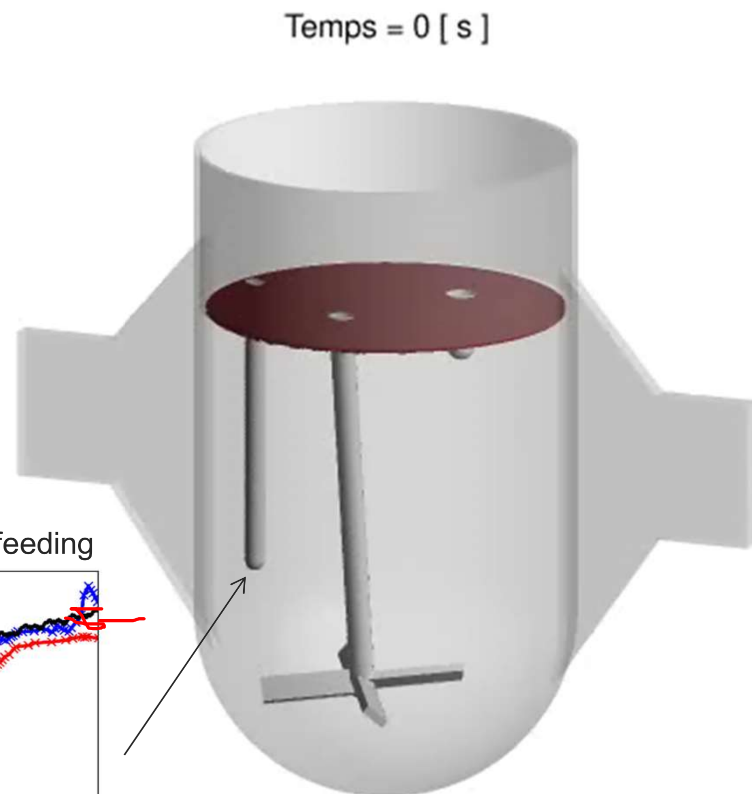
3 – Feed modelisation (3/3)

Validation of the feed modelisation at small scale



- Mix of calcine and glass fritt added at the top surface of the molten glass





- Evolution of the reacting raw materials during time

4 – Conclusion

- Cold crucible technology furnace is used for vitrification of HLW in La Hague plant since 2010 for the production of nuclear glass with up to 3%w of PGM

- The development of the CCIM carried out by the CEA Marcoule has required the numerical modelling of various physical phenomena

- PGM are of great concern due to their impact of the physical properties of the glass (viscosity, electrical conductivity, etc)

- Mathematical models helped to understand and control sedimentation phenomena in the furnace

- Simulation of feeding quantifies the kinetics of chemicals reactions taking place at the top of the glass

Thank you for your attention

CEA MARCOULE
BP17171
30207 Bagnols-sur Cèze Cedex
France
émilien.sauvage@cea.fr
+ 33 4 66 79 18 19