Rheological study of Platinum Group Metals aggregation in a glass melt

DE LA RECHERCHE À L'INDUSTRIE

Norma Maria Pereira Machado

Muriel Neyret (CEA Marcoule), Philippe Marchal and Cecile Lemaitre (Université de Lorraine)

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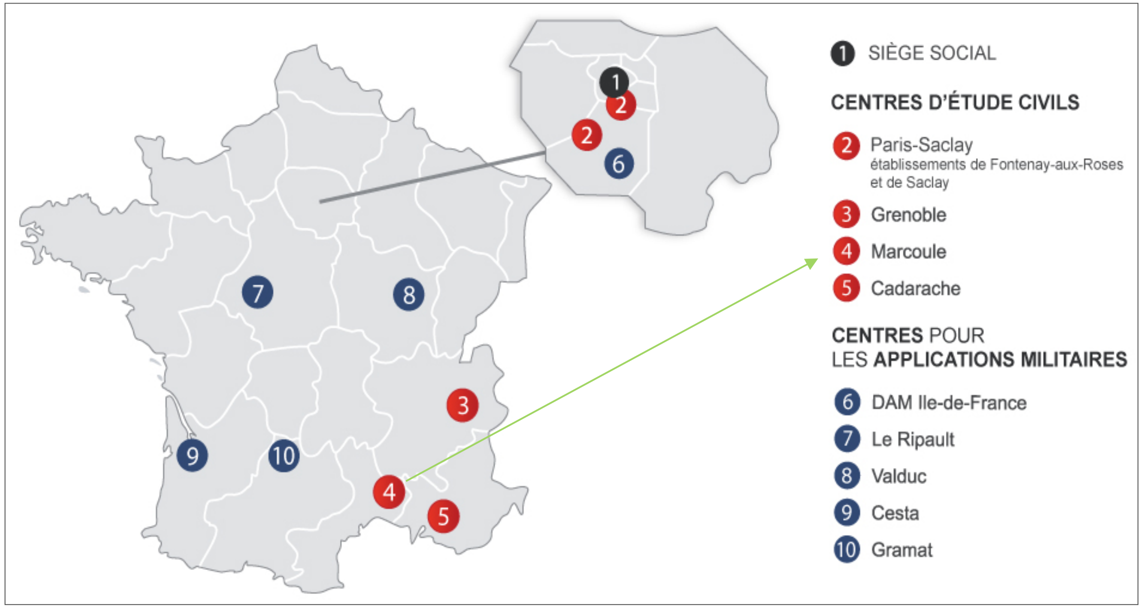
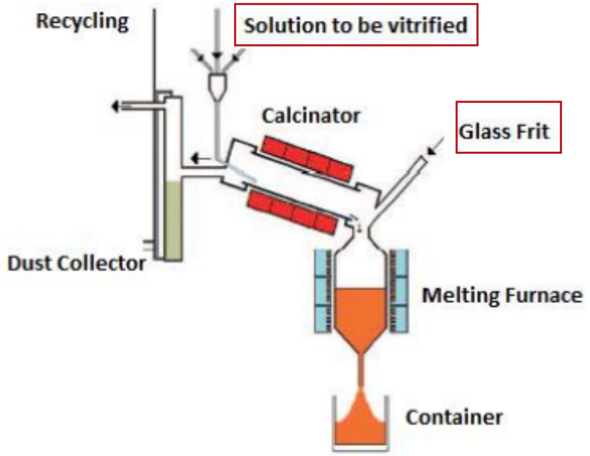
CEA Marcoule - LDMC

- **LDMC – Laboratory for the study and development of conditioning matrices,** part of the service responsible for vitrification studies and high temperatures processes
- Responsible for the **design, formulation, development and characterization of matrices for waste conditioning**
- Installations operate in a **non-radioactive** environment



Content

Nuclear Waste Conditioning

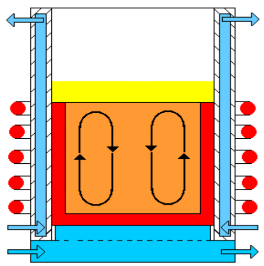


- Calcination
- Melting thanks to induced currents in the crucible (**Hot Crucible**) or in the glass (**Cold Crucible**)

Hot Crucible

- Induction heating oven which transfers its heat to the glass bath

Cold crucible



- A frozen glass layer, called self-crucible, is formed which creates a thermal and electrical insulation barrier between the crucible and the melt, preventing as well from the corrosive effect of the melt

Context

Nuclear waste in France

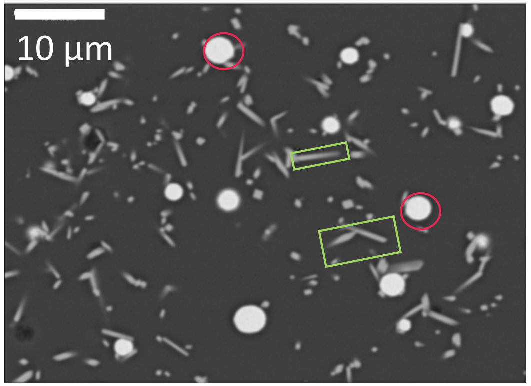
- High level waste are confined in a borosilicate glass matrix (R7T7)

Chemical composition : borosilicate glass (R7T7 glass)

	wt% Min.	wt% Max.
SiO_2	42.4	51.7
Al_2O_3	3.6	6.6
B_2O_3	12.4	16.5
Na_2O	8.1	11.0
FP* + Act* + PGE+ ZrO_2	4.2	18.5
RuO_2 + Pd + Rh	0	3.0

*FP: Fission Products; Act: actinides

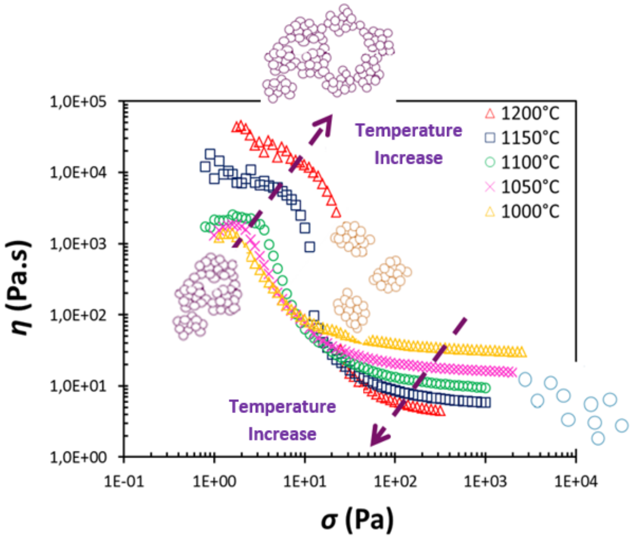
PGM PARTICLES:
Pd-Te **beads** (few µm)
RuO_2 needle shape particles(10-20µm)



- Platinum metal group (PGM) particles are almost insoluble in the glass leading to modifications in the glass properties

PGM particles influence in the rheological behavior

- **The glass with PGM particles has a shear-thinning behavior**



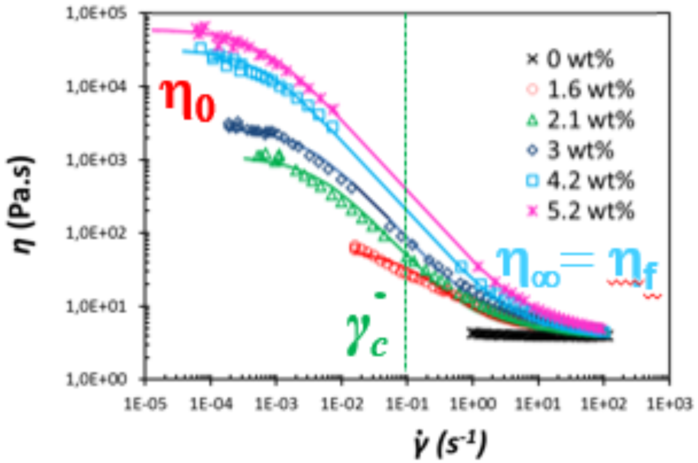
Viscosity of a simulated glass containing 4,2%wt of PGM particles, for different values of temperature, as a function the shear stress

- **Low shear:**
  - Presence of aggregates
  - Aggregate size and viscosity of glass increases with temperature and PGM content

- **High shear:**
  - Stirring destroys aggregates (individual particles)
  - Viscosity of glass decreases with temperature and increases with the content of PGM

C. Hanotin, J. Puig, M. Neyret, P. Marchal, Platinum group metal particles aggregation in nuclear glass melts under the effect of temperature, Journal of Nuclear Materials 477, 2016

Phenomenological modelling



Viscosity of simulated glass containing different PGM content at 1200°C, as a function the shear rate

▶ **Rheological behavior modelling**

- **η=f($\dot{\gamma}$, *T*, $\varphi\downarrow 0$)**
- Main parameters: Shear rate, Temperature, PGM content

Cross Model

Viscosity at **low shear** plateau — Viscosity at **high shear** plateau — Critical Shear Rate

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + \dot{\gamma}/\dot{\gamma}_c}$$

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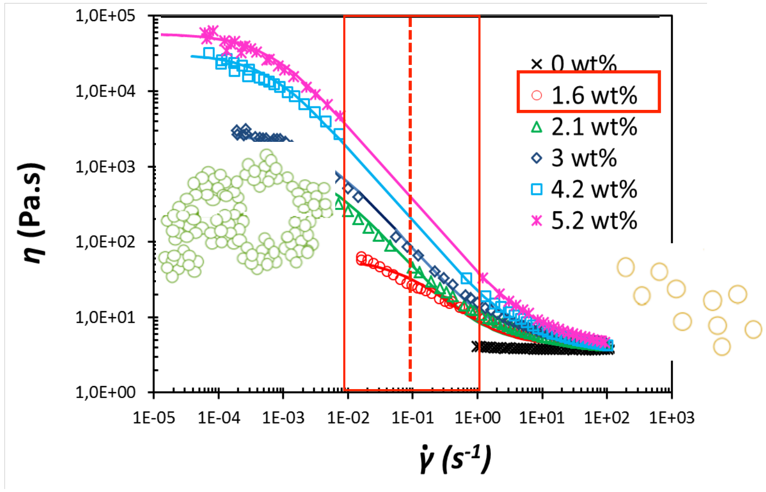
Aggregation Criteria



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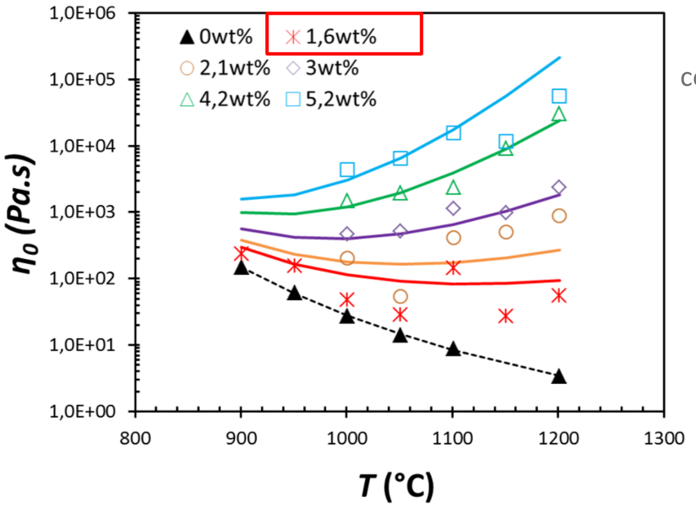

Viscosity of a simulated glass containing different PGM content as a function of temperature

▶ **Aggregation of PGM particles highlighted by rheological measurements for the following criteria:**

1. **Low shear rate: $\dot{\gamma}$ < 0,1 s^{-1}**
   $\eta=\eta_0$ for $\dot{\gamma}$ <10^{-2} s^{-1} = aggregated particles
   $\eta=\eta_{ff}$ for $\dot{\gamma}$ >10 s^{-1} = dispersed particles
   (PGM content 1,6%wt)

2. **Fluid matrix: T> 1100°C**

3. **Higher PGM content: ϕ>1,6wt%**

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Main Goals

1. Consolidation of the rheological model

- **Optimize the model's parameters**
- **Extend** the domain of the proposed model
- Analyze the impact of the **composition of the glass**

2. Proposition of a PGM particles aggregation model

- Establish the **aggregation kinetics** of the PGM particles
- Propose a **model estimating the size of the aggregates**

3. Establish a relation with sedimentation

- Calculate and measure **sedimentation rates** as a function of aggregate size and other influential parameters

Methodology

① Consolidation of the rheological model

- **Improve the rheological measurement protocol**
  - Identify the equipment's limits
  - Characterize the measurement reproducibility
- **Viscosity analyses as function of time**
  - PGM content impact
  - Temperature impact
- **Modeling integrating time**
  - Support on simulation of thixotropic fluids (GEMICO)
- **Testing of new parameters thermo-hydraulic simulation studies of the glass bath**

Methodology

② **Proposition of a PGM particles aggregation model**

A. Glass Approch (high temperature)

- **Development of an experimental protocol**
- **Experimental tests with glass**
- **Mathematical model**

B. Model suspension Approch (lower temperature)

- **Rheological tests on model suspensions → identify a representative suspension**
- **Different characterization tests for concentration analyses at lower temperatures**
  - RMN +Rheo (LEMTA)
  - Laser 3D (Institute de Physique de Nice)
  - Ultrasounds (CEA)

Methodology

③ **Establish a relation with sedimentation**

- Development of an experimental protocol
- Experimental tests with glass
- Mathematical model

Perspectives

Goals				
1. Rheological Model	2.Aggregation model		3. Sedimentation Link	
	Approach A	Approach B		
Measurement protocol consolidation	Measurement protocol consolidation	Identify Model suspension	Measurement protocol consolidation	2019
Tests using PGM glass	Tests using PGM glass	Experimental Tests	Tests using PGM glass	2020
Modelling	Modelling	Modelling	Modelling	
Simulation				2021

Thank you for the attention

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norma.pereiramachado@cea.fr

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