

# Thixotropic behavior of a glass melt containing PGM particles for nuclear interest

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## Abstract

Contrary to some other elements such as Iron, Nickel and Chromium, the Platinum Group Metals particles (PGM) are not incorporated chemically in molten glasses. These particles are generally found in nuclear borosilicate glasses resulting from the melting, at 1200°C, of a glass precursor and fission products issued from spent fuel reprocessing. During the melting step, the presence of these metals as suspended particles of a few microns has an impact on the rheological properties of the material, leading to a Non-Newtonian behavior. Their impact on the process is the object of characterization and modeling of many studies that have established that the melt presents a shear-thinning and thixotropic behavior. At high shear rate, the glass behaves as a suspension of individual particles, whose rheological behavior is controlled by the viscosity of the vitreous matrix. On the other hand, at low shear rate, below a stress threshold, and above a certain volume fraction in PGM particles, the formation of aggregates composed of needle-like Ru/RuO<sub>2</sub> chains and Pd-Rh-Te spherical particles, strongly influences the viscosity of the glass. In this work, a deeper analysis of the thixotropic behavior of a simulated nuclear glass melt containing 3.0 wt% (1.02 vol%) of PGM particles will be presented. Steady and transient state measurements were performed over a wide shear rate range using an imposed-stress rheometer at temperatures ranging from 1100 to 1250 °C. Using Houska model, this work shows that it is possible to predict the transient behavior of the sample from their steady-state rheological behavior.

**Keywords:** Melt, Platinum Group Metals (PGM), Thixotropy, Houska.

## 1 Introduction

In France, pressurized water reactors are in majority operating with Uranium Oxide fuel (UOX). At the end of its cycle in the nuclear reactor, the spent fuel still contains recoverable material, such as uranium (94 to 95%) and plutonium (1%), as well as high-level radioactive non-recyclable waste (4%). After the extraction of uranium and plutonium, the vitrification of the high-level radioactive waste is the standard immobilization treatment [1]. The vitrification consists in melting the nitrates salts of the waste (mostly converted to oxides in the calcination furnace heated at 400°C) and the glass frit in a melter, leading to the production of a complex amorphous material, which has around 40 different elements [2], [3]. Currently, the material is confined in a sodium alumino-borosilicate glass, called R7T7. The vitrification technology is based on the use of induction, in the crucible (hot crucible melter) or directly in the glass (cold crucible melter [1]). The nuclear glass is then poured into metal containers and then stored in wells before their future storage in deep geological formations [4].

During the elaboration at high temperature, most species to be confined react chemically with the vitrification additives to form a homogeneous liquid. Some elements, such as the Platinum Group Metals (PGM: RuO<sub>2</sub>, Pd, Rh) and their oxides, do not chemically incorporate into the nuclear glass melt and in the cast glass [5]. They can be found in the form of spherical alloys of palladium and rhodium with tellurium (1 to 5 μm) and ruthenium oxide in a needle-like form (10 to 20 μm). Even in small amounts (3 %wt), the PGM particles can interfere in the physical properties of the material, such as its viscosity and electrical conductivity [6]. Previous work has shown that they tend to aggregate and settle down, creating layers at the bottom of the crucible that can interfere with the process [7]–[9].

In view of the impact of the PGM particles on the physical properties of the nuclear glass melt, a deeper understanding of these modifications is needed. In particular, the rheological behavior of a fluid can be strongly affected by the particles aggregation kinetics as well as the flow. Nonetheless, the studies on the impact of PGM particles on the rheological behavior of a glass melt are limited due to the experimental difficulties encountered due to the very high temperature required to perform rheological measurements. Despite existing devices designed to operate accurately from room temperature up to a few hundred degrees, apparatus reaching the temperatures needed to study molten glass are still limited [10]. Nonetheless, some studies have shown that the glass melt viscosity is increased by the presence of PGM particles leading to a non-Newtonian behavior [6], [7], [9], [11].

Puig *et al.* designed an innovative device that combines a rheometer with an oven allowing rheological characterization of molten glass containing PGM particles over a broader shear and rate range, exploring the system with different platinum contents and at different temperatures up to 1300 ° C. It enabled the proposition of a new phenomenological model for the rheological behavior of these materials [9], [12], [13]. The model was conceived from rheological measurements of simulated nuclear glass melts containing PGM particles, both in steady-state and transient regime. Figure 1 shows the rheograms from the work of Hanotin *et al.* for a simulated nuclear glass containing 4.2 wt% of PGM particles at different temperatures. They exhibit a shear-thinning behavior and two Newtonian plateaus at low and high shear rates, which were well described by a simplified Cross model  $\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (\dot{\gamma}/\dot{\gamma}_c)^n}$ , where  $\eta_{\infty}$  and  $\eta_0$  are the viscosity at the high and low shear plateaus respectively,  $\dot{\gamma}_c$  is the critical shear rate and  $n=1$  [9].

At low shear rates and above a certain content of PGM particles, macroscopic aggregates appear, made of RuO<sub>2</sub> and Pd-Te chains, separated by thin layers of liquid which strongly increase the viscosity of the systems. In this first case, an increase in temperature lowers the viscosity of the matrix and favors aggregation through Brownian motion leading to an overall increase of the viscosity of the whole system. In contrast, at high shear rates, the system behaves as a suspension of small clusters and individual particles and its viscosity decreases classically by increasing temperature since it is then entirely controlled by the viscosity of the matrix [9].

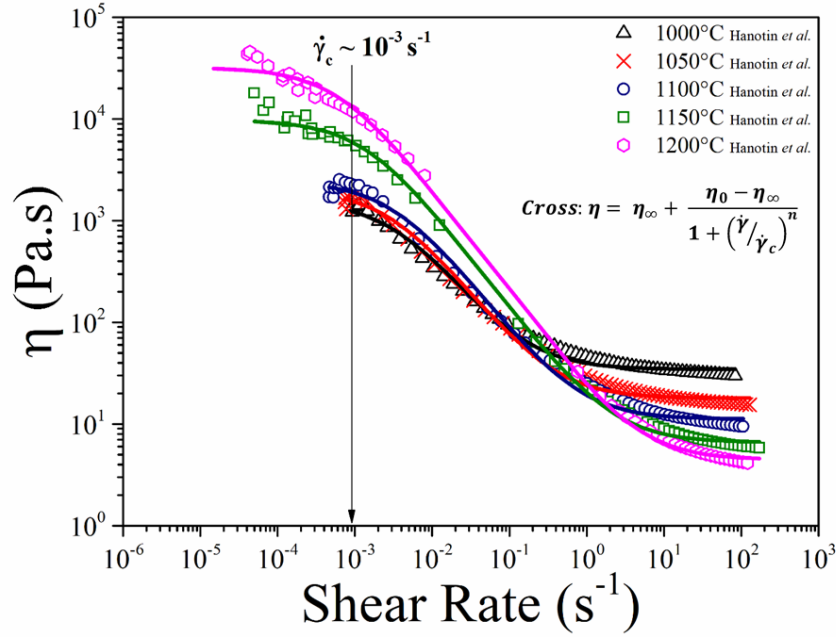


Figure 1 – Results of steady-state viscosity ( $\eta$ ) of a simulated nuclear glass containing 4.2 %wt of PGM particles in function of the shear rate for different temperatures extracted from Hanotin *et al.* [9]. The data were fitted with the simplified Cross model (continuous lines).

The study also showed a thixotropic behavior of the glass melt that increased with the PGM content, associated to the breakage of the aggregates under shear [13]. Differently from the shear thinning behavior, thixotropy is a time-related phenomenon associated with modifications of the internal structure of the material and is commonly observed for many substances. These modifications are generated by the competition of shear destructure and restructuring processes induced by flow and Brownian motion [14], [15]. Thus, experimental difficulties are encountered during the study due to its complexity and the mechanical inertia of the available apparatus which makes difficult to find reliable experimental data on the matter [16]. However, many studies address the mathematical modeling of the thixotropic behavior, being classified according to Mujumdar *et al.* into three categories: the phenomenological approach, the direct microstructure approach and the indirect microstructure approach [17].

In this work, a deep analysis of the thixotropic behavior of a simulated glass melt containing PGM particles is presented. Techniques adapted to the high temperatures are employed in order to characterize the impact of the shear rate, time and temperature on the rheological behavior of the melt. A mathematical modeling of the thixotropic behavior of glass melts containing PGM particles is presented for the first time using the Houska model, which can be viewed as a mesoscopic structural model well suited for the study of thixotropic materials. The adequacy of Houska in explaining and predicting the rheological behavior of the material provides then

an important input for the modeling of the vitrification process. In the following paragraphs, it will be shown that the modeling allows predicting the transient behavior of the samples without additional adjustable parameters than those determined in steady-state regime.

## 2 Materials and Methods

### 2.1 Materials

The borosilicate glass containing PGM particles used in this work was elaborated on a full-scale pilot unit installed at CEA Marcoule [4]. The unit follows the two step calcination-vitrification protocol and was equipped with a cold-crucible melter working at 1200°C.. The chemical composition of this simulated nuclear glass containing 3 wt% of PGM particles is shown in Table 1. The glass was cooled at room temperature and the studied material was extracted from the middle of the canisters. The PGM were presented in the form of needle-like RuO<sub>2</sub> ranging from 10 to 50 μm and the Pd-Te alloys presented in spherical particles with diameter ranging from 1 to 10 μm.

Table 1 - Chemical composition of the simulated nuclear glass samples containing 3 wt% of PGM particles.

Glass 3 wt% PGM									
SiO <sub>2</sub> (wt%)	B <sub>2</sub> O <sub>3</sub> (wt%)	Na <sub>2</sub> O (wt%)	Al <sub>2</sub> O <sub>3</sub> (wt%)	Alkali metal oxides (wt%)	Alkaline earth metal oxides (wt%)	Rare earth oxides (wt%)	RuO <sub>2</sub> (wt%)	Pd (wt%)	Others (wt%)
43.7	13.2	9.2	4.2	3.3	5.0	7.0	1.8	1.2	11.4

### 2.2 Rheological measurement at high temperatures

Due to the high temperatures needed for the characterization of a glass melt, an innovative device conceived in the laboratory [13] was used for all the rheological characterization presented in this work. The equipment, shown in Figure 2 [9], consists of a stress-imposed rheometer (Rheometrics Scientific SR5000) above a tubular furnace that can be heated up to 1500°C. A specific tool designed for this purpose, as indicated in the Figure 2, ensures the transmission of the torque from the rheometer to the crucible without disturbances effects. The characterization cell consists of a platinum-rhodium crucible (27 mm diameter; 40 mm height) located in the center of the furnace. The rotor is composed of a 30 cm long rod with the measurement geometry on the edge. The multiblade geometry chosen for this work allows an uniform distribution of the particles in the glass and prevents their sedimentation [13]. The crucible is filled with the shattered glass and heated to 1200 °C previously to the measurement. From the top to the bottom of the crucible, the temperature gradient is lower than 2 °C.

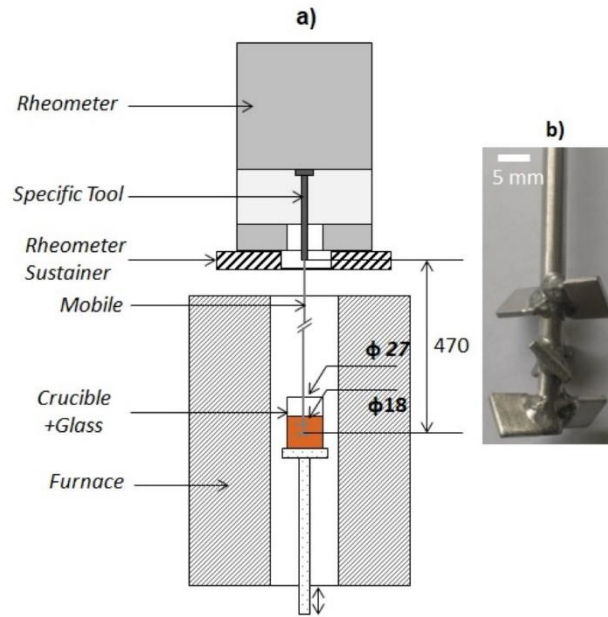


Figure 2 - a) High temperature measurement equipment (dimensions in mm), b) Mobile with a multiblade geometry.

The measured parameters such as torque ( $C$ ) and angular velocity ( $\Omega$ ) are linked to the shear stress ( $\sigma$ ), shear rate ( $\dot{\gamma}$ ), and shear strain ( $\gamma$ ) through geometrical factors  $K_\sigma$  and  $K_\dot{\gamma}$ :

$$\sigma = K_\sigma C$$

$$\dot{\gamma} = K_\dot{\gamma} \Omega$$

To determine  $K_\sigma$  and  $K_\dot{\gamma}$  the mixing device (multiblade + crucible) has been calibrated via a Couette analogy leading to  $K_\sigma = 8.79 \cdot 10^4 \pm 4.10^2 \text{ Pa N}^{-1} \text{ m}^{-1}$  and  $K_\dot{\gamma} = 2.1 \pm 0.01 \text{ rad}^{-1}$  with an annular gap of 4.5 mm [18], [19]. The use of this analogy has shown efficiency in translating the experimental data in the rheological behavior of the materials [20]–[23]. Puig *et al* [13] provided a complete description of the equipment and calibration procedure. The rheological measurements were carried out in steady and transient regime to further investigate the thixotropic behavior occurring in nuclear glass melts. The steady-state measurements were conducted by imposing successive stresses values from 0.5 to 500 Pa during 600 s. Transient step rate measurements were performed on the melt, varying the shear from 0.15 to 100  $\text{s}^{-1}$ . Although the instrument used for the experiments is a stress imposed rheometer, the choice of shear rate transient steps was based on the practicality of the calculation for subsequent application of Houska's equations. The duration of the experiments were chosen accordingly to the time due to the stabilization of the melt viscosity.

All tests above were conducted at four different temperatures: 1100, 1150, 1200 and 1250 °C. A pre-shear was implemented at the beginning and between subsequent tests at 40  $\text{s}^{-1}$  during 60

s to disperse completely the PGM particles in the glass removing memory effects from previous tests. In shear-rate experiments, because of the length of the cane that support the geometry precession phenomena can appear, leading to oscillations of the measurements. Nonetheless, the imprecisions in the measurements occur mainly at low shear regime, therefore under the range the experiments were conducted.

### 3 Structural Modelling

Houska *et al.* established a model for describing the rheological behavior of thixotropic fluids via a scalar parameter  $\lambda$  which allows to capture the structural evolution of the samples through a kinetic equation coupled to a rheological law [24]. The value of this parameter varies between 0 and 1 depending on whether the material is respectively in its most destructured or structured state, depending on the experimental conditions. This model is known for its effectiveness in describing the behavior of different fluids and is also used in fluid mechanics simulation codes [25]. For the glass containing PGM particles, the rheological equation that best described the behavior of the material is the Cross model. This equation is based on the idea of the existence of two Newtonian plateaus: one at low and another at high shear rate. The first Newtonian plateau is reached under very low shear rates, which are difficult to reach when the measurements are made in a shear-imposed mode. Hence, for studies carried at a range higher than the first plateau, the Sisko model becomes suitable as a rheological model since this equation is a simplified version of Cross i.e., includes only the shear-thinning zone and the high shear Newtonian plateau [26]. Sisko model must be adapted to take into account the time dependency of the samples due to their thixotropy. The equation is then modified to include a viscous coefficient that depends on the shear-dependent structure parameter ( $\lambda$ ), as shown in Eq.( 1 ):

$$\eta = \eta_{\infty} + \lambda K_0 \dot{\gamma}^{\alpha-1} \quad (1)$$

$$\frac{d\lambda}{dt} = -k_1 \dot{\gamma} \lambda + k_2 (1 - \lambda) \quad (2)$$

Where  $\eta_{\infty}$  is the plateau viscosity at the high shear rate, i.e. the viscosity at a highly dispersed state considering all critical parameters (shear rate, PGM content, etc). The  $\eta_{\infty}$ ,  $K_0$  and  $\alpha$  are obtained from viscosity measurements. Eq. ( 2 ) shows the equation describing the evolution of the structure parameter as a function of time for a constant temperature. The parameters  $k_1$  and  $k_2$  represent the de-structuring and structuring of the system, respectively. When  $t < 0$ , the imposed shear rate is  $\dot{\gamma}_0$  (the pre-shear imposed to the system) and when  $t > 0$ , the shear is fixed

at  $\dot{\gamma}$ . Based on this, the structure parameter can be calculated as a function of time, as showed in Eq. ( 3 ). The details of the calculus are shown in the annex.

$$\lambda(t) = \left\{ \lambda_0 - \frac{k_2}{\dot{\gamma}k_1 + k_2} \right\} \exp[-(\dot{\gamma}k_1 + k_2)t] + \frac{k_2}{\dot{\gamma}k_1 + k_2} \quad (3)$$

Where  $\lambda_0$  is the structure parameter when  $t = 0$ . Assuming that  $\dot{\gamma}_0$  had been applied long enough at negative times, then  $\lambda$  had reached an equilibrium value. Calculating  $\lambda$  for time tending to infinity, one obtains:

$$\lim_{t \rightarrow +\infty} \lambda = \lambda_\infty = \frac{k_2}{\dot{\gamma}_c k_1 + k_2}, \text{ for } t < 0, \lambda = \frac{k_2}{\dot{\gamma}_0 k_1 + k_2} \quad (4)$$

Hence, the structure parameter at  $t = 0$  has always the same value  $\lambda_0$  that can be defined as:

$$\lambda_0 = \frac{k_2}{\dot{\gamma}_0 k_1 + k_2} \quad (5)$$

Therefore, by replacing  $\lambda_0$  in Eq. ( 3 ), the equation for the structure parameter at  $t > 0$  is:

$$\lambda(t) = \left\{ \frac{k_2}{\dot{\gamma}_0 k_1 + k_2} - \frac{k_2}{\dot{\gamma}k_1 + k_2} \right\} \exp[-(\dot{\gamma}k_1 + k_2)t] + \frac{k_2}{\dot{\gamma}k_1 + k_2} \quad (6)$$

Considering the modified Sisko equation presented earlier and  $K = k_1/k_2$ , the apparent viscosity of the system can be written as follow:

$$\eta(t) = \eta_\infty + \left( \left\{ \frac{1}{\dot{\gamma}_0 K + 1} - \frac{1}{\dot{\gamma}K + 1} \right\} \exp[-k_2(\dot{\gamma}K + 1)t] + \frac{1}{\dot{\gamma}K + 1} \right) K_0 \dot{\gamma}^{\alpha-1} \quad (7)$$

Thanks to steady-state regime measurements on glass melt sample, the model parameters are obtained for each temperature. The structural parameter can be then defined in the studied shear rate range, as will be discussed in the next section.

## 4 Results and Discussion

### 4.1 Fitting model parameters in steady-state regime

Steady-state rheological measurements were made to observe the evolution of the viscosity of a technological glass containing 3.0 wt% of PGM particles with the shear rate at different temperatures (Figure 3). The melt showed a shear thinning behavior, with an abrupt decrease of the viscosity. The increase of the temperature led to a decrease of the viscosity, at the studied shear range. In the high shear flow regime, the viscosity of the matrix induces the disaggregation and the dispersion of the PGM particles in the glass melt. As a consequence, the



viscosity of the sample is mainly controlled by the viscosity of the matrix and decreases by increasing the temperature, contrary to what happens at low shear rate [9]. Previous work with the glass containing PGM particles demonstrated that the rheological behavior could be described by simplified Cross model, represented also by a shear thinning behavior and two Newtonian plateaus (at low and high shear rates) [9], [13].

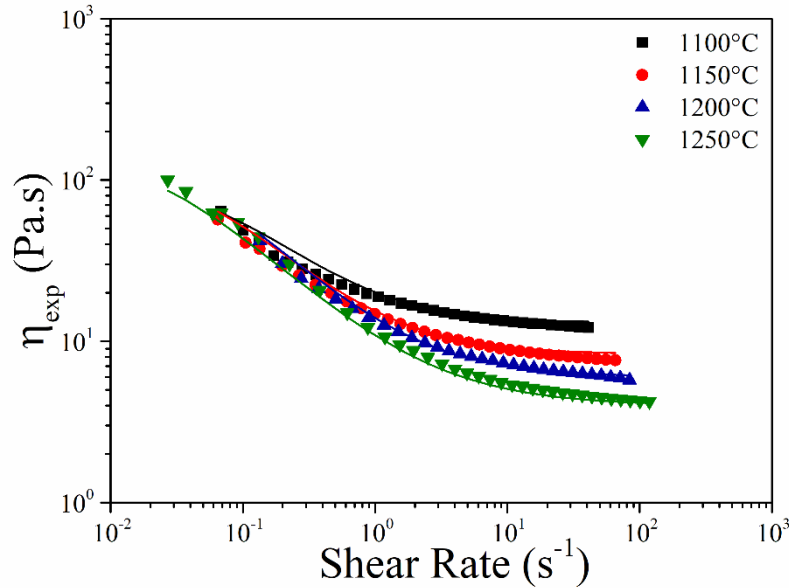


Figure 3 – Evolution of the glass melt containing 3 wt% of PGM particles steady-state viscosity as a function of the shear rate at 1100, 1150, 1200 and 1250 °C. The experimental data was fitted with the modified Sisko model showed in Eq.( 8 ).

In the current study, the experiments were conducted at shear-imposed mode, making it difficult to reach low shear rates. It was not possible to observe the low shear Newtonian plateau. Contrary to the high shear plateau that was present for all studied temperatures. The lack of the first Newtonian plateau implies the use of the modified Sisko model to fit the experimental data. Since the measurements were made in steady-state regime, it is necessary to consider Eq. ( 1 ) for  $\frac{d\lambda}{dt} = 0$ , resulting in:

$$\eta = \eta_{\infty} + \left( \frac{1}{\dot{\gamma}K + 1} \right) K_0 \dot{\gamma}^{\alpha-1} \quad (8)$$

Figure 3 shows that the Sisko modified equation fitted thanks to an ordinary least square method can describe properly the melt behavior at all studied temperatures. Although the four parameters ( $\eta_{\infty}$ ,  $K$ ,  $K_0$  and  $\alpha$ ) for each temperature were obtained in the steady-state regime, they can be used in the Houska model to describe the transient regime of the samples. Table 2 shows the parameters for all studied temperatures.

Table 2 – Parameters of Houska thixotropic model.

Parameters	1100 °C	1150 °C	1200 °C	1250 °C
$\eta_{\infty}$	13	8.0	6.0	4.0
$K$	15	24	35	57
$K_0$	115	177	285	400
$\alpha$	1.05	1.08	1.11	1.18

#### 4.2 Analysis of the model parameters

The temperature has a great impact on the viscosity of the melt containing PGM particles which, depending on the applied shear rate range, can either help the particles aggregation or their dispersion. At low shear rate and high temperature, hydrodynamic forces are low and favor the aggregation of the particles. It tends to increase the viscosity of the suspension even if an increase of temperature tends to decrease the viscosity of the matrix. In the other hand, at high shear rates, the particles are dispersed due to the hydrodynamics forces so the viscosity of the suspension evolves similarly to that of the matrix with temperature. Hence the understanding of the models parameters dependency with the temperature is essential for the study of the thixotropic behavior of the glass melt. Figure 4 shows that all parameters evolve linearly with the temperature. The dotted lines are for visual aid.

In Figure 4a the viscosity at the high shear plateau ( $\eta_{\infty}$ ) for all studied temperatures decreases gradually with the temperature, agreeing with the experimental data showed in Figure 3. As mentioned before, at high shear rate the hydrodynamic forces contributes to the dispersion of the aggregates formed in the glass melt. The increase in the temperature and consequently decrease in the viscosity, leads to a greater dispersion of the PGM particles in the melt. Hanotin *et al.* proposed an equation that describes the evolution of  $\eta_{\infty}$  in function of temperature for PGM glass melts [9]. Due to the non sphericity of the PGM particles, the rotation of the particles leads to the trapping of suspending fluid around them, a feature that can only be considered when the hydrodynamic volume fraction of the particles is take into account. Hence, the Quemadas's model is used to describe the viscosity in high shear flow coupled with the Vogel-Fulcher-Tamann's (VFT) law that represents the behavior of the continuous phase, as follow:

$$\eta_{\infty} = A \left( 1 - \frac{\varphi_0}{\varphi_{meff}} \right)^{-2} \exp \left( \frac{B}{T - T_0} \right) \quad (9)$$

Where  $A$ ,  $B$  and  $T_0$  are dimensional constants,  $\varphi_0$  is the initial volume fraction ( in this case  $\varphi_0= 1,02$  %) and  $\varphi_{meff}$  effective maximum packing fraction. In Figure 4a the experimental data are well fitted by the Eq. ( 9 ) with  $\varphi_{meff}=0.102$ ,  $A=0.008$  Pa.s,  $B = 4977$  °C and  $T_0= 402$  °C. The values obtained may vary slightly from those obtained by Hanotin *et al.* due to the differences that the glass batches may have from one to another. Figure 4b and c shows the increase of  $K_0$  and  $\alpha$  with the temperature, indicating a strong dependency of both parameters with the temperature.

The ratio between  $k_1$  and  $k_2(K)$  is showed in Figure 4d. The increase of  $K$  indicates a strong dependency with the temperature. Although the steady-state measurements reveal their ratio, to predict the material transient state behavior, it is essential to know  $k_1$  and  $k_2$  separately since both are connected to the system structure. The reorganization of the system structure is the result of a balance of the forces acting on the PGM particles and the impact of the matrix fluidity. Thus these changes are intrinsically related to the variation of the rheological behavior of the melt. The critical turning point where the material changes from a linear to non-linear behavior is characterized by a critical shear rate ( $\dot{\gamma}_c$ ) at which the viscosity decreases abruptly. Considering that at this point the Péclet number is close to unit, i.e., the thermo-mechanical competition reaches an equilibrium, the inverse of the critical shear rate can be understood as a mean characteristic time ( $t_c$ ) of reorganization of the structure leading to  $Pe = t_c \dot{\gamma}_c$  where  $t_c = 1/\dot{\gamma}_c$ . Puig *et al.* explored the variation of the critical shear rate for several compositions at 1200°C obtained via the simplified Cross model, as showed in Table 3. The variation of the parameter is of the same order of magnitude for all studied compositions at the same temperature [13]. Figure 1 shows the critical shear rate at which the viscosity abruptly decreases changing the behavior of the melt from Newtonian to shear thinning for the simulated glass containing 4.2 wt% of PGM particles [13]. For all temperatures, the sudden change happens around the same shear range, which can be approximate to  $10^{-3} \text{ s}^{-1}$ , as indicated in the figure, hence for the glass containing 3 wt% of PGM particles this same value can be adopted.

Table 3 – Variation of the critical shear rate ( $\dot{\gamma}_c$ ) for several PGM contents extracted from Puig *et al.* [13].

PGM (wt%)	1.6	2.1	3.0	4.2	5.2
Critical shear rate ( $\dot{\gamma}_c$ )	$1.1 \cdot 10^{-1}$	$5.8 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$	$7.2 \cdot 10^{-4}$	$5.7 \cdot 10^{-4}$

As mentioned earlier  $k_2$  is linked to the structuring of the system and is not influenced by the shear rate as exhibited in Eq. ( 2 ), thus  $k_2$  can be related to  $t_c$ . Therefore,  $k_2$  was considered

as constant for all temperatures and equal to the critical shear rate since  $t_c = 1/\dot{\gamma}_c = 1/k_2$ , where  $k_2 = 10^{-3} \text{ s}^{-1}$  as shown in Figure 4e. Nonetheless, the five parameters ( $\eta_\infty, K_0, \alpha, k_1, k_2$ ) alone are not enough to elucidate the evolution of the particles rearrangement. Hence, the calculation of lambda is essential to have an overall perspective of the structure over time and correlate the dependency of the rheological parameters with the temperature.

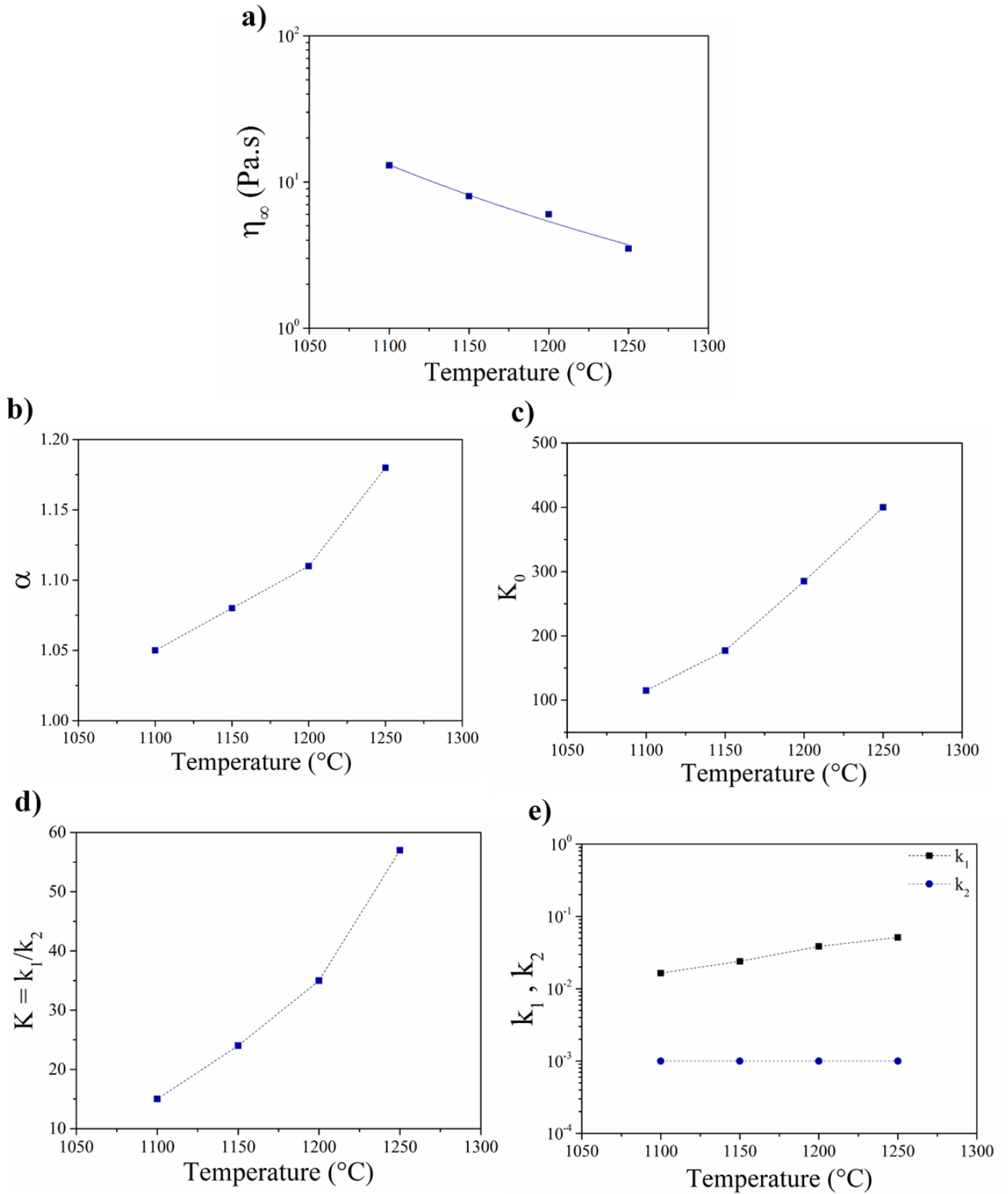


Figure 4 –Houska parameters as a function of the temperature: a) Viscosity at the high shear rate plateau  $\eta_{\infty}$  fitted with Eq. (9), b)  $K_0$ , c)  $\alpha$ , d) Ratio between  $k_1$  and  $k_2$  ( $K$ ) and e) evolution of  $k_1$  and  $k_2$ . The dotted lines are for visual aid.

Figure 5 shows the evolution of the structure parameter over time at a wide shear rate range for all studied temperatures. As mentioned earlier, when  $\lambda$  tends to zero, the structure is in its most

unstructured state, and conversely when it tends to one. For all temperatures,  $\lambda$  increases with time until it reaches a stable value. This behavior characterizes the build-up phenomena common with thixotropic fluids where the structure is rebuilt after an imposed shear rate corresponding to the chosen pre-shear [15]. The PGM particles have the tendency of aggregating at low shear rates due to the weakness of hydrodynamic forces compared to the effects of Brownian motion and attractive van der Waals forces [9]. Hence, the pre shear at a higher shear rate disperses the particles in the melt when the low shear allows the formation of aggregates leading to an increase of the viscosity due to the structuration of the system, followed by its stability when it reaches a maximum point of structuring, given the applied conditions. The graphs in Figure 5 also show that consistently  $\lambda$  decreases with the shear rate. The impact of the shear on the structure parameter is highlighted in Figure 6.

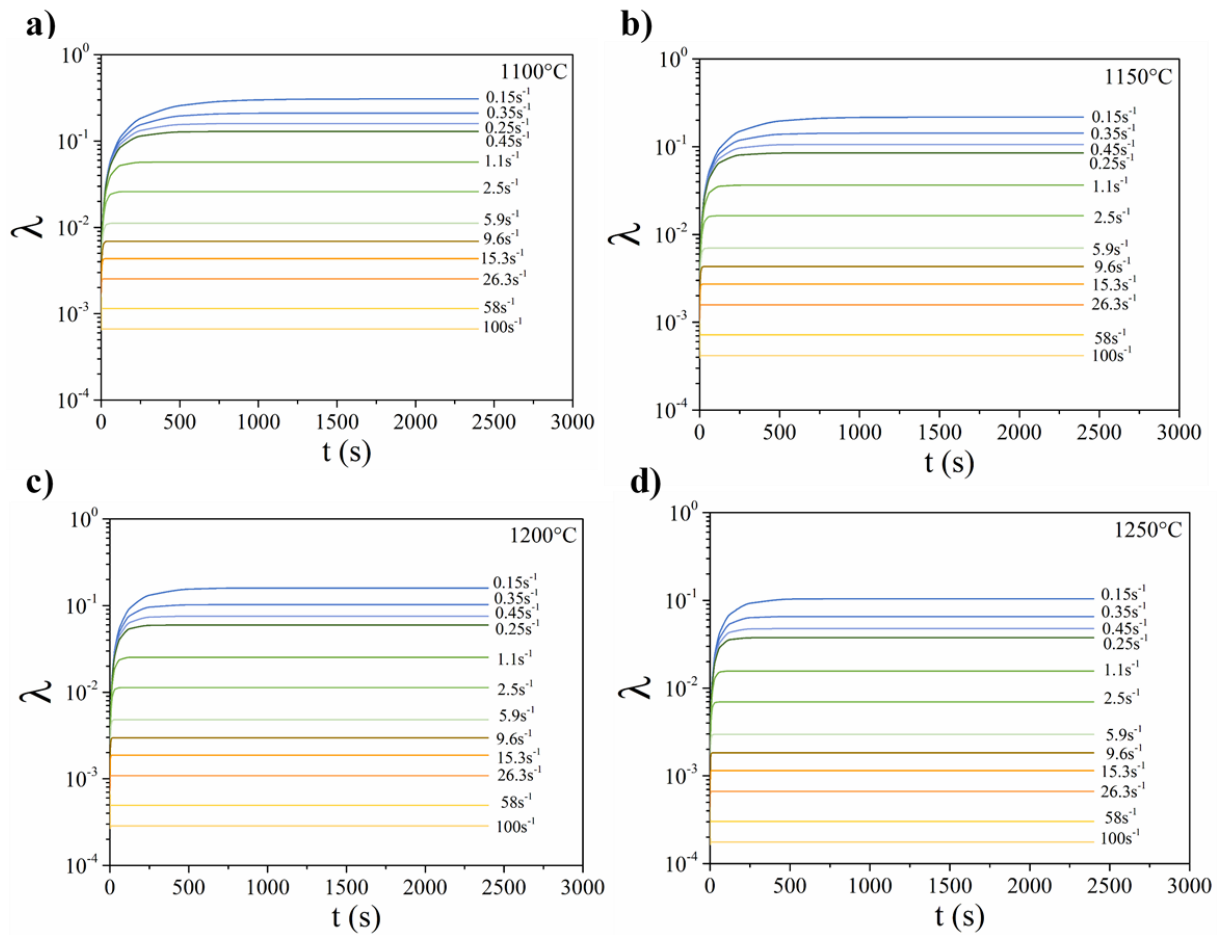


Figure 5 – Calculated  $\lambda$  as a function of time for all studied shear rates at a) 1100 °C, b) 1150 °C, c) 1200 °C and d) 1250 °C.

The evolution of  $\lambda$  as a function of the shear rate at a fixed maximum time ( $t = 2500$  s) was calculated for all temperatures, as shown in Figure 6, using Eq. ( 3 ). If the value of the structural parameter is extrapolated for lower shear rates, it reaches logically a plateau closer to one. At

low shear rate, the formation of clusters is intensified in comparison with high shear. The particle-particle interactions impacting in the PGM aggregation are enhanced at low shear rate [27] helping the clusters formation which causes an increase of the structuration of the system leading to an increase of viscosity for all temperatures. As a consequence, at low shear rate the rheological behavior of the system is controlled by the cluster network which is essentially insensitive to the temperature. So, logically,  $\lambda$  tends to one and is independent of the temperature. In contrast, at high shear rates, the system behaves as a suspension of small clusters and individual particles and its viscosity decreases by increasing temperature since it is then entirely controlled by the viscosity of the matrix. Thus a less structured system is formed with higher temperatures i.e.,  $\lambda$  tends to 0 and depends on the temperature.

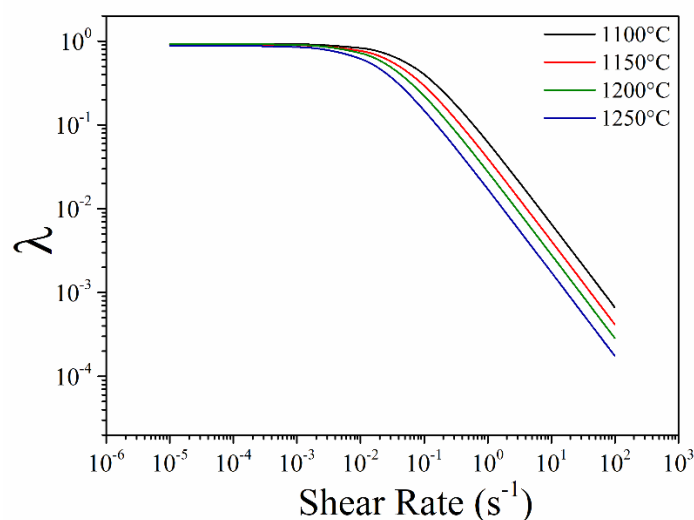


Figure 6 – Evolution of calculated  $\lambda$  with the shear rate for all studied temperatures.

#### 4.3 Prediction of the transient regime – Comparison with experimental results

One of the main difficulties in assessing the thixotropic behavior of a system lies in the experimental difficulties due to the complexity of the phenomena encountered [14], [15]. However, transient experiments are an interesting technique to investigate this behavior since they allow a temporal analysis of the viscosity evolution. Therefore, experimental data in transient regime were also obtained for the PGM glass melt for comparison with the Houska model. Figure 7 shows the experimental evolution of viscosity over time (symbols) for all four studied temperatures at different shear rates. As mentioned earlier, rheological experiments can exhibit artifacts, especially under extreme conditions. The graphs in Figure 7 illustrates these artifacts as fluctuations for low shear rate results (under  $0.35 \text{ s}^{-1}$  for example) at all temperatures. For all experiments, the melt viscosity increases over time until it reaches a stable value. The same phenomenon was observed as an increase of  $\lambda$  over time as shown in Figure 5. The growth

of both parameters ( $\eta$  and  $\lambda$ ) is indicative of the build-up of the suspension. For the experiments where the initial shear rate is smaller than the applied shear rate, the phenomenon is the opposite: the viscosity decreases until it reaches a stable value, corresponding to the breakdown of the structure.

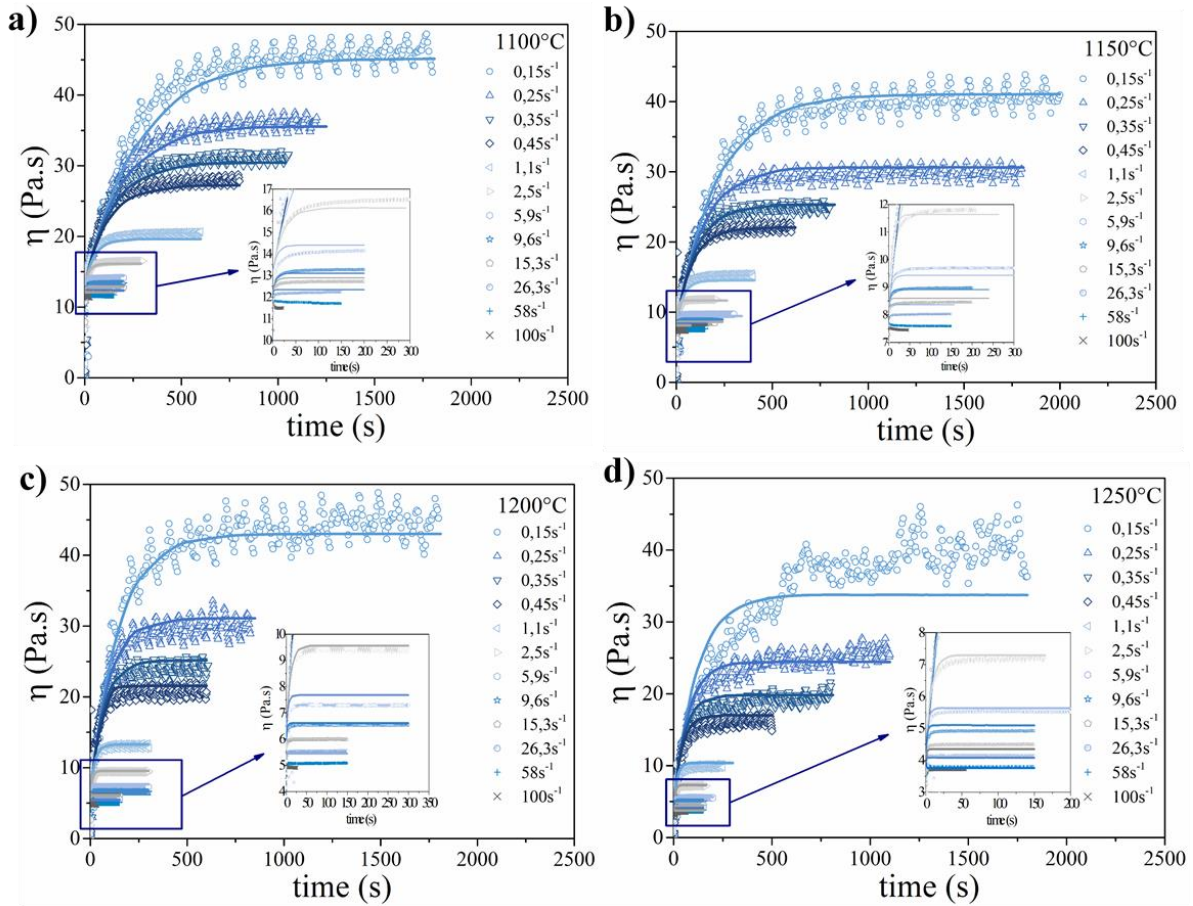


Figure 7 – Evolution of viscosity over time for different values of shear rate, varying from 0.07 s<sup>-1</sup> to 100 s<sup>-1</sup> at all studied temperatures. The lines correspond to the calculated apparent viscosity using Eq. ( 7 ) and the symbols correspond to the experimental data: a) 1100 °C, b) 1150 °C, c) 1200 °C and d) 1250 °C.

Based on the steady-state measurements previously made (Figure 3), important parameters that explain the rheological behavior of the melt were obtained. With these parameters, it was possible to predict the temporal evolution of the sample viscosity in transient regime by applying Eq. ( 7 ) without any additional fitting parameter. The continuous lines in Figure 7 represent the calculated viscosity of the melt for the four studied temperatures. It is worth noting the very close agreement between the prediction of the model, which parameters have been determined in steady-state regime, and the experimental results in transient regime over a very wide range of shear rates (0.15 to 100 s<sup>-1</sup>). The calculated viscosity follows the same behavior observed for the experimental data, increasing over time until it reaches an equilibrium plateau.



The Houska model showed its efficiency not only in describing the steady-state rheological behavior of the glass melt, but also in predicting the thixotropic behavior of the PGM glass in transient regime. Therefore, the proposed model and the associated characteristic parameters allow to describe and quantify with accuracy the thixotropic behavior of the glass melt.

## 5 Conclusions

The thixotropic behavior of a simulated nuclear glass melt containing 3 wt% of PGM particles was studied in this paper. Steady-state and transient measurements were conducted to disclose the rheological profile of the material. The impact of the shear rate, time and temperature on the melt was evaluated using a stress-imposed rheometer, working at high temperatures ranging from 1100 °C to 1250 °C. The initial analysis in the steady-state regime showed a shear thinning behavior of the melt, associated to a decrease of the viscosity with an increase of the temperature. Given the range of shear rate covered in this study, a modified version of the Sisko model proved to be adequate to describe the rheological behavior of the glass melt in the current experimental conditions.

A mathematical modeling of the thixotropic behavior of the system was presented for the first time to describe the rheological behavior of a suspension in a glass melt using the Houska model coupled with a modified Sisko model. The structure parameter  $\lambda$  calculated with the Houska equations allows to quantify at a mesoscopic scale the thixotropic behavior of the samples by numerically describing the structural state of the material. The evolution of  $\lambda$  over time evidenced a build-up phenomenon in the melt where PGM particles aggregates are formed over time due to Brownian motion associated to attractive forces, leading to an increase of the viscosity of the melt, until the material structure reaches an equilibrium. This is particularly evident at low shear rates where the weakness of hydrodynamic forces favors particles aggregation.

The value of the structural parameter was extrapolated at lower shear rates at an equilibrium time ( $t = 2500$  s) for all temperatures. Regardless of the temperature,  $\lambda$  exhibits a plateau close to one corresponding to a fully structured sample. This is consistent with the fact that at low shear rate, the material is more structured than at high shear rate. The temperature plays its part at high shear regime facilitating particles dispersion when the viscosity is decreased, creating a less structured material than at lower temperatures.

The parameters obtained in the steady-state regime were the input for the modelling of the viscosity of the melt. The resulting model, established in steady-state regime is compared with

experimental data obtained in transient regime at all studied temperatures. The model showed to be adequate to predict qualitatively and quantitatively the thixotropic behavior of the PGM glass in the transient regime. It is so, not only descriptive but also explicative and predictive of the rheological behavior of the simulated nuclear glass containing PGM particles. These observations are crucial for the rheological study of the glass melt not only because they are limited in the literature due to the extreme experimental conditions, but also on account of their strong impact on the vitrification process itself and its modeling.

## 6 Acknowledgements

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## 7 Annexes

*Calculation of the structure parameter ( $\lambda$ ) from the Houska model for thixotropic fluids:*

At  $t < 0$ , the fluid is subjected to a shear rate  $\dot{\gamma}_0$ . When  $t = 0$ , the shear abruptly increases to  $\dot{\gamma}$ , where  $\dot{\gamma} > \dot{\gamma}_0$ . The structure parameter can be calculated as a function of time. When solving the Eq. ( 2 ) for  $\dot{\gamma} = \dot{\gamma}_c = \text{constant}$ , the differential equation is then written:

$$\frac{d\lambda}{dt} + (\dot{\gamma}_c k_1 + k_2)\lambda = k_2 \quad (10)$$

Eq. ( 10 ) is a first-order linear ordinary differential equation. Hence, the solution is presented as follows:

$$\lambda(t) = C \exp(-(\dot{\gamma}_c k_1 + k_2)t) + \frac{k_2}{(\dot{\gamma}_c k_1 + k_2)} \quad (11)$$

Where C is an integration constant that can be determined using an initial condition, i.e. when  $t = 0$ .

$$\lambda(0) = C \exp[-(\dot{\gamma}_c k_1 + k_2) \times 0] + \frac{k_2}{\dot{\gamma}_c k_1 + k_2} \quad (12)$$

If we consider  $\lambda_0$  the structure parameter when  $t = 0$ , the calculated integration constant is:

$$C = \lambda_0 - \frac{k_2}{\dot{\gamma}_c k_1 + k_2} \quad (13)$$

Replacing C in Eq. ( 11 ) we have:

$$\lambda(t) = \left\{ \lambda_0 - \frac{k_2}{\dot{\gamma}_c k_1 + k_2} \right\} \exp[-(\dot{\gamma}_c k_1 + k_2)t] + \frac{k_2}{\dot{\gamma}_c k_1 + k_2} \quad (14)$$

When time is positive, i.e.  $t > 0$ , the shear rate is given as  $\dot{\gamma}_c = \dot{\gamma} = \text{constant}$ , so the Eq. ( 14 ) is rewritten as follows:

$$\lambda(t) = \left\{ \lambda_0 - \frac{k_2}{\dot{\gamma}k_1 + k_2} \right\} \exp[-(\dot{\gamma}k_1 + k_2)t] + \frac{k_2}{\dot{\gamma}k_1 + k_2} \quad (3)$$

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