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ScienceDirect

Procedia Materials Science 7 (2014) 156 – 162

Procedia  
Materials Science[www.elsevier.com/locate/procedia](http://www.elsevier.com/locate/procedia)

2nd International Summer School on Nuclear Glass Wasteform: Structure, Properties and Long-Term Behavior, SumGLASS 2013

## Rheological properties of nuclear glass melt containing platinum group metals

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### Abstract

Dispersions of undissolved palladium or ruthenium in nuclear glass can affect the glass flow during the vitrification process. As a consequence, one of the major challenges in nuclear glass elaboration is to understand and control the rheological behavior of glass melts. In this context, this work aims at describing accurately the rheological behavior of glass melts containing platinum group metals to better model the thermal hydraulics in vitrification process. A Searle viscometer has been used to characterize the non-Newtonian behavior of nuclear glass melt containing these noble metals versus temperature and shear rate. Obtained data have been compared to different reference models (Bingham, Ostwald ...) in order to find the appropriate relation describing rheological behavior of nuclear glass melts. The specific role of low shear rates on viscosity measurements has been highlighted. Finally, another investigation under a constant low shear rate has been performed at high temperature during a few hours with the view to clarify this role and the associated physical phenomenon.

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Selection and peer-review under responsibility of the scientific committee of SumGLASS 2013

Keywords: Viscosity; Nuclear glass; Platinum Group Metals; Non-newtonian behavior; Settling.

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### 1. Introduction

In the nuclear field, high level radioactive waste are vitrified into a borosilicate glass at 1100-1200°C. Glasses act as chemical matrixes to immobilize active components for a long time. In order to obtain suitable glasses to this application, it is necessary to control the vitrification process which melts nitrates salts of the waste (converted to oxides at high temperature) and oxides from a borosilicate glass. The nuclear glass formed is a complex material which has around 40 different containing glass precursors. However, in the French glass R7T7, some elements from

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the Platinum Group Metals (PGM) remain insoluble after the vitrification process. These high density particles (rhodium, ruthenium and palladium compounds), settle in the melting crucible and affect physical properties of the glass melt. In particular, the viscosity of R7T7 glass is modified, affecting the vitrification process described by Advocat et al. (2008).

As the "science of flow and deformation of the matter", rheology is a key tool for studying complex fluids, which had been described by Couarraze (2000) and Dupuis (2008). Glasses are amorphous materials which can be considered as a fluid from their melted state to their solid state. When solid particles, like PGM are dispersed in a glass melt, the medium can be considered as a simple suspension. Consequently, the rheological behavior of a nuclear glass melt depends on the concentration, the shape, the size distribution of particles and on the physicochemical interactions between them. These interactions have been recently detailed by Genovese (2012). Although these borosilicate glasses seem to be homogeneous, recent studies on physical and chemical interactions between PGM particles showed that these particles were not randomly distributed in the glass matrix. Using an analog suspension at ambient temperature, it had been determined that a physical mechanism of agglomeration occurred between RuO<sub>2</sub> particles in the melt. Moreover, the influence of the PGM concentration on physical properties (viscosity, electrical conductivity...) in a glass melt was studied by several authors: Krause and Luckscheiter (1991), Simonnet (2004), Grünewald et al. (2008).

Different rheological models have been tested including yield stress models like Bingham model or Ostwald - De Waele power law. Nevertheless, it was impossible to decide on the most suitable model because rheological data are lacking, especially at low shear rate, due to the limited accessible range of the viscometer used, lying between 1s<sup>-1</sup> and 100s<sup>-1</sup>. However, it is important to describe the rheological behavior of the samples in the low and very low shear rate ranges as numerical simulations tend to show that 80% of the melt is sheared below a few s<sup>-1</sup> during the process.

In this paper, the influence of PGM content on the viscosity of inactive nuclear waste glasses (R7T7 French glass) was quantified according to the melting temperature at shear rates ranging from 1s<sup>-1</sup> to 100s<sup>-1</sup>. The 2 PGM used in inactive glasses were ruthenium and palladium. By applying the lowest shear rate available with our viscometer (1.5s<sup>-1</sup> – 2s<sup>-1</sup>), information on viscosities were analysed. In addition, a new experimentation which consists on macroscopic observations and densities measurements has been achieved to describe physical phenomena like sedimentation and agglomeration in a melt under low shear during few hours.

## 2. Experimental

### 2.1 Sample preparation

Materials characterized in this study are 4 glasses with a chemical composition in the R7T7 chemical range. (Appendix A.1.) Samples were nominated using their respective PGM weight content (0%wt, 2.1%wt, 3%wt and 3.5%wt). These borosilicate glasses were made using the full-scale pilot unit installed at CEA Marcoule. Samples of these glasses were taken from the middle of canisters, which had been previously cooled at ambient temperature and cut in several pieces. According to microscopic observations and except PGM particles, glasses appeared homogeneous. Elemental composition of the glasses samples were analysed using X-ray fluorescence. These analyses confirmed that glass samples have a chemical composition similar to theoretical prepared glasses.

### 2.2 Viscosity measurements

Rheological measurements were carried out on a LAMY RM300i viscometer equipped with Searle geometry. A platinum crucible, containing glass samples, was placed in a center of a cylindrical furnace and heated up to high temperatures from 900°C to 1200°C. A platinum cylinder suspended from the viscometer was immersed and rotated in the melt. Shear rate was varied from 1s<sup>-1</sup> to 100s<sup>-1</sup>.

The apparatus was calibrated using a glass of known viscosity (BCL B3959) to ensure accuracy. Homogeneous glass usually behaves as an ideal fluid, following a Newtonian behavior which was described in Couarraze (2000):

$$\eta = T \cdot \dot{\gamma}$$

Where  $\eta$  is the viscosity in Pa.s, T is the shear stress in Pa and  $\dot{\gamma}$  the shear rate in s<sup>-1</sup>.

### 2.3 Dispersion characterization

Finally, in order to evaluate the influence of PGM particles at low shear rate and the associated physical phenomenon, an innovative experiment was realized. A glass sample with 3%wt of PGM particles was stirred under low shear rate at 1200°C during 21.5 hours in a platinum crucible by using the viscometer cylinder. After a quick cooling and an annealing operation at 600°C during 3 hours, a cylindrical piece of glass extracted from the crucible was cut horizontally in several pellets. Slices have been observed at macroscopic and microscopic scale and density of each pellet was measured using a hydrostatic balance. A similar experiment was also carried out on a glass sample with 3%wt of PGM without any stirring at high temperature.

## 3. Results and discussion

### 3.1. Influence of the temperature

Viscosity measurements of the four glass samples were fitted using the Vogel-Fulcher-Tamman equation:

$$\text{Log } \eta = A + B/((T - T_0))$$

Where  $\eta$  is the viscosity in Pa.s, A, B and  $T_0$  are constants and T is the temperature in Kelvin.

Viscosity curves and fitted values are respectively presented in figure 1 and table 1. It can be observed that the viscosity is more affected by the solid particles dispersed in the melt when the temperature increases. Indeed, below 950°C, relative differences in viscosity of the samples are lower than 10% which is close to the instrumental error. At 1200°C, the relative difference between a glass without particles and a glass containing 2.1%wt of PGM attains 17%. This increase is roughly linear up to 3%wt of PGM and is steeper beyond. To check whether this behavior is consistent with that generally observed with suspensions, further investigations are needed with samples containing higher concentrations of PGM.

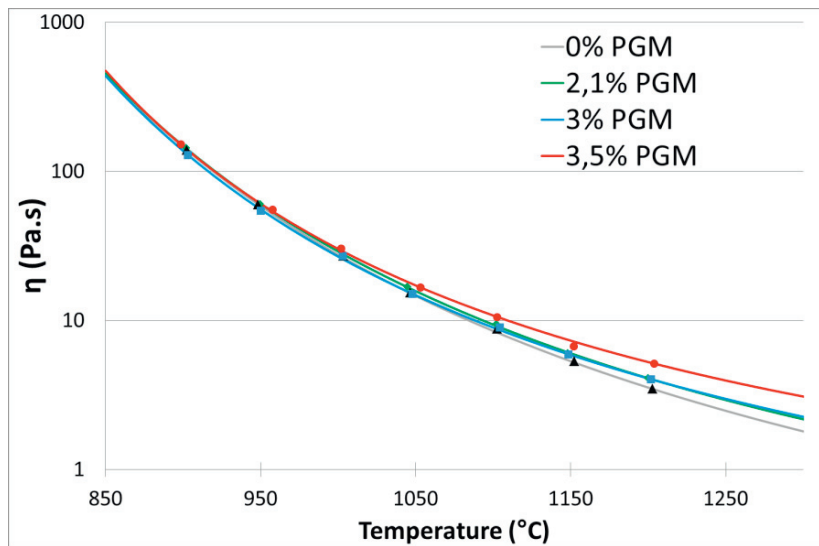


Figure 1: Curves viscosity-temperatures of the sample fitted using the VFT equation.

Table 1: VFT calculated constants values.

| PGM content (%wt) | A      | B    | T <sub>0</sub> |
|-------------------|--------|------|----------------|
| 0                 | -1.042 | 2027 | 418            |
| 2.1               | -0.724 | 1751 | 451            |
| 3                 | -0.468 | 1472 | 492            |
| 3.5               | -0.055 | 1186 | 532            |

### 3.2. Influence of the shear rate at 1200°C

Rheograms in figure 2.a indicate the evolution of the viscosity as a function of the shear rate at 1200°C. For a Newtonian fluid like the glass without PGM particles, viscosity remains constant, independent of the shear rate. However, by adding PGM in a glass, rheological properties are changed: the viscosity increases and becomes dependent on the shear rate, the samples exhibiting a shear thinning behaviour. For instance, the viscosity decreases by a factor 6 between  $1\text{s}^{-1}$  and  $100\text{s}^{-1}$  in the glass containing 3%wt of PGM. Furthermore, for the 3 samples containing PGM, it has been observed that the increase in viscosity due to the presence of particles is more marked at low shear rates than at high shear rates.

By measuring the evolution of the viscosity at a low shear rate during a few minutes (figure 2.b), it has been pointed out that viscosity is not stable in samples with PGM content higher or equal to 3%wt. Next experiments, presented in section 3.4, have been carried out over longer periods of time in an attempt to associate the change in the rheological properties of the samples to a physical structural mechanism, at a microscopic scale.

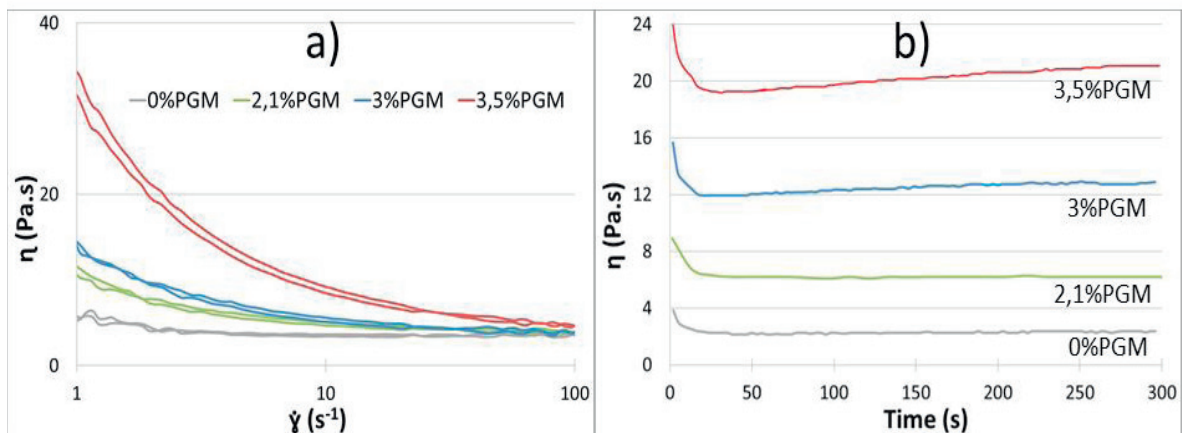


Figure 2 : Rheograms at 1200°C showing the viscosity evolution of the glass samples a) versus shear rate, b) versus time at  $1.5\text{s}^{-1}$ .

### 3.3. Towards a rheological model

Almost all the shear thinning fluids present newtonian regions at high and at low shear rates. These regions were not characterized in this work, because of the instrumental limitations. So, models proposed in this document concern the intermediate region [ $1\text{s}^{-1}$ - $100\text{s}^{-1}$ ].

Four models with two or three parameters (Yield threshold  $T_c$  and/or Index behavior  $n$  and Consistence  $K$  or Plastic viscosity  $\alpha$ ) have been tried to better model the rheological behavior of this region. Results of the fitting with these models for the viscosity data of glass with 3%wt of PGM are presented in table 2. According to correlation coefficients close to 1, all these models could be used to describe rheological behavior of that glass in that shear rate range. Index behavior  $n$  determined by Ostwald and Hershel-Buckley laws were in the range [0.7-0.9], which confirmed the shear-thinning phenomenon. Nonetheless, Bingham and Casson models were also in a good agreement. Therefore, according to those results, it has been proved that more data are needed in a wider shear rate range to determine the most suitable model in order to describe rheological behavior of glasses containing PGM particles. In a first step, data at low shear have been characterized in the next sub-section.

Table 2: Results obtained with the models used to fit viscosity data of the intermediate region [ $1$ - $100\text{s}^{-1}$ ] of the glass with 3%wt of PGM.

| Model                              | Ostwald            | Bingham                        | Hershel-Bulkley             | Casson  |
|------------------------------------|--------------------|--------------------------------|-----------------------------|---|
| Equation                           | $\tau = k\gamma^n$ | $\tau = \tau_c + \alpha\gamma$ | $\tau = \tau_c + k\gamma^n$ | $\sqrt{\tau} = \sqrt{\tau_c} + \sqrt{k}\sqrt{\gamma}$ |
| Yield threshold $T_c$ (Pa.s)       | /                  | 14.4                           | 8.0                         | 3.2   |
| Consistence $K$ or $\alpha$ (Pa.s) | 10.9               | 3.8                            | 5.9                         | 3.1   |
| Index behaviour $n$                | 0.74               | /                              | 0.90                        | /   |
| Correlation Coefficient $R^2$      | 0.991              | 0.996                          | 0.999                       | 0.998   |

### 3.4 Investigations under low shear rate

In order to evaluate the influence of the low shear on the structural change of the glasses, the viscosity of a sample containing 3%wt of PGM has been followed up with time under a constant shear rate of  $2\text{s}^{-1}$ .

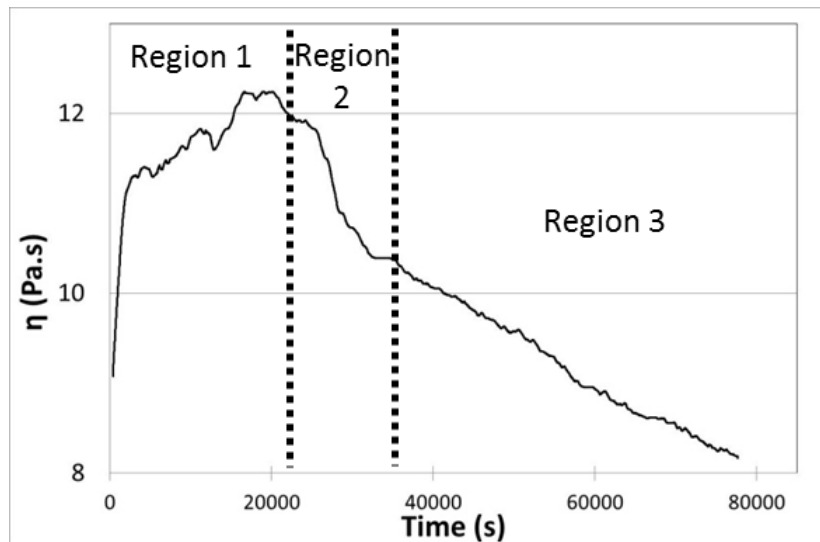


Figure 3: Evolution of the viscosity of glass with 3%wt of PGM particles under a shear rate of  $2\text{s}^{-1}$  as a function of time.

Figure 3 displays the resulting evolution of the viscosity where 3 different zones can be identified:

- The first part of the graph (Region 1) exhibits, at first, an abrupt increase of the viscosity probably due to a homogenization of the sample. Then, one can observe a relative stability of the viscosity which, however, increases continuously probably because of particle aggregation and entanglement of acicular particle of ruthenium dioxide.
- In the second region, the viscosity decreases rapidly. This phenomenon can be attributed to the settling of the particles. It leads to a decrease of the concentration of the suspension in the vicinity of the measuring tool (Searle geometry) and therefore to a decrease of the local viscosity of the sample.
- In the last part of the rheogram (Region 3), the viscosity decreases more slowly since the settling of the particles is hindered by important agglomerates of PGM particles present at the bottom of the crucible. The settling of the remaining particles in the neighborhood of the rotor is slowed down, by steric effect, by the agglomerates.

These interpretations have been strengthened by density measurements and photographs realised on different sections of the samples (see experimental section 2.3).

Photographs of Figure 4 confirm that almost all particles of PGM (black areas) have sediment at the bottom of the crucible at the end of the experiment under a shear rate of  $2\text{s}^{-1}$ . By comparison with the experiment without stirring, the results of Figure 4 clearly show that the phenomenon of sedimentation of PGM particles was accelerated by the shear, at least in the limit of the low shear rates accessible with our viscometer. This difference could be due to an acceleration of the particles aggregation induced by shear, leading to a quicker increase of the size of the aggregates and then to an enhancement of the settling. Of course, the application of a high shear rate would induce a desegregation of the agglomerates leading to opposite effect. That is why this interpretation is valid only within the limits of moderate shear rates.

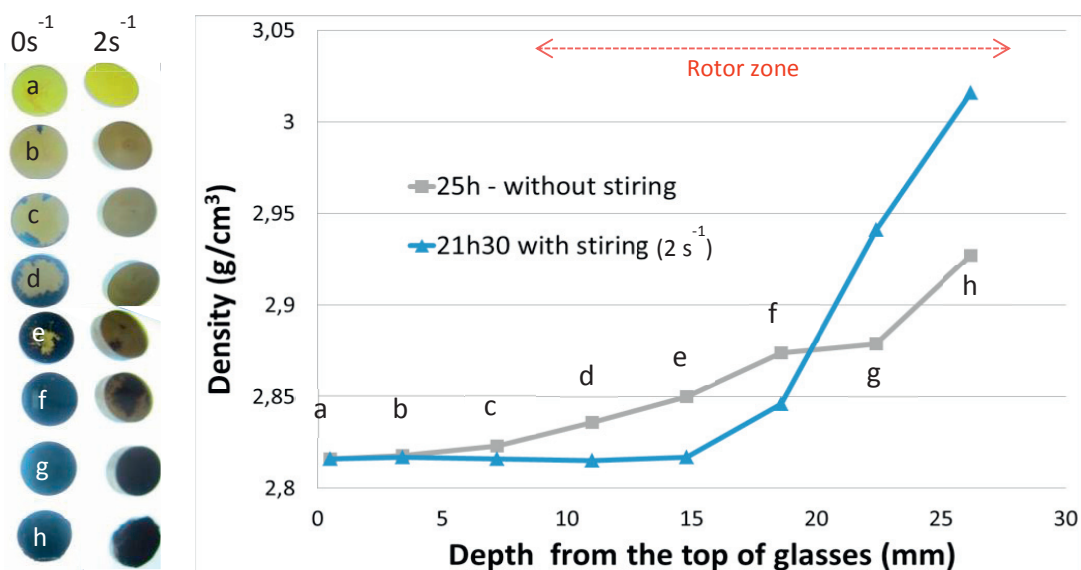


Figure 4: Glasses pellets with 3%<sub>wt</sub> PGM particles cut horizontally after experiments without any stirring during 25 hours and with a low shear rate ( $2\text{s}^{-1}$ ) during 21,5 hours. Density measurements (of the pellets) plotted from the top (a) to the bottom, of glasses (h).

#### 4. Conclusion

The PGM content of nuclear glass melts affects the viscosity, in particular in the studied intermediate shear rate range [ $1-100\text{s}^{-1}$ ]. The lower shear rates used in this study ( $1.5\text{s}^{-1}$  to  $2\text{s}^{-1}$ ) allowed to understand that viscosity evolves as a function of time at high temperature, which will affect the vitrification process. Using a low shear rate, it has been proved that physical mechanisms (like agglomeration) had an accelerating effect on the PGM settling. This effect could be stronger at lower shear rate. Therefore, it could be useful to investigate this range as a great part of the melt is sheared very slowly. Although a rheological model could be proposed in the intermediate shear rate range (Ostwald, Hershel-Bulkley or Casson are in good agreement), data at low shear rate have to be obtained in order to improve the description of the rheological properties of nuclear glass melt.

#### Acknowledgements

Author thanks AREVA for the financial support of this study.

#### Appendix A

##### A.1. Theoretical chemical compositions of the 4 glasses used in this study

| Oxides                         | 0%PGM theoretical glass (%wt) | 2,1%PGM theoretical glass (%wt) | 3%PGM theoretical glass (%wt) | 3,5%PGM theoretical glass (%wt) |
|--------------------------------|-------------------------------|---------------------------------|-------------------------------|---------------------------------|
| SiO <sub>2</sub>               | 45.1                          | 44.4                            | 43.7                          | 43.2                            |
| B <sub>2</sub> O <sub>3</sub>  | 13.9                          | 13.3                            | 13.2                          | 13.3                            |
| Na <sub>2</sub> O              | 10.2                          | 9.2                             | 9.2                           | 9.8                             |
| Al <sub>2</sub> O <sub>3</sub> | 4.8                           | 4.2                             | 4.2                           | 5.0                             |
| ZnO                            | 2.5                           | 2.4                             | 2.3                           | 2.4                             |
| CaO                            | 4.0                           | 3.8                             | 3.8                           | 3.8                             |
| ZrO <sub>2</sub>               | 3.0                           | 2.8                             | 2.8                           | 2.9                             |
| Rare-earth oxides              | 6.9                           | 6.2                             | 6.2                           | 6.2                             |
| MoO <sub>3</sub>               | 2.4                           | 2.2                             | 2.2                           | 3.2                             |
| RuO <sub>2</sub>               | 0                             | 1.3                             | 1.8                           | 2.3                             |
| Pd                             | 0                             | 0.8                             | 1.2                           | 1.2                             |
| Others                         | 7.2                           | 9.4                             | 9.4                           | 6.8                             |
| Total                          | 100.0                         | 100.0                           | 100.0                         | 100.0                           |

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