

**Cold crucible for HLW vitrification: Advances in the Feed and Platinum Group Metals (PGM) behavior modelling**

E. Sauvage\*, Z. Nabyl\* and P. Brun\*

\* CEA, DES, ISEC, DE2D, Univ Montpellier, Marcoule, France

**ABSTRACT**

A cold crucible induction melter is in operation in La Hague plant, which is operated by ORANO since 2010 for the vitrification of HLW arising from dismantling and decommissioning (D&D) operation and legacy reprocessing of high Molybdenum content fuel. The well-known advantages of the cold crucible compared to the hot metallic inductive melter are (i) a higher elaboration temperature (ii) an extended lifetime and (iii) a better homogeneity obtained by mechanical stirring and gas bubbling. As a result, the global production capacity is expected to be higher as well as the Platinum Group Metals (PGM) concentration in the glass.

During the melting, the glass generally shows a homogeneous liquid phase seeded with non-soluble heavy platinum-group-metal particles mainly made of rhodium, palladium and ruthenium dioxide. Previous studies reported spatial discrepancies of the local volume fraction of particles in the melt because of particles settling with time. This migration of particles towards less agitated bottom parts of the crucible affects the dynamical, electrical and thermal state of the melt because of the concentration-dependent electrical conductivity and viscosity of the suspension. A theoretical one-fluid transport model was developed with the help of small-scale experiments carried out with a HLW glass simulant. The model is coupled with existing 3D thermo-hydraulic numerical codes, thus enhancing the precision of heat flux predictions between the melt and the crucible.

The feed modelling is also under development. From vitreous precursors (Sodium alumino-borosilicate glass frit) and calcined waste (a mixture of about thirty oxides and nitrates compounds obtained after calcination step), a succession of processes such as impregnation, denitration, crystallization and dissolution occur to solubilize the waste into the vitreous network. Mainly focus on thermal and chemical (0D models) approaches the objective is to connect the reaction kinetics laws of thermally activated processes (denitration, crystallization, dissolution) to the magneto-thermo-hydraulic model to model both physics and chemistry of glass synthesis. The experimental methodology based on the characterization of thermo-activated reaction kinetics by differential and gravimetric thermal analysis (TGA/DTA) and the kinetic parameters identification (such as activation energy, reaction order, pre-exponential factor) is described. Moreover, an example of simulation integrating the chemical equation solved with CFD tools is presented and discussed.

**INTRODUCTION**

Vitrification is used in France to provide long-term containment of HLW) from the reprocessing of spent nuclear fuel. Vitrification is an atomic-scale incorporation of HLW into a glass. After melting and homogenization, the nuclear glass is poured into metal canisters that should be stored underground in a deep geological repository. In France, the technology used for vitrification has been based on induction melting for 40 years. This technology enables high power, low gassing and high cooling/heating rates. The induction furnaces were developed at CEA Marcoule on an inactive full-scale pilot plant.

**FRENCH RADIOACTIVE WASTE VITRIFICATION TECHNOLOGY PRESENTATION**

The overall process used for the vitrification of HLWs is a continuous process consisting of two steps: (i) the HLWs calcination in a rotating tube heated up to 400°C and (ii) the melting in furnaces in which the waste is mixed at high temperature (>1100°C) with glass frit. All gases emitted during the process are treated in-line with a dedicated off-gas treatment system including dust separator, condenser and scrubbing

columns. The vitrification furnace can be of two types: (i) an Inductive Hot Metallic Melter (IHMM) or (ii) a Cold Crucible Inductive Melter (CCIM). In the Orano's plant in La Hague (Normandy) commissioned in 1989, there are six production lines. Five are equipped with an IHMM and one with a CCIM since 2010. The CCIM, thanks to its cooled walls, can reach a higher maximum glass temperature, leading to a higher maximum glass throughput.

The main principles of CCIM are to heat the glass by direct electromagnetic induction despite the moderate electrical conductivity value of the molten glass, the crucible itself is cooled by an internal water cooling system. Therefore, there is a thin layer of solidified cold glass between the hot glass and the crucible preventing any corrosion. The molten glass is mechanically agitated with a rotary agitator and further surface homogenization is achieved with an air bubbling system.

Since 2010, the CCIM, located in the La Hague reprocessing plant, has produced three different nuclear glasses corresponding to three types of HLW:

- CSD-B canisters: intermediate level waste borosilicate glass for the vitrification of corrosive solutions from D&D operation.
- CSD-U canisters: high-level waste glass-ceramic for the vitrification of legacy highly corrosive UMo fission products from reprocessing of U-Mo-Sn-Al spent fuel.
- CSD-V canisters (R7T7 glass) High-level waste borosilicate glass for the vitrification of UOx fission products (ongoing PWR reprocessing activities).

The production of the CSD-U canisters is fully completed; see more details in [1]. For the CSD-V canisters, a test period of industrial production has begun last year. One thousand one hundred glass canisters have been produced with the CCIM so far.

The CEA mission is to give an industrial support to Orano La Hague plant, perform R&D and design of more efficient crucibles for future nuclear waste. Modelling and simulating the full vitrification process is a very efficient way to reach these objectives [2]. The rest of this paper is dedicated to present the last numerical simulation development in the field of the Platinum Group Metals particles simulation and the modelisation of the furnace feeding step.

## PLATINUM GROUP METALS (PGM) PARTICLES IN NUMERICAL SIMULATION

In the nuclear glass, noble metals particles are present at different concentrations depending on the waste type from 0.1%w to 3%w. They consist mainly of Ruthenium dioxide needles and Palladium-Rhodium spheres with typical size of few microns. These particles have a strong impact on the vitrification process through their influence on the glass physical properties, mainly: viscosity, density and electrical conductivity. Regarding viscosity, the PGM induced a non-newtonian behavior of the glass. Recent study shows and quantify a thixotropic behavior of the glass, which is a time dependency of the viscosity with the shear stress [3]. These phenomena will not be further detailed in this proceeding; we will focus on density and electrical conductivity.

### Sedimentation Modelling of Noble Metal Particles in the Glass during Vitrification

The particles sedimentation in the glass is considered with two types of models. The first is a one-phase Eulerian model, which was developed for individual sedimentation phenomenon. The local concentration of C particles is calculated with the following equation:

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

with  $\tau$  the Stokes terminal velocity ( $\sim 1$ mm/s),  $\alpha = 4,65$  the hindering exposure,  $\kappa$  hydrodynamic diffusivity and  $C_a$  the maximum concentration. Parameter values were identified from specific settling experiments in hot glass at rest. The Stokes terminal velocity value is very low due to the small particle size and high glass viscosity. Consequently, the particles individual sedimentation is almost non-existent at the process scale and characteristic time. The second type of sedimentation is what is called "cloud settling". It is simply modeled by a dependence of the glass density with the particle concentration:

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

with  $\rho_f$  the density of glass without particle and  $\beta_p = \frac{\rho_p}{\rho_f} - 1 \approx 2,1$ . This second effect takes place in the case where specific areas enriched with particles are present. Rayleigh-Taylor instabilities lead to a high sedimentation rate of the entire enriched zone.

Both models are used in full process simulation to predict industrial scale sedimentation.

### Noble Metal Particles Effect on Electrical Conductivity of the Glass

As the particles tend to settle in the hot glass, in-situ measurement of electrical conductivity at high temperature is very difficult. To circumvent this problem, an inactive glass sample with a uniform particle distribution was sent for X-ray micro-tomography to the European Synchrotron Radiation Facility (ESRF, ID19). Three-dimensional data of particle shape and distribution were obtained with a spatial resolution of 0.16 microns. Electrical conduction simulations were performed on subdomains of the complete dataset with low conductivity value assigned for glass ( $10^0 \Omega^{-1}m^{-1}$ ) and high conductivity for particles ( $10^6 \Omega^{-1}m^{-1}$ ). More than 200 calculation boxes on the real shape of 3D particles in glass have been defined. The range of particulate volume concentrations is [0;20]%v.

Figure 1 shows on the left a view of a calculation box. The particles are in gray. On the right of Figure 1, the effective conductivity is plotted against the particle concentration. The shape of the result is a typical percolation curve. For a low concentration, the effective conductivity increases slowly up to a specific concentration, the percolation concentration ( $C_p$ ) at which the conductivity increases by three orders of magnitude. This concentration corresponds to when a continuous path of particles is present in the glass between the two virtual electrodes. This percolation concentration is about 5.5%v, a fairly low value, explained by the needle shape of  $RuO_2$ . However, in the vitrification process, the maximum concentration of particles is 3%w corresponding to 0.8%v quite far from the percolation threshold. Nevertheless, certain operating conditions could lead to locally concentrating the particles and reaching the threshold. At this time, the Joule-heated glass process may have trouble dissipating enough power into the glass.

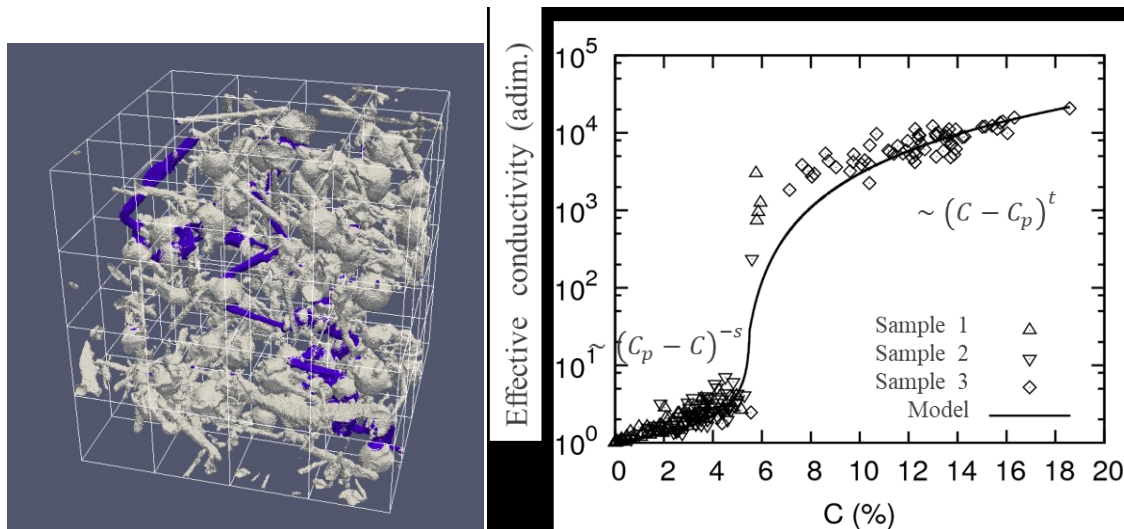


Fig. 1. On the left, 3D micro-tomography X-ray data of an inactive glass, the metal particles are in grey. The box is  $40 \times 40 \times 40 \mu m^3$ . The blue color shows current flowing in a continuous path of particles between the top and bottom of the box. On the right, the percolation curve of the effective conductivity obtained with 200 calculation cells.

A continuous mathematical law, giving the glass electrical conductivity as a function of the particle concentration has been identified. This law is used in full-scale, industrial simulation to predict the effects of particle concentration on process electrical parameters.

### FEEDING MODELLING

The modeling work of the chemical reactions occurring in the “cold cap” began with the thesis work of K. Paraiso [4]. The objective was to add to the existing simulations [2], a modeling of the chemical aspects involved during the nuclear glass synthesis, in particular during the supply of glass frit and calcine.

In this perspective, a kinetic modeling of the reaction mechanism was sought, based on thermal analysis data according to a methodology developed by the PNNL-DOE teams [5]. Different measurements on TGA and DSC are carried out at different heating rates, from 10 to 40°C/min on an initial mixture of glass frit and calcine. The RUN re-RUN method identifies chemical reactions as the sum of four overlapping thermally activated reactions. Fig. 2 shows the Kissinger plot of the four reactions peak and the modelling of the reaction rate at 30°C/min with the four reactions.

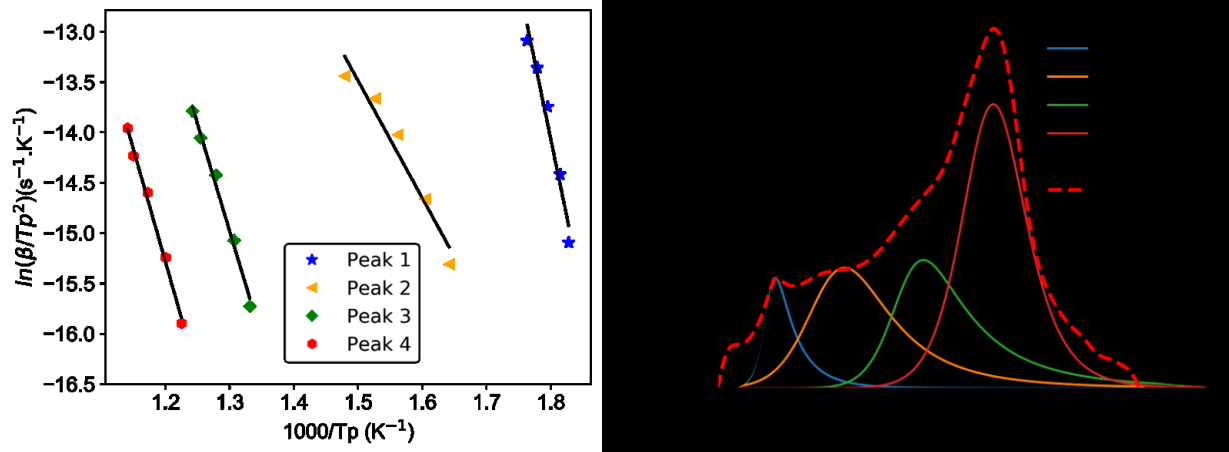


Fig. 2. Reaction rate of chemical reactions taking place when heating a glass frit and calcine mixture calculated from TGA measurement. Four overlapping reactions were identified.

Mathematical equation of the  $n^{\text{th}}$  order chemical kinetics equation is:

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

with  $w_i$  the weight coefficient as  $\sum_{i=1}^4 w_i = 1$ ,  $E_i$  activation energy,  $n_i$  reaction order and  $A_i$  pre-exponential factor.

This equation is generalized by adding advection and diffusion terms. Then, it is solved in computational fluid dynamics software (Ansys-Fluent). For validation purposes, a confrontation between the experiments and the numerical result is carried out on mock-up scale. The glass is melted in a one-liter platinum crucible with mechanical stirring to be representative of the industrial process. Once the temperature has stabilized at 1200°C, 10 g of glass precursors are added to the glass free surface. The temperature measurement shows a drop of 10°C during the time that all the precursors melt and homogenize. Illustrations of the experiments are shown in Figure 3.

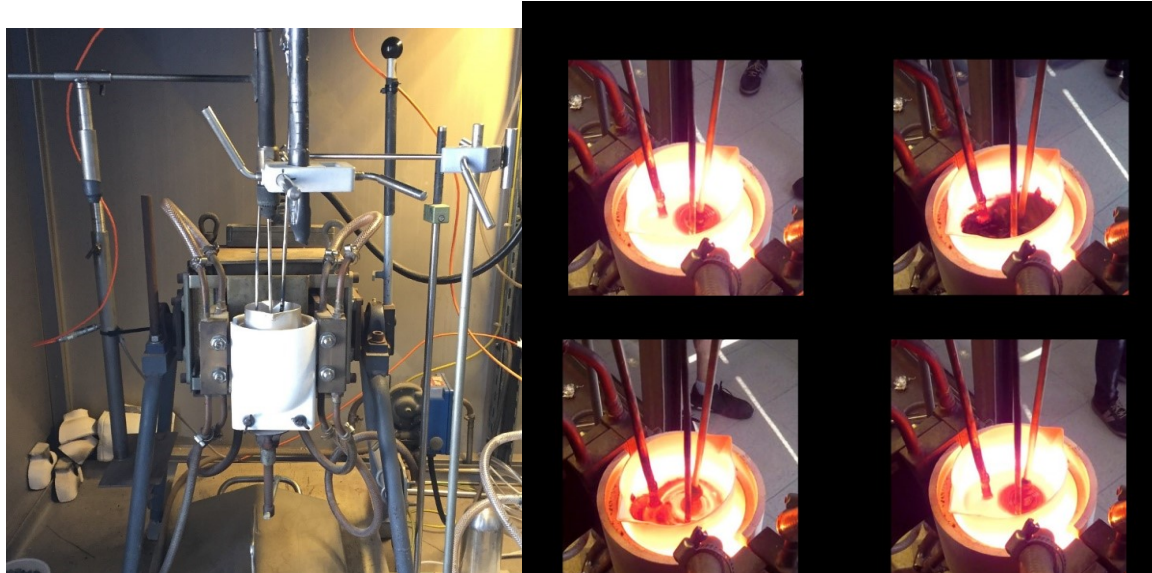


Fig. 3. Overview of the mock-up: platinum crucible (~one liter) heated by Joule effect - Stirrer - Thermocouples, on the right, photos of the reactive surface before and after adding 10g of glass precursor to the surface.

The simulation of the entire model is carried out with Ansys-Fluent. The temperature field results from Joule heating in the platinum and heat losses at the side of the crucible and at the free surface. Fig. 4 shows the initial temperature field in glass and platinum. Raw, cold material is added to the free surface in the simulation. The chemical reactions kinetics are solved at the same time as the fluid flow. The temperature drop measured with a thermocouple in the experiment is comparable to that calculated. The 10 g of glass precursors have an influence on the temperature distribution in the glass for about three minutes.

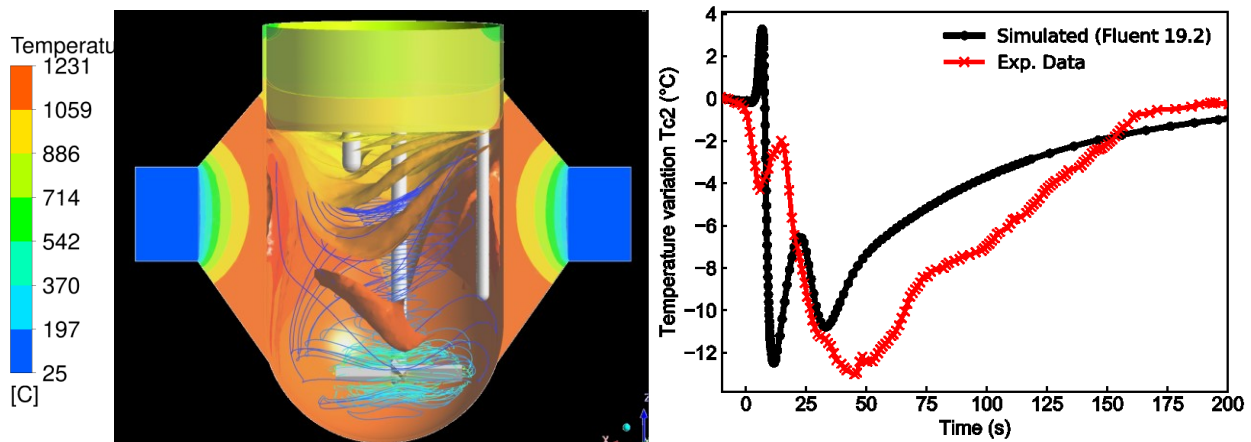


Fig. 4. Temperature field on the platinum crucible and in the glass (left) and temperature drop after addition of glass precursors to the surface at  $t=0s$  (right). Numerical and experimental temperatures are plotted.

## CONCLUSION

CCIM, developed at CEA Marcoule, has been in operation at the La Hague plant since 2010. Production test campaigns for UOx glass containing particles of PGM up to 3%w, started. Numerical simulation has helped the development and optimization of the CCIM, particularly in its latest upgrade on (i) the phenomenon of sedimentation risk (individual and cloud settling) and (ii) the chemical reactions taking place at the glass surface. The modeling of the kinetics is coupled with the fluid flow resolution and the

thermal field. The reaction time in the process could be quantified.

#### **REFERENCES**

- [1] Renaut, C., Leveel, É., Chanu, T., Darvey, F., Renouf, S., & Charles, M. (2020). Orano achève la vitrification des solutions de produits de fission des combustibles UNGG. *Revue Générale Nucléaire*, (5), 50-53.
- [2] G. Barba Rossa, Modélisation multiphysique de l'élaboration de verre en creuset froid, Thèse de doctorat, Université de Grenoble Alpes, 2017.
- [3] 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. 153618. 10.1016.
- [4] Paraiso, K., Sauvage, E., Schuller, S., Hocine, S., Lemaitre, V., & Burov, E. (2022). Characterization and modeling of chemical reactions taking place during the vitrification of high level nuclear waste. *Journal of Nuclear Materials*, 569, 153878
- [5] J. Chun, D. Pierce, R. Pokorny and P. Hrma : Cold-cap reactions in vitrification of nuclear waste glass, *Thermochimica Acta*, 559 (2013) 32-39

#### **ACKNOWLEDGEMENTS**

The authors thank CEA, EDF and ORANO for their financial support.