Incorporation of Noble Metals in High-Level Waste Borosilicate Glass: Focus on Vitrification Process Developments – 14067

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ABSTRACT

Ruthenium, palladium and rhodium, which belong to noble metals group (NM), are fission products in high-level waste (HLW) resulting from reprocessing of nuclear spent fuel. All HLW vitrification facilities have experienced operational problems that can be related to the presence of NM in the melter. These metals, and their alloys and compounds, have very low solubility in glass and modify the glass properties such as viscosity or electrical conductivity. These dense metals also tend to settle to the bottom of the melter. Whatever the melting process, the specific properties and behavior of NM could decrease the process throughput and increase the melter downtime.

To avoid these problems CEA and AREVA have studied behavior of NM in borosilicate glass over the years. Several technological improvements such as multiple bubbling and mechanical stirring have been implemented on the Hot Crucible Melter (HCM) following R&D studies in order to increase throughput and NM content in glass. The behavior of NM was taken into account in the design of the new Cold Crucible Induction Melter (CCIM). As a consequence, the CCIM should be able to increase glass throughput with the same NM content as the HCM.

INTRODUCTION

All high-level waste vitrification facilities have experienced operational problems arising from the presence of noble metals in the melter, related to their specific properties and behavior in the glass.

Ruthenium, palladium and rhodium, which belong to noble metals group(NM), are fission products in high-level waste (HLW) resulting from reprocessing of nuclear spent fuel. Most of the high-level waste in France arises from reprocessing UOX fuel containing a significant proportion of NM in relation with their burnup.

At the La Hague plant in France, noble metals in solution enter the vitrification units in two separate flow streams: fission products and fines. Shearing and fuel dissolution result in a nitric acid solution containing the uranium, plutonium, and fission products. This solution contains small, solid particles composed of Zr, Mo and noble metals (Ru, Pd, Rh). These small particles, known as “fines”, are then separated from the dissolution solution by centrifugation and constitute the fines solution. The fission products solution is obtained after separation of the uranium and plutonium.

The French vitrification process includes two steps: calcining of the waste solutions, followed by melting of the glass. It is a semi-batch process in which frit (containing glass precursors) and calcine (containing the fission products) are continuously supplied to the molten glass, which is periodically poured into canisters. As the glass melter technologies developed by the CEA and operated commercially by AREVA have not modified the overall process flowsheet, this article focuses only on the melting step. The glass melter technologies discussed here were developed to process HLW from UOX fuel. Their high noble metals content was therefore one of the criteria taken into account in developing the vitrification process, in particular for thermal hydraulic modeling of the glass melt.

The behavior of NM in borosilicate glass is first briefly described, before reviewing the R&D studies carried out in a full-scale inactive pilot with a Hot Crucible Melter (HCM). The paper then shows how innovative R&D solutions and their implementation in the La Hague reprocessing plant have contributed to increase the performance of the HCM. Finally, the capability of the Cold Crucible Induction Melter (CCIM) to vitrify the UOX fission products waste is discussed, with the results of R&D tests on a full-scale inactive pilot.

NOBLE METALS IN GLASS

This article concerns borosilicate glasses simulating the active glasses produced in the R7 and T7 units of the La Hague plant. The chemical composition of R7T7 glass is indicated in Table I.

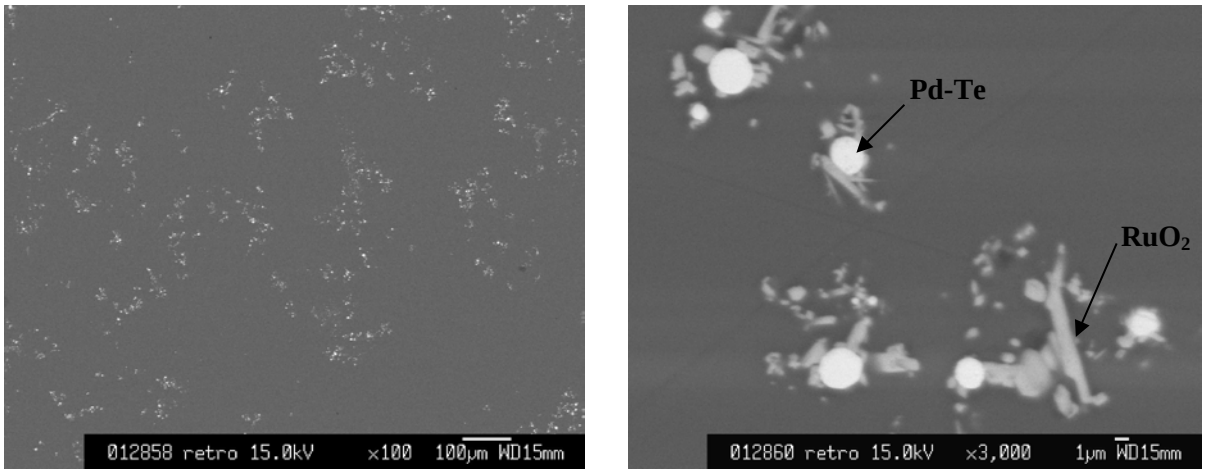
Table I. R7T7 glass composition domain

	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* + NM + ZrO_2	4.2	18.5
RuO_2 + Pd + Rh	0	3.0

*FP: Fission Products; Act: actinides

In the inactive glass, rhodium is simulated by palladium. The noble metals used for R&D studies are therefore limited to ruthenium and palladium.

The microstructure of this glass is well known [1; 4]. Microstructural analysis of the glass by Scanning Electron Microscopy (SEM, Fig. 1) shows a homogenous black opaque vitreous matrix, with a microstructure including a regular distribution of microscopic platinoids: the RuO_2 phase is present as acicular particles of about 10 µm, and metallic Pd-Te alloys as beads a few micrometers in diameter.



SEM image ×100 SEM image×3000

Fig. 1. SEM images of UOX glass microstructure [1]

Most of the physical properties of the glass are modified by the presence of noble metals. Its rheological behavior in particular is strongly influenced by their presence [2]. Molten R7T7 glass without NM exhibits Newtonian behavior: its viscosity is constant regardless of the shear rate. When NM are present, it becomes a shear thinning fluid: its viscosity increases when the shear rate diminishes (Fig. 2).

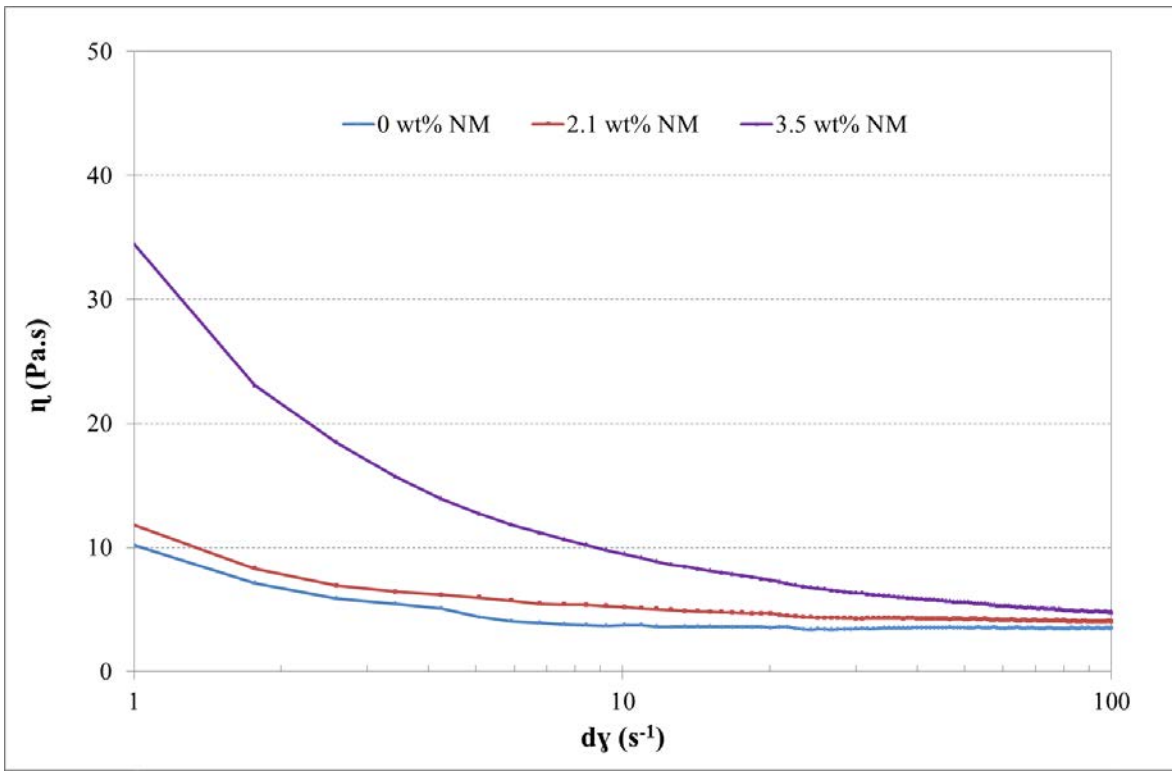


Fig. 2. Viscosity versus shear rate of R7T7 glass containing different NM concentrations (1200°C)

At high shear rates (above 30 s-1), the viscosity is also observed to increase with the NM content (Fig. 3).

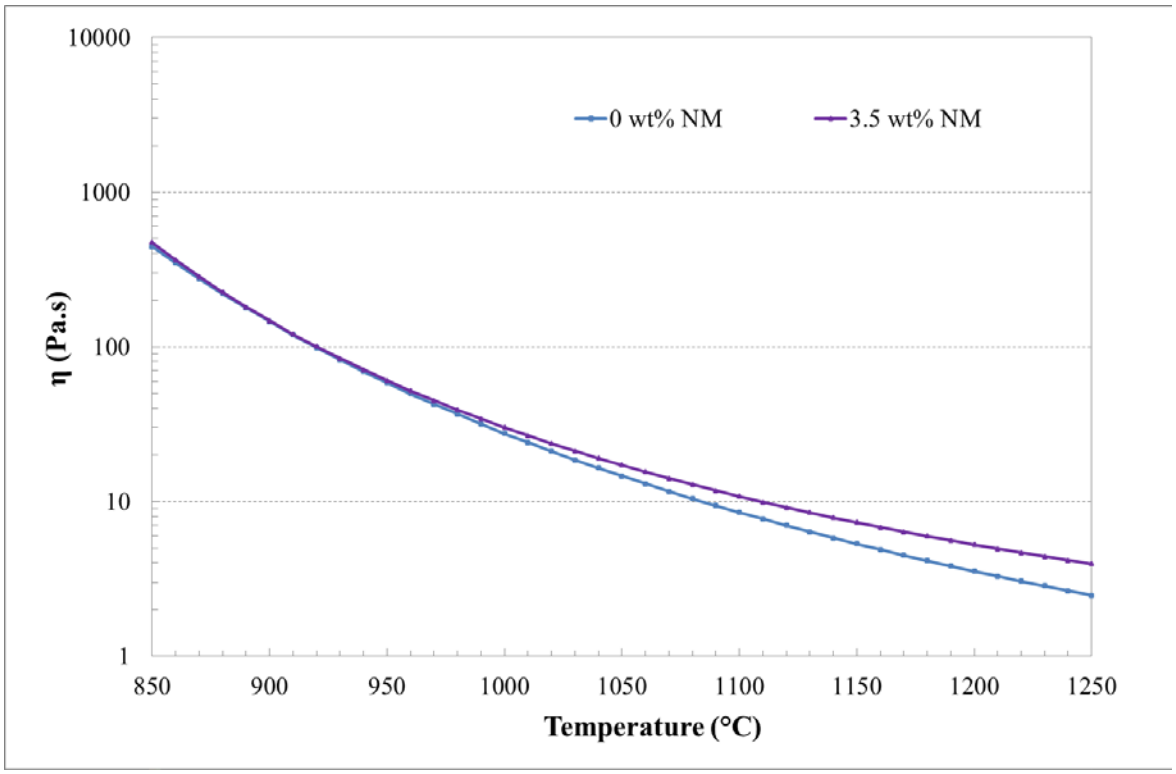


Fig. 3. Viscosity versus temperature of R7T7 glass with different noble metals concentrations

R&D TESTS WITH HOT CRUCIBLE MELTER

Description of the Hot Crucible Melter

The hot crucible melter has been operated commercially at La Hague since 1989 in R7 and 1992 in T7. A full-scale pilot unit used for R&D studies is installed at Marcoule [3].

The HCM comprises (Fig. 4):

- four heating inductors,
- inductors for the glass pouring and drain nozzles,
- a dome section connected to the calciner, equipped with stirrers to homogenize the molten glass (only in the last development),
- bubbler pipes,
- temperature probes at various heights in the glass and on the melter wall.

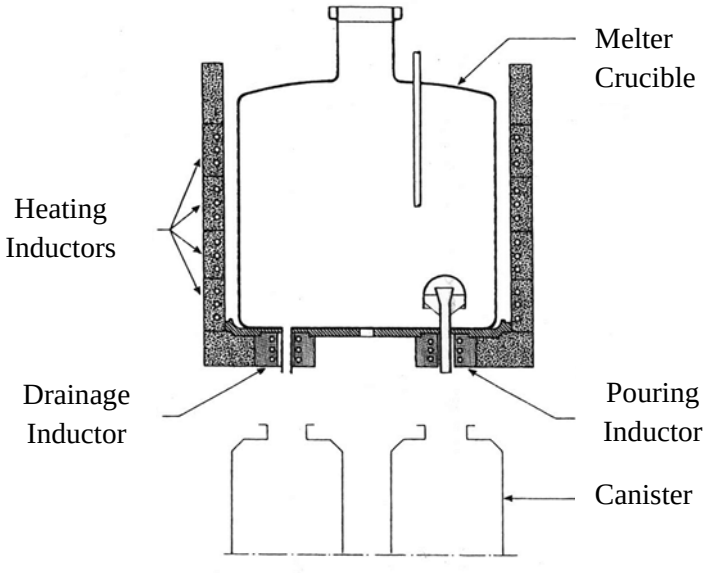


Fig. 4. Original Hot Crucible Melter design

The metal wall of the melter is heated by Joule effect using current provided by a stack of inductors surrounding the melter; the metal wall of the melter directly heats the glass by conduction.

The glass synthesis temperature is limited to 1100°C in this type of furnace; at higher temperatures problems related to the mechanical strength of the metal melter and corrosion of the melter by the molten glass may occur.

The melter is continuously supplied with calcine and glass frit. It is stopped to pour the glass into a canister.

This melter has an R7T7 glass production capacity of 25 kg/h for a molten glass surface area of 0.26 m^2.

Tests description and results

The R&D tests described in this section were carried out at Marcoule in the full-scale pilot of the commercial process. The tests were performed on inactive surrogates of solutions containing fission products and fines. The glass samples synthesized were inside the R7T7 composition range (Table I). Two tests were carried out with glass containing no NM and three others with glass containing large amounts of NM (between 2.5 and 2.8 wt%).

The tests were performed with high NM concentrations to exacerbate the undesirable phenomena, mainly problems in pouring the melt, and material settling at the bottom of the melter [4]. It should be noted that other tests with lower NM concentrations were performed without encountering operational difficulties.

All the tests were carried out in a hot crucible melter, with different glass melt stirring technologies. The main results are shown in Table II.

Table II. Trial runs with HCM

		Run 1	Run 2	Run 3	Run 4	Run 5
NM content wt%	**RuO_2 mesured**	/	2.6	/	1.6	1.5
	RuO_2 expected	0	2.5	0	1.7	1.6
	Pd mesured	/	/	/	1.2	0.9
	Pd expected	0	0	0	1.1	1.0
Technological configuration		mono-bubbling	mono-bubbling	multi-bubbling	multi-bubbling	multi-bubbling + mecanical stirring
Mass in melter after run / Total glass mass (wt%)		< 1	15	<1	6	<1
Glass melt temperature (°C)		1050	1040	1110	1110	1100

Comparing Runs 1&2 and Runs 3&4 clearly shows that the heel enrichment is related to the presence of noble metals. The addition of NM reduced the mass transfer rate in the melt by increasing its viscosity. Heat transfer from the heated wall of the melter to the center was therefore limited. The thermal power necessary to heat the cold products falling onto the surface of the melt and to sustain the glass-forming reaction was therefore also reduced. This resulted in the presence of partially dissolved elements in the glass that settled to the bottom.

The objective of the HCM optimization studies was to enhance heat transfer in the melter. Thermal homogeneity of the molten glass was the goal, together with the highest possible glass flow rates (shear thinning of glass containing NM).

The addition of several bubbler pipes increased the mean temperature of the melt by favoring heat exchange between the wall and the center of the melter. Continual improvements such as optimization of the melter insulation and operating conditions (refining before pouring) also improved the thermal homogeneity of the molten glass. This improvement effectively reduced the holdup mass (Run 2 vs. Run 4).

The addition of two mechanical stirrers further improved mixing of the melt. No material settling was observed at the bottom of the melter when fabricating a glass containing nearly 3 wt% NM (Run 4 vs. Run 5).

INDUSTRIAL RESULTS

The incorporation of NM in glass in the R7 & T7 vitrification facilities has always been a major industrial challenge. As mentioned before, noble metals are not easily digested by the glass and their presence (even in small amounts) affects the rheological behavior of the melt: glass viscosity increases, glass rheological behavior becomes non-Newtonian. R&D by the CEA demonstrated the ability of R7T7 glass to incorporate up to 3 wt%. Due to process qualification and to ensure the 3 wt% limit is never exceeded, the R7T7 vitrification facilities operate with an industrial limit of 2.8 wt%. The operator limits the NM content below this value to always have a qualified glass.

Since the beginning of commercial operation in the La Hague facility, several technological enhancements have been made to the melter design to improve mixing capability. Initially, the R7/T7 melters were only equipped with a single bubble stirring device which effectively limited heel enrichment phenomena as the fission product solutions destined for vitrification had only limited NM content. As a result, no fines were incorporated in the glass canisters. Starting in 1990, multiple bubbling was progressively implemented. The design evolved from one bubbler pipe in the melter to three in order to improve the thermal homogeneity of the glass melt. From 1993, the melters were equipped with four bubbler pipes whose position and shape were optimized through hydrodynamic modeling.

In parallel with the technological enhancement of the melter, NM incorporation in the glass increased as a result to 1.6 wt%. Fines were incorporated in the glass for the first time in T7 in 1992 which increased the NM content in glass. Based on the feedback from T7, R7 started incorporating fines in glass in 1995.

However, this technological enhancement of melter mixing capability was not considered sufficient to address industrial needs. As a result, mechanical stirring was implemented in the melters in 1996 with the following objectives:

- improve glass bath temperature homogeneity,
- better distribute the frit and calcined FP in the melter,
- accelerate the production rate as a result by limiting the residence time.

The incorporation of noble metals in glass consequently increased to 2−2.1 wt%. Some years later, the NM content (from FP and fines) was even higher as fission products and actinides incorporation was deliberately set at a lower level.

In recent years, the changing characteristics of reprocessed spent fuels have posed the problem of an increase in the proportion of NM in the fines. In 2006, it was decided to optimize waste incorporation in the glasses produced in the R7 and T7 facilities. At this point, it was decided to conduct a continuous improvement program through close monitoring of the vitrification operations. A task group was created with the following members:

- The CEA, which joined the LCV (CEA-AREVA Joint Vitrification Laboratory, R&D and R&T provider) in 2010 [5],
- AREVA (Industrial Operator),

- AREVA/E&P (AREVA's engineering organization, former SGN).

The objectives of this approach were to monitor specific production campaigns in the R7 and T7 facilities with the aim of:

- improving the operating parameters (such as temperature, bubbling, stirring setpoints), based on the industrial feedback and process expertise of the different stakeholders,
- improving process surveillance by setting up control and remediation procedures.

This approach proved successful and ended in 2012 with the definition of an improved operating standard for the melters, which is currently used by R7 and T7 operators. The noble metals content in the glass increased to an average of 2.4 wt% without any pouring problems or any material settling at the bottom of the melter. This average value takes into account canisters containing no fines (the NM remain around 1.5 wt%) that can be produced occasionally during short periods.

The average incorporation of noble metals per year in the R7 and T7 facilities has varied since the start of operation, as shown in Fig. 5.

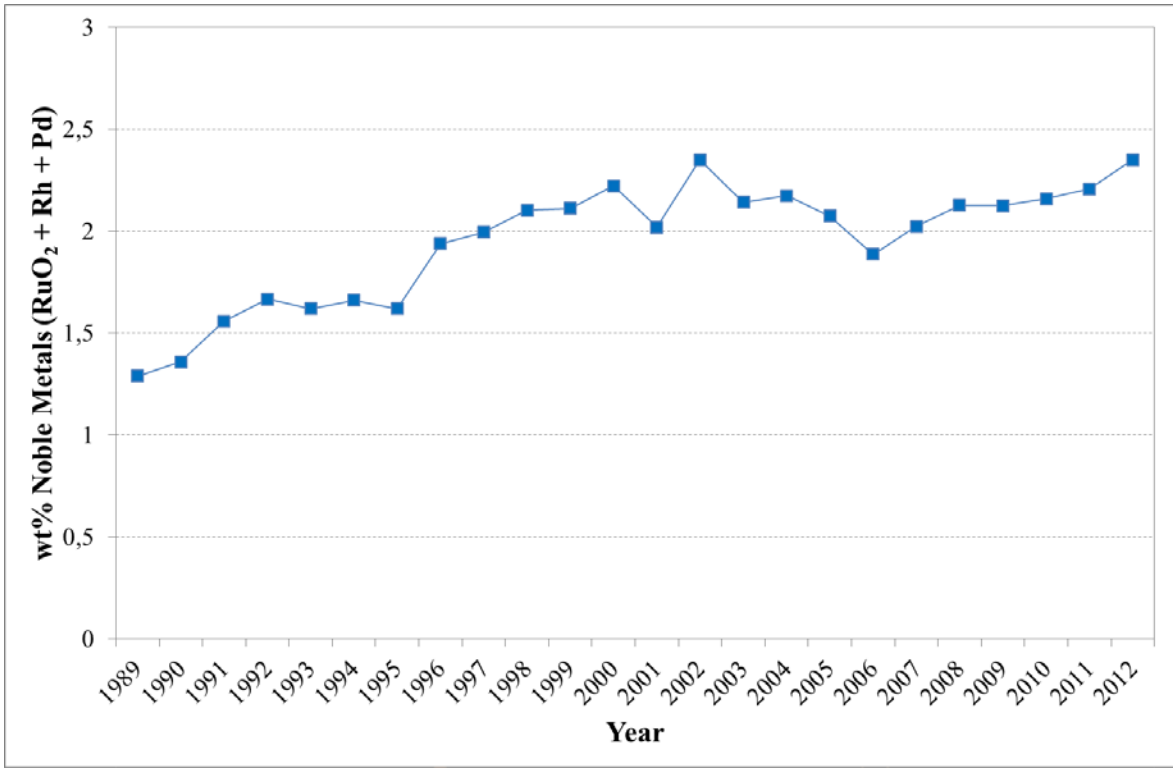


Fig. 5. Average mass of NM incorporated at La Hague over time

R&D TEST WITH COLD CRUCIBLE INDUCTION MELTER

Description of the melter

The Cold Crucible Induction Melter has been operated commercially at La Hague since 2010 to vitrify decommissioning effluents and solutions produced by reprocessing U-Mo fuel. The vitrification of high-level waste from reprocessed oxide fuels (UOX fuels) in a CCIM is currently pending approval by the French Nuclear Safety Authority. A full-scale pilot unit used for R&D studies is installed at Marcoule [3].

The cold crucible induction melter comprises (Fig. 6):

- an inductor,
- a crucible or sectorized shell that is transparent to the magnetic field,
- a dome assembly connected to the calciner, and equipped with a stirrer,
- temperature measurement probes,
- a sectorized slab that is transparent to the electromagnetic field, equipped with pouring valves and gas injectors.

The glass in the crucible is heated directly by eddy currents generated by the inductor surrounding the shell. The currents dissipate power by Joule effect that heats the calcine and glass frit to form the glass melt.

The cooling of the crucible creates a thin layer of solidified glass which coat the surface of the crucible in contact with the glass, thereby protecting it from the corrosive melt. The technology also allows the temperature to be increased (up to 1300°C for some new glass formulations).

Thermal hydraulic studies allowed stirring and mixing of molten glass to be modeled and optimized from the equipment design stage by taking into account the specific behavior of noble metals.

The melter crucible is continuously supplied with calcine and glass frit, even during pouring. The melter is fed continuously with NM without rinsing.

This melter has a maximum R7T7 glass production capacity of 36 kg/h for a molten glass surface area of 0.33 m^2.

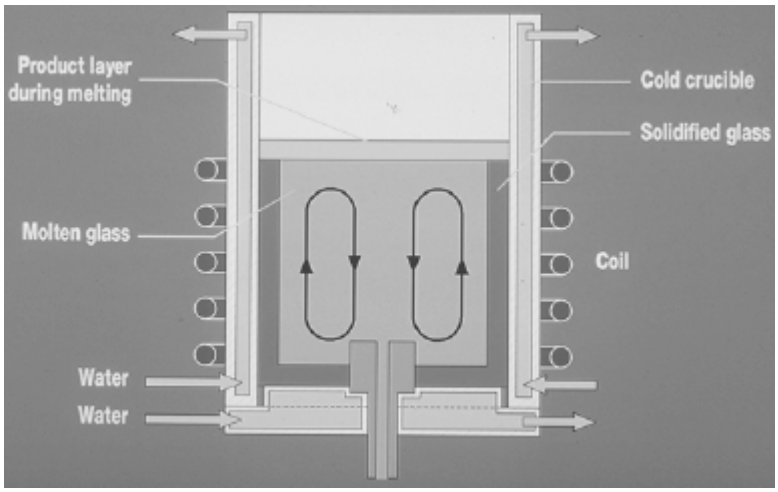


Fig. 6. Cold Crucible Melter

Test description and results

The full qualification program for vitrification of UOX solutions in a cold crucible melter included 16 tests, one of which was of extended duration (440 h) [1]. All the tests were performed with NM concentrations between 2.1 and 3 wt%. No glass production problems arising from the presence of NM were observed during the 16 tests. The test described here was one of the tests in the program qualification.

The R&D test described here was carried out at Marcoule in a full-scale pilot of the commercial process implemented at La Hague. The tests were performed on inactive surrogates of the solutions containing fission products and fines. The resulting R7T7-type glass contained 18.5wt% (FP + Act. + NM + ZrO2), including 3wt% NM.

The glass fabrication temperature was 1200°C. About 2.8 metric tons of glass were poured during the 90 hours test. Samples were taken from each pour. The analyzed glass corresponded to the expected formulation, with a homogeneous composition and microstructure identical to the description earlier in this article.

Quantitative analysis results for RuO_2 and Pd obtained by X-ray fluorescence are indicated below (Fig. 7). The theoretical RuO_2 and Pd concentrations calculated from the material balance are also indicated.

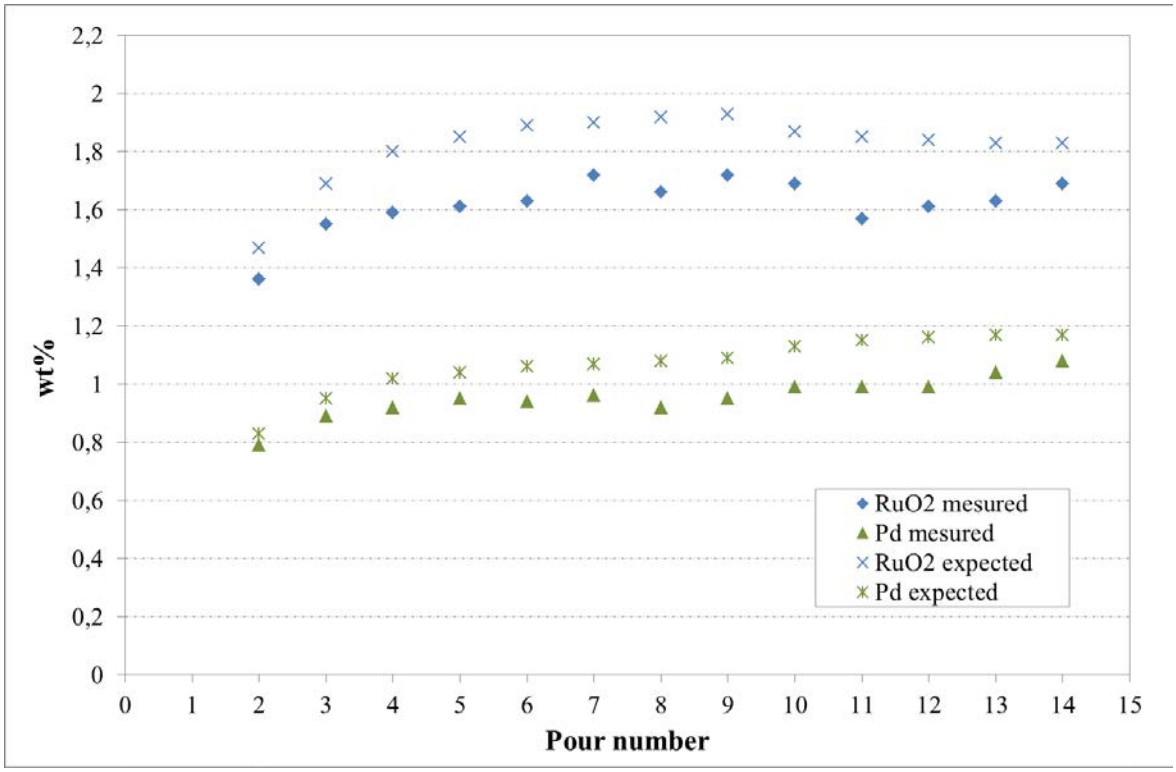


Fig. 7. RuO_2 and Pd content in poured glass

There was a discrepancy between the theoretical and analyzed concentrations of palladium and ruthenium. The difference remained stable throughout the test, and was mainly due to the X-ray fluorescence analysis method. Although quantitative analysis of noble metals by this method is difficult, and a systematic bias is observed, the measurement repeatability is satisfactory (about 2%). The stability of the deviation between the analyzed and expected concentrations of NM shows that there is no cumulative effect in the melter.

The stability of the measured content in the poured glass also shows that the NM in the feed stream are found in the final glass. These analysis results were confirmed by observations after the test: no material settling was observed in the melter.

This test shows that it is possible in a cold crucible melter to produce a homogeneous glass containing 3 wt% noble metals without any major difficulties and without settling.

CONCLUSIONS

The high noble metals content of R7T7 glass significantly modifies its rheological behavior. To allow satisfactory flow of the glass in the melter and during pouring, studies were conducted on optimizing the stirring and the heat transfer properties of the melt. The R&D tests showed that mechanical stirring and multiple bubbling were necessary in HCM to produce glass containing about 3 wt% NM without encountering operational problems.

The permanent contact between the R&D and industrial operating teams allowed each of these optimizations to be implemented quickly in the facilities at La Hague. The gradual increase in the NM content of the glass produced since the startup of the vitrification units perfectly illustrates this collaboration.

The R&D tests with the CCIM have shown that the new melter is capable of producing glass with 3 wt% NM of the same quality as in a hot crucible melter, with nearly 40 % greater production capacity (36 kg/h instead of 25 kg/h).

These tests show that controlling the thermal hydraulics of the melt is a key parameter in the production of glass with high noble metals content.

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