Methodology of Qualification of CCIM Vitrification Process Applied to the High-Level Liquid Waste from Reprocessed Oxide Fuels - 12438

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ABSTRACT

The vitrification of high-level liquid waste from reprocessed oxide fuels (UOX fuels) by Cold Crucible Induction Melter is planed by AREVA in 2013 in a production line of the R7 facility at La Hague plant. Therefore, the switch of the vitrification technology from the Joule Heated Metal Melter required a complete process qualification study. It involves three specialties, namely the matrix formulation, the glass long-term behavior and the vitrification process development on full-scale pilot.

A new glass frit has been elaborated in order to adapt the redox properties and the thermal conductivity of the glass suitable for being vitrified with the Cold Crucible Induction Melter. The role of cobalt oxide on the long term behavior of the glass has been described in the range of the tested concentrations. Concerning the process qualification, the nominal tests, the sensitivity tests and the study of the transient modes allowed to define the nominal operating conditions. Degraded operating conditions tests allowed to identify means of detecting incidents leading to these conditions and allowed to define the procedures to preserve the process equipments protection and the material quality. Finally, the endurance test validated the nominal operating conditions over an extended time period. This global study allowed to draft the package qualification file. The qualification file of the UOX package is currently under approval by the French Nuclear Safety Authority.

INTRODUCTION

In France, high-level liquid waste arising from nuclear fuel reprocessing has been successfully vitrified for more than 30 years with three major objectives: durable containment of the long-lived fission products, minimization of the final waste volume, and suitability for an industrial context. CEA and AREVA have acquired unique experience in the field of high level liquid waste vitrification through continuous efforts to improve both technology and associated matrix formulations.

As a result, AREVA has replaced one existing Joule-heated metal melter (JHMM) in a production line in the R7 facility at the La Hague plant by a cold crucible induction melter (CCIM) [1]. Among others, this technology has three main advantages: vitrification of a broad spectrum of waste because of the upper reachable melt temperatures, increase of glass production capacity, and increase of melter lifetime because of the lower wall temperature (formation of a thin solid glass layer).

Two different types of nuclear waste have been already or will be very soon conditioned using CCIM technology. In April 2010, the vitrification of decontamination effluents from the La Hague UP2-400 facility has been successfully started [2]. The first vitrification run is foreseen concerning the high-level liquid waste from reprocessed spent U-Mo fuel used in gas cooled reactor [3].

This paper describes the dedicated CCIM qualification program performed for the vitrification of high-level liquid waste from reprocessed oxide fuels (UOX fuels). The produced glass in the process experiments is the simulated borosilicate high-level waste glass. In the first part, the paper presents the general qualification methodology and focuses on the glass formulation and its long term behavior. In the second part, it describes the process experiments performed on full-scale pilot.

GENERAL QUALIFICATION METHOD

As a preliminary step of CCIM industrialization on active waste, a qualification program on inactive surrogate solutions is needed, in order to define the properties of the resulting glass and the operating conditions of its elaboration. The CEA vitrification R&D division has developed a global approach (**Fig. 1**). This approach implicates three specialties, namely the matrix formulation, the glass long-term behavior and the vitrification process development on full-scale pilot.

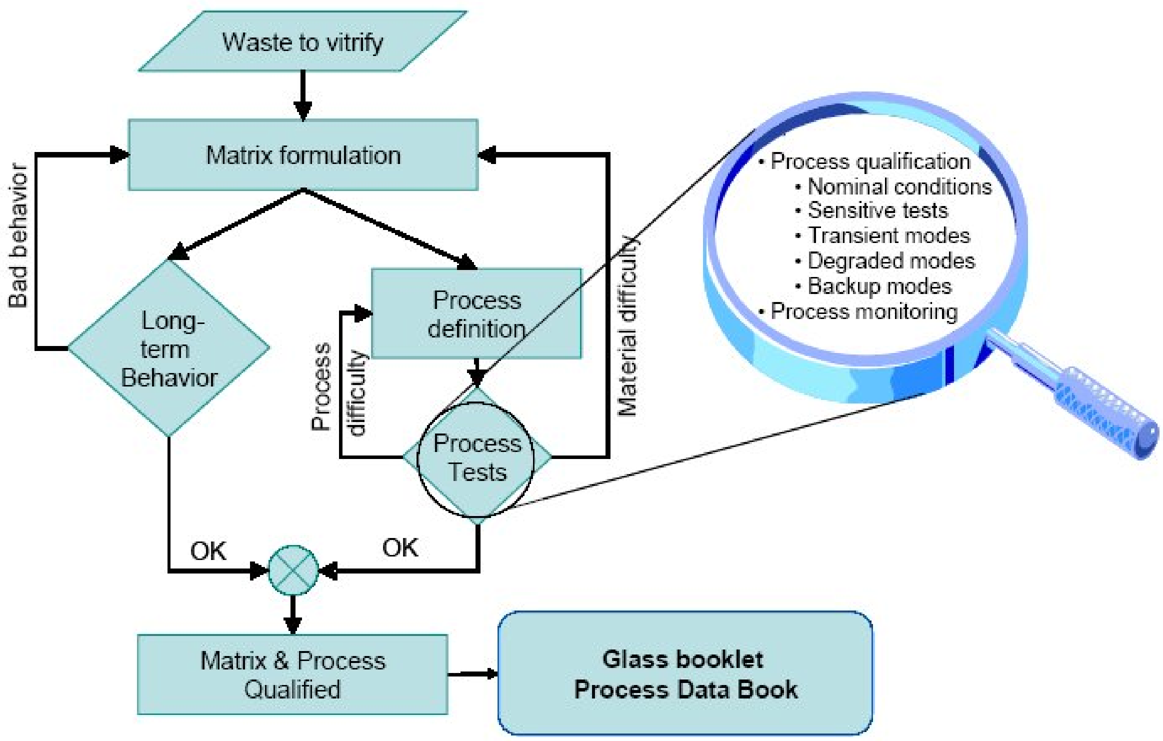


Fig. 1 : Process and matrix qualification methodology

Concerning the vitrification of high-level liquid waste from reprocessed oxide fuels (UOX fuels), the material is the well-known simulated borosilicate high-level waste glass. Its chemical composition, its microstructural properties and its long-term behavior are the same as those produced at present in La Hague facility. The following methodology was applied on the corresponding inactive glass:

- Formulation and characterization of a UOX vitreous matrix adapted to the fabrication in CCIM,
- Realization of different full-scale pilot tests with inactive surrogate solutions. The glass produced in the pilot was characterized in detail on samples taken in the canister after cooling for each test.

GLASS FORMULATION AND CHARACTERIZATION

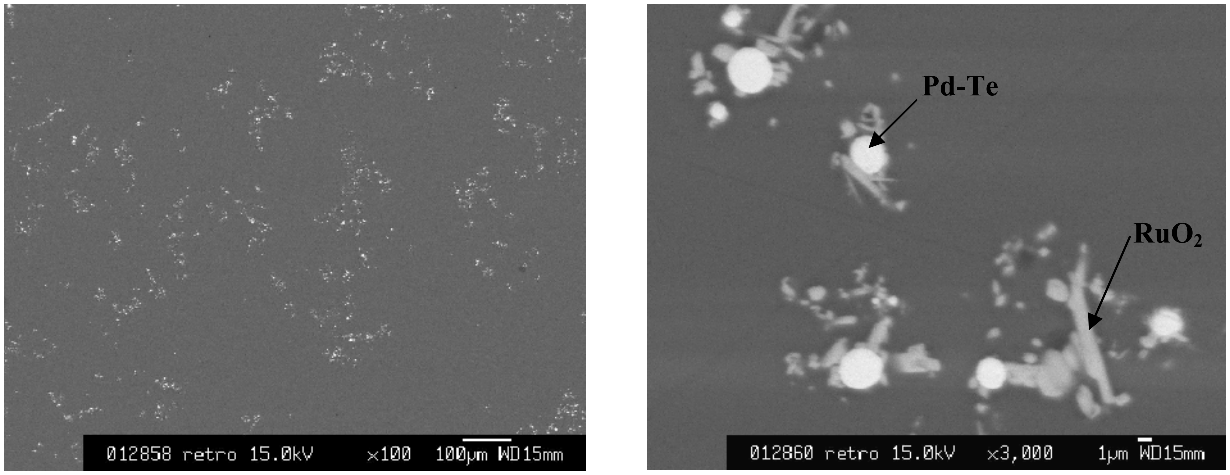
Matrix formulation

In order to produce the expected glass in optimal conditions, the redox property and the thermal conductivity of the glass have to be adapted to the Cold Crucible Melter requirements. The glass redox has to be adjusted to avoid glass foam phenomena. The thermal conductivity has to be low enough to enable the induction heating into the glass. Consequently, a new glass frit has been formulated on the basis to the one used with the Joule Heater Metal Melter.

The reference glass composition considered in the study is the simulated borosilicate high-level waste glass loaded with 17.5 wt% of fission products + actinides simulants + noble metals + Zr fines, and with 2.14 wt% of platinoids (only Ru and Pd were used). This composition is presented on **Table II**.

Microstructural analysis of the glass elaborated on full-scale pilot has been performed by Scanning Electron Microscopy (SEM, **Fig. 2**). Each sample revealed a homogenous black opaque vitreous matrix, with a microstructure including a regular distribution of microscopic platinoids: RuO_2 phase has short stick shape of about 10 µm and metallic Pd-Te are beads of some micrometers. This microstructure is the one expected for simulated UOX glass.

Moreover, several physical and mechanical properties of the glass were measured. For example, the density, the viscosity, the thermal conductivity, the electrical resistivity, the coefficient of thermal expansion, the glass transition temperature, the Young modulus and the Vickers hardness were determined among other properties. They are all similar to those measured on the inactive JHMM produced glass.



SEM image x 100 SEM image x 3000

Fig. 2 : SEM images of UOX glass microstructure

Long-term behavior

CEA assesses the long-term behavior of UOX glass using the $V_0 \rightarrow V_r$ [4]. For this glass qualification program, the volatility and the matrix behavior under irradiation are the same as those described for the well-known UOX glass already qualified. However, considering the leaching resistance, a complete study was needed and was conducted in order to describe the role of cobalt oxide, which is an additional element in the formulation. Particularly, several papers [5;6] explain that Co-based secondary silicate phases could be formed. So the question is: could the formation of such phases impact the leaching resistance of the matrix, especially the residual rate (V_r) ?

The study was achieved in two steps. First, the initial alteration rate was determined at 100°C by traditional Soxhlet experiments. A value of 1.5 ± 0.3 $g.m^{-2}.d^{-1}$ was measured. This is close to the usual data founded for UOX glass (1.7 ± 0.6 $g.m^{-2}.d^{-1}$, [4]). This value indicates that cobalt has no impact on the initial alteration rate.

Secondly, the potential impact of the formation of Co-based phases on the residual alteration rate was quantified using mechanistic model called GRAAL [7;8]. The main result is that within the range of the cobalt concentration of our study, the impact of cobalt on the residual alteration rate is inferior to 1.5%, that mean, very far from the usual standard deviation (20%).

These data confirm that the chemical durability of the UOX glass matrix produced in our conditions by CCIM vitrification process is similar to the well-known UOX glass produced by JHMM vitrification process.

QUALIFICATION METHOD FOR VITRIFICATION PILOT TESTS

The CCIM process qualification has consisted in different types of full-scale pilot tests with inactive surrogate solutions:

- The nominal, the sensitivity and transient mode tests have determined the operating parameters which guarantee that the industrial-scale glass has the same characteristics as those synthesized at the laboratory scale. A new approach using design of experiments has been used to set the process conditions required to produce a homogeneous material.

- The degraded mode tests have defined the operating parameters to preserve the process equipment and the material properties.
- Finally, a 19-days endurance test has demonstrated that the process is reliable, and that the material properties remain constant over time.

Vitrification Pilot Description

The qualification program was carried out at Marcoule in the full scale pilot of the active vitrification cell (**Fig. 3**). The feed solution and additives are supplied to the calciner. The resulting calcine is then mixed with glass frit in the melter. The cold crucible melter is continuously supplied with calcine and intermittently with glass frit. 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 main monitored parameters are temperature and stirring parameters (stirrer and bubbler).

The off-gas treatment unit recycles particle matter and purifies the gas streams before stack release. It is composed by a dust-scrubber (tank with a baffled column equipped with a backwashing system), a triple-pass condenser with a water-cooled shell, a perforated plate recombination column for nitrous fumes and a perforated plate scrubbing column. Liquid samples are taken periodically from each of the four process devices to estimate the quantity of volatilized or entrained species.

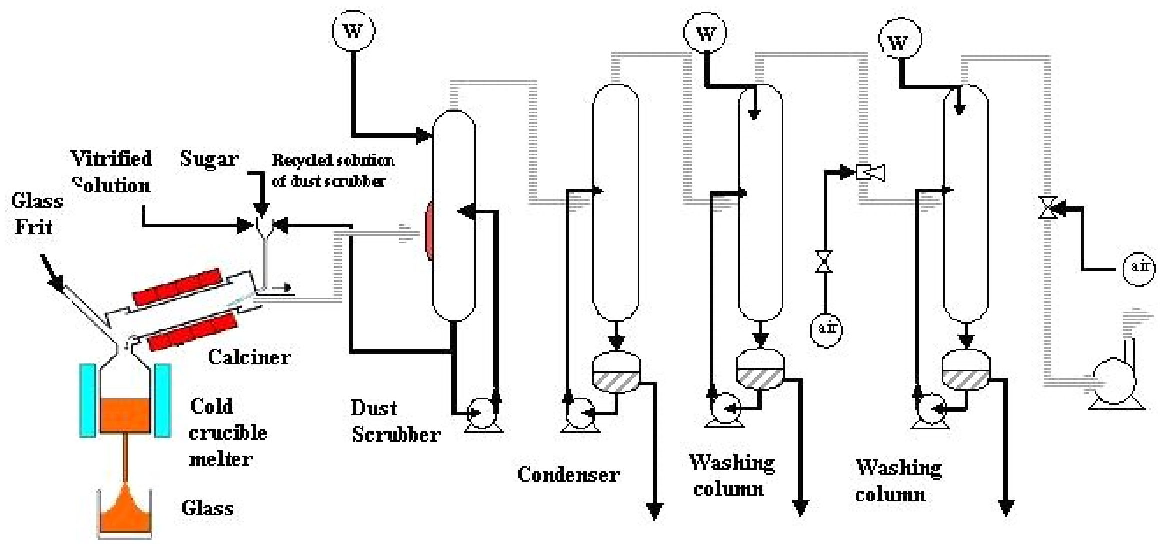


Fig. 3 : Full-scale vtrification pilot

Nominal Operating Modes

The objective of the sensitivity operating conditions tests was to define the parameters values required to synthesize a homogenous reference glass with the same properties as the laboratory reference glass. The calcining parameters were defined by prior tests without vitrification and could not be modified during the vitrification process. The impacts of the melt stirring conditions (stirrer and bubbler) and the glass synthesis temperature were evaluated from the process stability, the volatility phenomena and the material quality. A new approach using design of experiments has been used to set the process conditions. The objective was to determine an optimized operating range for these parameters. Nine operating conditions were fixed and are indicated in **Table I**.

For each experiment conditions, three consecutive elaboration/pour cycles were realized in order to obtain thermal equilibrium and to validate the process results. The elaborated glass was systematically analyzed.

Table I : Process operating conditions sensitivity tests
(Min.: minimal value of the range, Med.: medium value of the range, Max.: maximal value of the range)

	Température (°C)	Stirrer rotation speed (rpm)	Stirrer position from the bottom of the melter (mm)	Injector flow rate (NL/h)
Experiment 1	MAX	MED	MIN	MAX
Experiment 2	MAX	MIN	MAX	MED
Experiment 3	MAX	MAX	MED	MIN
Experiment 4	MED	MED	MAX	MIN
Experiment 5	MED	MIN	MED	MAX
Experiment 6	MED	MAX	MIN	MED
Experiment 7	MIN	MAX	MAX	MAX
Experiment 8	MIN	MIN	MIN	MIN
Experiment 9	MIN	MED	MED	MED

This matrix of experiments allows to define very precious data in the description of the CCIM process concerning the variation of the electric and magnetic parameters, the variation of the thermal parameters, the realization of the pour and the variation of the elements volatility. More precisely, it is now possible to classify the major operating factors. For example, the study concerning the element volatility is showed on **Fig. 4**. The results indicate first, that for this range of variation the melting operating conditions have no impact on the ruthenium volatility (element sensitive to the calcination operating conditions), and secondly, that the temperature, then the injectors flow rate were the most impacting factors on cesium, sodium and boron volatility. The stirrer rotation speed and its position had no preponderant impact. It has to be noted that these volatility variations can’t be detected from the glass elemental analysis.

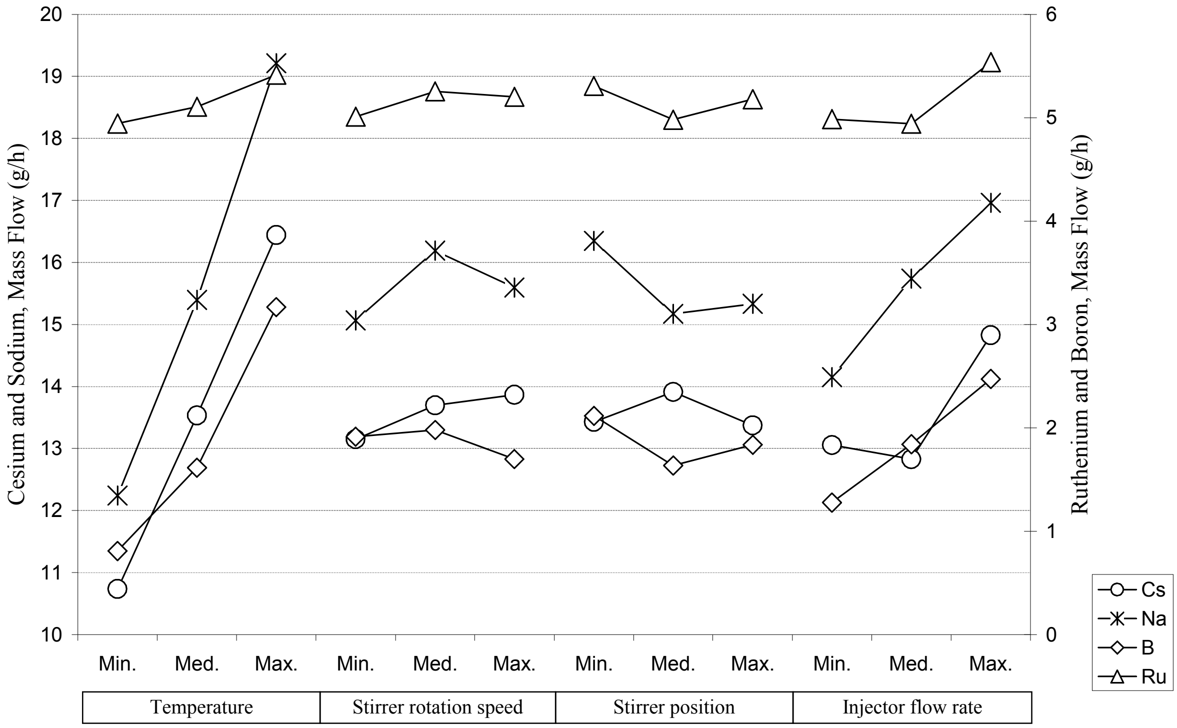


Fig. 4 : Impact of the process operating conditions on the element volatility
(Min.: minimal value of the range, Med.: medium value of the range, Max.: maximal value of the range)

This design of experiments study showed also that, as expected, the thermal distribution in the melt is better for high temperatures, high flow rates and high stirrer rotation speeds. Particularly, these conditions are looked for having a regular pour. Therefore, the recommended and validated nominal parameters are the following ones:

- ~ 1200 °C for the glass temperature in the crucible, obtained by regulating the generator power,
- ~ 60 rpm for the stirrer rotation speed,
- ~ 600 L/h (at Normal conditions: 101325 Pa and 0°C) for the flow rate from each bubbler ,
- ~ 36 kg/h for nominal throughput.

These nominal operating conditions were tested for a one week long experiment and for the endurance test (see further paragraph).

For the reference glass produced under nominal operating conditions, three glass samples were taken while the melt was poured: at the beginning, the middle and the end of the pour. The X-rays Fluorescence elemental analysis are presented in **Table II**. This table shows the analyzed glass chemical composition, the theoretical one's (named reference glass) and the expected glass composition calculated from mass measurement of the calcine and the glass frit. These data showed that the glass is still homogeneous at the beginning, the middle and up to the end of the pour. Very good agreement is observed between the theoretical and expected glass compositions and the chemical analysis results. Only platinoids are measured lower than expected in the glass mainly due to ruthenium analytical uncertainties. X-rays fluorescence method is not very accurate for the quantification of platinoids.

Table II : Analysis data for the reference glass elaborated under nominal operating conditions

	Reference glass composition (wt%)	Expected glass (wt%)	Analyzed glass (wt%)		
			Beginning	Middle	End
SiO_2	44,35	44,31	44,30	44,33	44,41
Al_2O_3	4,18	4,18	4,23	4,23	4,24
B_2O_3	13,34	13,33	13,28	13,04	13,09
Na_2O	9,22	9,23	9,15	9,15	9,14
Cr_2O_3	0,05	0,05	0,09	0,09	0,09
Fission Products + Actinides Simulant + Nobles Metals + Zr fines	17,50	17,55	17,45	17,46	17,44
Platinoids	2,14	2,14	1,88	1,88	1,91

Several microstructural characterizations were carried out on glass samples. The observed microstructures are the same as shown in **Fig. 2**. In each case the glass was homogeneous with well-dispersed micro-aggregates of ruthenium oxide and metallic Pd-Te beads.

The equipment performance in a melting facility is estimated by calculating the decontamination factor under active conditions equivalent to the decontamination factor under inactive conditions. For each compound, the decontamination factor was calculated as the ratio of the output content to the input content. Twelve elements were analyzed in the off-gas treatment system. Only the decontamination factors for ruthenium, cesium, sodium and boron are indicated (**Table III**). For example, the DFcv equal to 50 for the cesium means that 2 percents of the element is not vitrified and is present in the off-gas equipments.

As generally observed, the elements massively retained in the calcining-vitrification process are those that are contained only in the glass frit, such as boron. This is due to the fact that the frit is feeding at the end of the calciner and is less sensitive to the calciner flow rate. In this respective order, cesium, then ruthenium, and then sodium are quite volatile elements. Ruthenium is known to be volatile during calcination (sugar is added to reduce the volatility), and high temperatures reached by the CCIM process allow also the formation of volatile borate BO_4^{x-} associated to alkaline (like Na or Cs).

Table III : Process decontamination factors for reference glass under nominal operating conditions

	DFcv (calcination vitrification)	Dfpsep (particle separator)
Ru	85	3
Cs	50	3
Na	200	3
B	1500	6

Transient Operating Modes

During transient phases, the operating parameters must be adjusted to guarantee the chemical composition and microstructure of the final glass and to avoid strong volatility. The following tests were chosen considering the presence of volatile elements and various startup options:

- Different glass frit loading startup configurations (150 to 200 kg) were tested to determine the procedure for obtaining a homogeneous glass with acceptable composition. The analysis for the first melt exhibit no enrichment or depletion of any of the glass constituent elements. We may therefore conclude that any possible high volatility of some elements during the startup phase has no consequences on the glass composition.
- Short and extended tests of calciner standby period during 2, 8 and 40 hours (CSP) were also realized. In operation, those periods occur when the process is no longer supplied with UOX solution and frit. For the melter, the CSP can be considered equivalent to a glass soaking period. Short and extended CSPs did not disturb the crucible and off-gas treatment management cycles, nor were any differences in behavior identified under CSP operating conditions. It did not affect the material, as shown by the results of chemical analysis and microstructural characterizations. It will not be necessary to modify the glass elaboration conditions during reasonably short calciner standby periods.

Degraded Operating Modes

Operating incidents can lead to process deviations from nominal operating conditions. Degraded operating modes must be examined to minimize their impact on the process equipment and on the material quality. Means of detection are determined and management procedures are defined. In our case we chose to study the following degraded modes.

- An interruption in the glass frit feeding was realized in order to evaluate the consequences on the material and its impact on process control. This test allowed determining the suitable means of detecting frit feed clogging, and showed that no impact was detected on the material quality or on the process.
- The restarting of a full of glass melter was realized to demonstrate that under the rated operating conditions, a crucible which had to be cooled down after an incident with maximum holdup, can be restarted. The feasibility of start-up was successfully demonstrated.
- The interruption of stirring, the exit of the melting temperature and rotation speed stirrer range were also tested. The properties of the final glass were preserved and no impact on the process was detected.
- The loss of gas sparging was finally tested. The parameters have been adjusted in order to guarantee the quality of the glass.

It was shown that the management modes applied to cope with these situations successfully preserved the material quality and did not disturb the crucible and off-gas treatment behavior.

Endurance Test

The main objective of the endurance test was to demonstrate that the process and the material properties remain constant over the time. The endurance test lasted 440 hours days compared with

90 hours for the other tests. 71 pours were achieved, corresponding to 35 standard glass containers at La Hague. It represents 14.4 tons of glass elaboration during this period.

No major operating difficulties were encountered during the three-week test. The reference glass composition was produced under nominal conditions without any problem in the crucible.

No variation in the chemical composition and microstructure of the glass poured into the canisters was observed throughout the test, including the last pour.

CONCLUSION

The vitrification of high-level liquid waste from reprocessed oxide fuels (UOX fuels) by Cold Crucible Induction Melter is planed by AREVA in 2013 in a production line of the R7 facility at La Hague plant. Therefore, the switch of the vitrification technology from the Joule Heated Metal Melter required a complete process qualification study. It involves three specialties, namely the matrix formulation, the glass long-term behavior and the vitrification process development on full-scale pilot.

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