Vitrification of Molybdenum-Rich High-Level Solutions by the Cold Crucible Melter Process - 11502

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ABSTRACT

Vitrification of high-level liquid waste is internationally acknowledged to minimize both the environmental impact resulting from waste disposal and the volume of conditioned waste. In France, the high-level liquid waste arising from nuclear fuel reprocessing has been successfully vitrified for more than 20 years with three major objectives: durable containment of the long-lived fission products, minimization of the final waste volume, and operability in an industrial context.

To improve vitrification performance, AREVA has replaced the existing melter in one of the cells of the R7 line at La Hague with a cold crucible melter. The cold crucible is a compact water-cooled vessel in which the radioactive waste and glass additives are melted by direct high-frequency induction. Because the heat is transferred directly to the melt, high operating temperatures can be achieved with no impact on the melter itself. The new process allows us to vitrify legacy high level liquid waste from reprocessed spent U-Mo-Sn-Al (UMo) fuel used in gas cooled reactors: the high molybdenum content of the waste makes it very corrosive and also requires a special high-temperature glass formulation to obtain sufficiently high waste loading factors (10–12% molybdenum oxide).

A glass-ceramic matrix has been developed by the CEA to immobilize UMo solutions: it comprises a vitreous major phase encapsulating secondary phases measuring less than a hundred micrometers. The secondary phases are formed by phase separation and crystallization phenomena during cooling of the molten glass in the canister. The physical and microstructural properties of the UMo glass in the solid and liquid states were determined over the full specified range of compositions and process operating parameters. The impact of the sample position in the canister was also taken into account, given the sensitivity of crystallization phenomena to the thermal cooling scenario. A demonstration of the long-term behavior of UMo glass-ceramic has also been carried out.

The industrial feasibility of this process has been demonstrated in a full-scale pilot facility with inactive surrogate solutions. The process was qualified by the following tests:

- *Nominal, sensitivity, and transient-mode tests*: ranges of glass compositions and parameter values were defined that ensure the production of glass with the same properties as the laboratory reference glass, and with acceptable element volatility.
- *Degraded operation*: management modes were defined to prevent any impact on the material properties after the return to nominal conditions.
- *Endurance testing*: a 21-day endurance test demonstrated that the process is not subject to variations and that the material properties remain constant over time.

More than a hundred UMo glass canisters were produced during the test campaigns in the inactive pilot facility. This paper presents the results obtained in these qualification programs.

INTRODUCTION

In France, the vitrification of high-level liquid waste produced by nuclear fuel reprocessing has been successfully performed for more than 30 years with three major objectives: durable containment of the long-lived fission products, minimization of the final waste volume, and operability in an industrial context. As a result, CEA and AREVA have acquired unique experience in the field of high-level waste vitrification through continuous efforts to improve both the technology (from hot to cold crucible melter) and the associated matrix formulations, with constant emphasis on quality and volume reduction, leading to the design and qualification of the cold crucible melter (CCM) technology. Some legacy solutions obtained by reprocessing spent UMo fuel in the former UP2-400 plant during the 1970s are still stored at La Hague. These solutions are less radioactive than the current fission product concentrates coming from ongoing reprocessing activities, but are very rich in molybdenum. AREVA is committed to conditioning these wastes using the CCM technology [5].

With this objective, a glass-ceramic matrix has been developed by the CEA to immobilize these UMo solutions: it comprises a vitreous major phase encapsulating secondary phases measuring less than a hundred micrometers. The secondary phases are formed by phase separation and crystallization phenomena during cooling of the molten glass in the canister. The physical and microstructural properties of the UMo glass in the solid and liquid states were determined over the full specified range of compositions and process operating parameters. The impact of the sample position in the canister was also taken into account, given the sensitivity of crystallization phenomena to the thermal cooling scenario. A demonstration of the long-term behavior of UMo glass-ceramic has also been carried out. The industrial feasibility of this process has been demonstrated in a full-scale pilot facility with inactive surrogate solutions.

GENERAL QUALIFICATION METHOD FOR CONTAINMENT GLASS FORMULATION

Acceptance criteria for the final material must first be defined to orient the glass formulation procedure [1]. The following specifications are determined:

- Required standard wasteform composition and variation range,
- Required process-related fabrication constraints,
- Expected matrix properties after fabrication,
- Expected waste volume reduction factor.

The first formulation step identifies a range of vitreous material compositions suitable for incorporation of the waste elements. The composition range is selected on the basis of the expertise acquired by the CEA in waste containment glasses. The compositions within the range are tested to assess their potential, and one or more compositions are selected for optimization and more thorough characterization. The tests focus in particular on the processing temperature, the properties necessary to ensure satisfactory process control (e.g. viscosity and electrical resistivity), micro-homogeneity, and chemical durability. Following this laboratory study of nonradioactive materials in which the radioactive species are replaced by nonradioactive isotopes or surrogate elements, a reference glass is specified. The reference glass is validated by fabricating a nonradioactive sample in a pilot unit at a scale representative of the actual fabrication process. A sensitivity study is then carried out to determine the impact of variations in certain

parameter values on the feasibility of fabricating the matrix and on the characteristics of the final material. The operating range is validated by performing tests in the vitrification pilot facility, taking into account the worst-case operating configurations. The final phase of the formulation study necessary before accepting the containment matrix involves a long-term behavior assessment. These findings are intended to corroborate the chemical durability test results obtained during the previous studies; they are supplemented by studies of irradiation stability and an assessment of the long-term alteration phenomena liable to affect the material. Depending on the radioactive elements present in the waste and the properties of the matrix, it may be advisable to include an additional validation step in which the matrix is fabricated and characterized with radioactive waste samples [2].

Formulation of a Glass Matrix for Containment of UMo Solutions

Considering elements present in the UMo high-level waste feed solutions (**table I**), the molybdenum and phosphorus loading capacity of the glass is unquestionably critical for the waste loading capability of the containment matrix. Molybdenum loading is limited to about 4 wt% in R7 glass.

Table I. UMo solution main characteristics

Composition (g/L)	MoO_3	137
	P_2O_5	42
	Na_2O	11
	Other	15
Volume		250 m^3
Activity		< 222 10^{10} Bq/L

At higher values a water-soluble segregated yellow molybdic phase could appear in the glass. Phosphorus cannot be loaded to above a few percent in this type of glass because it forms silicates liable to diminish the chemical durability of the residual glass. It was therefore decided to investigate at laboratory scale a different composition range than R7/T7 glass to take into account the specificity of the UMo solution composition. We chose to begin with a range based on SiO_2, Na_2O, Al_2O_3, P_2O_5, B_2O_3 and MoO_3. Tests were also conducted with various additives: CaO to stabilize molybdenum in the form of durable calcium molybdate crystals, ZrO_2 and ZnO to enhance the chemical durability of the final glass and the homogeneity of the glass melt. The limits of the composition range were determined from the results obtained during CEA tests in the 1960s and 1970s with compositions capable of being fabricated at temperatures below 1200°C. The target value of the melting temperature is between 1200°C and 1300°C, however, made possible by the use of a cold crucible melter. The following simplified composition range (less than 6 compounds) was investigated to test their ability to incorporate high content of molybdenum and phosphorous:

- SiO_2: 32 to 44 wt%
- Al_2O_3: $\leq$ 5 wt%
- B_2O_3: 15 to 22 wt%
- Na_2O: 12 wt%
- P_2O_5: $\leq$4 wt%
- MoO_3: 10 to 12 wt%
- Tested additives: CaO, ZnO, ZrO_2, Li_2O.

Over 100 glass samples were fabricated and characterized in this range. The results (**Figure 1**) for each composition are normalized for the three constituents with the greatest impact on the final material within the studied range: SiO_2, Al_2O_3, P_2O_5. Three glass families were identified within the domain, in addition to highly refractory matrices unsuitable for fabrication below 1300°C:

- Glasses that are translucent after quenching (SUMo1-Type glass),
- Opaque glasses (SUMo2-Type glass),
- Macroscopically heterogeneous matrices.

SUMo1-10a and SUMo2-12a glass compositions were deduced from the first and second families, containing respectively 10 and 12 wt% of MoO_3 taking into account the whole waste composition. They were selected for further optimization, together with SPNM′ glass (main components: SiO_2, P_2O_5,Na_2O, MoO_3) melted in reducing conditions. The qualities of reduced SPNM′ glass for vitrification of UMo solutions were observed during another formulation study; although this composition is not part of the selection range, its advantageous chemical durability and viscosity characteristics are related to the oxidation state of molybdenum, which is reduced to +IV instead of +VI in the general oxidizing conditions [3]. Following this optimization and characterization phase, SUMo2-10d glass (optimized from SUMo2-12a) containing 10 wt% of MoO_3 was selected as the reference formulation; its composition is also indicated in **Table II**. Due to variations in the waste loading factor and uncertainties on compositions of UMo solution and glass additives introduced in the process as glass frit, glass composition variations are also taken into account.

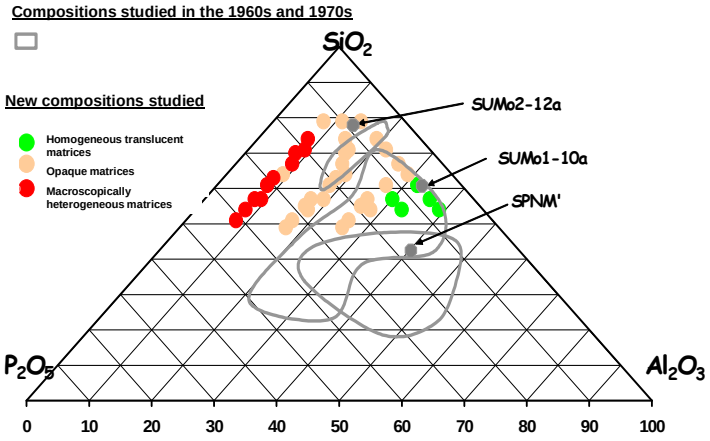

Figure 1. Glass composition range of the preliminary formulation study

Table II. UMo reference glass composition (wt%)

SiO_2	38.7
Na_2O	9.4
B_2O_3	13.9
Al_2O_3	7.1
P_2O_5	3.1
MoO_3	10.0
ZnO	6.0
ZrO_2	3.3
CaO	6.1
Other	2.4

The reference UMo glass, SUMo2-10d, is a vitreous material fabricated at 1250°C. It is an opaque glass-ceramic. In the molten state the melt is homogeneous, but phase separation and crystallization phenomena occur after cooling in the canister. The glass-ceramic is characterized by secondary phases dispersed in an encapsulating borosilicate glass matrix. The secondary phases are mostly found in beads of nanometer or micrometer scale, or even in aggregates of a few tens of micrometers (**Figure 2**). Some beads appear homogeneous at micrometer scale, while others appear to be multiphase beads. The “homogeneous” beads contain mainly molybdenum, phosphorus, calcium, zinc and sodium. Several crystalline and vitreous phases can be identified in the “multiphase” beads and “aggregates”: calcium molybdate, calcium or zinc phosphates, as well as an interstitial vitreous borosilicate phase. Considering the possible impact of the cooling scenario on phase separation and crystallization phenomena, the glass fabricated at laboratory scale is based on the extreme cooling scenarios expected in the waste canister. The same microstructure is also observed for all possible compositions of the domain considered. Only slight differences in crystal size are observed.

The following properties were determined for the reference UMo glass and for UMo glass with maximum and minimum molybdenum and phosphorous content over the composition range considered. All these glasses were synthesized at 1250°C. Chemical durability tests in Soxhlet mode at 100°C yielded r_0 values around 2.6 $g \cdot m^{-2} d^{-1}$ which is comparable to the r_0 value obtained for R7 glass The molten glass properties are also compatible with fabrication in a cold crucible melter: a viscosity of around 40 dPa·s at 1250°C and an electrical resistivity of about 7 Ω·cm at 1250°C. The maximum range molybdenum and phosphorus content in the final glass determined the melting temperature range, which must be higher than the phase separation temperature in order to maintain a homogeneous melt in the crucible. The phase separation temperature depends on the molybdenum and phosphorous concentrations in the glass [4]. For the purposes of this formulation study, the sensitivity study thus consisted in determining the extreme acceptable variations for these parameters: melting temperature, molybdenum and phosphorous contents.

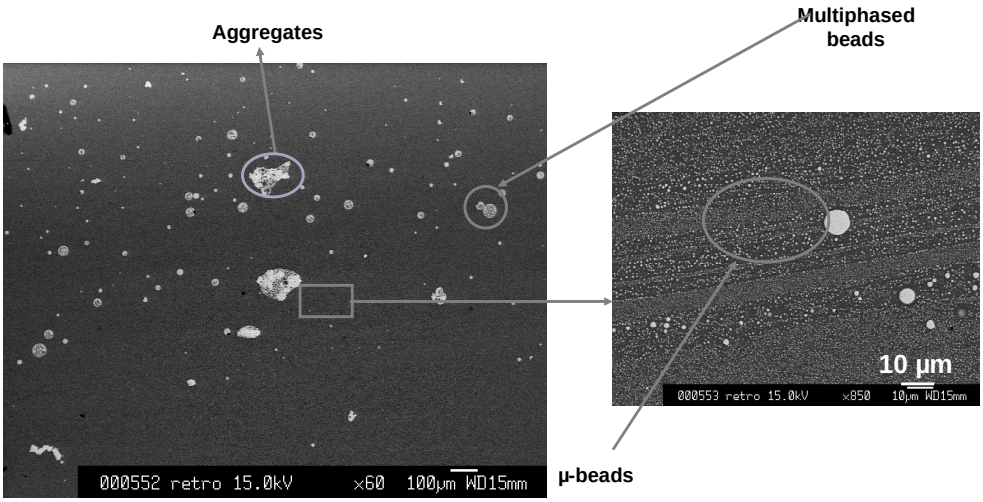

Figure 2. UMo glass microstructure

Long-Term Behavior

The long-term behavior of the matrix was also investigated, and particularly the matrix behavior under irradiation and its leaching resistance.

The irradiation behavior was studied using a few tens of grams of UMo glass doped with americium and curium produced in the Atalante complex at Marcoule to determine the location of the actinides in the matrix and to ensure that the matrix properties were conserved after having accumulated the dose levels expected for this type of glass. Americium was added to the vitrification feed mixture to simulate all the actinides and to demonstrate that they tended to concentrate in the calcium molybdates and calcium phosphates. This result confirms those obtained during inactive tests with neodymium as the trivalent actinide surrogate.

All the leaching experiments were carried out on glass samples synthesized in a cold crucible melter under conditions representative of the industrial process. A large body of experimental leaching data was obtained to establish a law describing the variations in the initial alteration rate as a function of the pH and temperature. These dynamic-mode experiments (with very high solution renewal rates to maintain initial rate conditions) were carried out over a wide pH range (7 to 11) at 30°C and 90°C. Rate drop measurements were performed in a static system at 50°C on the benchmark glass and on a glass with molybdenum and phosphorus concentrations at the upper limit of the range. In each case, canister core samples and edge samples were taken because the crystal size varies according to the glass cooling conditions: they are generally larger in the center of the canister where cooling is the slowest. The data confirm that the chemical durability of the glass-ceramic matrix is comparable to that of homogeneous borosilicate glasses for the alteration rate regimes investigated (initial rate and rate drop).

VITRIFICATION PILOT TESTS

The qualification program was carried out at Marcoule in the full scale pilot of the future active vitrification cell (**Figure 3**). The feed solution and additives are supplied to the calciner. The resulting calcine is then mixed with glass frit in the melter. The off-gas treatment unit recycles particle matter and purifies the gas streams before stack release.

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, stirrer speed, and gaz flow rate via injectors.

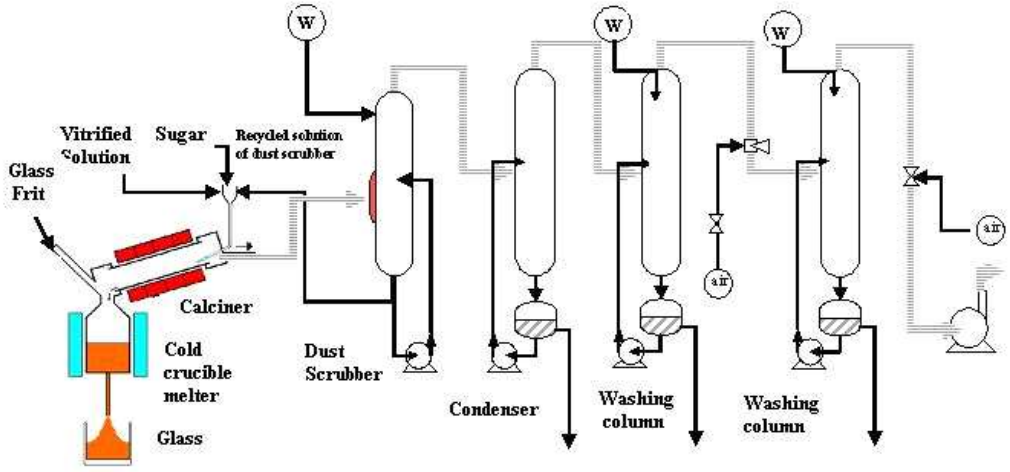

Figure 3. Full scale vitrification pilot

Nominal, sensitivity, and transient operating mode tests covering nominal process operation were performed first, followed by an investigation of degraded modes and an endurance test to finish the process qualification study.

The glass fabricated in the pilot was characterized in detail on samples taken during pouring as well as in the canister. Samples were taken at different positions along a vertical cross section of the canister (**Figure 4**). The samples were analyzed to verify the good agreement between theoretical and analyzed composition. Several microstructural characterizations were carried out on these glass samples. Durability and other properties were also determined on glass produced at pilot scale in order to verify that the glass produced had the expected characteristics.

Figure 4. Location of UMo glass samples taken along a vertical cross section of the canister

Nominal Tests

The objective of the nominal tests was to define the nominal 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 temperature in the molten glass was fixed by previous results obtained at laboratory scale. Only the stirrer rotation speed and the flow rate of the gaz injectors were subject to variation. The final choice of the nominal parameters was based on the results of glass characterization, volatility and stability of process operation.

Nominal CCIM parameters during the synthesis of the selected reference glass were:

- ~ 1250°C for the glass temperature in the crucible, obtained by regulating the generator power,
- ~ 50 rpm for the stirrer rotation speed,
- ~ 400 L/h (at Normal conditions: 101325 Pa and 0°C) for the flow rate from each of the gaz injector.
- ~ 45 kg/h for nominal throughput.

Sensitivity Tests

- The first type of sensitivity tests concerned waste loading. The waste loading is related to the molybdenum and phosphorous concentration in glass. The impact of variations in the melt stirring conditions and glass synthesis temperature on material quality and on volatility phenomena were also studied. The tests objective was to validate an operating range for these parameters over the entire composition domain, to maintain the nominal throughput.

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. Considering the presence of volatile elements and various startup options, the following tests were chosen:

- Startup tests with glass frit or with glass to determine the procedure for obtaining a homogeneous glass with acceptable composition
- Short and extended tests of calciner standby period (CSP). In operation, those periods occur when the process is no longer supplied with UMo solution and frit. For the melter, the CSP can be considered equivalent to a glass soaking period.

We have shown that startup with glass frit or glass is possible for the CCIM. The analysis findings for the first melt show 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.

Moreover, 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 characterization. It will not be necessary to modify the glass fabrication conditions during reasonably short calciner standby periods.

Degraded Operating Modes

Operating incidents can cause the process to deviate 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 five degraded modes:

- the impact on the material of an interruption in the glass frit feeding: the purpose of this test was to determine the consequences of glass frit feed failure on the material and its impact on process control; another objective was to determine a suitable means of detecting frit feed clogging;
- the consequences of restarting a full melter, 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, and to determine the impact on material and process;
- the impact of an interruption of stirring and the countermeasures necessary to guarantee the properties of the final glass;
- the impact of exiting the melting temperature range, and the necessary countermeasures;
- the impact of the loss of gaz sparging, and the necessary countermeasures.

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 21 days compared with 5 days for the other tests.

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, nor did any difficulties appear during pouring of the 18 tons of glass fabricated during this period.

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 specific feature of UMo solutions (high molybdenum and phosphorus content), the objective of minimizing the final waste volume as far as it is reasonably achievable with respect to acceptance for ultimate disposal, and the requirement of processing this solution in the existing AREVA vitrification facility were taken into account to develop a high waste loading glass-ceramic matrix which benefits from the advantages of the Cold Crucible Melter.

The formulation and process qualification program were carried out at laboratory and pilot scale. A full scale pilot of the industrial vitrification process was used for the R&D program, as well as to train operators and to validate the design options.

This process qualification methodology applied to the UMo solutions allowed us to draft the package qualification file for new glass-ceramic packages. In addition to the technological data, this file also describes the study of the glass composition range and of its long-term behavior.

The qualification file of the UMo package is currently under approval by the French Safety Authority. AREVA has planed to startup the vitrification of the legacy UMo solutions in cold crucible melter at the La Hague Plant in 2011.

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