Qualification of In-Can Melting Process Applied to Vitrification of High Activity Waste Solutions (HAWS) at the CEA's Valduc Center: Description of Process and Equipment, Methodology and Initial Results – 10022

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ABSTRACT

The CEA's Valduc Center has selected vitrification for specific High-Activity nuclear Waste Solutions (HAWS) containing radioactive decay products of plutonium and large quantities of salts. This choice has lead the CEA Marcoule to develop a compact "in-can" batch melting process in which the melting pot is disposable and serves as the primary canister for the solidified glass. This process is particularly suitable for the treatment of small waste quantities (less than 10 m^3 per year) and low flow rates (5 to 10 L/h) which do not justify the use of a Cold Crucible Induction Melter. The unit capacity is approximately one hundred kilograms of glass a week operating alternately between feeding during the day and surveillance at night.

The existing nonradioactive test bed was originally used for testing at CEA Marcoule from 2005 to 2008 and was modified in 2009. In order to be fully representative of the glove box to be implemented at CEA Valduc, a new nonradioactive pilot-scale unit in which the core process (furnace and dust scrubber) is completely enclosed with glove box simulation was built at CEA Marcoule in 2008. The equipment includes all the systems and components necessary to perform full-scale tests: feed system, furnace and complete off-gas treatment system. The results obtained in term of volatility, material, etc. are indicated for the two types of tests carried out in this facility between 2005 and 2008: feasibility tests to choose between vitrification in the metal melting pot with or without prior calcining, and optimization tests to qualify the process. The main conclusion drawn from the tests is the feasibility of direct in-can vitrification. This configuration was preferred to calcination-vitrification because of its simplicity for implementation in a glove box.

Finally, the first test runs performed in 2009 on the new pilot unit with liquid feed representative of the current HAWS stored at CEA Valduc are described. The first was a nominal test to verify that no problems arose in vitrifying solutions under the specified conditions; the second was a performance test with the objective of determining the maximum capacity of the facility in terms of liquid feed and glass throughput rate. The glass product was visually homogeneous and was chemically and morphologically analyzed. Off-gas treatment system (OGTS) assessments determined preliminary decontamination factors for the OGTS components and allowed comparison with the previous pilot unit.

INTRODUCTION

In order to treat a fraction of the nuclear waste arising from the activities of the CEA's Valduc Center, demonstration experiments were carried out in a large-scale calcination-vitrification facility at CEA Marcoule equipped with a resistance furnace suitable for the "in-can" melting process [1, 2, 3, 4]. First the feasibility of vitrification was confirmed, a configuration was defined, and the process was optimized. The second stage involves process qualification in a new representative facility.

This paper describes the existing nonradioactive facility initially used for the feasibility and optimization tests. Eight demonstration runs were completed between 2005 and 2008 in this facility with different liquid feeds. The results obtained in terms of volatility, material and process control are discussed.

The new representative facility is then described together with the beginning of the process qualification procedure with nominal and maximum capacity tests. Preliminary decontamination factors of the process are also indicated for various equipment with a comparison between the facilities.

FIRST SERIES OF DEMONSTRATIONS: 2005–2008

All the demonstration runs involved process feed during the day alternating with a surveillance period at night. The objective for each test was to produce 108 kg of glass, equivalent to about 40 hours of feed per week.

Description of the Representative Test Bed
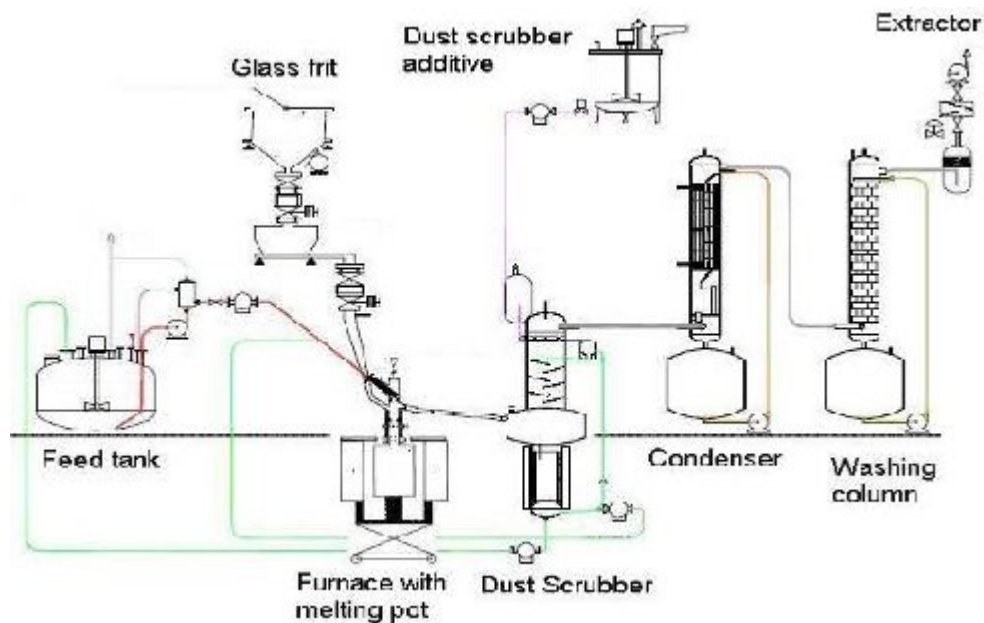
Figure 1. Diagram of full-scale pilot in direct vitrification configuration

The test bed includes all the equipment necessary for a one-week test of the in-can melter: vitrification furnace, particle separator, condenser, scrubbing column, and exhaust blower, installed on three levels. **Figure 1** shows the unit in the direct vitrification in-can melting configuration. Glass is produced in an expendable melting pot which becomes the disposal canister at the end of the test. The melter is supplied directly with the vitrification feed solution and with glass frit. The feed streams are supplied through a connecting sleeve between the melting pot in the furnace and the particle separator; the entire process is

depressurized. Particulates in the furnace exhaust stream are trapped by scrubbing in a particle separator and recycled to the melter via a pump. The off-gas passes through a condenser and a scrubbing column.

Furnace and melting pot

The furnace used from 2005 to 2009 consists of refractory bricks with two independent electrically heating zones to accommodate melting pots of different materials and thicknesses depending on the tests (**Figure 2**). The heating zones are rated at 9 kW for the lower section and 7 kW for the upper section. It is also equipped with three thermocouples (one in each zone and one in contact with the bottom of the melter).

Figure 2. Initial vitrification furnace used for testing in 2005 to 2009.

The new furnace in use since 2009 is mounted on a on a separate frame from the test bed. It consists of two parts, a stationary cylindrical dome mounted on level 1 and a hearth supporting the melting pot on level 0. A mechanical lifting platform controls the vertical position of the hearth beneath the cylindrical dome (**Figure 3**).

Figure 3. Vitrification furnace that is currently being used.

The furnace is designed and dimensioned for use in a glove box. The dome comprises nine 5.5 kW heating elements secured to the top of the furnace and extending vertically around the melting pot. The new furnace has only one heating zone. It is also equipped with a thermal expansion absorber to prevent deformation of the melting pot.

Furnace-particle separator connecting sleeve

For the initial tests (runs 1 & 2), the connector was a simple vertical tube between the melting pot and the calciner (whether or not the latter was used) through which the process liquid and glass frit were supplied. It was progressively improved with provisions for declogging the vertical portion, for supplying the feed solution directly on the melting pot centerline, and for exhausting the off-gas to the particle separator. It is also air-cooled and includes water cleaning nozzles.

Off-gas treatment

The off-gas treatment system comprises a particle separator, a condenser, and a scrubbing column. The particle separator consists of a tank with a baffled column equipped with a backwashing system. The plates are sprayed by a pump with solution drawn from the tank, which is electrically heated to maintain the solution stirred and at the boiling point; the solution level is maintained constant with makeup water. Particulates trapped by the separator are recycled to the mixing pot. In 2009 a new particle separator dimensioned for the process flow rates was installed. Unlike the previous model, spraying is controlled by an airlift with a constant-level flow regulator and the particle separator column is topped by a bubble-cap tray to improve liquid-gas contact. It can also be supplied with a complexing agent in the case of fluorinated solutions to limit equipment corrosion.

After particle removal the gas enters the condenser where the steam is condensed. The condensates are recovered in a dedicated tank. Behind the condenser, the process off-gases pass through a sprayed packed NOx recombination column. The entire process is maintained depressurized by an exhaust blower.

Liquid samples are taken periodically from each of the three process devices to estimate the quantity of volatilized or entrained species. Each device is also equipped for level and temperature measurements, and for inlet and outlet pressure measurements.

Control and Monitoring

The test bed is fully instrumented and operated remotely via a programmable logic controller and a digital control system with a multi-screen display. All the process parameters can be monitored, logged, and recorded to provide historical trend information. The control system includes warning thresholds on each critical measurement and automatic shutdown sequences to assure safe operation of the system. The system was updated to integrate all the modifications implemented in the facility.

Feasibility Tests: Runs 1 to 4

Two tests (runs 1 and 2) were performed at Marcoule in 2005 to decide between the calcining-vitrification and direct vitrification process configurations.

In the "calcining-vitrification" configuration the solution is fed to the calciner by means of a metering pump via a mixing pot. The calciner is a rotary kiln producing a dry residue in the form of granules. Sugar is supplied to the kiln as a calcining additive. At the lower end of the calciner the glass frit is supplied in the form of flakes. The resulting mixture of granules and flakes drops into the melter.

The test solution was a nonradioactive simulant representative of a mixture of the contents of Valduc tanks spiked with silver and chlorine, elements found in other effluents to be processed whose behavior in the glass

and in the process must be assessed. The waste loading in the glass was 31%. Both tests were carried out in 304L stainless steel melting pots 5 mm thick. The setpoint temperature for the standby and feed sequences for both tests was 1140°C in contact with the melting pot to ensure a temperature of 1100°C in the glass. The feed rates and other process parameters are indicated in **Table I**.

Table I. Process Parameter Values

Runs	Feed rate (L/h)	Glass throughput (kg/h)	Recycle rate (L/h)	Sugar (436 g/L) feed rate (L/h)	Oxide mass in solution (g/L)
1	4	2.4	0.5	2.4 then 1.6	202.5
2	5.5 to 2.5	3.4 to 1.6	0.5	0	202.5

With regard to the power input, about 4 kW were necessary to maintain the molten glass at the setpoint temperature during standby, and about 1 kW per liter of feed solution was consumed in both configurations. The difference concerns the power supplied to the furnace: 0.25 kW/L of feed solution in the case of calcining-vitrification (the remaining power was supplied to the calciner) and at least 1 kW/L of feed solution in the case of direct vitrification (power saturation occurred at the beginning of the test).

Direct vitrification has undeniable technological advantages including ease of process control and simplified equipment due to the elimination of the calciner. Calcining-vitrification would have imposed calcining requirements for each tank (sugar quantity, calciner setpoint temperatures, etc.).

Observations of the glass have showed that this process is capable of producing a homogeneous glass with the desired properties (dense, good incorporation of the nuclear waste and no residual glass frit, low viscosity at high temperature). Macroscopic beads consisting mainly of Ag and Cd were observed to settle on the bottom of the crucible. The chlorine loading was only 0.5% instead of the target value of 1%. Chemical analysis (**Table II**) showed a significant cadmium deficit and a strong enrichment by melting pot constituents (Fe, Ni, Mn). The oxygen partial pressure was measured using a zircon electrode and the Heraeus Electro-Nite Rapidox system[5]. This measurement is based upon the potential difference between an iridium working electrode and a zirconia reference electrode. These pressures showed that the glass melts were highly reduced ($10^{-11.5}$ atm for run 1 and $10^{-8.5}$ atm for run 2), and that calcining-vitrification with sugar added in large quantities results in greater reduction of the melt than direct vitrification.

Table II. Glass Compositions for Runs 1 & 2

Oxides	Target Glass (Runs 1 & 2) (wt. %)	Analyzed Glass (Run 1) (wt. %)	Analyzed Glass (Run 2) (wt. %)
SiO_2	43.13	45.92	40.72
Al_2O_3	7.43	6.66	9.92
Na_2O	15.01	12.6	12.98
B_2O_3	13.46	NA	11.77
Fe_2O_3	1.27	7.54	6.07
Cl	1.00	0.50	0.30
CdO	3.07	0.27	2.64
NiO	0.13	0.22	0.37
MnO_2	0.01	0.16	0.14
Cr_2O_3	0.16	1.65	1.14

Two tests (runs 3 & 4) were performed in 2006 to definitively validate the choice of direct vitrification and to collect additional process data. The feed parameter values are shown in **Table III**.

Table III. Process Parameter Values for Runs 3 & 4

Runs	Feed rate (L/h)	Glass throughput (kg/h)	Recycle rate (L/h)	Waste loading (%)	Oxide mass in solution (g/L)
3	8	4.2	0.5	31	161.82
4	6	2.8	0.5	25.5	118.3

SEM analysis of the glass samples showed satisfactory homogeneity with some chromites, but the glass surface in the canister contained bubbles around which metallic cadmium was detected. As the glass was highly reduced and the cadmium volatilization temperature is 765°C, it is very likely that the cadmium reduced to metallic form and volatilized; this hypothesis tends to corroborate the observation that the glass was more reduced during run 1 than run 2.

These tests definitively validated the feasibility of direct vitrification by in-can melting, but highlighted some difficulties — especially the reduction of the molten glass due to corrosion of the metal pot and the high volatility of cadmium.

Optimization tests: Runs 5 to 8

Tests were carried out at laboratory scale to mitigate the difficulties encountered during the technological tests. Iron oxide was added to the melt as a redox buffer and analyses showed that glass was no longer reduced ($10^{-1.5}$ atm) with massive addition of iron oxide (12.5% in the glass). The objective of runs 5 to 7 was to validate the use of Fe_2O_3 additive during a full-scale test. Run 5 was the benchmark test without iron additive; iron was added via the feed solution in run 6, and via the glass frit in run 7. The test objectives, the solutions and frit compositions, and the target glass are summarized in **Table IV**.

Table IV. Summary of Runs 5, 6 and 7

	Run 5	Run 6	Run 7
Objective	Benchmark	Iron additive in feed solution	Fe_2O_3 additive in glass frit
Surrogate feed solution	Benchmark	Benchmark doped with iron to obtain 9 wt% additional Fe_2O_3 in the final glass	Benchmark
Glass frit	Benchmark	Benchmark	Benchmark doped with Fe_2O_3 to obtain 9 wt% additional Fe_2O_3 in the final glass
Target glass	Average glass	Average glass doped with iron oxide	
Melting pot material	NS30 (10 mm)	NS30 (5 mm)	Al_2O_3-clad Inconel 601 (5 mm)

Run 5 had to be interrupted after producing only 65 kg of glass. Runs 6 & 7 produced about 108 kg of glass, but a heating resistor malfunction during run 6 resulted in uneven heating.

Analysis of the off-gas treatment confirmed the effectiveness of adding iron. The most volatile element was fluorine followed by cadmium and sodium (same order of magnitude). Most (about 90%) of the fluorine from the melting pot was trapped in the particle separator. One of the objectives of adding iron was to limit the cadmium volatility related to the reduction of the glass, and this objective appears to have been attained, at least during standby operation. The other objective of adding iron — to limit the reduction of the glass — also appears to have been achieved based on the measured oxygen partial pressures: $10^{-9.4}$ atm for run 5, $10^{-3.2}$ atm for run 6, and $10^{-1.4}$ atm for run 7.

Composition analysis (**Table V**) showed that the glass was chemically homogeneous with the exception of run 6, for which the partial heating resistor failure prevented suitable convection in the glass. The glass

compositions were generally enriched in Fe, Ni, Cr, and Mn with respect to the theoretical target composition and slightly depleted in Cd due to corrosion of the metal pot coupled with the reduction of the glass leading to cadmium volatilization.

Table V. Glass Compositions for Runs 6 & 7

Oxides	Target glass runs 6 & 7 (wt. %)	Analyzed glass run 6 (wt. %)		Analyzed glass run 7 (wt. %)
		Bulk glass	Near wall	
SiO_2	44.13	45.89	41.88	44.42
Al_2O_3	2.36	2.57	2.41	2.57
Na_2O	14.39	13.52	12.87	13.22
Fe_2O_3	12.55	11.84	15.66	12.91
F	1	0.58	0.80	0.60
CdO	2.96	2.58	2.94	2.66
NiO	0	0.30	0.98	0.37
MnO_2	0	0.10	0.21	0.06
Cr_2O_3	0.16	0.48	1.86	0.45

The objective of run 8 was to validate the minimum Fe_2O_3 concentration in the glass at technological scale to limit the reduction of the melt and cadmium volatilization. Iron oxide was added via the glass frit and a 310S stainless steel melting pot (in wt% :Ni 19.1% Cr 25.6% Fe 53.7% Mn 0.90% C 0.045% Si 0.63%) was used.

Analysis of the off-gas treatment showed that optimizing the additive limited the cadmium release from the melt compared with massive iron additive from 9% to 6% ($m_{off-gas}/m_{feed} \times 100$), which corresponds to flows of 0.078 g/h on standby and 7.35 g/h during the feed phase.

 Table VI shows that most of the elements were recovered in the condenser — especially sodium and cadmium, which were released massively into the off-gas stream. The most volatile element was sulfur (about 13% of the feed quantity was recovered in the off-gas treatment). The glass was not reduced ($P_{O2} \sim 10^{-1.1}$ atm). It was chemically homogeneous, but enriched in melter constituents (about 7 to 8% Fe_2O_3 rather than the target of 5.6%).

Table VI. Element Distribution in the OGTS

Element	Cd	Na	Fe	S
Mass recovered in the off-gas treatment system (volatilization from melting pot) (g)	196	483	11	13
wt% of feed stream recovered in the off-gas treatment	6	2	0.2	12
wt% of element flowing out of the melter recovered in particle separator	21	23	45	32
wt% of element flowing out of the melter recovered in condenser	75	74	53	68
wt of element flowing out of the melter recovered in scrubbing column	4	3	2	0

The tests carried out from 2005 to 2008 validated the feasibility of direct vitrification by in-can melting, yielding a homogeneous material with the desired characteristics in terms of chemical durability. Indeed, the initial alteration rate (measured by boron release) in pure water, at 100°C (soxhlet tests), is less than 3.3 $g/m^2/j$. This value is consistent with those obtained on laboratory glasses and show a good chemical resistance behavior. The process was also optimized for operational implementation.

BEGINNING OF PROCESS QUALIFICATION: 2009–…

Having enhanced the reliability of the process, we decided to implement the core process (furnace and particle separator) at Marcoule for maximum representativeness. Since its installation three tests have been carried out in 2009, including an acceptance test and the first two tests in the process qualification program.

Process Qualification Program

The process qualification program included five types of tests to specify the conditions necessary to obtain a homogeneous material:

- Tests to determine the nominal operating parameters guaranteeing the quality of the material fabricated at industrial pilot scale by final characterization of its physical and chemical properties compared with the same material synthesized in the laboratory.
- Two types of sensitivity tests:
  – Chemical composition sensitivity tests similar to laboratory studies intended to synthesize the glass composition potentially most difficult to fabricate at full scale, considering the technological performance of the selected vitrification process.
  – Tests of sensitivity to the operating conditions to specify possible parameter variation ranges acceptable for the material and for the process.
- Transient mode tests to determine melter control parameters during the startup and standby phases.
- Degraded mode tests to identify procedures for offsetting or mitigating the impact of incidents on safety, on the process equipment, and on the material.
- Tests of suitability for actual process effluents, since some basic data remain hypothetical due to the deployment of new processes.

In this program, the tests chosen for these glasses were based on the rheological and thermal properties, on the risk of crystallization or phase separation, and on the presence of volatile compounds. Nominal and maximum capacity tests were carried out in the full-scale pilot described below.

Acceptance Test: Run 9

This test was carried out for acceptance of the facility producing glass under nominal operating conditions with a realistic nonradioactive surrogate solution. The glass production rate was intentionally limited to 5 kg/h, corresponding to a solution feed rate of 4 L/h with recycling at 1 L/h. The processing temperature was 1100°C at the thermocouple in contact with the bottom of the melter.

The test revealed a gradient of about 25°C between the upper and lower portions of the canister, and about 70°C between the low portion and the bottom between the three temperature measurement points. The power required to maintain the molten glass at 1100°C during the standby phase is about 10 kW. The power necessary to produce the glass from the frit-solution mixture is about 3.5 kW per liter of feed solution supplied at the beginning of the test with an empty melter, to 1 kW/L of solution. This corresponds to the results obtained with the previous furnace, but the undersize power supply units made it impossible to estimate the power required at the beginning of the test.

Nominal Test: Run 10

This test was carried out under nominal conditions for the solution. The conditions were identical with run 9, without the test phases inherent in acceptance testing and with a setpoint temperature of 1100°C equal to the mean of two measurements in contact with the upper and lower portions of the melting pot. The results were the same as for run 9, confirming the process repeatability.

The main difference in the off-gas treatment was that after a week of production the particle separator was flushed into a buffer tank to recycle the solution back to the melting pot and appreciably improve the decontamination factor (DF_{pot}).

Maximum Capacity Test: Run 11

This was a test of process sensitivity to the operating conditions, during which the maximum solution feed rates were determined with respect to the melter and the particle separator. For this test the solution feed rate was 10 L/h with 0.5 L/h recycling. No difficulties were observed during the test; the device is capable of operating at full capacity. The test was carried out during the fourth quarter of 2009; the results are still being interpreted and the samples are still being analyzed. Only the observations and analyses of the final material will allow validation of the maximum throughput of this facility.

COMPARISON OF DECONTAMINATION FACTORS BETWEEN FACILITIES

The decontamination factors can be compared for the process equipment in the two facilities with respect to cadmium, sodium, sulfur, and iron. The decontamination factors are calculated from samples taken in the off-gas treatment system at the end of the tests before and after particle separator solution flushing at the end of the week. DF_{pot} characterizes the element release from the melting pot due to volatility or mechanical entrainment. The order of magnitude of these values was reproducible from one test to another in the former unit.

Table VII. Process Decontamination Factors of the 2 Facilities

Element:	Cd			Na			Fe			S		
	Former	New		Former	New		Former	New		Former	New	
		Bef.	Aft.		Bef.	Aft.		Bef.	Aft.		Bef.	Aft.
DF_{pot} (melting pot)	16	30	63	45	35	74	427	332	1174	9	9	19
DF_{sep} (particle separator)	1	2.3	1.1	2	2.3	1.1	2	4.4	1	1	3	1.3
DF_{cond} (condenser)	20	5	5	12	6	7	27	12	15	25	6	6
$DF_{process}$ (total)	320	345	346	1080	483	570	23058	17430	17610	225	162	148
% of feed stream recovered in the off-gas treatment	6.1	3.3	1.6	2.2	2.9	1.3	0.2	0.3	0.1	11.7	11.4	5.3

The DF values for the condenser diminished in the new facility, whereas the DF increased for the particle separator; this generally occurs when the upstream device is shut down, i.e. in this case in the bubble-cap tray particle separator, which thus appears to be more effective than the preceding version. It may also be noted that the percentage each element recovered in the off-gas system is lower with the new test bed (Run 10) than with the preceding one (Run 8). This difference is mainly attributable to the change in the particle separator solution management procedure at the end of the week.

CONCLUSION

Since 2005 CEA Marcoule has been developing an "in-can melting" vitrification process for specific High Activity Nuclear Waste Solutions at CEA's Valduc Center. The tests carried out to date have validated the feasibility of this process and confirmed the direct vitrification option in which the liquid and solid feed streams are supplied directly to a disposable melting pot.

Difficulties involving the material and the process were encountered (reduction of the glass melt coupled with strong cadmium volatility) but were mitigated during the reliability development tests resulting in a robust process. The glass produced is homogeneous.

CEA Marcoule began process qualification testing in 2009 in a new facility using equipment representative of the devices that will be installed in a glove box at CEA Valduc. After testing under nominal operating conditions and a test of process sensitivity to operating conditions, the program will continue as described in the article. By beginning with tests under nominal conditions, it is possible to quickly detect possible issues, and thus to modify the operating conditions or the glass composition range if necessary.

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