

Development of In-Can Melting Process Applied to Vitrification of High Activity Waste Solutions (HAWS): Glass characterizations and process tests results - 12442

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ABSTRACT

The CEA has selected vitrification for specific High-Activity nuclear Waste Solutions (HAWS) containing large quantities of salts. This choice has led 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 m³ 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.

In order to be fully representative of the glove box to be implemented, 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 nominal tests were performed in 2009 and 2010 to verify that no problems arose in vitrifying solutions under the specified conditions. Two different liquid feeds representatives of the current HAWS stored and future solutions were used. The transient runs were carried out in this facility in 2010. Their objectives were to validate the glass product with different operating conditions and to determine optimum parameters for transient phases such as decreased volatility during standby phases.

Finally, all the material obtained under nominal conditions or different operating conditions (e.g. initial glass frit quantity, standby temperature or restart procedure of feeding after night surveillance) have been characterized and described. The impact of transient phases on the process is then discussed in terms of volatility, thermal balance, etc., and compared with nominal tests results. Off-gas treatment system (OGTS) assessments determined preliminary decontamination factors for the OGTS components and allowed comparison between the two types of solutions and for different operating parameters.

INTRODUCTION

In order to treat a fraction of the nuclear waste arising from some activities of CEA, 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]. First the feasibility of vitrification was confirmed, a configuration was defined, and the process was optimized [4]. The second stage involves process and material qualification in a new representative facility.

This paper describes the new representative facility together with the process qualification procedure. This program includes 5 types of tests (nominal, 2 types of sensitivity tests, transient and degraded mode) and the nominal and the transient tests have been completed and those results presented in this paper.

The nominal tests were performed in 2009 and 2010 to verify that no problems arose in vitrifying solutions under the specified conditions. Two different liquid feeds representative of the current HAWS and of future solutions were used. The results obtained in terms of process control, material and volatility are discussed.

The transient runs were carried out in this facility in 2010 to validate the glass product with different operating conditions and to determine optimum parameters for transient phases such as decreased volatility during standby phases. The impact of transient phases on process is then discussed in term of volatility, thermal balance, etc. Preliminary decontamination factors of the process are also indicated for the pot/scrubber system with different operating parameters.

NONRADIOACTIVE PILOT-SCALE UNIT

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

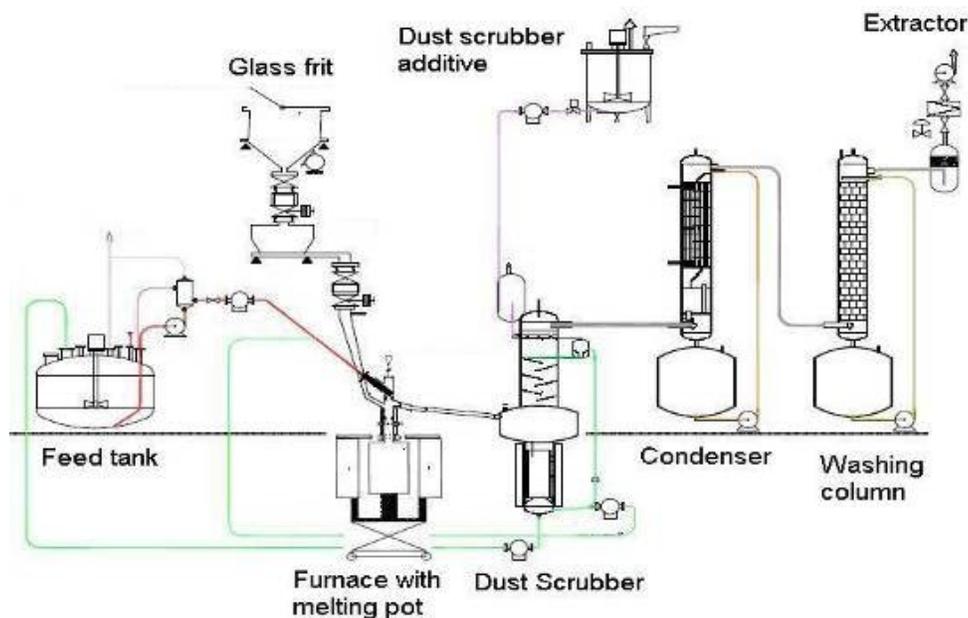


Figure 1. Diagram of full-scale pilot in direct vitrification configuration

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 new furnace in use since 2009 is mounted 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 2**).



Figure 2. Vitrification furnace currently in use

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 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

The connector tube between the melting pot and the particle separator is equipped for declogging the vertical (all runs) and inclined (since run 2010#1) portions, for supplying the feed solution directly on the melting pot centerline, and for exhausting the off-gas to the particle separator. It was air-cooled for the first nominal run (2009#2) and subsequently water-cooled (since run 2010#1) 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 an airlift 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 and particulates trapped by the separator are recycled to the mixing pot. 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 NO_x 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.

PROCESS QUALIFICATION: 2009–...

Since the implementation of the core process (furnace and particle separator) at Marcoule for maximum representativeness, ten tests have been carried out, including an acceptance test (run 2009#1) and some 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 (runs **2009#2** and **2010#1**).
- 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 (run 2011#1 and 2011#3).
 - Tests of sensitivity to the operating conditions to specify possible parameter variation ranges acceptable for the material and for the process (runs 2009#3 and 2009#4).
- Transient mode tests to determine melter control parameters during the startup and standby phases (runs **2010#2** and **2010#3**).
- Degraded mode tests to identify procedures for offsetting or mitigating the impact of incidents on safety, on the process equipment, and on the material (run 2011#2).
- 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. Tests were carried out in the full-scale pilot are indicated previously and these described below are in bold.

NOMINAL TEST

Objectives and procedure

Both tests under nominal operating conditions consisted in determining the nominal parameters. The tests were conducted for the following purposes:

- Ensure the quality of the material produced in an industrial pilot facility by final characterization of its physical and chemical properties (homogeneity, chemical composition, etc.).
- Provide data on the process and the material balance (decontamination factors for the equipment, melter, dust scrubber, etc.) at full scale under inactive conditions.
- Validate the nominal parameters for all the process equipment.

The first test (2009#2) was performed with a surrogate effluent solution representative of the process input, known as the “A” solution, and the second (2010#1) with a “B” solution.

The “A” solution was a 4 N nitric acid solution with 170 g/L of dry solids, consisting of nitrate salts (mainly cadmium and sodium at equivalent oxide concentrations of 60 and 90 g/L, respectively) and other elements (Fe, Ca, F, Cl, S, etc.) at concentrations not exceeding 6 g/L.

The “B” solution was a more acidic (7 N) nitric acid solution also containing nitrate salts (mainly magnesium and gallium at equivalent oxide concentrations of 14 and 5 g/L); the concentrations of the other elements (Cd, Ca, Na, F, Cl, etc.) did not exceed 4 g/L and the dry solid content was about 55 g/L. This solution also contained silver.

A typical test procedure under nominal operating conditions is shown in **Figure 3**.

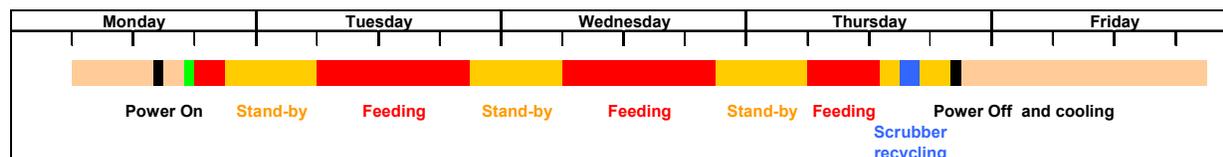


Figure 3. Typical test procedure under nominal operating conditions

The duration of the feed sequence depended on the vitrification feed solution (concentration, dry matter): about 22 hours for the “A” solution and 40 hours for the “B” solution. Except for this difference, the procedure was the same: after a week of operation, the dust scrubber was drained into a buffer pot in order to reinject the trapped particulates into the melting pot and thus increase the process depollution factor.

Process

The nominal process parameters used for these tests are shown in the following table.

Table I. Process Parameter Values for Runs 2009#2 and 2010#1

Runs	Temperature (°C)	Feed rate (L/h)	Glass throughput (kg/h)	Recycle rate (L/h)	Waste loading (%)	Oxide mass in solution (g/L)
2009#2	1100	4	5	0.5	13.6	170
2010#1	1100	5	2.7	1	10.2	55

The glass production rate for test 2009#2 was intentionally limited to 5 kg/h, which limited the liquid feed rate.

The process setpoint temperature was the mean temperature value measured at two points in contact with the upper and lower walls of the melting pot. The setpoint temperature (1100°C) was maintained within 4°C during the feed sequence and within 1°C during standby with the exception of transient operating

phases (feed startup and shutdown, melter shutdown, etc.). The molten glass temperature was measured during test 2010#1 to validate the effectiveness of a simpler regulating system based on temperature measurements in contact with the melting pot wall. The results are shown in **Figure 4**.

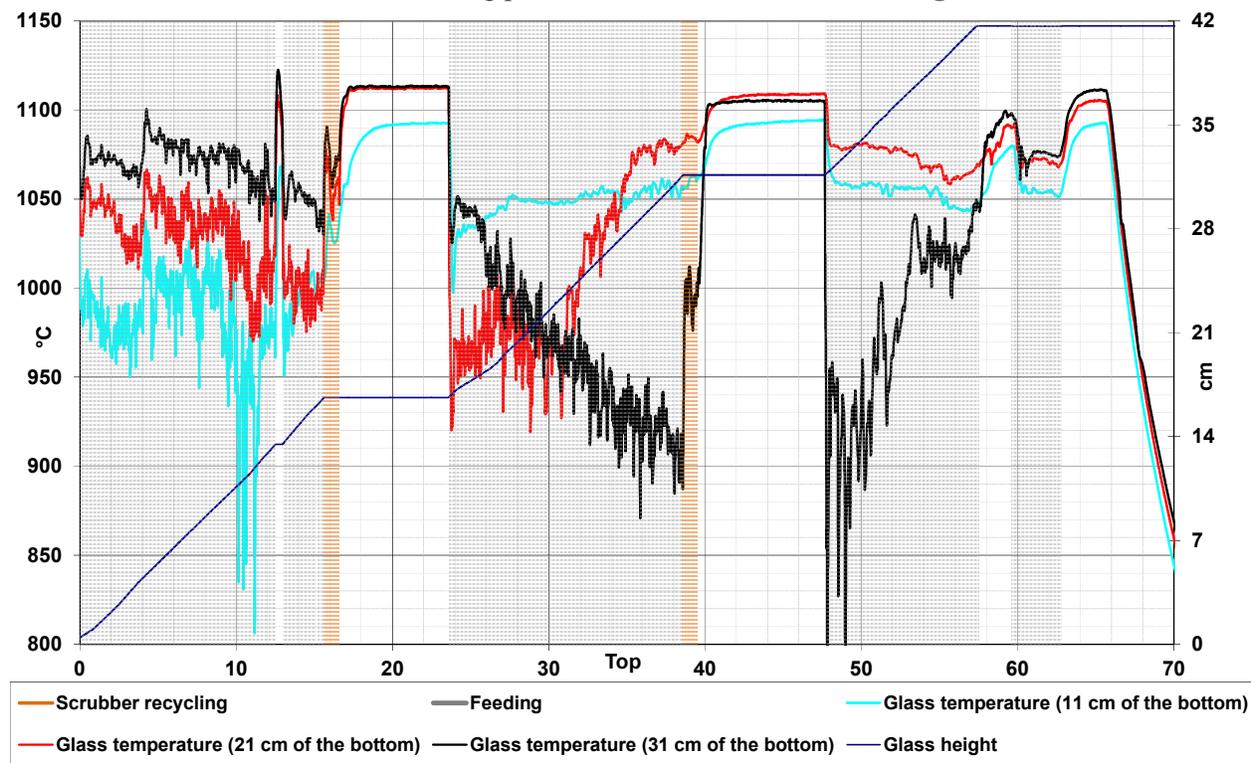


Figure 4. Glass temperatures and glass height for Run 2010#1

During standby, a temperature rise can be observed in the measured zones, whether or not they were immersed in molten glass. This is logical considering that during the feed sequence the melt is partially covered and its surface is cooled by the arrival of cold material. In addition, the production of gases (steam, NO_x , etc.) cools the measurement points situated outside the melt.

During the feed sequence, the temperature behavior measured at different height is reproducible according to the glass level. The temperature first gradually decreases until the molten glass surface reaches the measuring point. The temperature then rises during the time necessary to produce about ten centimeter of glass in the melting pot. Once the melt level is 10 cm above the measuring point, the temperature stabilizes until the end of the test.

The power required to maintain the melt in the molten state during the standby phase is about 10 or 11 kW. During the feed phases, the power required in the melter is 4.5 kW/L/h for the “B” solution and about 4.2 kW/L/h for the “A” solution. However, much of this power is dissipated in the furnace structures and in the connecting sleeve between the pot and the dust scrubber. The data (available for test 2010#1) allowed us to inject about 0.5 kW into the melt during the standby phase and about 1.6 kW/L/h of “B” solution.

The melting pot can be cooled by natural convection or by forced convection by supplying compressed air to the melter. Pot 2009#2 was cooled naturally, and pot 2010#1 by forced convection; the difference between the two methods was 28 hours to reach a temperature of 50°C. A temperature of 50°C wall was reached naturally in 72 hours compared with 44 hours when compressed air was supplied to the melter once the melting pot wall temperature dropped below 600°C.

Analyses of the off-gas stream showed that the flows observed for both tests are acceptable, with no significant impact on the resulting glass composition. Nevertheless, the volatilization flow levels obtained for nominal test 2010#1 (“B” solutions) were at least ten times lower than those calculated during the

tests with “A” solutions. During the feed sequence the volatilization flows did not exceed 1.3 g/h regardless of the element considered, although for example values of 26 g/h for Na or 7 g/h for Cd were reached for the “A” solutions (compared with 1.1 g/h and 0.6 g/h for the “B” solutions). Nevertheless it must be noted that the solutions have different characteristics and that the conditions taken into account for the nominal test 2009#2 were not optimized (off-gas treatment problems, air-cooled sleeve, etc.). In both cases the greatest volatility was observed during the first feed phase.

Glasses

Chemical analysis of the glass samples showed that the “A” glass was of uniform composition throughout the canister volume. The composition was similar to the expected one except that sulfur was present in smaller quantities. Slight cadmium was enrichment (4.9%) was observed at the bottom of the pot together with pot constituents (Ni, Fe, Cr). The “B” glass was generally homogeneous and close to the expected composition, although slight silver depletion was observed. Unlike the “A” tests, no Ni or Cr enrichment was observed in the glass, suggesting limited corrosion of the melting pot.

Table II. Glass Compositions for Runs 6 & 7

Oxides	“A” glass (run 2009#2)		“B” glass (run 2009#2)	
	Target glass (wt%)	Analyzed glass (wt%)	Target glass (wt%)	Analyzed glass (wt%)
SiO ₂	47.56	47.24	45.55	45.89
Al ₂ O ₃	4.14	4.14	4.97	4.90
Na ₂ O	14.07	14.00	13.14	13.26
Fe ₂ O ₃	5.68	5.80	5.65	5.75
F	0.16	<0.2	0.3	<0.3
CdO	4.59	4.60	0.68	0.68
NiO	0.08	0.38	0.00	0.00
SO ₃	0.27	0.23		
Cr ₂ O ₃	0.09	0.24	0.00	0.00
Ga ₂ O ₃			0.88	0.80
MgO			2.57	2.85
Ag ₂ O			0.38	0.23

The differences in color visible to the naked eye (“yellow” glass and “black” glass) at the bottom of the pot (**Figure 5**) are probably due to differences in the size distribution of silver nodules dispersed in the glass matrix.

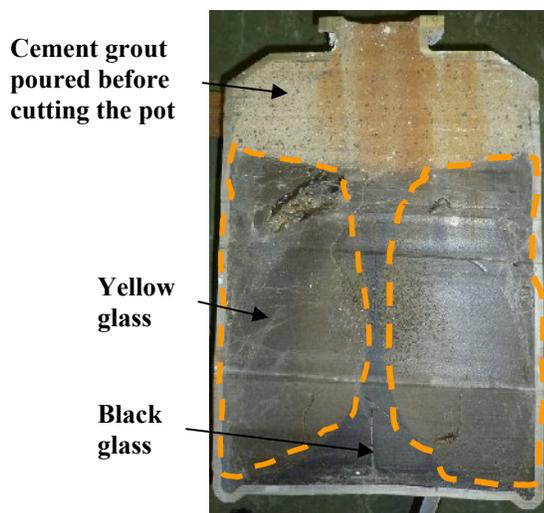


Figure 5. Cutaway melting pot – Run 2010#1

The measured glass properties are indicated below.

Table III. Physical and chemical properties measured for the “A” and “B” glass specimens

Property	“A” glass		“B” glass	
	Pilot scale	Laboratory scale	Pilot scale	Laboratory scale
P(O ₂) (atm)	10 ^{-0.5}	Not measured	10 ⁻²	Not measured
Viscosity (dPa·s at 1100°C)	40	41	59	62
Density (Room temp.)	2.71 ± 0.01	2.695 ± 0.002	2.704 ± 0.002	2.673 ± 0.002
Density (1100°C)	2.405 ± 0.002	Not measured	2.383 ± 0.001	Not measured
Glass transition temperature (°C)	491 ± 6	484 ± 6	485 ± 6	494 ± 6
Thermal conductivity (W/m·K)	5.8 ± 0.5	Not measured	7.5 ± 0.5	Not measured

The oxygen partial pressure measured with a Rapidox analyzer [5] shows that the two glass specimens are not reduced. The measured densities and glass transition temperatures are comparable for technological and laboratory glass specimens. The thermal conductivity of the “B” glass was higher than for the “A” glass, probably because of the much higher NiO and Fe₂O₃ absorber content in the “A” glass (6.3% and 0.3%) than in the “B” glass (5.8% and 0%).

SEM observations and EDS analyses showed that “A” and “B” glasses were homogeneous. It may be noted that the “B” glass contains silver nodules uniformly distributed in the matrix.

For each test, glass samples were taken from the middle of the canister (zone 2) and near the wall (zone 6) for leaching testing in renewed pure water (Soxhlet conditions) to determine the initial alteration rate at 100°C. The rates measured from the normalized boron mass losses are summarized in **Table IV**.

Table IV. $r_0(B)$ and daily mass losses measured during Soxhlet leach tests at 100°C

		$r_0(B)$ g/m ² /d	$\Delta m/(S \cdot \Delta t)$ g/m ² /d
“A” glass	Pilot scale 2009#2 middle	3.9 ± 0.6	3.1
	Pilot scale 2009#2 wall	3.5 ± 0.5	2.9
	“A” glass (laboratory scale)	3.7 ± 0.6	3.3
“B” glass	Pilot scale 2010#1 middle	2.7 ± 0.4	3.8
	Pilot scale 2010#1 wall	4.0 ± 0.6	3.1
	“B” glass (laboratory scale)	3.3 ± 0.5	2.7

These values show satisfactory glass chemical durability. The initial alteration rate of the “A” glass in test 2009#2 is of the same order of magnitude as for the “A” glass fabricated at laboratory scale. This is also true for the nominal “B” glass formulation.

These two tests under nominal operating conditions produced glass samples generally meeting our expectations, and allowed us to measure the characteristic properties (viscosity, density, thermal conductivity, chemical durability) of the “A” and “B” glass. The Inconel 601 melting pots exhibited good corrosion resistance during these tests.

These tests also allowed us to determine the nominal operating conditions:

- a nominal process temperature of 1100°C;
- a maximum glass production rate of 5 kg/h;
- a liquid feed solution flow rate of 5 L/h or less if the glass production rate exceeds the preceding maximum value;
- a liquid recycle rate of 0.5 L/h for a nominal solution feed rate 5 L/h.

TRANSIENT TEST

Objectives and procedure

Transient mode tests are operating tests at rated capacity dedicated to a study of transient modes (standby and startup). The objective is to assess the effects of transient process phases on melter behavior (convection cells, melting pot skin temperature, etc.), on the process parameters, and on the resulting glass quality to determine the optimum operating modes. They were performed at the rated capacity of the test bed and at the rated temperature during the feed sequence, 1100°C.

These tests were carried out for the following purposes:

- study the startup phase (first addition of frit),
- study the standby phases (temperature changes during standby),
- obtain a homogeneous glass with the desired composition,
- provide data on the process and on the material balance (decontamination factors for the equipment, melter, dust scrubber, etc.) for the startup phase, the feed phases, and the corresponding standby phases.

The tests were carried out with the “A” solution (test 2010#2) and “B” solution (test 2010#3). The standby temperatures tested were 1060°C, 1080°C and 1100°C, with initial glass frit masses of 3 kg (2009#2) and 5 kg (2009#3). Only the “B” test is discussed here.

Process

The process parameters were the same as for test 2010#1 during the feed sequence. The observations reported for test 2010#1 are applicable here, except that the melter power level observed during the standby phase ranged from 9 kW (1060°C) to 11 kW (1100°C).

The off-gas stream was analyzed to calculate the volatility of the elements during these phases and corroborated the results obtained during the nominal test. Adding a larger mass of frit (5 kg instead of 1 kg) generally appeared to limit the volatility (**Table V**). Conversely, recycling particulates from the dust scrubber for 15 minutes before the resumption of the feed streams following a standby phase or lowering the temperature during the standby phases did not significantly diminish the volatility of these elements.

Table V shows the element weight percent values at the outlet of the pot according to the height of glass for the tests performed with “B” solutions with different frit masses on startup.

Table V. Elements (wt%) found at the outlet of the pot for “B” tests with a glass height of 45 cm

Element	“B” glass	
	1 kg glass frit Run 2010#1	5 kg glass frit Run 2010#3
Nd	4.7%	3.0%
Mg	3.3%	2.5%
Cd	4.3%	3.6%
Na	0.7%	0.2%

It may be noted that the weight percentages recovered at the outlet of the pot were lower when the startup was performed with 5 kg of frit. This gain is also visible for all the elements during filling of the melting pot.

The decontamination factor, DF , of a device is the ratio of inflow to outflow. It is calculated for a time t as the mass inflow rate divided by the mass outflow rate. The decontamination factors are calculated from

samples taken in the off-gas treatment system at the end of the tests after particle separator solution flushing at the end of the week.

$DF_{Pot-Scrubber}$ values were calculated for each chemical element for the pot-scrubber unit:

$$DF_{Pot-Scrubber} = \frac{F_A \times [A] + F_F \times \%F + F_R \times [R]}{F_C \times [C] + F_W \times [W]}$$

where F_A volume flow rate of vitrification feed solution
 $[A]$ concentration of the element in the vitrification feed solution
 F_F mass flow rate of glass frit
 $\%F$ weight percentage of the element in the glass frit
 F_R recycling volume flow rate
 $[R]$ concentration of the element in the particle separator
 F_C condensate volume flow rate
 $[C]$ concentration of the element in the condenser
 F_W overflow rate from NOx column
 $[W]$ concentration of the element in the NOx column

The pot-scrubber decontamination factor ($DF_{pot-scrubber}$) characterizes the release of each element from the melter + scrubber system into the condenser. The causes thus may be either the production of volatile species in the melter, or the entrainment of particles in the process gas stream. The decontamination factors can be compared for the pot-scrubber system with respect to cadmium, sodium, fluorine, neodymium and gallium.

Table VI. Overall depollution factor for the melting pot and dust scrubber for the tests with “B” solution

DF pot-scrubber	Nd		Cd		Na		F		Ga	
	2010#1	2010#3	2010#1	2010#3	2010#1	2010#3	2010#1	2010#3	2010#1	2010#3
	~ 875	~ 850	~ 245	~220	~ 2680	~2030	~ 200	~160	~ 2000	~1760

The results by decreasing order of relative volatility are: fluorine, cadmium, neodymium, gallium, and sodium. The DF observed for this test are very satisfactory, and comparable to those of nominal test 2010#1.

Glasses

The glass synthesized during the transient mode test was similar in every respect to the glass obtained in the nominal test. The observations for the nominal glass samples are reproducible for these samples as well. Chemical durability measurements were also performed and support the results obtained earlier. The measured values were $r_0(B)_{middle} = 1.9 \pm 0.3 \text{ g/m}^2/\text{d}$ and $r_0(B)_{wall} = 3.8 \pm 0.6 \text{ g/m}^2/\text{d}$.

CONCLUSION

Since 2005 CEA Marcoule has been developing an “in-can melting” vitrification process for specific High Activity Nuclear Waste Solutions. 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. 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.

The nominal mode tests performed in 2009 and 2010 were used to determine nominal operating conditions for the process:

- a nominal process temperature of 1100°C
- a maximum glass production rate of 5 kg/h
- a liquid feed solution flow rate of 5 L/h or less if the glass production rate exceeds the preceding maximum value
- a liquid recycle rate of 0.5 L/h for a nominal solution feed rate 5 L/h.

They also produced glass samples generally meeting our expectations, and allowed us to measure the characteristic properties (viscosity, density, thermal conductivity, chemical durability).

The first test of transient operation in 2010 yielded glass consistent with expectations and showed that reducing the temperature had no significant effect on the volatility of the constituent elements. However, a significant impact on the release of elements at the beginning of the test was observed with a larger initial quantity of glass frit on startup.

The process qualification program will now continue with tests of degraded operating modes.

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