French HLW Vitrification History and Major Achievements

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The vitrification of High-Level liquid waste (HLW) produced from nuclear fuel reprocessing has been carried out industrially for over 40 years by Orano with three main objectives: containment of fission products, reduction of the final volume of waste and optimization of plants efficiency in an industrial context. Since the beginning of the French vitrification history in the 50's, continuous efforts have been made to improve processes and technologies and to adapt matrix formulations in accordance with waste features and Waste Acceptance Criteria (WAC).

The vitrification process operated by Orano includes two main steps (Figure 1). First, the nitric acid solution containing the highly radioactive fission products and the noble metals-rich fines suspension are evaporated and calcined into a rotative furnace, the calciner. Then, the resulting calcine is mixed with glass frit and heated in the melter. The gas generated by evaporation and calcination are cleaned by an off-gas treatment system (OGTS). The first stage of the OGTS is a wet dust scrubber which allows most of the dust carry-over to be directly recycled into the process.

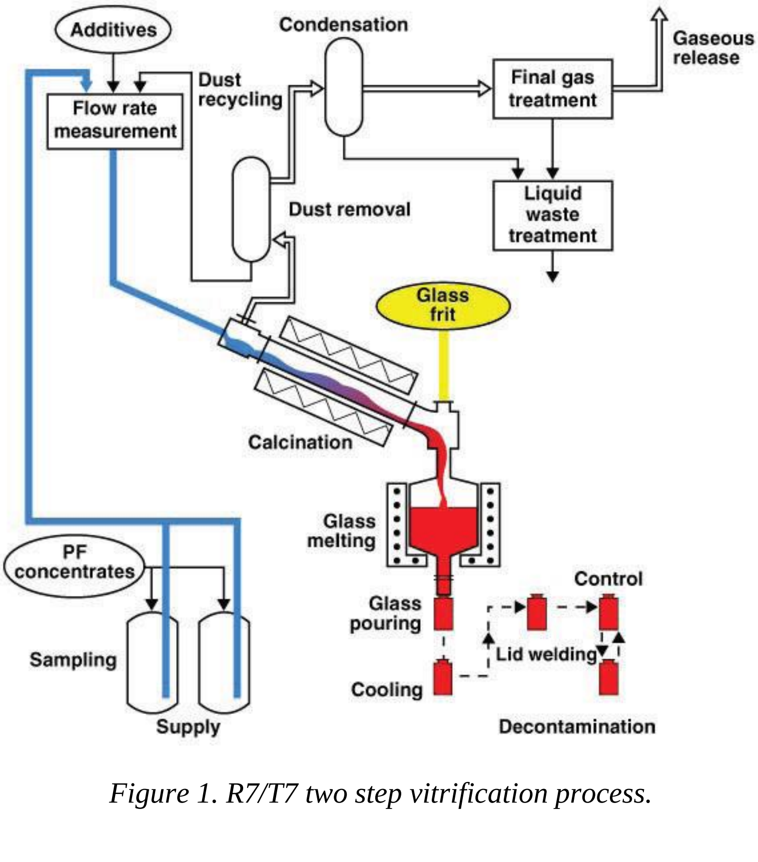

Figure 1. R7/T7 two step vitrification process.

Based on the industrial experience gained in the Marcoule Vitrification Facility (namely AVM), the vitrification process was implemented at a larger scale in the late 1980's at the Orano "La Hague" commercial recycling plant in the R7 and T7 vitrification facilities to be operated in line with the UP2-800 and UP3 reprocessing plants. R7 and T7 facilities are both equipped with 3 vitrification lines.

The Induction Heated Metallic Melter (IHMM) has been first developed and successfully operated for over 40 years with continuous improvements of the process through operational feedback and R&D

programs [1]. In this technology (Figure 2), the metallic wall of the melter is heated by Joule effect through electromagnetic currents provided by a stack of coils surrounding the melter. The metallic wall of the melter directly heats the glass by thermal conduction. The glass is heated up to a temperature of around 1100°C. The melter is continuously supplied with calcine and glass frit during glass processing, feeds are stopped to pour the glass into the canister. The IHMM has a 25 kg/h glass production capacity and the molten glass surface area is around 0.26 m^2.

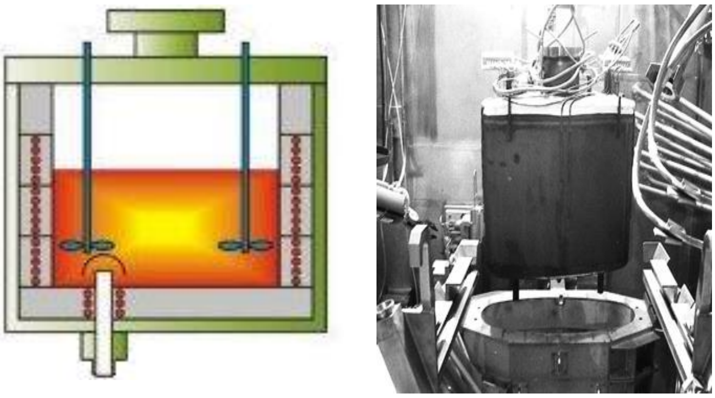

Figure 2. (a) IHMM design principles. (b) Picture of a IHMM in hot cell

Thanks to CEA (French Alternative Energies and Atomic Energy Commission) and Orano long term R&D experience in vitrification processes, the complete industrial experience acquired by Orano operation teams, the close support from engineering team of Orano Projets and the permanent contact between those entities, this specific organization has managed to support efficiently various improvement programs and contributed to significantly improve the vitrification operation at La Hague plant. The major programs that have contributed to operation improvement have been: an upgrade of the calciner to increase the feed throughput; the optimization of the IHMM technology and operation in order to improve its capacity to operate with high noble metals (NM) incorporation rate and high melting throughput; a major update of operation guidelines for the key equipment in order to consider years of industrial feedback and up to date R&D knowledge; and the improvement of reliability and remote in-cell maintainability.

The Orano continuous improvement policy has also led to the development and implementation of the Cold Crucible Induction Melter (CCIM) technology. The CCIM is characterized by currents directly induced inside the molten glass by a coil (Figure 3). These electromagnetic currents heat the glass inside the melter by the Joule effect. The segmented structure of the crucible enables penetration of electromagnetic field into its volume. Absorption of electromagnetic radiation allows the glass to be heated directly without heating the crucible.

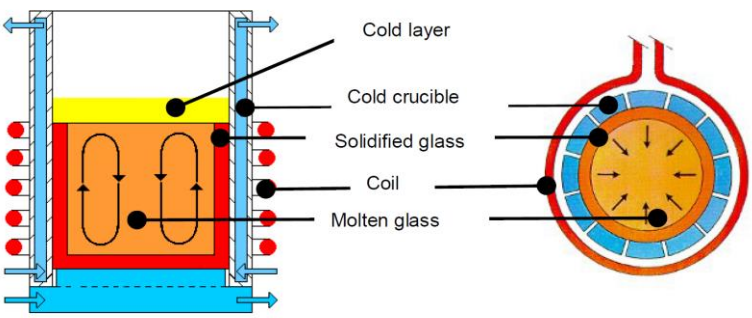

Figure 3. Direct induction melting principle

This technology can be used to vitrify various types of chemical waste. By allowing higher waste loading it also minimizes the total volume of packaged waste. Furthermore, the presence of the cold layer minimizes the impact of the composition of the waste on the lifetime of the crucible.

The CCIM has started hot operation at La Hague plant in April 2010 and has now been in commercial operation for over 12 years. The implementation of the CCIM has been a major breakthrough as it had to be installed in place of an IHMM, in a highly radioactive cell into which human access was prohibited, and without impacting the existing structures and upstream or downstream equipment. The CCIM was first used to vitrify effluents from the La Hague UP2-400 facility D&D operations [2]. This waste stream was vitrified into a borosilicate glass at a temperature of around 1250°C to reach significant waste loading. A dedicated glass frit formulation was developed to avoid foaming phenomena during the treatment as the effluents had a high content of cerium. Around 220 canisters were produced. The CCIM was then used to vitrify around 250 m^3 of high-level liquid waste from reprocessed U-Mo-Sn-Al spent fuel, used in Gas Cooled Reactors (GCR), that were produced during the mid-1960s at La Hague plant. These “UMo” solutions were less radioactive than the current fission products concentrates coming from ongoing reprocessing activities, but were very rich in molybdenum and phosphorus. The high molybdenum and phosphorus contents made the molten glass extremely corrosive and required a special high-temperature glass formulation to obtain sufficiently high waste loading (12 wt% in molybdenum oxide). Since 2020, the CCIM has been operated for the vitrification of the very high-level fission products coming from the ongoing reprocessing activities at La Hague Plant. The “R7T7” UOx glass has an average incorporation rate of 1 Ci/g and can be loaded with up to 3 wt% of NM (RuO_2 + Rh + Pd).

As a result, Orano, supported by CEA, has developed a unique experience in the field of design, construction, and operation of HLW vitrification facilities with high record of safety, reliability, and product quality in line with reprocessing plant operation objectives. Based on this experience, the consortium of the DEM&MELT project which gathers Orano, CEA, ECM Technologies and ANDRA (French national radioactive waste management agency) has developed a specific In-Can vitrification tool designed to match the requirements and constraints from D&D projects. The DEM&MELT In-Can vitrification process is a robust, simple, and versatile in situ vitrification process. It is designed for high or intermediate level waste and is compact enough to be implemented in an existing facility or close to the waste to be treated. It has been developed to treat both liquid and solid waste, to produce a small amount of secondary waste and to minimize investment and operating costs.

DEM&MELT is an In-Can process for thermal treatment and vitrification of solid and liquid radioactive waste (Figure 4). The canister (or “can”) is directly used as a melter — and renewed after each batch — to stabilize and condition the waste, with or without additives, and to form a dense, monolithic, stable, and durable matrix.

Figure 4. (a) Schematic diagram of the DEM & MELT process. (a) DEM&MELT scale 1 pilot unit built and commissioned at CEA Marcoule

The technology was tested at pilot scale with waste of various types [3]: namely alpha liquid waste (full qualification of the process with around 20 pilot tests), solidified fission products, liquid fission products solution, zeolites, silicotitanates, sand, ashes and co-precipitation slurries. The tests carried out confirm the simplicity, robustness and versatility of the process. The technology makes it possible to achieve high rates of waste incorporation into the matrix while guaranteeing good performance of the wasteform — especially with regards to its durability in order to limit the release of radioelements into the biosphere — and ensures very low volatility of the radioelements during thermal treatment. The main results are presented in the table hereafter.

Waste	WL oxides *	Radionuclides volatility	Wasteform
HL Solid fission products	10 %	0.6 wt% Cs	Glass
HL Liquid fission products	10 %	0.2 wt% Cs	Glass
Alpha-contaminated liquid waste	Confidential		
Ashes	50 %	-	Crystallized glass
Zeolites	50 %	0.08 wt% Cs	Glass
Mix of zeolites, slurries, silicotitanates and sand	80 %	<0.5 wt% Cs; <0.1 wt% Sr	Crystallized glass
Mix of zeolites, silicotitanates and sand	60 %	0.04% wt% Cs; 0.01% wt% Sr	Glass
Coprecipitation slurries	40 %	0.007 % Sr	Glass

Table 1. Pilot tests main results

$$* \, \boldsymbol{WL_{ox}}(\%) = \frac{sum\ of\ oxide\ masses\ composing\ the\ waste\ (kg)}{mass\ of\ wasteform\ (kg)} \times 100$$

[1] A. Garcia, L. Gauquelin, M. Gassies, J. Lauzel, Ph. Mahut, E. Boudot, S. Betremieux, S. Ben Lagha, L. Meslin, JF. Hollebecque, "New Operation Records for La Hague R7/T7 Vitrification Facilities: A Success of a continuous Improvement Program", GLOBAL 2015, Paris, France

[2] Régis Didierlaurent, Eric Chauvin, Jacques Lacombe, Christian Mesnil, "Cold crucible deployment in La Hague facility: the feedback from the first four years of operation", WM2015 Conference, March 15 – 19, Phoenix, Arizona, USA

[3] Régis Didierlaurent, Laurent David, Maxime Fournier, Caroline Michel, Jean-François Hollebecque, "DEM&MELT In-Can Melter Solution: from Demonstration Tests to Industrial Design", WM2022 Conference, March 6 – 10, 2022, Phoenix, Arizona, USA