

The Industrial Experience Feedback and R&D Ensure the Longevity of French Vitrification Facilities - 15503

Christian LADIRAT *, **Jean-François HOLLEBECQUE ***, **Eric CHAUVIN ****

** CEA, DEN, DTCD, SCDV, F-30207 Bagnols-sur-Cèze, France.*

*** AREVA NC, Tour AREVA, 1 place Jean Millier, F-92084 Paris La Défense, France*

ABSTRACT

The French vitrification of High Level Liquid Waste (HLLW) developed since the beginning of the 1960s led to the successive completion of four industrial vitrification facilities: PIVER facility (1969), Marcoule vitrification facility (1978), and R7 (1989) and T7 (1992) vitrification facilities on La Hague site.

R&D has involved containment glass formulation and characterization of glass properties, development of modular technologies specifically tailored to be operated in shielded cells, and development of the vitrification process on full scale prototype. Industrial support has then provided by the R&D team during all phases of commissioning and operation of these industrial facilities.

The initial choices of industrial facility design, as well as technologies to enhance flexibility and modularity, allowed an evolution of the vitrification process over time.

Maintaining the R&D capabilities on containment glass, process and technology development at full scale size is essential to anticipate treatment of the new effluent and propose innovative industrial technologies. Fueling R&D with industrial feedback ensured the longevity of industrial vitrification facilities and development capabilities for future projects.

INTRODUCTION

France, in the development of its nuclear power industry, has chosen to make optimum use of and recycle fissile material contained in the spent fuel from its reactors. A UP1 reprocessing plant at Marcoule was built to handle the fuel from gas-cooled natural uranium reactors and two UP2 and UP3 plants were built on the La Hague site to process fuel from light water reactors (LWR). Vitrification was quickly chosen for the solidification of High Level Liquid Waste (HLLW). Demonstrating its industrial feasibility and its containment performance over the long term has been an ongoing concern. To do this, the vitrification process was developed in France by jointly conducting laboratory studies on materials, technological development of equipment and the construction and operation of industrial scale vitrification facilities associated with existing reprocessing plants.

For each type of waste to be treated and for each fabrication or upgrade project of an industrial plant, research and development simultaneously focused on studies to formulate a glassy containment matrix, on the design preparation process tailored to the glassy matrix specifications and the development of equipment specifically suited to use in shielded cells. Feedback from operating and managing existing vitrification industrial facilities is an essential source of information. It is taken into account in the development of studies to improve or adapt the entire vitrification process.

The development of vitrification in France is presented through the commissioning background of the various vitrification industrial facilities. The assigned objectives, initial choices of technology, basic R&D implemented, industrial guidance support applied and lessons learned from each facility are illustrated to show the changes in the French process. Anticipating R&D studies that incorporate feedback is also essential to prepare for future developments in running facilities.

GLASS AS CONTAINMENT MATERIAL AND ITS PRODUCTION PROCESSES

HLLW, pre-concentrated to reduce the volume, are temporarily stored in constantly agitated and cooled stainless steel tanks. Their activity related to the burn-up fraction of the fuel treated, may reach $3.75 \cdot 10^{13}$ Bq/L and the heating power generated is sizeable (up to 7 W/L). These nitrate solutions (1 to 2 N) are generally characterized by high physicochemical complexity.

The purpose of HLLW vitrification is to:

- convert waste from a liquid to a solid state
- reduce the volume in interim storage and storage
- obtain a material that meets the safety requirements needed by interim storage and storage.

The material intended for the containment of Fission Products and actinides (FP) contained in these solutions must have very special properties, due to chemical issues. In the 60s, glass was chosen by France and the international community as the containment material for fission product solutions, due to the flexibility of its amorphous structure that enables it to contain many chemical elements. This research to find a glass compound is a compromise between the properties of the material and the technological feasibility of producing it on an industrial scale. France chose alumino-borosilicate glass as the containment material for fission product solutions resulting from the treatment of fuels from "graphite gas" and "light water" reactors.

The main operations to convert the solution to be treated to a vitrified waste package are as follows:

- Evaporation of water
- Drying and calcination which converts most of the elements to oxides by decay of the nitrates except the alkalis and certain alkaline earths. This operation takes place in a temperature range between 100 and 400°C.
- The preparation of the glass by reaction with the calcine obtained from the previous operation with raw materials which are generally a glass already formed called glass frit and which mainly contribute the formative elements of the glass system such as silica. These reactions generally require temperatures between 1,050°C and 1,300°C depending on the glass mix to be produced. These operations must be carried out by a process along with a technology compatible with operation in a high level radioactive environment;
- Pouring the glass and producing vitrified waste packages;
- Treatment of the gases produced during the various steps above.

INDUSTRIAL VITRIFICATION FACILITIES IN FRANCE

PIVER Pilot Facility at Marcoule

PIVER operated from 1968 to 1980. The evaporation, calcination and vitrification operations took place in a nickel-based stainless steel crucible so as prevent corrosion by the molten glass heated by induction; the glass bath obtained was then poured into a container.

PIVER's main objectives were to demonstrate the feasibility of obtaining vitrified waste packages, validate process data obtained on non-radioactive test rigs with actual solutions under industrial conditions, validate the heating by induction principle of the melter and recommend a glass package interim storage principle.

This PIVER pilot facility helped qualify HLLW vitrification on an industrial scale and, in particular, the technology of induction-heated metallic crucible and its casting system. However, this method was not used on an industrial scale in France because of its excessively low productivity (around 5 kg/h of glass) due to its intermittent nature.

The PIVER operation records are given in Table I below.

TABLE I: PIVER operating records

Volume of reprocessed effluent	25 m ³
Weight of glass produced	12 metric tons
Number of glass canisters	164
Total βγ activity	1.5 10 ⁵ TBq

At the same time as the PIVER operation, CEA redirected R&D towards the development of a continuous process, with the technology related to it, to achieve productivity compatible with fuel reprocessing plant needs.

Marcoule Vitrification Facility (AVM)

The Marcoule vitrification facility (AVM) is associated with the UP1 reprocessing plant. It operated from 1978 to 2012 with a processing capacity of 40 L/h of gas-graphite type HLLW and a glass-making capacity of 15 kg/h. The AVM, during its operation, vitrified all the fission products from the UP1 plant as well as the high level activity effluents from plant decontamination.

R&D involved in the preliminary phase of this industrial project had to apply simultaneously to studies of glass material for containment and technological studies of equipment.

Formulation studies helped determine a glass composition suitable for containment solutions coming from UNGG-type fuel reprocessing; these studies were supplemented by in-laboratory production and characterization of active glass in Marcoule's VULCAIN shielded cell. The functionalization of each device was considered, in the technological studies of the process, to enable the design of equipment tailored to the desired processing capabilities and the ability to optimize their control during operation. Each device was dedicated to a process function.

The implemented process mainly involved two stages: firstly, evaporation-calcination of fission product solutions and secondly, melting of calcine, produced beforehand, in the melting furnace along with the addition of a glass frit containing the glass system. An off-gas treatment system completed the process (Fig. 1)

- The calcining unit, consisting of a rotating tube heated by a resistance furnace, fed by HLLW and also additives and a recycled solution coming from the off-gas treatment, and enables the following operations: evaporation, drying of residue and partial conversion to oxides of the nitrates in the solutions. The use of an organic calcining additive, decaying under the influence of temperature, facilitates the fragmentation of the calcine.
- The vitrification furnace consisted of an induction-heated metal canister to hold the calcine from the rotary tube as well as the glass frit. The glass was prepared at a temperature of about 1,100°C, and was poured every 8 hours into refractory stainless steel containers - each container accommodating

three successive 120-kg pouring steps. After welding on a lid and external decontamination, these containers could be transferred for interim storage.

- The calciner off-gas was treated in several pieces of equipment to successively stop the dust that would be continuously recycled to the calcination tube, condense steam and recombine nitrous vapors. These successive operations, supplemented by a ruthenium specific filter based on iron oxides, washing columns and high efficiency filtration stages to obtain decontamination factors allowing the release of these gases in the atmosphere, in compliance with chemical and radioactive standards.

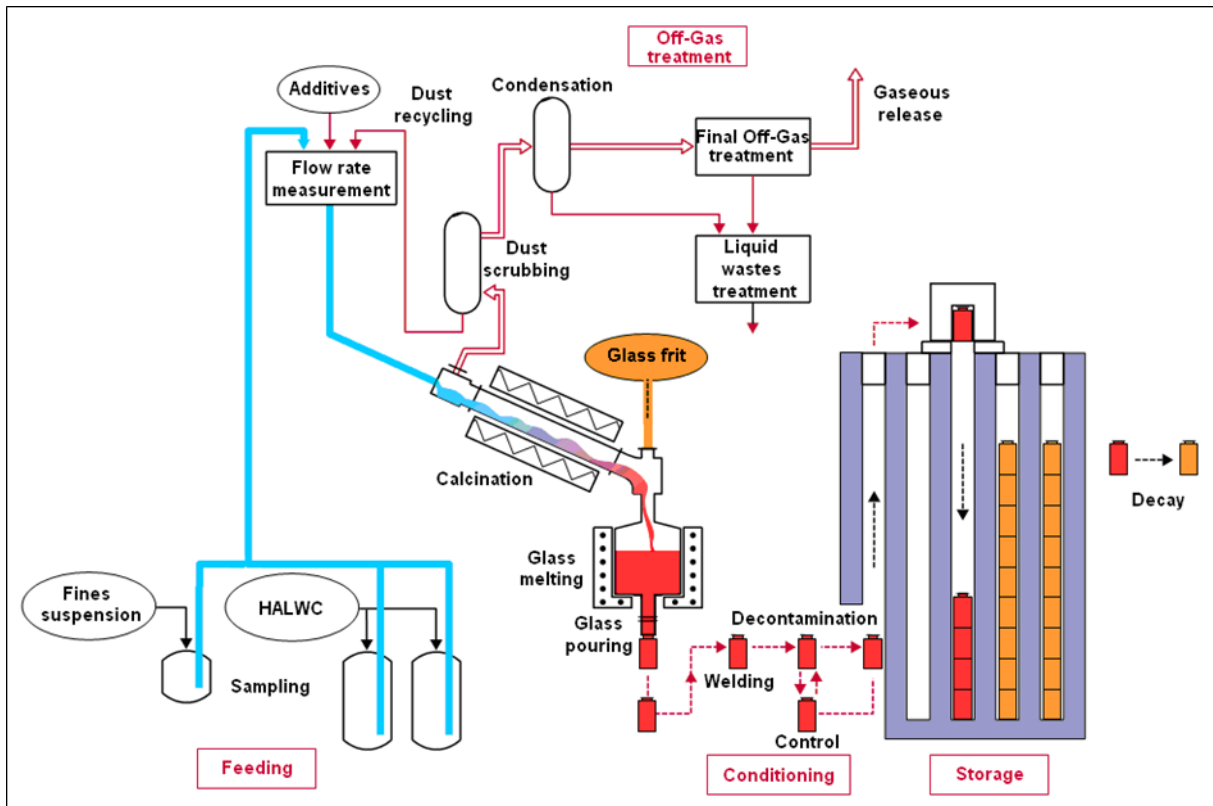


Fig. 1: Continuous vitrification process

The main initial objectives of the industrial facility were to:

- Implement a continuous process with a set of devices dedicated to each function of the process.
- Understand the management of technological waste generated by the operation of the process by endeavoring to minimize its volume and recommend industrially acceptable packaging
- Validate the principles adopted for maintenance under actual operating conditions.

The AVM, during its operation, vitrified all HLLW from the UP1 plant as well as the high level activity effluents from plant decontamination. The operating records are given in Table II.

TABLE II: AVM operating records

Volume of reprocessed effluent	2,870 m ³
Weight of glass produced	1,220 metric tons
Number of glass canisters	3,306
Total βγ activity	22 10 ⁶ TBq

The main lessons learned from the operation of the Marcoule Vitrification facility are as follows:

- The principle of having separate equipment for each of the process functions helped perfectly tailor operating parameters to the changes in the chemical compositions of solutions to be vitrified,
- The high volatility of ruthenium, in small amounts due to the low burn-up of reprocessed fuels, was partially controlled by the continuous recycling of solutions from dust-scrubber and supplemented in the other gas treatment devices. The use of a reducing agent has been recommended for the vitrification of solutions with high ruthenium content in future La Hague vitrification facilities.
- Corrosion, due to fluoride in the solutions to be vitrified, was controlled by a significant addition of aluminum in the dust-scrubber. This addition is, however, strongly penalized by its significant contribution of non-radioactive aluminum oxide to be taken into account in the formulation of the glass. Minimizing or removing fluorine in the reprocessing process has been incorporated into future studies.
- Changes, during operation, in the compositions of solutions to be vitrified have shown that it was not enough to define a single glass composition but a range of acceptable chemical composition. Formulation studies were repeated in the 90s to define glass specifications detailing a range of glass compositions and operating parameters related to their fabrication.
- Experience of operating the calciner helped identify critical points and to learn the service life of the various mechanical components and propose new design specifications to enable simplified replacement of the various components such as rollers, heating elements, and sealing rings.
- The operation of the induction-heated, cylindrical, metallic, melting pot has generally been satisfactory. Foreseeable deformations of the melting pot were, through experience, gradually controlled by adjusting operating parameters. The service life of this equipment could reach 8,000 hours at over 1,000°C. The internal temperature gradients have also shown that it is not possible to extrapolate diameter-wise to achieve higher capacities. An ovoid metallic melting furnace was developed.
- All the process operations such as maintenance of process equipment, but also filling the container, welding of its lid, operations for treating technological waste, were carried out in a single cell. The level of contamination reached increased the difficulties of operations such as cleaning the canisters prior to interim storage.

R7 AND T7 VITRIFICATION FACILITIES AT LA HAGUE

The R7 and T7 are associated with the UP2-800 and UP3 reprocessing plants respectively, located at La Hague. They were commissioned for industrial operation in 1989 and 1992. The solutions to be vitrified come from LWR civilian fuel reprocessing. Both of these facilities has three vitrification lines with an

initial capacity for solution processing of 60 l/h, and a glass-making capacity of 25 kg/h. Canisters from the R7 and T7 facilities hold 400 kg of glass from two successive pours of 200 kg.

The project's R&D was initiated in the late 70s. It developed the material, process and technology aspects.

Material Development

The main objective was to find a glass formulation for the containment of high level liquid waste from all types of light water reactor fuel to be processed at the La Hague plant. The main challenges were to increase the oxide load factor of the glass from fission products and taking into account the specific power of the waste as well as the flow of fines coming from the fuel dissolution solutions' clarification step.

Feedback from AVM operation has shown the need have, rather than a single glass composition which is difficult to produce consistently due to changes over time in the compositions of the solutions to be vitrified, a range of acceptable compositions that in operation can be obtained from a composition of glass frit.

Formulation studies have led to an R7T7 glass, named after the facility in which it is developed (Table II), predominantly (80%) consisting of SiO₂, B₂O₃, Al₂O₃ and Na₂O. Silicon, aluminum and boron play a network formation role, i.e. they polymerize the glass system through their strong bonds; alkalines are modifying elements that, generally open the glass network; they help lower the melting point, reduce viscosity and increase reactivity of the molten glass, which facilitates its preparation. The FP and actinide oxides content is currently limited to 18.5w% (TABLE III). With the exception of platinoids in the glass in the form of RuO₂ crystals and metallic phases (Pd, Rh, and Te), R7T7 glass is, after generation and natural cooling, homogeneous on a microscopic scale. Platinoids uniformly distributed in the glass matrix do not affect the containment properties of the glass produced.

TABLE III: Average chemical composition of the R7T7 glass produced

Range of chemical compositions for R7T7 glass produced in the industrial facilities at La Hague			
Oxides	Interval specified for the manufacturer (w %)		Average composition of industrial glass (w %)
	min	max	
SiO₂	42,4	51,7	45,6
B₂O₃	12,4	16,5	14,1
Al₂O₃	3,6	6,6	4,7
Na₂O	3,5	11,0	9,9
CaO		4,8	4,0
Fe₂O₃		< 4,5	1,1
NiO		< 0,5	0,1
Cr₂O₃		< 0,6	0,1
P₂O₅		< 1,0	0,2
Li₂O	1,6	2,4	2,0
ZnO	2,2	2,8	2,5
Oxides (PF+Zr+ actinides) + Suspension of fines	7,5	18,5	17,0
Actinide oxides			0,6
SiO₂+B₂O₃+Al₂O₃	> 60,0		64,4

Technological Development

The main devices such as the calciner and melting pot were the subject of specific development to tailor them to the new processing capabilities required and industrial operating conditions. This equipment should be modular and easily interchangeable by limiting the number of wear parts so as to reduce the volume of technological waste produced.

Calciner dimensions have increased to double its capacity compared to that of AVM and its modular design enables the replacement of wear parts such as rollers and sealing rings. Heating is provided by eight sets of resistors that can be replaced independently. Figure 2 shows the structure of a fully removable calciner in a shielded cell.

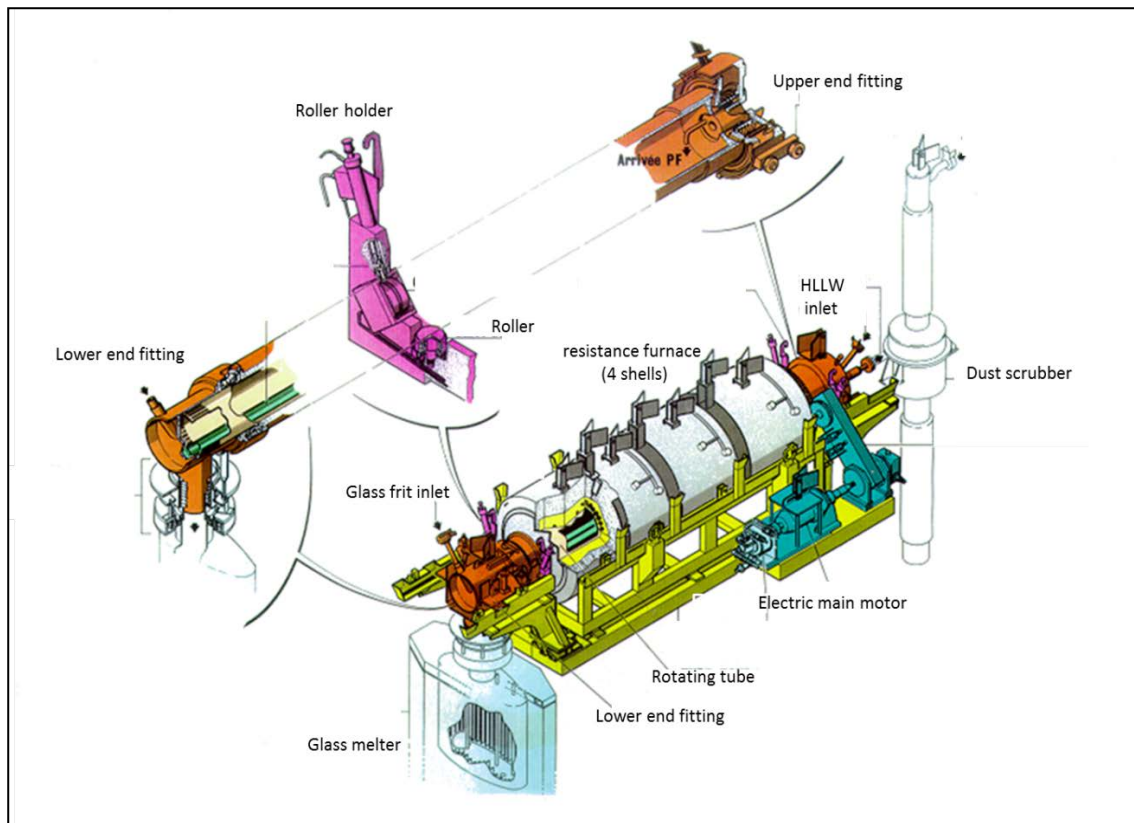


Fig. 2: Structure of the calciner

An ovoid melting pot has been developed to meet the increasing capacity needs in relation to the AVM melter. The medium frequency induction heating has been maintained and can reach glass melting temperatures of around 1,100°C in the pot center. As the melting pot is fed continuously with calcine produced in the calciner and glass frit, the pouring nozzle is penetrant and equipped with a siphon cup. A glass hold-up in preparation is thus maintained in the melting pot after each glass pouring. To facilitate glass preparation, the melting pot was fitted with gas injection sparging rods. Figure 3 shows a diagram of the melting pot.

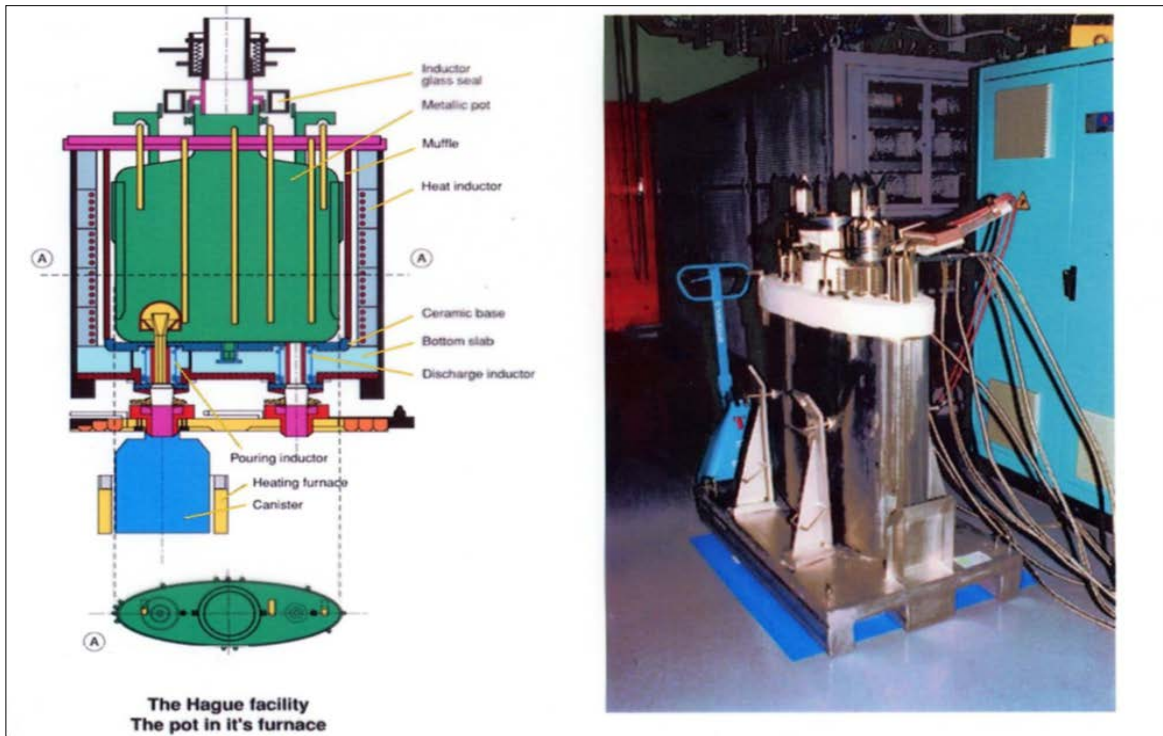


Fig. 3: Metallic melting pot

Process Development

The complete vitrification process has been carried out on a full scale pilot using solutions of non-radioactive simulated waste. The chemical composition of the glass has been adapted according to the observations made on the technology glass produced. The conditions for generating glass have been studied in a wide range of operating parameters and a concept of operation parameters to be complied with has been defined to ensure that the glass batch is properly prepared and can be poured into the glass container. Process improvements, such as the use of reducing agents to limit ruthenium volatilization in the glass formulation, have been validated.

Design of the Facilities

Two facilities R7 and T7 (Figure 4) have been designed so as to perform operations in different shielded cells according to their radiological characteristics and contamination capacity. In order to ensure production continuity of each facility while allowing regular maintenance, three process lines for glass production have been installed in three vitrification cells. Treatment operations on technological waste produced are carried in a special common cell located crosswise above the vitrification cells. Glass container filling stations are located in a common shielded cell, less prone to contamination, below the vitrification cells. The glass canisters to be filled are docked under the melting furnaces and never enter the vitrification cells. In this way, the decontamination and mechanical processing of canisters are facilitated up to the interim storage phase.



Fig. 4: Design layout diagram of a facility in The Hague

Industrial Support

The start-up of the first R7 facility was very gradual. The first solutions to be vitrified were formed from fission product oxide solutions only and adjusted to be close to the reference conditions studied during development. The solutions coming from solvent rinsing and clarification have not been taken into account.

A very significant impact from the platinoid group of elements (Pd, Ru, etc.), that had been simulated during the process development phase, on the viscosity of the bath of molten glass and the conditions of chemical reaction between glass frit and calcine soon became clear. The increase in viscosity caused an extension to pouring time and induced, in association with the decrease in reactivity, the formation of slow resorption hold-up. Another consequence has been to limit the service life of the melting pots to about 2,000 hours.

Industrial support R&D has been set up on the non-radioactive prototype. Tests using the platinoid group elements have been undertaken to quickly obtain new operating conditions. A medium-term program, on the melting pots, was initiated to define a new, more temperature-resistant material and to implement mechanical stirring as a supplement to stirring by gas injection for glass waste loading increasing. The modularity of the vitrification lines has enabled an experimental melting pot to be test in actual conditions before gradually generalizing its use to all the vitrification lines. In this new version, a melting pot produces over 150 glass canisters, which represents changing one melting pot per year per vitrification line.

HLLW chemical composition has changed during the 20 years of operation. A medium to long-term research program helped anticipate developments. After testing, for example, on the non-radioactive

prototype to assess the maximum capacity and potential consequences on other devices, the evaporative capacity of the calciner was increased by successive steps on La Hague vitrification lines, with analysis of changes to parameters for the entire facility. An increase in capacity of 50% was obtained.

Installation of a Cold Crucible Melter

The need for vitrification of different decommissioning and legacy effluents led to the development of specific glass matrices and a new melting furnace based on cold crucible technology. For instance for legacy effluent a glass-ceramic matrix containing 10 to 12w% of molybdenum oxide was developed. This glass –ceramic need to reach a temperature of about 1,250°C adding that the melt is a very corrosive glass matrix, only the CCIM was able to process it. The CCIM was installed in a R7 facility shielded cell instead of a metallic pot melting furnace.

The R&D program required more than 10 years to develop. The melting furnace and all of its operating parameters were qualified on an inactive prototype absolutely identical to the one to be installed in a shielded cell. This qualification program lasted three years and defined the operating parameters in a nominal situation but also in transitional and degraded situations of glass production. A 400-hour+ run validated all operating parameters at the end of the program.

A program to train the operators preceded cold crucible commissioning on the La Hague site in 2010. R&D teams have reinforced the startup teams for the interpretation of the recorded process data. Operating recommendations made by the development teams were jointly transformed into industrial processes.

The operating records of the R7 and T7 facilities are shown in TABLE IV below:

TABLE IV: Operating records of the R7 and T7 facilities

Data at end 2013	R7	T7
Volume of reprocessed effluent	9,933 m ³	7,169 m ³
Weight of glass produced	3,690 metric tons	3,326 metric tons
Number of glass canisters	9,287	8,347
Total βγ activity	139 10 ⁶ TBq	132 10 ⁶ TBq

The main lessons learned from the operation of the R7 and T7 facilities are as follows:

- The design ensures the proper operation of the facility with two main production lines and one maintenance line. Technical developments can be commissioned and validated gradually on one line before being generalized to all facilities. One of the lines can be specialized for a type of waste and thus increase the range of waste that can be treated in the facility.
- Effective integration of solutions of fines containing a significant proportion of platinoids required significant support from technological development and glass material research teams.
- Continuous adaptation of the process and technological equipment has allowed solving numerous process issues and treating new HLLW streams. This has ensured 25 years of high performance operation and to have a tool suited to the challenges of coming years focused on new fuels and reducing operating costs.

- Exchanges between operations teams from active facilities and research and development teams on glass materials, process and technology, are essential to ensure long-term operation and enable the necessary adjustments.
- Regular interpretation of operating parameters allows, with the help of magneto-thermal-hydraulics models developed, to see the appearance of slow phenomena, anticipate difficulties, solve them and plan, for example, the end-of-life of melting pots.
- The initial design of the facilities and the modular equipment have helped significantly improve the process and implement a new melting technology.

CONCLUSIONS

In France, the development of the vitrification of liquid high-level waste was carried out in two areas simultaneously: research on glass materials, production processes and technologies needed for industrial implementation in shielded cells in non-radioactive environments, and industrial implementation in actual operating conditions which provided feedback and key lessons learned for further development.

The development cycle before industrial implementation is about 10 years. As for the life cycle of an industrial plant it is more than 30 years. To improve its performance and adapt to future changes that will occur during its operation, maintaining research and development teams on materials and processes is essential to provide strong industrial support in the early years of service life, to prepare for the ever-necessary changes to processes and to anticipate future developments in fuels to be reprocessed and new effluents that will be treated using a vitrification process. A non-radioactive prototype would appear to be essential to test all process upgrades and to prove that there is no negative impact on the quality of the glass produced.

The CEA and AREVA created, in 2010, a Joint Vitrification Laboratory for materialize a strategic partnership designed to consolidate and develop operational excellence and scientific research in the treatment and packaging of radioactive waste via high temperature processes. This laboratory's missions are to provide scientific and technical support to industrial activities, to develop new processes and technologies, to perform basic research and develop into materials, and to develop modeling and simulation of implemented processes and technologies. In view of the opening of a future deep geological repository, papers on scientific knowledge of the various types of vitrified waste packages are drawn up to have answers to questions that will arise from storage operators, but also the public.

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