BOROSILICATE GLASS HLW STABILITY DURING LONG TERM INTERIM STORAGE

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Abstract

France has chosen a recycling strategy to manage nuclear spent fuels. This strategy relies on high level waste immobilization into a borosilicate glass waste form in order to meet both interim storage and final geological disposal safety requirements. Interim storage facilities at La Hague recycling plant have been designed to last more than an hundred years (concrete structure) factoring the need for a glass waste form durability using for instance natural or forced convection principles. This period of time during interim storage contributes to the final disposal cost optimization by allowing the radioactive decay of the main contributors to thermal power dissipated in the early years after glass production.

In parallel to the thermal design of the interim storage, lots of studies have been carried out on the glass thermal and irradiation stabilities. Thermal treatment experiments consolidated by modeling show that the glassy state is expected to be stable during the interim storage period, with no crystallization induced by the glass thermal history. Moreover, the impact of the radiations (beta and alpha decays) expected in interim storage has been studied by external irradiation, glass actinide doping technique and molecular dynamic simulation. The results have demonstrated that the glassy state will not be modified during the interim storage period and the glass will fully preserved its role of conditioning material.

1. INTRODUCTION

The separation of reusable material from used nuclear fuel allows the recovery of the main part of radionuclides into a small volume of high activity, heat generating solutions called High Level Waste (HLW). In order to provide the best level of safety for human and environment, it is necessary to immobilize this HLW into a very stable and durable waste form, able to contain the radionuclides for several thousands of years. Vitrification of HLW is the internationally recognized standard to both minimize the impact to the environment resulting from waste disposal and the volume of conditioned waste. Many countries such as the USA, France, the United Kingdom, Germany, Belgium, Japan, Russia, have vitrified HLW.

In France, the vitrified wastes are produced complying with product quality stringent conditions (process conditions, glass chemical composition, thermal power, dose rate). These limits are the results of the

optimization of what the various needs at the production, the interim storage, the canister transportation and the final disposal facilities. Hence, Integration of final disposal is thought ever since the glass production step.

Once vitrified, the high level waste canisters must also be kept safe. In France, the long-term disposal for HLW still needs to be commissioned. Interim storage is the current solution developed in France to manage HLW canister and is thus becoming a key facility in the closed fuel cycle. Orano commissioned two sort of interim storage facilities, with a capacity greater than 20,000 canisters.

The efficiency of the interim storage facility also rely on the stability of the glass canisters and more especially of the glassy state, submitted to the interim storage conditions, i.e. a specific thermal history and a self-irradiation stress coming from the decays of fission products and minor actinides. To that respect, studies about the thermal and radiation stabilities of the nuclear glass have been performed.

The current paper presents firstly the glass HLW interim storage strategy and facilities and secondly the main results obtained by the scientific researches performed to test the glass thermal and radiation stabilities.

These interim storage facilities ensure long-term canister stability, in terms of physicochemical evolution for glass.Interim storage role in the nuclear cycle global view.

1.1. Canister characteristics

In France, vitrification is performed by a two-step process, calcination of HLLW followed by vitrification of the obtained calcined product added to a glass frit at 1100°C (Fig. 1): HLLW composed of fission products and minor actinides are thus incorporated into a borosilicate glass matrix [16].

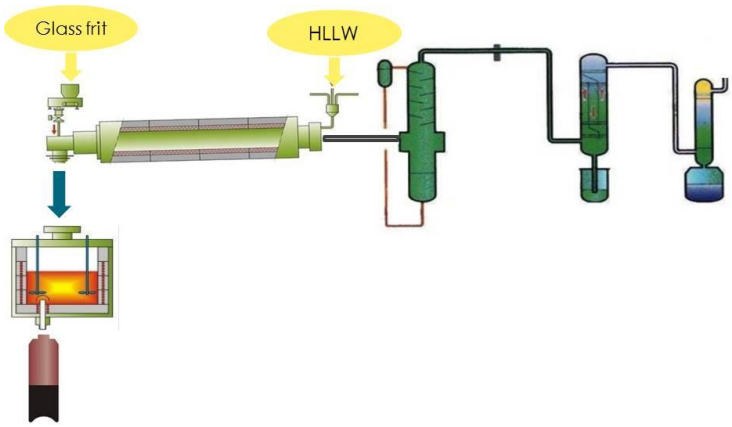

FIG. 1: Two-step vitrification process operating in La Hague Plant.

Vitrification step produces a canister filled by a glass, called vitrified HLW canister. The vitrified HLW canister is a steel canister 43 cm (17 inches) in diameter and 1.4 m (55 inches) in height (Fig. 2). The total volume is about 180 liters (47.5 US gallons) and is filled with about 400 kg (882 pounds) of glass containing 65 kg (143 pounds) of HLW (about 15% to 18.5% in weight of FP and actinide oxides).

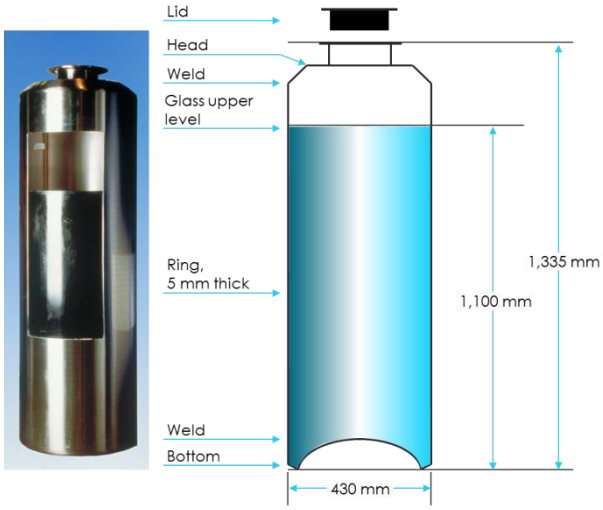

FIG. 2. Vitrified HLW canisters.

Dose rate is around 1.4 x10^4 Gy/h. Thermal heat is approximately 2.5 kW per canister at the production step, 1.6 kW after 10 years, and 0.6 kW after 50 years (Fig. 3). After 100 years, ^{432}Am which half-life period is around 430 years have a more and more important contribution to heat power in comparison to ^{137}Cs/^{137m}Ba and ^{90}Sr/^{90}Y radionuclides.

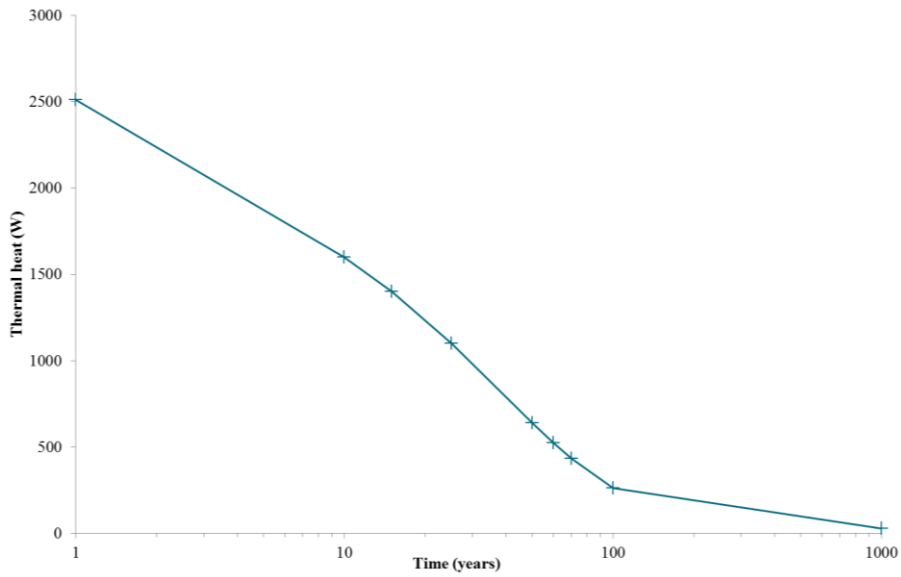

FIG. 3. Thermal heat decay for a typical canister produced in La Hague vitrification facilities.

All parameters followed during the production allowed to produce a glass which properties are consistent with the limits of transportation and final disposal (for example, plutonium weight, heat power, …) .

In France, the vitrified wastes are produced respecting parameter limits (process conditions, glass chemical composition, thermal power, dose rate). These limits are the compromise of what is needed at the production, the interim storage, the canister transportation and the final disposal facility. Hence, Integration of final disposal is thought since the glass production step.

1.2. Interim storage facilities

After production, vitrified HLW canisters need to cool down before the final repository. Interim storages have been built to perform this step before transportation and final disposal.

Glass canisters have been stored in the R7 facility since 1989 and in the T7 facility since 1992. These two facilities allow the vitrified HLW canister first cooling step just after vitrification process when the initial thermal power is over 2 kW. They are cooled by a forced ventilation system: air is coming in direct contact with canisters. R7 interim storage capacity is 4500 canisters in five modules of a hundred pits; each pit can stack up to nine canisters. T7 interim storage design is nearly the same as R7: four modules of a hundred pits, each pit offering a storage capacity for nine canisters (3600 canisters), see Table 1.

TABLE 1. INTERIM STORAGE FACILITIES AT LA HAGUE PLANT

Facility	Operation start-up	Capacity	Number of modules	Ventilation type
R7 interim storage	1989	4500	1	Air-forced
T7 interim storage	1992	3600	1	Air-forced
E/EV/SE	1996	4320	2	Natural
E/EV/LH	First module in 2013	3888	2	Natural
	Second module in 2017	3888		
E / EV / LH2	Coming in 2022	8424	2	Natural

When thermal power is under 2 kW, canisters are moved to one of the other interim storage facilities at La Hague plant (E/EV/SE, E/EV/LH and E/EV/LH2 coming). Functions to be done by these facilities are:

— Reception of canisters from R7 and T7 facilities;
— Unloading of canisters and transfer to pits;
— Interim storage of canisters in the pits;
— Removal of the canister from the pits.
— Two main criteria were taken into account to size the ventilation system:
  - Glass temperature limit must be kept lower than 500°C. The maximum allowable temperature for the material is defined taking into account glass crystallization characteristics, depending on glass composition. With regards to R7T7 glass, the minimum crystallization temperature is about 610 °C. That means that stored glass in the equilibrium state has to be kept at a maximum temperature of 510 °C;
  - Concrete temperature limit must be kept lower than 90°C.

These facilities were designed with natural air ventilation allowing heat canisters decreasing to 500 W thermal power (limit for final repository). Natural air is flowing into a metallic sleeve enclosing each pit, thus cooling air is not in contact with the canisters and can be led to the stack without any high level filtration. These facilities are composed of pits (between 180 and 324 pits per module), each pit offering a storage capacity of twelve canisters (Table 1).

This interim storage concept has undeniable advantages: very simple concept, passive, modular, common handling zone for several modules. Many improvements were brought to the design from E/EV/SE to E/EV/LH, in particular:

— Corrosion resistance and durability of concrete structures were improved optimising the choice of inox and changing the formulation concrete to avoid chlorination and carbonation;
— Compactness, 30% less surface necessary and 13th canister in each pit is possible;
— Design, the position of dilatation joint at the upper part of the pit. On the first design, each pit was equipped with a dilatation joint positioned in the lower zone of the pit, where the temperature is the lowest and might be a zone of condensation.

Interim storage facilities are the link between vitrified HLW canisters production and the final repository allowing the radioactive decay of confined radioelements as the geological repository design is strongly driven by waste's thermal behaviour. This decay heat generation makes necessary a cooling step preventing glass temperature from rinsing above the maximum allowable temperatures for glass and its environment.

Thanks to this design, interim storages are able to guarantee the best conditions to preserve the vitrified HLW canisters from alteration maintaining a temperature compatible with its stability. Lot of modelling works have been done to confirm that whatever the position of the canister is, the temperature remains below 510°C. It is particularly true for canister located at the hotter position in the pit, corresponding to the top of the pit (see Fig. 4)

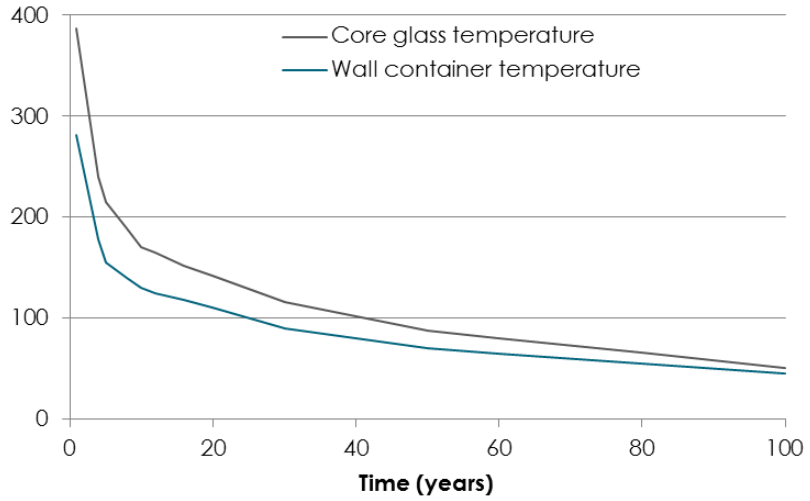

FIG. 4. Glass temperature of a canister located at the top of a pit.

2. STUDIES DONE ON THE VITRIFIED WASTE PRODUCED

2.1. Thermal stability

The nuclear glass are obtained from the quenching of a glass melt prepared in the in the vitrification furnace. From a thermodynamic point a view the glass at solid state is out of equilibrium conditions and could transform into a more stable form, a crystalline material. Crystallisation phenomena in glassy materials obeys to nucleation and growth laws that are limited by kinetic reasons. As an example, some studies performed on natural basaltic glasses have shown the preservation of the glassy state with no devritrification during the 1 million years of natural ageing after their fabrication [1].

In the case of the nuclear glass, specific studies have been performed on SON68 glass (name of the laboratory glass of type R7T7 used for research purpose) to evaluate the risk of devitrification during the glass thermal history of the interim storage conditions. Long term thermal treatments have been performed, at 550 and 450°C for one year, and have shown no crystallisation of SON68 glass. Moreover, some scientific studies were also performed to evaluate the nucleation and growth laws of the main crystalline phases that can be induced by thermal treatments in a temperature range of 630 to 1170°C, either from isothermal or thermal gradient heat treatments [2-4]. The nucleation and growth kinetics of these phases were determined by optical microscopy and SEM. A modelling approach was developed to evaluate the crystallisation rate of the glass with time and then applied in this temperature range. The main conclusions obtained are the following:

— Three main crystalline phases have been observed, i.e. zincochromite, cerianite and powellite phases (See Fig. 5). Taking into account the glass chemical composition a maximum of around 4wt% of crystalline phase could be formed and would require an optimized thermal treatment, far away from the glass thermal history after its fabrication;

— The activation energy associated to the crystallisation phenomena is associated to the one of the glass viscous flow;
— From the modelling work, the time necessary to induce a full crystallisation of these phases is estimated to be of around 50000 years at a temperature of 690°C. This crystallisation time increases by a factor of 103 with a decrease of temperature of 100°C.

Therefore, these results have shown that the risk of crystallization of the nuclear glass under interim storage and subsequent disposal conditions is very limited, and that the glassy state should be fully preserved.

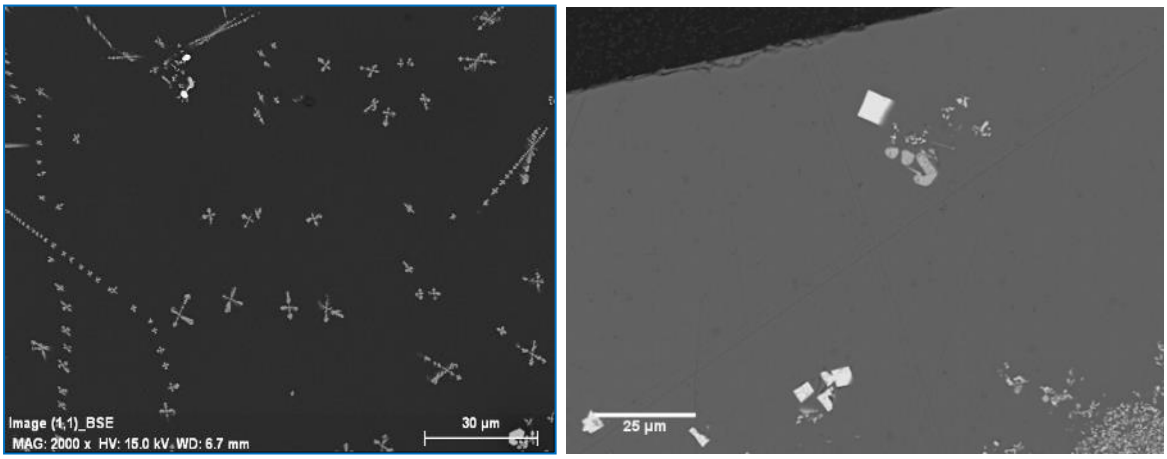

FIG. 5. Example of crystallization observed in a nuclear glass after thermal treatment.

2.2. Radiation stability

Nuclear glass is submitted to beta and alpha decays coming respectively from the radioactive decays of fission products and minor actinides and also to gamma transition emitted by of the excited nucleus [5]. The beta decays, gamma transition and also the alpha particles emitted in alpha disintegrations loss most of their energy to the glass structure by electronic excitation and ionization of the atoms. The recoil nuclei of alpha disintegrations mainly loss its energy by nuclear collisions with the atoms of the glassy network, inducing displacement cascades.

During the first hundred years of interim storage the level of absorbed dose form beta decays and gamma rays is of around 4 to 5 GGy, and is called electronic dose. In the same time, the level of absorbed dose from the recoil nuclei of alpha decays is of around 0.02GGy and is termed nuclear dose (See Fig. 6).

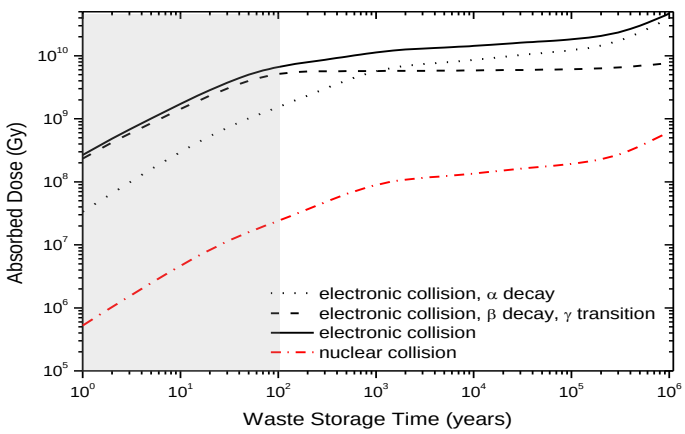

FIG. 6. Evolution of the absorbed dose of a nuclear glass of type R7T7 with time. The gray rectangle highlights the interim storage period.

The effects of the beta dose on the nuclear glass structure and properties was mainly studied at CEA by irradiating non-radioactive glass with a high energy electron beam (of around 2.5MeV energy) [6-12]. This experimental approach allows to perform bulk irradiation of the glass and therefore to use characterization tools such as ESR, NMR and Raman spectroscopy, to characterize the structural response of the material to such level of electronic dose of several GGy.

It has been shown that simple silicate and borosilicate glasses can undergo significant structural transformations, mainly involving point defect generation, boron coordination changes, modification of the glass polymerization level, changes of the mean angle between silica tetrahedral, and molecular oxygen formation. Nevertheless it was reported that the level of the structural transformation is influenced by the glass chemical composition. For instance, a mixed alkali effect appeared to decrease the changes, and the addition of transition metals or lanthanide elements to the glass can decrease or completely suppress the glass structure modification. It was suggested that the various redox states of transition metals or lanthanides act as traps for the electrons and holes generated by the interaction between the electrons and the glassy network, and consequently reduce or prevent the generation of point defects and any subsequent structural transformation. Therefore the chemical complexity of the glass is a positive factor that reduces its sensitivity to ionizing radiation. This certainly explains why few structural changes, with no modification of the glassy state, were observed in the studies of complex SON68 type nuclear glass irradiated by beta particles up to 4GGy.

To address the effect of alpha decays a multi-faceted approach has been used at CEA [13-15] based on:

- The fabrication and subsequent study of specific glass enriched in short half-life actinides;
- Ion or neutrons irradiations to mimic the nuclear and electronic damage induced by alpha decays;
- Molecular dynamic simulations of nuclear damage generated by heavy ions induced displacements cascades, that mimic the recoil nuclei effects.

In the last 15 years, great progress has been accomplished towards the understanding of the effects of alpha decay on nuclear glass structures and properties. It has been shown that alpha decay accumulation in nuclear glass induces slight changes of macroscopic properties (density and mechanical properties), no modification of the glassy state with a glass microstructure that remains homogeneous without any phase separation and crystallization, a slight modification of the glassy structure, with modifications of both short and medium range orders. The main structural changes are a partial conversion of boron from a tetrahedral coordination number to a trigonal one, an increase of the non-bridging oxygen atoms concentration and a modification of the ring statistic and angles in between the glass polyhedra. The final structure seems to be the result of the ballistic melting in recoil nuclei tracks and the subsequent α particles partial damage repair due to a thermal self-healing mechanism in the α particles tracks. It results in a new homogeneous glassy state, similar to that obtained by a very high quenching rate of a molten glass, with slightly modified macroscopic properties. Their variations with dose seem to be controlled by the accumulation of recoil nuclei track overlapping, according to a direct impact model. The saturation of the structural changes is therefore observed at a nuclear dose of around 40MGy (or 4×10^{18} α decay/g, Fig. 7.).

The results obtained from the radiation stability studies have shown that the glassy state is preserved all along the duration of the interim storage period. Few structural changes and modification of the macroscopic properties are induced by both beta and alpha decays that are limited in amplitude and for which a saturation of the variation with dose have been observed. These results show that the main function of the glass that is to contain the radioactive isotopes will also be preserved during the interim storage period.

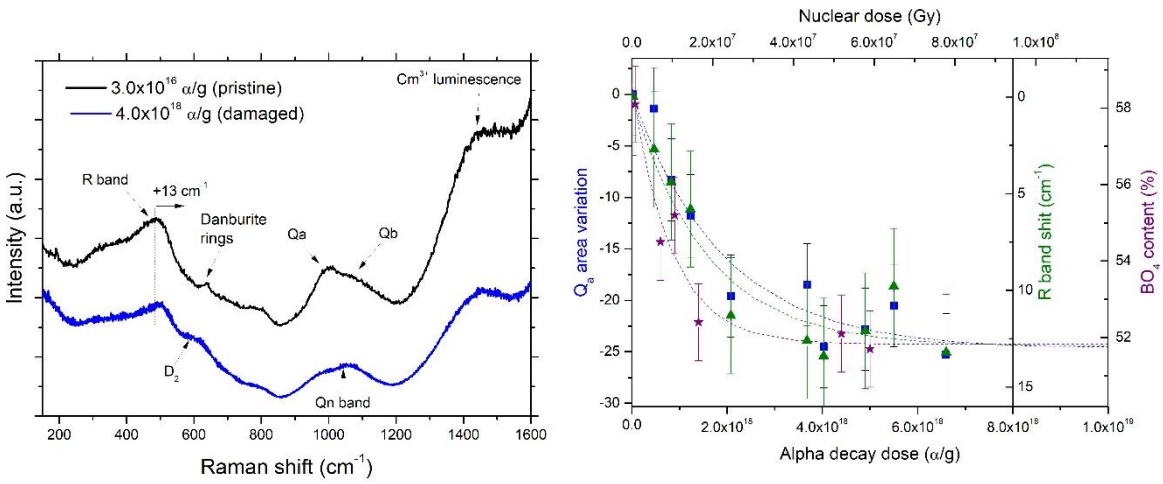

FIG. 7. Structural evolution of the laboratory ISG glass doped with ^{244}Cm. a) Raman spectra at two alpha decay dose, b) evolution of structural parameters with alpha decay dose.

3. IN THE PERSPECTIVE OF CIGEO DISPOSAL FACILITY

3.1. The Cigeo disposal repository and its provisional industrial capacity

The French National Radioactive Waste Management Agency (Andra) is responsible for the long term management of radioactive wastes produced in France. This stated-owned Agency is in charge of the design and the construction of disposal facilities in France. After 15 years of research, in 2006 the Planning Act took the decision that the management of High Level and Intermediate Level Long Lived radioactive Waste should be based on disposing them in a geological formation.

Therefore Andra launched the basic designed phase of the Cigeo disposal facility in 2014 and the detailed designed phase in 2016. The Cigeo is a deep geological concept of repository at a depth of 500 meters, situated on the boundary between the Haute-Marne and the Meuse departments. Its goal is the disposal of the most highly radioactive wastes with long-lived radionuclides which neither meet the waste acceptance criteria of operational waste disposal facility nor those of the in study intermediate disposal facility. This is particularly the case for the vitrified HLW stainless canisters. If the licence is granted around 2021 by a construction authorization decree, the Cigeo could receive the first waste package around 2030.

The underground facility will be separated in two package disposal sections:

— The repository zone for ILW-LL Waste.
  - This zone consists in tunnels that are a few hundred meters long, for ten meters in diameters. It is supposed to dispose of around 176 000 different waste packages. It will be operated from around 2030 to 2095. An industrial pilot phase will perform operational tests during around five years.

— The repository zone for HL Waste.
  - This zone consists in cells of around hundreds of meters long and around 70 cm in diameter. It is designed to dispose of around 56 000 vitrified HLW stainless canisters. This zone is supposed to dispose of around 1000 HLW stainless canisters with very low thermal heat around 50 W for test in an industrial pilot phase from 2030 to 2035. It is also designed to dispose of around 55 000 vitrified HLW stainless canisters with high thermal heat (< 500 W). It should be operated from 2080 to 2145.

3.2. Industrial management of the vitrified HLW stainless canisters

Both Andra and the French waste producers (Orano, CEA, EDF) elaborated a program document as a design basis for the sizing of the Cigeo. In this document, the waste producers provided the forecast radioactive

waste inventory, in compliance with the recycling of the spent fuel generated by French nuclear power plants. The waste producers also proposed an annual program of provisional expeditions of waste package from theirs sites to the Cigeo repository site. This program meets both the thermal sizing of the HL Waste zone and industrial constraints such as spent fuel recycling program, thermal necessary decay, interim storage, transportation.

In this context, at this time, it is supposed that the 55 000 vitrified HLW stainless canisters should be send from 2080 to 2095 with stream between 0 to 850 waste packages a year; and from 2085 to 2015 with a constant stream of 850 waste packages a year.

The totality of the 55 000 vitrified HLW stainless canisters will be produced at the La Hague recycling plant. After a period of interim storage in this site, they will be transported ~~up~~ to the Cigeo facility. Orano has an industrial experience of cask design and operations for waste transportation. At their reception on the Cigeo facility the vitrified HLW stainless canisters will be placed in a steel overpacks in order to prevent glass leaching during a period of time corresponding to the thermal phase.

The modular conception of the interim storage facilities for the vitrified HLW stainless canisters is based on the building of a new module every five years, as illustrated in the figure below (Fig. 8).

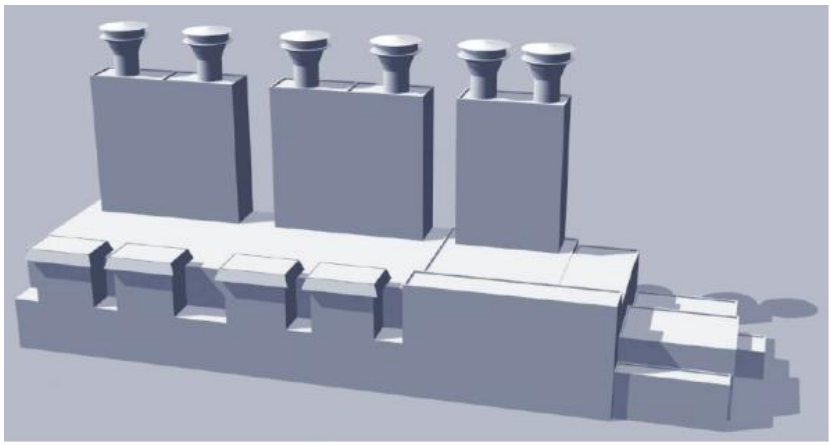

FIG. 8. Modular design of interim storage facility in La Hague plant.

This modular conception allows Orano and EDF, the owner of the vitrified HLW stainless canister to manage the necessary decay period of time. The figure bellow (Fig. 9) illustrates the forecast increase of the storage capacity of storage provided by the modular conception and operation from 2006 up to 2040.

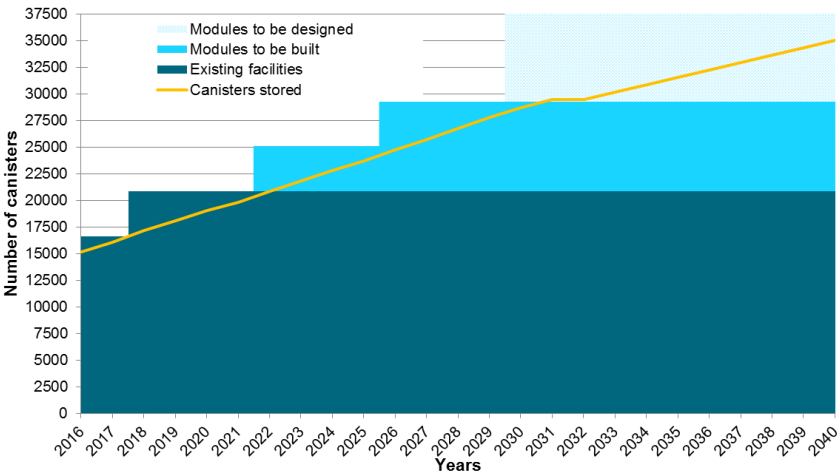

FIG. 9. Evolution of interim storage capacity for vitrified HLW canisters.

It must be noted that if the thermal waste acceptance criteria imposed by the conception of the HLW zone has been 500 W since the very beginning of the project, Andra is performing Thermo-Hydro-Mechanical optimization of the conception that could lead to a new threshold around 400 W.

Those levels of heat will impose a period of decay from 75 to 85 years, depending on the vitrified HLW stainless canister. The modular conception and exploitation of the interim storage facilities in La Hague factor these design constraints.

The interim storage strategy and capacity in the La Hague plant contributes to the final disposal cost optimization, and it is important part of the nuclear cycle global view.

4. CONCLUSIONS

This paper has presented the current solution to manage the heat power decrease of vitrified HLW in the first decades after production. Interim storage concept chosen in France has the following advantages: very simple concept, passive, modular, common handling zone for several modules. It is the best way to implement successfully the cooling step of HLW vitrified canisters which is a crucial issue in glass storage.

Scientific studies have been performed to evaluate the glass behaviour under the conditions of an interim storage facility, i.e. a glass submitted to a specific thermal history and to a self-irradiation induced by both beta and alpha decays. These studies have shown that the glassy state will be preserved all along the duration of the interim storage period and that the main function of the glass that is to contain the radioactive isotopes will also be maintained.

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