



**HAL**  
open science

## HLW Waste conditioning and long-term performance

Florence Bart, Christophe Poinssot, Stephane Gin, Sylvain Peugot, Céline Roussel

► **To cite this version:**

Florence Bart, Christophe Poinssot, Stephane Gin, Sylvain Peugot, Céline Roussel. HLW Waste conditioning and long-term performance. Ehud Greenspan. Encyclopedia of Nuclear Energy, Elsevier Inc., pp.564-576, 2021, 978-0-12-819732-5. <10.1016/B978-0-12-819725-7.00221-X>. <cea-04815419>

**HAL Id: cea-04815419**

**<https://cea.hal.science/cea-04815419v1>**

Submitted on 2 Dec 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

# HLW Conditioning and long-term Performance

In : “Encyclopedia of nuclear energy” Elsevier 2021

## Authors

### **Florence Bart**

CEA French Atomic Commission - Energy Division - Marcoule Center

Dismantling and Waste Conditioning Department

*florence.bart@cea.fr*

### **Christophe Poinssot**

Deputy CEO and Scientific Director at French Geological Survey (BRGM)

*c.poinssot@brgm.fr*

### **Stéphane Gin**

CEA French Atomic Commission - Energy Division - Marcoule Center

Dismantling and Waste Conditioning Department

Long Term Behavior Laboratory

*stephane.gin@cea.fr*

### **Sylvain Peugeot**

CEA French Atomic Commission - Energy Division - Marcoule Center

Dismantling and Waste Conditioning Department

Highly Radioactive Material Laboratory

[sylvain.peuget@cea.fr](mailto:sylvain.peuget@cea.fr)

### **Céline Roussel**

ORANO group

R&D Vitrification Project Manager

*celine.roussel@orano.group*

## **Abstract**

This chapter is devoted to high level waste management. A synthesis of the high level waste (HLW) typology and key characteristics is given, showing that nuclear glass and spent nuclear fuel need to be considered for long term disposal, depending on national strategies. A rationale for selecting a relevant conditioning process is then presented, describing the parameters and constraints to take into account. A brief description of the vitrification processes, the sole industrially deployed conditioning process for HLW, is then presented. The vitrified waste interim storage strategy is described. The knowledge about the long term performance of HLW, spent nuclear fuel and nuclear glass, in geological disposal is then detailed. Finally, the development of alternative conditioning processes for HLW are briefly presented.

## Summary

1. Introduction
2. Synthesis of the HLW typology and key characteristics
3. Rationale for selecting a relevant conditioning process
4. Description of the HLW conditioning processes, the sole industrially deployed conditioning process for HLW
5. Vitrified waste interim storage
6. Long term performance of HLW in geological disposal
7. Development of alternative conditioning processes for HLW

## 6.10.1 Introduction

The operation of nuclear reactors, as well as their associated fuel cycles: uranium production, enrichment, fuel fabrication and reprocessing in some cases, generate radioactive waste. Radioactive waste also results from the use of radioactive materials in research, medicine, education and industry. In some countries, radioactive waste is also generated in support of defense activities. This means that practically all States have to consider the management of radioactive waste and to make sure it is managed in a safe manner with due regard to the level of radioactivity and in compliance with national regulations, often based on, or in harmony with, IAEA safety standards (IAEA, 2018).

High level waste (HLW) are waste with levels of activity concentration high enough to generate significant quantities of heat by the radioactive decay process and/or waste with large amounts of long lived radionuclides. Disposal in deep, stable geological formations usually several hundred meters or more below the surface is the generally recognized option for disposal of HLW.

## 6.10.2. Synthesis of the HLW typology and key characteristics

### **HLW typology**

After use, Spent Nuclear Fuel becomes a highly radioactive material, due to the presence of minor actinides and fission products created by nuclear reactions. Spent Nuclear Fuel (SNF) is considered as a high level waste in some countries (USA, Sweden, Finland, Spain, Canada, etc.) or a potential future energy resource in others (France, Japan, UK, Belgium). In the first case, SNF will be disposed after some decades of interim storage ('once through fuel cycle'). In the second case, is planned to be reprocessed to recover fissile materials for future use ('closed fuel cycle'). The majority of States have adopted the policy of direct disposal of spent nuclear fuel, while several States with the largest nuclear programs (France, India, Japan, the Russian Federation, the United Kingdom and China) have adopted the policy of reprocessing nuclear fuel and recycling the separated material. Germany and the United States of America have changed their policy from reprocessing and recycling to direct disposal and are currently planning spent fuel repositories.

### **Basic characteristics of Spent Nuclear Fuel (Poinsot, 2012)**

A PWR spent fuel assembly is comprised of four 580-lm thick Zircaloy fuel rods of 9.5 mm in diameter and 4-m long, inside which are stacked uranium oxide fuel pellets (Johnson, 1988). The free volumes of the fuel rods are initially filled with He at 25 bar. After irradiation, the fuel pellets are fractured in roughly 15 fragments due to the presence of a steep thermal gradient and contain minor actinides (produced by neutron capture) and fission products (produced by fission reactions), which are either trapped in the UO<sub>2</sub> lattice or remain present as metal or oxide solid phases within the UO<sub>2</sub>.

Part of the fission products are gases, which are for the larger part (95%) trapped within the UO<sub>2</sub> matrix, whereas the remaining gases are released in the free volumes of the rod and contribute to significantly increasing the internal rod pressure (up to 50–60 bar in room conditions). In addition, the distribution of fission reactions is not completely homogeneous within the rods and the zones with very high fission rates have a specific microstructure with smaller grains and a higher porosity. In the case of UOX rods, such zones occur as an external rim, and for MOX fuels, these zones occur in the Pu-rich agglomerates from the initial microstructure.

Furthermore, fuel cladding is also damaged during the in-reactor period due both (i) to the external corrosion by primary circuit water leading to hydrogen uptake, and (ii) to the irradiation-induced

mechanical hardening. Finally, it is important to stress that nuclear fuel is not designed to be a durable waste form, but to host the fission reaction inside the reactor and to produce electricity. This means that it is severely damaged after irradiation and, furthermore, not in thermodynamic equilibrium due to the fast quenching upon reactor shutdown.

Therefore, its long-term durability and confinement properties are more difficult to demonstrate compared to a homogeneous and specifically-designed matrix such as nuclear glass.

### **Basic characteristics of high level liquid waste coming from SNF reprocessing**

SNF contains about 2% fissile material (1% remaining  $^{235}\text{U}$ , 1% plutonium and minor actinides) that can be isolated (reprocessed) and recycled as a new fuel. The HLW accounts for over 95% of the total radioactivity produced in electricity generation if a reprocessing policy is followed. It originates from a liquid residue from reprocessing spent nuclear fuel to extract the uranium and plutonium for reuse. The liquid contains most of the radioactivity from the original spent fuel.

In the reprocessing option, more waste streams need to be dealt with in addition to the HLW itself. These other waste streams include intermediate level structural waste such as hulls and nozzles from fuel assemblies, and intermediate level process waste, for example sludge from liquid effluent treatment. Typically, 1 ton of reprocessed PWR fuel generates about 0.1 m<sup>3</sup> of HLW, 2.5 m<sup>3</sup> of ILW, 1.5–3 m<sup>3</sup> of LLW (all values are after conditioning, including the waste package/container) and 950 kg of uranium which can be reused for new fuel production (AIEA 2018). The most important other waste streams produced in reprocessing spent fuel is the long lived ILW composed of the hulls and endcaps of the metal tubes that contained the fuel, and other parts of the fuel elements. These can be embedded in a matrix of cement inside a steel container or can be compacted into steel cylindrical containers similar to those containing the HLW.

Conventional aqueous (PUREX type — plutonium and uranium recovery by extraction) reprocessing generate a complex solution containing some 40 chemical elements which must be continuously stirred and cooled to dissipate its thermal power.

The fission product solution produced by the PUREX process is the initial highly radioactive liquid waste to be considered for conditioning. It is a nitric solution (typically 1-2 N) containing a complex mixture of species (about 100 g.L<sup>-1</sup>), partially precipitated, including mainly Cs, Sr, Mo, Zr, minor actinides (Np, Cm, Am), lanthanides, platinum group metals (Pd, Ru, Rh), plus alkaline and alkaline earth cations, and corrosion products from stainless steel, nearly the whole periodic classification.

Conserving this fission products solution in the liquid state is not a sustainable option considering security and safety concerns on the long-term, and this initial high level liquid waste (HLLW) have to be transformed to produce a chemically durable and heat- and radiation-resistant solid matrix tailored for final disposal nuclear glass wasteforms, as explained later on.

### 6.10.3 Rationale for selecting a relevant conditioning process

The conditioning of fission products solutions is aimed at (1) turning waste from the liquid to the solid state, (2) reducing the volume to be stored and, then, disposed of, and (3) getting a material which complies with the safety requirements peculiar to storage and long term disposal. More precisely, the conditioning material has to present satisfactory properties of resistance to self-irradiation (alpha, beta and gamma emitters), thermal stability (heat production associated with radioactivity), and

chemical durability (taking into account environmental disposal conditions). The wasteform is meant to stabilize the waste during packaging, an interim storage period, transportation, disposal in a geological repository, and post closure disposal period. The deep geologic disposal is considered to be the most suitable option for disposing higher activity radioactive wastes worldwide because of the predicted effectiveness of many natural geological systems in reducing the transport of radionuclides that can be augmented by robust engineered barriers, thereby enhancing disposal facility performance.

Early research routes were first focused on mica- or feldspath-type crystalline materials prior to being re-oriented to vitreous materials in the late fifties (Vernaz, 2014). During the sixties, glass was selected by the world's community as the confinement material for fission products solutions, due to the structural flexibility of its disordered structure that enables glass to confine many chemical elements. The aim is not a mere embedding, but an atomic-scale confinement, since radionuclides are intimately incorporated in the glass structure.

Glasses were selected in the 1970s primarily for the following reasons (Jantzen and Ojovan, 2019):

- Vitrification technologies are known and reliable large scale non-nuclear commercial technologies
- More cost-effective process than ceramics
- High solubility of waste components in the glass and tolerance to variation in waste composition
- Low raw materials costs
- Sufficiently high durability to ensure long-term performance
- Continuous, high-throughput, operation of glass melters
- High resistance to damage from radiation and radioactive decay
- Reasonably well understood corrosion/release mechanisms for a homogeneous wasteform
- Existence of natural analogues.

The use of the vitrification process (see figure 1) for conditioning of fission product has been chosen by many countries, such as France, Belgium, the United Kingdom, the United States of America, Japan, the Russian Federation, South Korea, India, China. Except for alkali-aluminophosphate glass used in Russia, alkali-borosilicate glass has been universally selected as the vitreous wasteform convenient for fission products solutions immobilization.



Figure 1 Simulated non-radioactive nuclear glass

Determining a glass composition means making a compromise between the material properties and the technological feasibility of its industrial-scale fabrication (Jantzen and Ojovan, 2019)(Vernaz, 2009). (Hyatt, 2019).

The main following criteria are considered:

- Waste loading : the wasteform must be able to accommodate a significant amount of waste (typically 20 weight %) in order to minimize final volume of waste canisters to be disposed in deep geological ;
- Industrial feasibility, considering that the processes need to be remote operated, in hot cells facilities
- Durability : low rate of dissolution to minimize the release of radioactive and chemical constituents in the biosphere during very long period of time (typically 100 000 years), radiation stability
- Compatibility with the intended disposal environment—compatible with the near-field environment of the disposal facility.

#### 6.10.4. Description of the HLW conditioning processes, the sole industrially deployed conditioning process for HLW

Two kinds of industrial vitrification technologies are available: JHM, Joule Heated Melter and CCIM, Cold Crucible Induction Melters.

Two kinds of Joule Heated Melters are used in nuclear glass industry (figure 2):

- The ceramic melter, known as “LFCM” for Liquid Fed Ceramic Melter,
- Joule Metallic Melters.

The LFSM process consists in heating the glass by an electric current flowing between electrodes that are immersed in molten glass (approximately 1150°C). The furnaces are big-sized ceramic furnaces, they show extended lifetime compared to metallic pots (several years). The melter is directly fed with the liquid waste, evaporation and calcination steps take place on the molten glass surface. This continuous process is implemented in Belgium (Pamela), USA (DWPF and WVDP), Japan (TVF), Russia (Mayak), India (Trombay) and Germany (CEK).

Joule Metallic Melter technologies for processing nuclear glass are implemented in France (Marcoule Vitrification facility, La Hague Facility), United Kingdom (WVP), India (Tarapur). The Joule heated melters are smaller than ceramic melters (containing typically 400 kg of glass), with a shorter lifetime, and metallic pot need to be changed after typically one year. They have a maximum operating temperature around 1150°C. The vitrification process is a continuous two steps process, on line performed in two separate devices: evaporation-calcination of fission product solutions, and the vitrification of the calcinate previously produced. Heat is induced in the crucible walls, which heat the glass.

The CCIM is selected for processing glass or glass ceramic wasteform when higher melting temperatures (1200–1300°C) are required. In this case, heat is directly induced in the molten glass and the crucible walls are cooled. There is a self-forming crucible, which is a thin cooled glass liner, a few centimeters thick, protecting the metallic walls of the furnace from molten glass corrosion. This

technology is implemented industrially in France (La Hague facility), the induction melter being replaced by a CCIM on figure2, and in Korean for low and intermediate level waste.

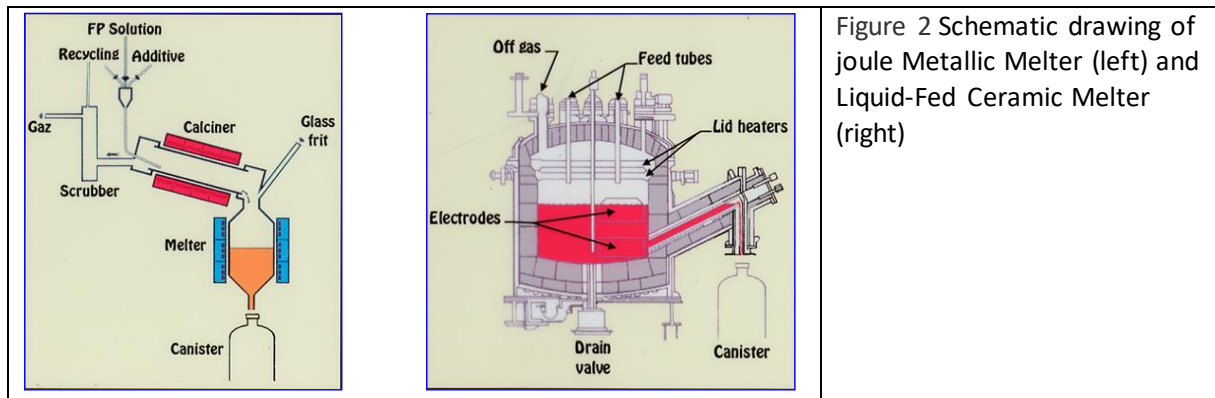


Figure 2 Schematic drawing of joule Metallic Melter (left) and Liquid-Fed Ceramic Melter (right)

Typical nuclear glass compositions are given in table 1 (Malkowsky, 2020) for countries that are industrially producing high level nuclear glass.

Country	Facility	Type of glass: composition in wt. %
Russia	EP500 PA "Mayak"	NAP: 53.3 P <sub>2</sub> O <sub>5</sub> · 15.8 Al <sub>2</sub> O <sub>3</sub> · 1.6 Fe <sub>2</sub> O <sub>3</sub> · 23.5 Na <sub>2</sub> O · 5.8 miscellaneous <sup>1</sup>
Belgium	Pamela	NAP: 70.7 P <sub>2</sub> O <sub>5</sub> · 7.1 Al <sub>2</sub> O <sub>3</sub> · 22.2 Fe <sub>2</sub> O <sub>3</sub>
Belgium	Pamela	ABS : 52.7 SiO <sub>2</sub> · 13.2 B <sub>2</sub> O <sub>3</sub> · 2.7 Al <sub>2</sub> O <sub>3</sub> · 4.6 CaO · 2.2 MgO · 5.9 Na <sub>2</sub> O · 18.7 miscellaneous
France	AVM Marcoule	ABS: 46.6 SiO <sub>2</sub> · 14.2 B <sub>2</sub> O <sub>3</sub> · 5.0 Al <sub>2</sub> O <sub>3</sub> · 2.9 Fe <sub>2</sub> O <sub>3</sub> · 4.1 CaO · 10.0 Na <sub>2</sub> O · 17.2 miscellaneous
France	AVH R7/T7 La Hague	ABS: 45.1 SiO <sub>2</sub> · 13.9 B <sub>2</sub> O <sub>3</sub> · 4.9 Al <sub>2</sub> O <sub>3</sub> · 4.0 CaO · 9.8 Na <sub>2</sub> O · 22.3 miscellaneous
Germany	Karlsruhe	ABS: 60.0 SiO <sub>2</sub> · 17.6 B <sub>2</sub> O <sub>3</sub> · 3.1 Al <sub>2</sub> O <sub>3</sub> · 5.3 CaO · 7.1 Na <sub>2</sub> O · 6.9 miscellaneous
UK	WVP Sellafield	ABS: 47.2 SiO <sub>2</sub> · 16.9 B <sub>2</sub> O <sub>3</sub> · 4.8 Al <sub>2</sub> O <sub>3</sub> · 5.3 MgO · 8.4 Na <sub>2</sub> O · 17.4 miscellaneous
US	DWPF Savannah River	ABS: 49.8 SiO <sub>2</sub> · 8.0 B <sub>2</sub> O <sub>3</sub> · 4.0 Al <sub>2</sub> O <sub>3</sub> · 1.0 CaO · 1.4 MgO · 8.7 Na <sub>2</sub> O · 27.1 miscellaneous
US	WVDP West Valley	ABS: 45.8 SiO <sub>2</sub> · 8.4 B <sub>2</sub> O <sub>3</sub> · 6.1 Al <sub>2</sub> O <sub>3</sub> · 11.4 Fe <sub>2</sub> O <sub>3</sub> · 1.4 MgO · 9.1 Na <sub>2</sub> O · 17.8 miscellaneous
US	WTP Hanford (under construction)	ABS: 50.0 SiO <sub>2</sub> · 20.0 B <sub>2</sub> O <sub>3</sub> · 5.0 Al <sub>2</sub> O <sub>3</sub> · 25.0 Na <sub>2</sub> O
Japan	Tokai Vitrification Facility	ABS: 46.7 SiO <sub>2</sub> · 14.3 B <sub>2</sub> O <sub>3</sub> · 5.0 Al <sub>2</sub> O <sub>3</sub> · 3.0 CaO · 9.6 Na <sub>2</sub> O · 21.4 miscellaneous
India	WIP Trombay	ABS: 30.0 SiO <sub>2</sub> · 20.0 B <sub>2</sub> O <sub>3</sub> · 25.0 PbO · 5.0 Na <sub>2</sub> O · 20.0 miscellaneous
India	AVS Tarapur	ABS: 34.1 SiO <sub>2</sub> · 6.4 B <sub>2</sub> O <sub>3</sub> · 6.2 TiO <sub>2</sub> · 0.2 Na <sub>2</sub> O · 9.3 MnO · 43.8 miscellaneous

Table 1 : Typical nuclear glass compositions for countries that are industrially producing high level nuclear glass (Malkowsky, 2020).

## 6.10.5. Vitrified waste interim storage

### Background

The vitrified wastes are produced complying with product quality conditions (process conditions, glass chemical composition, thermal power, dose rate) which are the results of the optimization of production parameters, the interim storage conditions, the canister transportation and the final disposal facilities.

These high level waste canisters must be kept safe, whatever a decision concerning long-term disposal for HLW, interim storage is therefore worldwide necessary to manage glass canisters during several decades. In France for example, nuclear glass canisters (about 30 000 canisters) are safely placed in interim storage since the beginning of the industrial production (1978 for Marcoule Vitrification facility and 1989 for La Hague Vitrification facility).

The efficiency of the interim storage facility relies on the stability of the glass canisters and more especially of the glass itself, submitted specific thermal conditions (from 400°C after production to less than 200°C after 10 years) and submitted to a self-irradiation stress coming from the decays of fission products and minor actinides. Dose rate is around  $1.4 \times 10^4 \text{ Gy}\cdot\text{h}^{-1}$ . 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. After 100 years,  $^{432}\text{Am}$  (half-life period = 430 years) has a more and more important contribution to heat power in comparison to  $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$  and  $^{90}\text{Sr}/^{90\text{Y}}$  radionuclides.

As an example, the French vitrified HLW canister is a steel canister 43 cm (17 inches) in diameter and 1.4 m (55 inches) in height (figure 3). 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). US glass canisters produced at DWPF are larger, 10 feet tall and 2 feet in diameter.

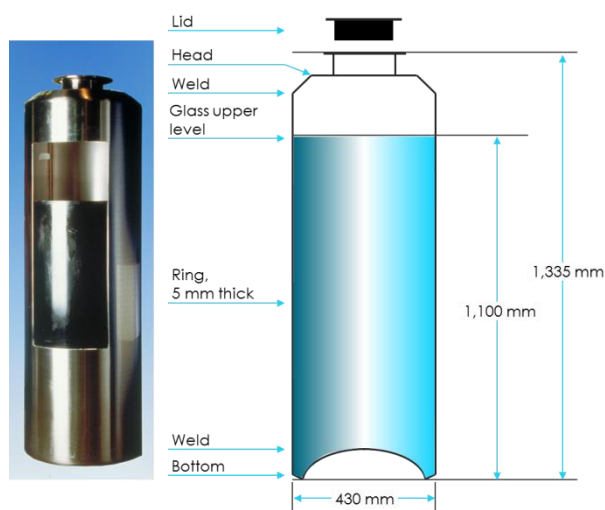


FIG. 3 Vitrified HLW canisters produced by ORANO La Hague (France)

After fabrication, glass canisters are cooled by a forced ventilation system. When thermal power is decreased (typically,  $< 2 \text{ kW}$  for la Hague Facility), canisters are moved to an interim storage with natural air ventilation. The interim storage must guarantee that glass is kept at temperature lower than the glass crystallization temperature, which is depending on glass composition. In the case of borosilicate nuclear glasses, the minimum crystallization

temperature is about  $600 \text{ }^\circ\text{C}$ , and that is why the facility is designed to keep the canisters at temperatures lower than  $500 \text{ }^\circ\text{C}$ .

### Thermal stability

The nuclear glass are obtained by quenching of a glass melt prepared in the in the vitrification furnace. From a thermodynamic point of 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 obey 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 devitrification during the 1 million years of natural ageing after their fabrication (Crovizier, 2003).

In the case of the nuclear glass, specific studies have been performed on simulated and industrial nuclear glass to evaluate the risk of devitrification during 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 the 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 (Orlhac et al., 1999 and 2001).

Optical microscopy and SEM experimental studies were used to determine the nucleation and growth kinetics of these phases. A modelling approach was developed to evaluate the crystallisation rate of the glass with time and then applied in this temperature range. Three main crystalline phases have been observed, i.e. zincochromite, cerianite and powellite phases (figure 4). 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. From the modelling work, the time necessary to induce a full crystallisation of these phases is estimated to be of around 50 000 years at a temperature of 690°C. This crystallisation time increases by a factor of 100 with a decrease of temperature of 100°C, meaning that at 200°C, crystallization phenomena are negligible.

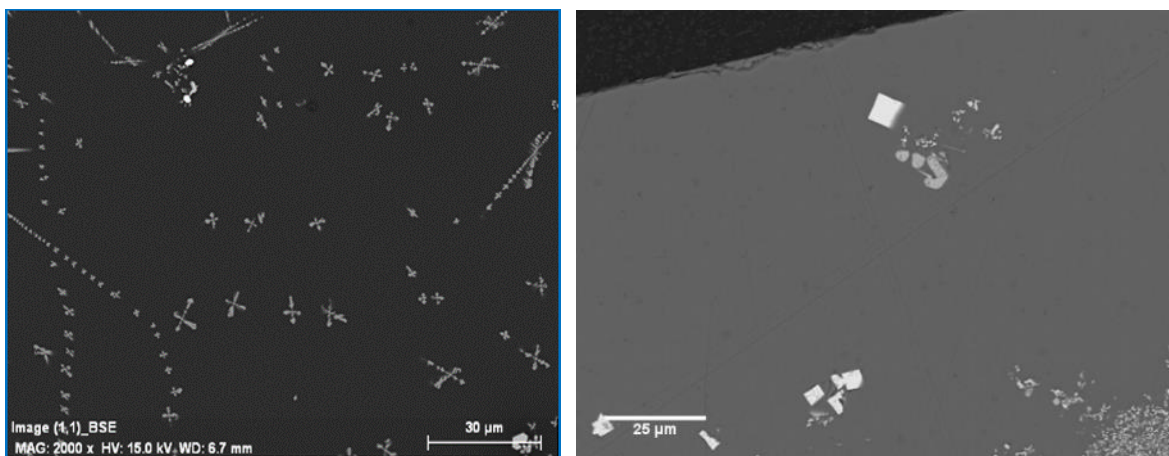


Figure 4 Example of crystallization observed in a borosilicate nuclear glass after thermal treatment: zincochromite, cerianite and powellite are the white crystals surrounded by the glass which is darker.

### **Radiation stability**

Nuclear glass are 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 (Malkowsky, 2021)(Mir, 2016 and 2017)(Weber, 2013). The beta decays, gamma transition and 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 lose 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 from beta decays and gamma rays is of typically 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 0.02 GGy and is termed nuclear dose (See figure 5).

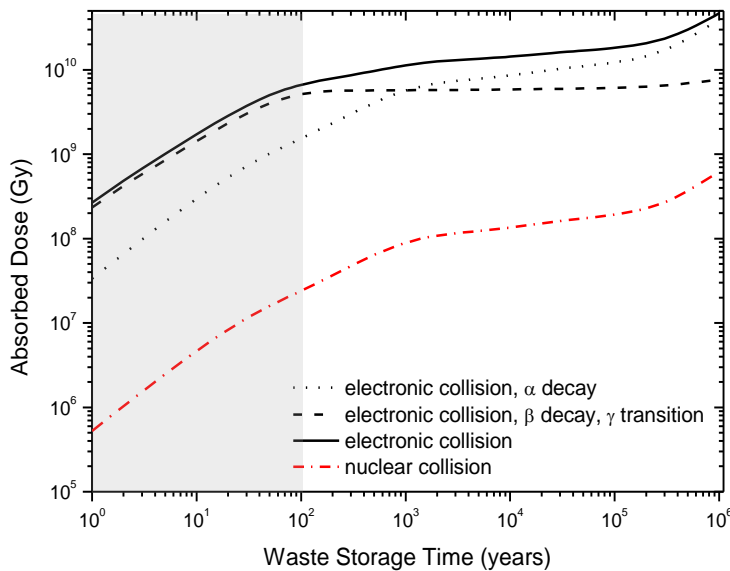


Figure 5 . Evolution of the absorbed dose of a nuclear glass with time. The gray rectangle highlights the interim storage period.

It has been shown that (Mir 2016 and 2017), under beta irradiation, simplified 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 into 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 nuclear glass irradiated by beta particles up to 4GGy.

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 (Peuget, 2014). 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 is the result of the ballistic melting in recoil nuclei tracks and the subsequent alpha particles partial damage repair due to a thermal self-healing mechanism in the alpha 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 is 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 40 MGy (or  $4 \times 10^{18}$  alpha decay/g)(figure 6).

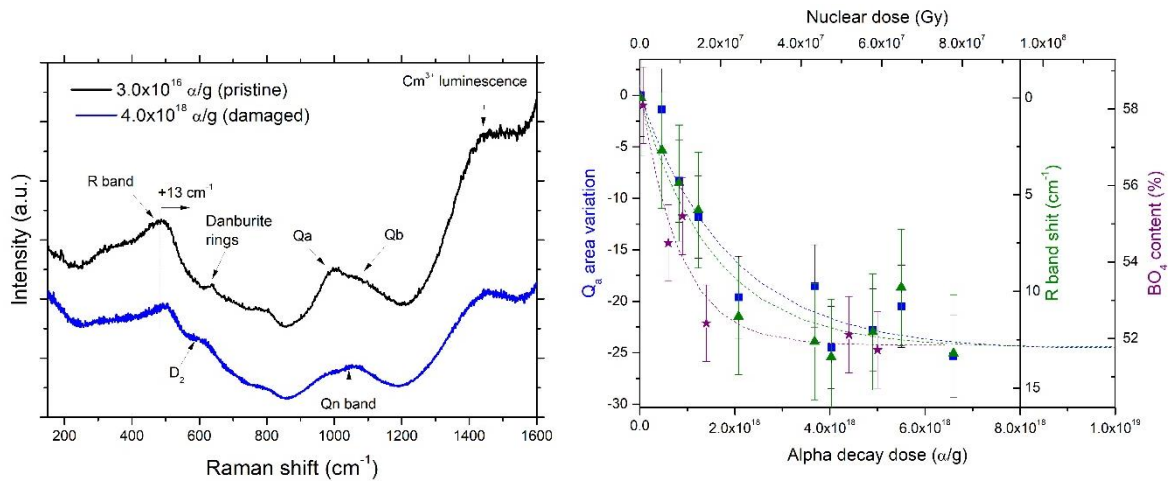


Figure 6 : Structural evolution of the laboratory ISG glass doped with  $^{244}\text{Cm}$ . a) Raman spectra at two alpha decay dose, b) evolution of structural parameters with increasing alpha decay dose

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 be preserved during the interim storage period.

## 6.10.6. Long term performance of HLW in geological disposal

### Background

There is presently a broad consensus among technical experts that the preferred method of ensuring long term management of HLW (Spent Nuclear Fuel and Glass) is isolation in a deep geological disposal facility, which provides passive, multibarrier isolation of radioactive materials from biosphere (AIEA, 2018).

Emplacement in carefully engineered structures buried deep within suitable rock formations provides the long term stability typical of a stable geological environment. At depths of several hundred meters, in a tectonically stable region, processes that could disrupt the disposal facility are so slow that the deep rock and groundwater system remain practically unchanged over hundreds of thousands or even millions of years.

In the geological disposal, high level waste packages will be exposed to underground water after several thousands of years, with ongoing corrosion of over- and primary containers, and that is why long term behavior of glass under leaching is widely described since decades. A schematic representation of spent fuel assemblies and glass package is shown on figure 7 (Poinssot, 2012).

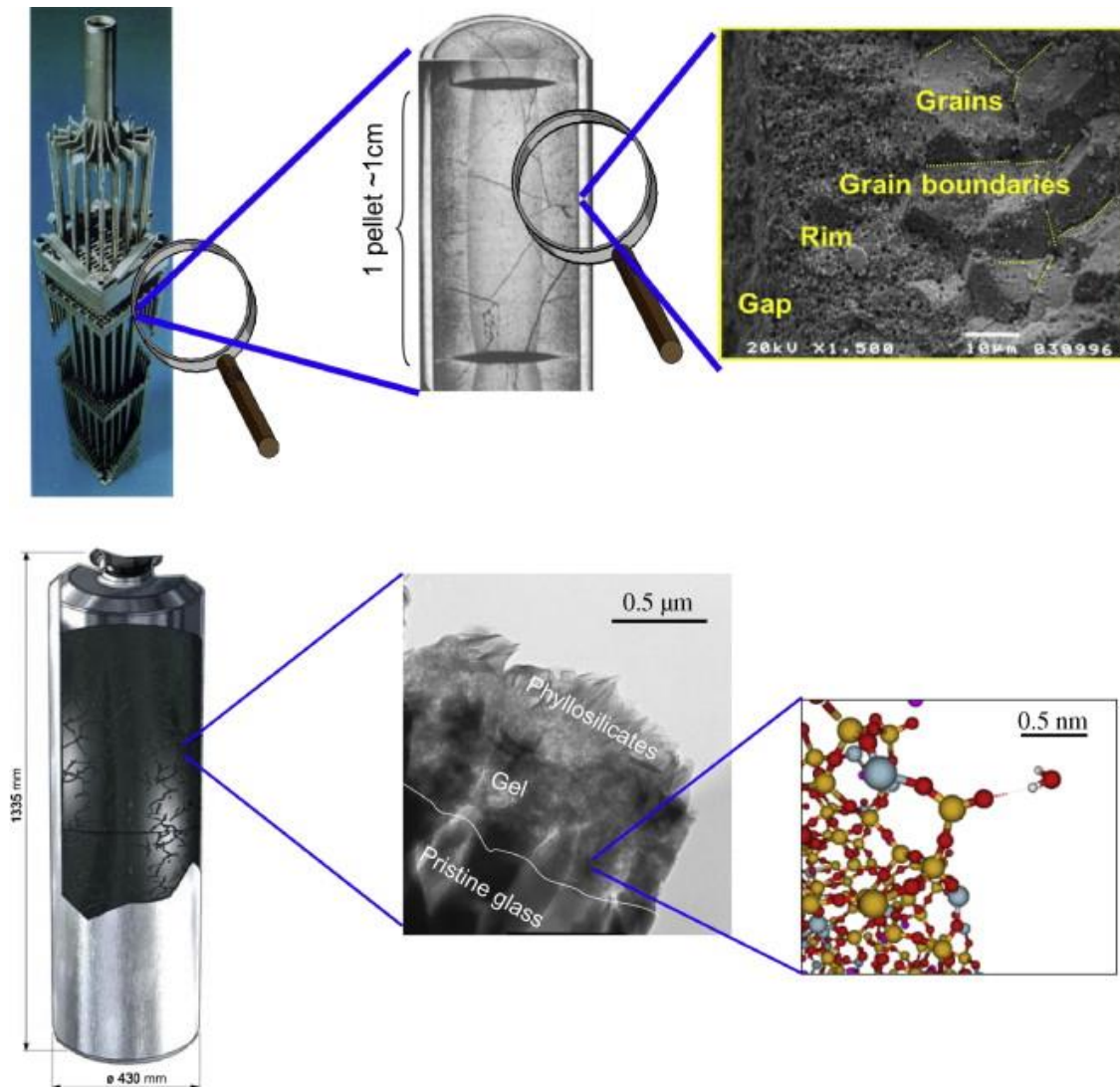


Figure 7 :

Top: schematic representation of a spent fuel assembly comprised of numerous fuel rods (center), which are made of an external Zircaloy cladding filled with UO<sub>2</sub> sintered pellets. After irradiation, these pellets are strongly modified (right). Bottom: schematic representation of a glass package (left) showing the primary canister made of stainless steel filled with borosilicate glass. Glass is fractured due to rapid cooling after the elaboration and forms a gel and crystalline phases when leached by water (center). At atomic level (right), glass displays an amorphous structure with a short range order

Down : schematic representation of a glass package (left) showing the primary canister made of stainless steel filled with borosilicate glass. Glass is fractured due to rapid cooling after the elaboration and forms a gel and crystalline phases when leached by water (center). At atomic level (right), glass displays an amorphous structure with a short range order

(Poinssot, 2012)

In order to describe the long-term performance of waste forms, it is necessary to consider the different steps of their lifetime, in relation with the environmental conditions of the waste packages (wasteform, metallic containers and surroundings materials such as concrete and host rock, clay or granite).

Two boundary conditions are considered, associated with two scenarios.

- First situation: the waste package remain intact, without any interaction with the surrounding environment. The package undergoes only an internal modification and is exposed to energy exchanges involving heat and radioactivity (residual alpha, beta and gamma radioactivity and neutrons in spent fuel). No mass transfer occurs between the system and the external environment. These conditions are close to interim storage conditions.
- Second situation: the evolution of waste forms in a water-saturated open system. Once the leaktight container is breached, the waste matrix is subjected to aqueous alteration and can exchange matter with nearfield materials, such as cementitious materials and host rock. Migration of the radioactive elements then becomes possible.

A transient state between both of the above-described scenarios corresponding to the evolution of waste forms in an open unsaturated medium must also be considered, when the nearfield environment is not entirely resaturated with groundwater when canister breaches.

As a general rule, a waste form will successively undergo these three different types of boundary conditions. The first period corresponds to the lifetimes of the container and overpack.

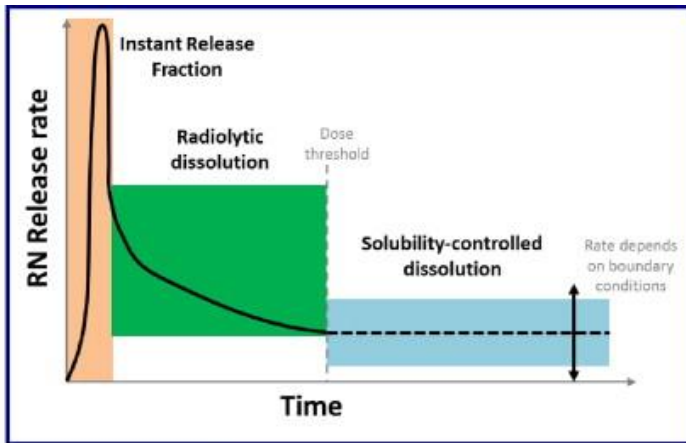
The occurrence of the open system/unsaturated conditions scenario will depend on the water re-saturation rate of the nearfield. It is therefore strongly site-dependent. It may last longer if gas bubbles (i.e. hydrogen) are produced due to metal corrosion (due mainly to the waste containers) and avoid the complete resaturation. At long term, the waste form will be placed in open and saturated conditions.

A simplified representation of the influence of the main physical and chemical parameters on spent fuel and glass source terms is given on figure 8 (Poinssot, 2008).

The water transport and solution chemistry are key factors regarding the long-term durability of both matrices. However, the mechanisms through which spent fuel and glass may release their RN are quite different. First, spent fuel is very sensitive to radiolysis whereas glass is not, second and most important, part of the RN within spent fuel are instantaneously released in contact with water (instant release fraction or IRF) whereas the RN in the glass are only released when glass dissolves.

### **Keys elements of the evolution of SNF in a repository**

The RN release from spent fuel in contact with water, such as in a geological disposal site, can conceptually be broken down into two main fractions (Johnson, 1988). The first fraction involves the rapid release of the labile activity corresponding to the radionuclide inventory on the free surfaces of the fuel, and the release of the grain boundary inventory, over a period of several months to several years. This fraction is often referred to as the Instant Release Fraction (IRF). The second fraction corresponds to the slow release of activity as the UO<sub>2</sub> matrix dissolves, and may last several thousands of years. The release of most of the activity from the spent fuel rod, i.e. the activity contained in the grains, is thus controlled by the fuel dissolution kinetics (Ewing, 2015)(Jegou, 2007)(Ferry, 2006) (Kerleguer, 2020).



Type of Boundary Condition	Spent Nuclear Fuel		Nuclear Glass	
	Phenomena	Significance	Phenomena	Significance
Chemical	Matrix dissolution, precipitation of secondary phases, recombination of radiolytic species	+++	Glass dissolution, precipitation of secondary phases	+++
Hydraulic	Water renewal rate over the very long term when alteration is controlled by solubility	++	Water renewal rate and diffusion of silicon in the nearfield	+++
Thermal	Rate of chemical reactions	+	Rate of chemical reactions	++
Radiological	Radiolytic dissolution, He production within a fuel pellet	+++	Self irradiation, Radiolysis, He production	+
Mechanical	Fuel fracturing	-	Glass fracturing	+
Biological	Fuel dissolution	-	Glass dissolution	-

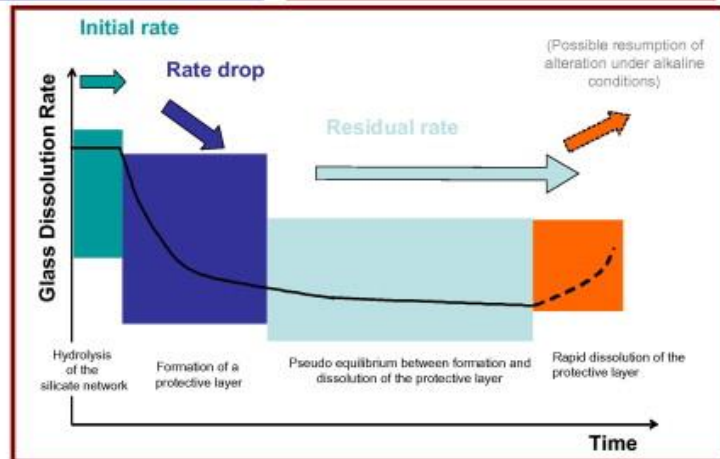


Figure 8 Synthesis of the direct effects of the main constraints applied to waste forms in geological disposal sites (table) and their relative significance regarding the source term. Schematic representation of the main kinetic regimes of the spent fuel (up) and glass (down)

The water transport and solution chemistry are key factors regarding the long-term durability of both matrices. However, the mechanisms through which spent fuel and glass may release their RN are quite different. First, spent fuel is very sensitive to radiolysis whereas glass is not, second and most important, part of the RN within spent fuel are instantaneously released in contact with water (instant release fraction or IRF) whereas the RN in the glass are only released when glass dissolves.

## Key elements of the long term behavior of glass in deep disposal

The vitrification process involves chemically bonding radionuclides to an aluminoborosilicate network, except for a very small amount of them, which are retained in the small undissolved noble metal particles. From a long-term behavior point of view, this means that radionuclides confined in such a material cannot be released in the environment if the glass remains undissolved. The solid-state diffusion process, even if thermally assisted, remains negligible. Radioactive decay produces heat and radiation damage and its potential effect is another key issue regarding the long-term stability of this type of waste form.

No significant impact of alpha/beta/gamma activity is expected on stage I (initial dissolution rate). For stage II corresponding to the residual rate regime, explored irradiation conditions seem to have very low effect both on the alteration rates and on the morphology of the alteration layer but some secondary effects can be observed such as modifications in the production of radiolytic species (Tribet, 2020). During glass alteration, RN are more or less retained in alteration products formed at the glass surface (gel and crystalline phases). The retained fraction mainly depends on the predominant redox form of each RN, which needs to be related to the water composition, the redox potential and the pH. The mobile fraction is made of aqueous species (potentially promoted by ligands) and colloids. Many data are available in the literature for actinides and fission products (Gin, 2017), including some from integrated mockups and in situ tests, showing that under anoxic and reducing conditions expected in most of geological repositories, the solubility of most of long lives RN is very low.

Explaining the Long-Term Behavior approach requires identifying the governing mechanisms and developing models to overestimate their influence (Poinsot, 2012)(Ribet, 2009).

Glass alteration is described, whatever the glass composition, by the different reactions involved that are : interdiffusion (proton - alkali ion exchange), hydrolysis (Si-O-Si bond rupture), dissolved species recondensation so as to form an amorphous alteration gel which constitutes a diffusive barrier between the glass and the solution, and the precipitation of secondary crystalline phases.

These reactions are structured as four simultaneous processes which are likely to be described in terms of kinetics:

- the oxide glass is turned into a porous, hydrated, hydroxide-type phase (the gel);
- this glass hydration reaction is limited by the water diffusion transport into the pristine glass, through the gel layer already formed: in other words; the gel has a passivating effect;
- the gel is dissolved on its external surface at a rate which is a function of the solution composition and renewal conditions;
- secondary phases precipitate, thereby consuming passivating-zone formers.

At laboratory scale, the residual rate can be measured either thanks to static experiments at a high surface-to-volume ratio ( $S/V$ ), or using a single-path-flow-through test at a low flow rate and a silica doped solution. When these protocols are applied to a large range of glasses, in most cases, a constant or a near-constant rate is observed, which is 3–4 orders of magnitude lower than the initial rate (the maximum dissolution rate corresponds to pristine glass in contact with pure water) and leads to rates of a few nm per year for UOX-type borosilicate glasses.

Modelling the long term behavior of nuclear glasses is needed to describe the glass alteration kinetics over a very large period of time, including the final residual rate regime, thanks to a mechanistic model

such as the french GRAAL model (GRAAL meaning Glass Reactivity with Allowance for the Alteration layer) (Frugier, 2018) (Poinssot, 2012)(Frugier, 2008).

GRAAL is modelling the alteration of the glass, taking into account the evolution with time of the equilibria between the passivating layer, the secondary phases that may precipitate, and the composition of the liquid phase in interaction with the solid phases. Graal is correlated with a reactive transport model (such as HYTEC), and connected with a thermodynamical data base.

The long-term glass dissolution rate also depends on chemical and hydraulic factors that influence the fate of silicon. Silicon is the main glass former and this element is therefore involved in most of the chemical processes governing the glass dissolution process (Grambow, 2001)(Gin, 2018). As the host rock is chosen for its low permeability and diffusivity, it can be expected that if the barriers placed in between the glass and the host rock do not prevent the saturation conditions with respect to the silica-rich passivating layer, the dissolution rate will be low. The low rate achieved when saturation conditions prevail is called the “residual rate” or “final rate”. These terms refer to the fact that no thermodynamic equilibrium between the glass and solution can ever be achieved and that no surface layer can completely protect the glass.

Performance assessment of geological nuclear waste repositories requires also modeling of the long-term evolution of the aqueous alterations of the fractured nuclear glass block, because the time scales under consideration are of several thousands of years and hence beyond the range of any direct experimental perspectives (Repina, 2020).

Furthermore, in-situ glass corrosion experimentations on radioactive glasses have been carried out, giving some indications of the performances which are obtained for nuclear glass in representative repository conditions (see a review in (Gin, 2017)). Tests related to the geological disposal of intermediate and high level glasses have been carried out on three types of glasses with different compositions (borosilicates or aluminosilicates) in different natural environments, over several years. The results show very thin altered glass thicknesses, with the same orders of magnitude (a few microns) for the different glasses and environments, and typical of a process controlled by diffusion and point to the formation of a passivating alteration layer was observed, as observed for non-radioactive simulated glasses.

## Development of alternative conditioning processes for HLW

A titanate-based fully crystallized wasteform, SYNROC, was invented by Australian scientists from ANSTO in the late 1970s (Ringwood, 1988)(Gregg, 2020). The original form of Synroc, a multiphase ceramic wasteform based on stable and leach resistant titanate minerals was directed toward the immobilization of PUREX wastes from the reprocessing of nuclear fuels. Geologically stable titanate minerals—perovskite, hollandite, zirconolite and rutile are the main phases of Synroc.

The Synroc wasteforms are obtained thanks to HIPing processes. However, a current limitation is the lack of demonstration of this type of process at an industrially relevant scale within a nuclear facility.

## Conclusion

The management of high level waste, spent nuclear fuel (SNF) and nuclear glass, is a key point in the nuclear industry, all around the world, since many decades, and for the future also. Two kinds of HLW need to be taken into account : SNF is considered as a high level waste in some countries (USA, Sweden, Finland, Spain, Canada, etc.) or a potential future energy resource in others (France, Japan, UK, Belgium). In the last case, vitrification of the fission products coming from fuel reprocessing is the industrial process implemented in these countries, resulting in an industrial maturity wich is now demonstrated. Disposal in deep, stable geological formations usually several hundred meters or more below the surface is the generally recognized option for disposal of HLW. The description of the long term behavior of SNF and nuclear glass benefits from many international studies, showing that such glassy wasteform is relevant for HLW conditioning.

## List of references

AIEA (2018). Status and Trends in Spent Fuel and Radioactive Waste Management - IAEA Nuclear Energy Series – N° NW-T-1.14 (2018)

Crovisier, J.L., T. Advocat, and J.L. Dussossoy (2003). Nature and role of natural alteration gels formed on the surface of ancient volcanic glasses (Natural analogs of waste containment glasses). *Journal of Nuclear Materials*, 321, 91-109.

Delattre, O., et al. (2013). Crystallization Kinetics of Apatite and Powellite in a Borosilicate Glass under Thermal Gradient Conditions. XIII International Conference on the Physics of Non-Crystalline Solids, X. Zhao, K.L. Ngai, and C. Liu, Editors. Elsevier Science (Amsterdam) 3-9.

Ferry C., et al. (2006). Specific outcomes of the research on the spent fuel long-term evolution in interim dry storage and deep geological disposal. *Journal of Nuclear Materials*. 352. 246 – 253.

Frugier, P. et al. (2018) Modeling glass corrosion with GRAAL. *NPJ Materials Degradation* 2:35 ; doi:10.1038/s41529-018-0056-z

Frugier, P. et al. (2008). SON68 nuclear glass dissolution kinetics: Current state of knowledge and basis of the new GRAAL model. *Journal of Nuclear Materials* 380. 8–21.

Gin, S. (2018). Dynamics of self-reorganization explains passivation of silicate glasses. *Nature Communications*. 9. 2169.

Gin, S., et al. (2017). Radionuclides containment in nuclear glasses: an overview. *Radiochimica Acta*, 105(11), 927-959.

Gregg D.J. et al (2020) Synroc technology: Perspectives and current status (Review). *Journal of the American Ceramic Society*, 103(10), 5424-5441

Grambow, B. and Müller R. (2001). First-order dissolution rate law and the role of surface layers in glass performance assessment. *Journal of Nuclear Material*. 298. 112-124.

Hyatt N.C., Ojovan M.I., (2019). Special Issue: Materials for Nuclear Waste Immobilization. *Materials*, 12, 3611

Jegou, C. et al (2007). Spent fuel UO<sub>2</sub> matrix alteration in aqueous media under oxidizing conditions. *Radiochimica Acta* 95. 513–522.

Jantzen C.M., and Ojovan M.MI, 2019. On Selection of Matrix (Wasteform) Material for Higher Activity Nuclear Waste Immobilization (Review). *Russian Journal of Inorganic Chemistry*, 64(13), 1611–1624.

Johnson, et al. (1988). Spent nuclear fuel. In *Radioactive waste form for the future*, W. Lutze, R.C. Ewing (Eds.), Elsevier Science Publishers B.V. 635-698

Kerleguer, V. (2020). The mechanisms of alteration of a homogeneous U<sub>0.73</sub>Pu<sub>0.27</sub>O<sub>2</sub> MOx fuel under alpha radiolysis of water. *Journal of Nuclear materials*. 529.51920.

Lutze W. and Ewing R.C.,1988. *Radioactive Waste Forms for the Future* (Elsevier, Amsterdam)

Malkovsky V.I. et al. (2020). The Influence of Radiation on Confinement Properties of Nuclear Waste Glasses. Science and Technology of Nuclear Installations Article ID 8875723, 14 pages

Mir, A.H., et al. (2017). Electron and electron-ion sequential irradiation of borosilicate glasses: Impact of the pre-existing defects. Journal of Nuclear Materials, 489, 91-98.

Mir, A.H., et al.(2016). Surface and bulk electron irradiation effects in simple and complex glasses. Journal of Non-Crystalline Solids, 453, 141-149.

Orlhac, X., et al., (2001). Determination of the crystallized fractions of a largely amorphous multiphase material by the Rietveld method. Journal of Applied Crystallography, 34, 114-118.

Orlhac, X. et al.(1999). Study of crystallization mechanisms in the French nuclear waste glass. MRS Proceedings, 556, 263-270.

Peuget, S. et al. (2014). Specific outcomes of the research on the radiation stability of the French nuclear glass towards alpha decay accumulation. Journal of Nuclear Materials, 444(1-3). 76-91.

Poinssot C. and Gin S. (2012) Long-term Behavior Science: The cornerstone approach for reliably assessing the long-term performance of nuclear waste. Journal of Nuclear Materials 420. 182-192

Repina M. et al. (2020) Reactive transport modeling of glass alteration in a fractured vitrified nuclear glass canister: From upscaling to experimental validation. Journal of Nuclear Materials. 528. 151868.

Ribet, I. et al. (2009) Long-term behavior of vitrified waste packages. Proceedings of Global Conference 2009 Paris, France

Ringwood A.E. et al. (1988). "Synroc". In: Lutze W, Ewing RC, editors. Radioactive waste forms for the future. Amsterdam. 233-334.

Tribet M. et al. (2020). New Insights about the Importance of the Alteration Layer/Glass Interface. The Journal of physical Chemistry C., 124, 10032-10044.

Vernaz E. 2009. Nuclear Waste Conditioning. CEA Monograph, CEA Saclay and Groupe Moniteur (Éditions du Moniteur, Paris).

Vernaz E., Bruezière J., (2014). History of Nuclear Waste Glass in France. Procedia Material Science 7, 3-9

Weber W.J. (2014). Radiation and Thermal Ageing of Nuclear Waste Glass. Procedia Materials Science 7. 237 - 246

Ewing, R. (2015) Long-term storage of spent nuclear fuel. Nature materials. 14. 252-257