

Glasses and Ceramics for High-Level Waste Immobilization: An Overview

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Abstract. According to their activity level, the radioactive wastes are categorized as high-, intermediate- and low-level waste. This report is mostly concentrated on high-level waste, which includes liquid waste from the first cycle of spent fuel reprocessing and solids into which such liquid waste has been converted. The disposal of the high-level radioactive waste consists of placing radioactive waste in a storage facility or repository, so that it is safe from unintentional disturbance in a manner which also prevents escape of any of the waste material for extremely long time periods. However it has shown to be the weakest point of the nuclear power. In this report, an overview is given of the most used materials for nuclear waste immobilization: glasses and ceramics, their properties, different types and a comparison between them. The radioactive waste is immobilized when it has reduced its potential for dispersion of contaminants in the environment and conversion of a waste into a wasteform by solidification (vitrification, cementation, bituminization) and embedding.

Different types of glasses and ceramics are under development and further research.

Keywords: disposal, radioactive waste, vitrification, cementation.

1 Background

The radioactive wastes contain unstable elements that decay and emit ionizing radiation which can be harmful to humans and the environment [1]. According to their state, the radioactive wastes can be liquid, gaseous, and solid. The gaseous waste contains airborne radionuclides which are released in the atmosphere after they have decayed into non-radioactive products. The liquid waste comes mostly from spent fuel reprocessing and few of the processes for decreasing the radioactivity in the liquid waste. These processes include evaporation, ion exchange, fixation in solids (solidification), filtration, centrifugation, etc. Solid waste mostly comes from contaminated equipment and it is generated as a result of the maintenance and repairs of the nuclear power facilities. The solid radioactive waste is pressed, so that the volume is reduced, and afterwards, some immobilisation process, like vitrification takes place, depending on the activity of the waste [2].

According to their activity level, the radioactive wastes are categorized as high-, intermediate- and low-level waste [3]. Low-level waste includes items that have become contaminated with radioactive material or have become radioactive through exposure to neutron radiation. A total of 90% of all radioactive waste is low-level waste. Intermediate-level waste (ILW) constitutes about 7% of the total radioactive waste [4] and has decay-heat levels lower than 2 kW/m³. On the other hand, high-level waste's decay heat is above that threshold. HLW generate 95% of the total radioactivity of produced waste [3]. High-level waste includes liquid waste from the first cycle of spent fuel reprocessing and solids into which such liquid waste has been converted. Its typical activity is about 10⁴–10⁶ TBq/m³ [5]. There are mainly two types of fuel cycles:

once-through and closed, depending on whether the spent fuel is reprocessed or not [6]. When the spent fuel is not processed any further, it is considered a high-level waste [5]. The spent fuel typically contains 95–96% uranium with ²³⁵U concentrations similar or slightly above that in natural uranium, 1% plutonium, 0.1% other actinides and 3–4% fission products [5]. The use of 10 t of uranium fuel generates around 1.5 m³ high-level waste, 0.115 m³ vitrified high-level waste, and 0.35 m³ intermediate-level wastes [6].

2 High-Level Radioactive Waste Disposal

The radioactive waste management covers the entire technological cycle – from their generation, through preliminary treatment, processing, transportation, to their turning into appropriate condition for temporary storage and subsequent disposal [3].

The disposal of the high-level radioactive waste consists of placing radioactive waste in a storage facility or repository, so that it is safe from unintentional disturbance in a manner which also prevents escape of any of the waste material for extremely long time periods (hundreds of thousands of years) [7], however it has shown to be the weakest point of the nuclear power.

If the spent nuclear fuel is not considered as a high-level waste, other measures have to be implemented. After the storage (wet and/or dry), the spent fuel is mostly reprocessed by hydrometallurgical PUREX (Plutonium Uranium Redox Extraction). The PUREX process consists of several steps: dissolution of the fuel (reception at the reprocessing plant, storage, shearing, dissolution, and clarification); uranium and plutonium separation from fission products; purification of plutonium and uranium, and converting

them into oxides; operations for conditioning solid wastes and effluent treatments. It is a process with liquid-liquid extraction ion-exchange method used to reprocess spent nuclear fuel, in order to extract primarily uranium and plutonium. The solidified waste form can be stored conveniently, shipped, and disposed of. The glass waste is expected to resist leaching by water for hundreds of years [8].

3 High-Level Radioactive Waste Immobilization

Radioactive waste immobilisation means that the waste is provided with solid and stable material host, like glass or ceramics, so that it will be easily stored. Immobilization of HLW prevents contamination of the biosphere with radioactive elements [9]. The main immobilisation technologies that are available commercially and have been demonstrated to be viable are vitrification, cementation, and bituminisation [7]. Vitrification involves melting of waste materials with glass-forming additives so that the final vitreous product incorporates the waste contaminants in its macro- and micro-structure. The use of predominantly crystalline ceramic waste-forms (ceramication) has also been proposed including single-phase ceramics such as zircon to accommodate a limited range of active species such as plutonium and multiphase systems such as Synroc to accommodate a broader range of active species [10].

A system of multiple barriers ensures that waste radionuclides decay below exemption levels before there is any possibility of their release. The first barrier is the waste-form in which the radionuclides are held. That could be the spent fuel's ceramic matrix or a carefully designed vitreous or cementitious system. The next barrier usually is a metallic package or container, which provides absolute containment but for limited periods of time compared to the half-lives of some of the long-lived nuclides. Careful design of backfill materials and the host rock of the repository which ideally should have high radionuclide sorption capability, delay the release of radioactive materials to the environment and biosphere. Multi-barrier systems are designed depending on the disposal option (near surface, deep underground) and the engineering barrier system used. If the disposal facility remains intact, the radionuclides could reach the biosphere only if the waste-form is dissolved in groundwater and the radioactive solution migrates to the surface. That is why the leaching resistance (the inability of the material to be dissolved in particular medium) plays an important role in the selection of the waste-form material for ultimate disposal in an underground repository [9].

4 Glass as a Solvent for High-Level Waste

Glass is used to dissolve the HLW and the outcome of the vitrification process is a glassy homogeneous product castable into stable and suitable forms (large glass blocks). Glasses are amorphous materials with a topologically disordered structure of interconnected structural blocks. Upon heating, glasses continuously change most of their properties to those of a liquid-like state in contrast to crystals (where such changes occur abruptly at a fixed

temperature or the melting point) – called glass transition temperature. Under suitable conditions, it is possible for the glass to incorporate up to 25–30 wt% HLW. The choice of glass composition is a compromise between high HLW solubility, manageable glass formation temperature, and low leach ability in repository environments [10].

The glass has several advantages as a material used as matrix for highly radioactive waste immobilisation. It is a good solvent for HLW, can be processed at reasonably low temperatures, and is very tolerant of variations in waste composition. Furthermore, the glass exhibits reasonable chemical durability and radiation resistance, and can accommodate changes occurring during radioactive decay of HLW constituents [9].

The vitrification technology comprises several stages, starting with evaporation of excess water from liquid radioactive waste, followed by batch preparation, calcination, glass melting, and ending with vitrified waste blocks and potentially small amounts of secondary waste. In the one stage process both waste calcination and melting occurs in the melter. Here, the vitrification process glass forming additives are mixed with concentrated liquid wastes and so a glass-forming batch is formed. This batch is then fed into the melter where further water evaporation occurs, followed by calcination and glass melting which occur directly in the melter. In a two stage process the waste is calcined prior to melting. Thin film evaporators are typically used and the remaining salt concentrate is mixed with the necessary additives and depending on the type of vitrification process is directed to one or another process apparatuses [10].

Waste vitrification is attractive because the process provides high capability to immobilise various elements. Meanwhile the technology is simple and can be adapted from glass production industry and the resulting waste-form has small volume. The glasses show high chemical durability in natural waters and high tolerance to radiation damage. Also, the process is able to destroy hazardous organics in the waste while chemically incorporating the waste inorganic constituents into a stable glass often with significant volume reduction which contributes towards reduced disposal costs [10].

The drawbacks of vitrification are due to high initial investment cost, high operational cost and complex technology requiring well qualified personnel. Because of that vitrification is economically expedient when relatively large volumes of radioactive waste with relatively stable composition are available such as HLW or operational radioactive wastes from nuclear power plants [10].

There exist several different types of glasses. The borosilicate glasses can dissolve easily wide range of waste compositions, can be modified in order to optimize their properties, possess flexibility regarding the waste loading and are able to incorporate many different kinds of waste elements. In addition, they maintain good durability within given composition ranges. However borosilicate glasses require a high processing temperature. They are suitable for the immobilization of plutonium and can accommodate high concentrations of actinides.

Table 1. Typical properties of HLW Glasses [10]

Glass	Density [g/cm ³]	Compressive strength [MPa]	Normalised leaching rates, 28th day [(g/cm ² ·d) × 10 ⁻⁴]	Thermal stability [°C]	Damaging dose [Gy]
Borosilicate	2.7	[22.0; 54.0]	0.3 (Cs); 0.2 (Sr)	> 550	> 10 ⁹
Phosphate	2.6	[9.0; 14.0]	1.1 (Cs); 0.4 (Sr)	> 450	> 10 ⁹

Phosphate glasses possess good atomic bonding characteristics. However these glasses are less stable thermally than their silicate equivalents, less durable in aqueous environments, have lower melting temperatures, lower melt viscosities and substantially different temperature-viscosity behaviour than their silicate equivalents. In addition, they have poor chemical durability and low thermal stability. Phosphate melts are highly corrosive in nature. However, phosphate glasses require low formation temperatures and possess high solubility for sulphates and metal oxides. There is a new family of lead iron phosphate glasses that have good glass-forming characteristics, reasonable thermal stabilities, and excellent chemical durability. These glasses are not as corrosive as the earlier phosphate compositions and prepared at temperatures in the range 800–1000°C, which is some 100–250°C lower than the borosilicate compositions. However, their durability in aqueous solutions decreases. This can be improved by the addition of CaO.

Rare earth oxide glasses or “Loffler” glass contain 55 wt% of lanthanide oxides, and have high solubility for uranium, plutonium, and americium which make them potential host for those elements’ immobilisation. There are other alternative glasses with high silica contents and better leaching resistances than the borosilicate compositions. They possess good durability and superior resistance compared with borosilicate glasses. These glasses require higher temperatures for melting than the borosilicate compositions. They can accommodate up to 20 wt% UO₂ depending on the cooling velocity and possess good chemical durability and good mechanical integrity. Sintered glasses enable reduction in the processing temperature of several hundred degrees and elimination of evaporation losses [10].

The main properties of borosilicate and phosphate glasses are summarised in Table 1.

Borosilicates and phosphates have been accepted as the two main glass types for nuclear waste immobilisation. The exact compositions of these nuclear waste glasses are tailored for easy preparation and melting, avoidance of phase separation and uncontrolled crystallisation, and acceptable leaching resistance. As an example, at the reprocessing plant in La Hague, France, high-level waste is calcinated, mixed with borosilicate glass powder and melted in an induction furnace at 1100°C. The steel canisters into which the molten mixture is poured are 1.34 m long and 0.43 m in diameter. One canister can hold the HLW from 1.3 tHM of reprocessed spent fuel [5]. Vitrification programmes are also carried out in Sellafield, UK; West Valley, USA; Mayak, Russia; and others [10].

5 Ceramics as a Solvent for High-Level Waste

The cementation is a very old technique that requires simple, robust equipment and cheap raw material, and it has low energy demand [7, 11]. Summary of cementitious waste form’s advantages and drawbacks is shown in Table 2.

In 1950, it was suggested that high level radioactive waste could be immobilized in a poly-phase ceramics. Single-phase minerals can host a large number of nuclides and can be used as a monophasic waste-form. However, monophasic ceramics are difficult to fabricate and poly-phase compositions are more common. The composition of the poly-phase ceramic is tailored to that of the waste composition to achieve complete and reliable immobilisation of the waste constituents [7].

Table 2. Advantages and disadvantages of the cementitious waste form [7, 11]

Advantages	Disadvantages
<ul style="list-style-type: none"> • Good compressive strength; • Good leach resistance; • Good resistance to freeze/thaw treatment; • Proved behaviour at aging (for up to 50 years); 	<ul style="list-style-type: none"> • Low waste loading – • Large volume – high disposal costs; • Problems with processing of historical wastes; • Unknown behaviour for long-term storage periods (for centuries)

The most widely studied ceramic waste form has been a single phase sodium zirconium phosphate. These compounds have low thermal expansion and structural flexibility to accommodate a large number of multivalent ions. The latter property allows the incorporation of large share of the nuclides present in a typical commercial high-level waste. The studies of simulated waste forms based on this form have shown reasonable leach resistance. The material’s structure allows waste loadings up to 20 wt% [12].

The most well-known poly-phase ceramic is synthetic rock (Synroc), which was developed by Ringwood and co-workers in Australia in the 1970s. Synroc is a titanate-based ceramic containing several mineral phases, and non-stoichiometric titanium oxides. The pH of the leachant has a relatively small effect on the durability of Synroc [11]. The properties of Synroc composites are outlined in Table 3.

Synroc is chosen as a waste form because it is a titanate ceramic based on naturally occurring minerals, which incorporate actinide elements in nature. It is dried and calcined under reducing conditions and hot pressed at 1100–1170°C, adding 2 wt% Ti to lower the mobility of volatiles and keep Mo metallic thereby avoiding formation of water-soluble molybdates [7].

Table 3. Properties of Synroc composites [11]

Flexural strength	[MPa]	65
Compressive strength	[MPa]	350
Young's modulus	[MPa]	1.4×10^5
Microhardness	[g/mm ²]	> 950
Density	[g/cm ³]	[4;6]
Thermal conductivity	[W/m·K]	2
Thermal expansion coefficient	[K ⁻¹]	11.0×10^{-6}
Leaching rate	[g/(m ² ·d)]	[10 ⁻² ; 10 ⁻³]

A wide range of cations of different charges can be incorporated into the crystalline phases of the Synroc. A number of different kinds of Synroc have been reported with their composition depending on the proposed application [7, 13]:

- **Synroc-C:** developed for immobilization of commercial waste from the reprocessing of spent power reactor fuel; composed of Ba, Al, Ca, Zr titanates. The processing temperature varies from 1280°C to 1380°C. The titanate minerals can incorporate into their crystal structures nearly all of the elements present in the radioactive waste. Synroc-C, was intended mainly for the immobilisation of liquid HLW arising from the reprocessing of light water reactor fuel and it can hold up to 30 wt% HLW.
- **Synroc-D:** for defence waste; contains nepheline instead of hollandite as host for Cs, Rb and Ba.
- **Synroc-E:** has improved long-term stability;
- **Synroc-F:** used for unprocessed spent fuel containing significant amounts of uranium and plutonium. It is enriched in pyrochlores, and has been developed for the disposal of unprocessed spent fuel from light water and CANDU reactors.

Early work on Synroc processing relied on preparing precursor materials by conventional powder methods (mechanical grinding and mixing). Later work has concentrated on the use of wet chemistry processes [7].

6 Comparative Analysis of Glasses and Ceramics

An overview of the properties of the glasses and ceramics as immobilization materials for high-level waste is given in Table 4.

Glasses and ceramics are chosen for immobilization of the HLW mainly because they have long-term resistance to radiation damage. However, both of them show good chemical characteristics and they have simple manufacturing. Glasses incorporate 25–30% HLW, while the ceramics' waste loadings are up to 20%, using sol-gel structure. Both of them are suitable solvents for HLW. The use of the ceramics as a HLW solvent depends on the ability of the crystalline phases to accept chemical species. Glasses can be extremely resistant to aqueous corrosion, while that can be a problem for the ceramics. The most important drawback of the glasses as immobilization materials for HLW is that the process is very expensive, while the ceramics can be found at low cost.

Table 4. Comparative analysis of glasses and ceramics as immobilisation matrices' materials

Glasses	Ceramics
<ul style="list-style-type: none"> • used to dissolve the HLW to form a glassy (vitreous) homogeneous product that can be cast into suitable forms incorporation up to 25–30 wt% HLW into a glass; • a good solvent for HLW; • can be processed at reasonably low temperatures; • very tolerant of variations in waste composition; • exhibits reasonable chemical durability; • radiation resistant; • can accommodate changes occurring during radioactive decay of HLW constituents; • can be made extremely resistant to aqueous corrosion; • can be made out of wide ranges of compositions; • the basic glass-making process is simple and robust; • very expensive 	<ul style="list-style-type: none"> • Waste loadings up to 20 wt%; • required to contain as much nuclides as possible; • required to possess sufficient leach resistance for a long period of time; • The use of ceramic materials depends upon the ability of the crystalline phases to accept a broad spectrum of chemical species within their lattices; • low leach rates for many crystalline phases; • long-term resistance to radiation damage; • high waste loading; • excellent thermal and mechanical stability; • simple processing; • low cost

7 Conclusion

Finding permanent and safe solution for managing high-level radioactive waste is of crucial importance for achieving a progress in changing public's opinion about nuclear power. Several approaches for waste immobilization are implemented for now: vitrification, bituminisation and cementation. Via the vitrification, the waste is mixed with glass-forming chemicals in a furnace to form molten glass that then solidifies in canisters, thereby immobilizing the waste. Many countries are using the borosilicate glass as a wasteform for immobilization of the HLW, but other types of glasses are being developed such as phosphate (lead iron phosphate), Loffler glass, or other alternative glasses. The borosilicate glass is mostly chosen for its easy preparation and melting, controllable crystallization and acceptable leaching resistance. Generally glasses have several advantages as a material used as matrix for highly radioactive waste immobilisation. They are a good solvent for HLW, can be processed at reasonably low temperatures, and are very tolerant of variations in waste composition. Furthermore, the glass exhibits reasonable chemical durability and radiation resistance, and can accommodate changes occurring during the radioactive decay of HLW constituents. Compared to borosilicate glass, the phosphate glass has similar density and can withstand the same dose rates. However it has considerably lower compressive strength, lower thermal stability, and significantly higher leaching rates.

Other matrix materials are the ceramics. There are two types of ceramics suitable for the immobilization of high-level waste: single-phase and poly-phase ceramics. Single-phase minerals can incorporate considerable amounts of radionuclides (around 20%), but are more expensive and difficult to manufacture. Poly-phase compositions are more common and their composition can be tailored to that of the waste composition in order to achieve complete and reliable immobilisation of the waste constituents—hosting more impure nuclides. The most studied poly-phase ceramic is Synroc which has multiple varieties. Although the ceramics have lower waste loading than glasses and therefore larger volumes of immobilised waste arise, they have shown good resistance to freezing and high temperatures and are compatible waste form for the high-level waste. Moreover, Synroc exhibits significantly higher compressive strength and has higher density than both borosilicate and phosphate glasses. On the other hand, Synroc's leaching rates are higher than the glasses' rates.

In general both glasses and ceramics have suitable mechanical and physicochemical properties that allow for long-term immobilization of highly radioactive waste. Currently, there are several materials that are applied as matrix materials and new types of glass and ceramics with better properties are under development.

References

- [1] U.S. NRC (accessed July 24 2017) Backgrounder on Radioactive Waste [].
- [2] Bromova E., Vargoncik D., Sovardina M. (2013) Nuclear Energy – Online Interactive Book, Simopt, CZ, ISBN 978-80-878751-05-0.
- [3] WORLD NUCLEAR ASSOCIATION (accessed July 24, 2017) Radioactive Waste Management [].
- [4] WORLD NUCLEAR ASSOCIATION (accessed July 24, 2017) What Are Nuclear Wastes and How Are They Managed? [].
- [5] IAEA (20016) Storage and Disposal of Spent Fuel and High Level Radioactive Waste.
- [6] IPFM (2011) Spent Fuel from Nuclear Power Reactors, Princeton, NJ, United States.
- [7] Ojovan M.I., Lee W.E. (2005) An Introduction to Nuclear Waste Immobilisation, Elsevier, ISBN 0-080-44462-8.
- [8] Ojovan M.I. (2011) Handbook of Advanced Radioactive Waste Conditioning Technologies, Woodhead Publishing, ISBN 978-0-85709-095-9.
- [9] Donald W.I., Metcalfe B.L., Taylor R.N.J. (1997) The immobilization of high level radioactive wastes using ceramics and glasses. *Journal of Materials Science* **32** 5851-5887.
- [10] Ojovan M.I., Batyukhnova O.G. (2007) Glasses for Nuclear Waste Immobilization. Presented at WM'07 Conference, February 25 - March 1, 2007, Tucson, AZ, United States.
- [11] Wang L., Liang T. (2012) Ceramics for High Level Radioactive Waste Solidification. *Journal of Advanced Ceramics* **1** 194-203.
- [12] Sheetz B.E., Agrawal D.K., Breval E., Roy R. (1994) Sodium Zirconium Phosphate (NZP) as a Host Structure for Nuclear Waste Immobilization: A Review. *Waste Management* **6** 489-505.
- [13] Gugov I., Kleitman M., Malakova A., Ivanova K., Georgiev G. (2017) Immobilization of liquid low-level waste from Kozloduy NPP by drying and subsequent sintering with inorganic additives. Presented at BULATOM 2017, Varna, Bulgaria, 2017.