

Review

Glass Crystalline Materials as Advanced Nuclear Wasteforms

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Abstract: Glass crystalline materials (GCM) are of increasing interest as advanced nuclear wasteforms combining the advantages of vitreous and crystalline matrices. The GCM are versatile wasteforms envisaged for a wider use to immobilise various types of both radioactive and chemically hazardous wastes. They can be produced either via low temperature sintering using precursors composed of glass frit, oxides, and crystalline phases or through conventional melting aiming to produce first a parent glass, which is then crystallised by a controlled thermal schedule to obtain target crystalline phases within the GCM. Utilization of GCM is highlighted as a perspective wasteform for immobilization of partitioned radionuclide streams.

Keywords: high level radioactive waste (HLW); radionuclide partitioning; immobilisation; melting; sintering; crystalline matrix; vitreous matrix; glass crystalline materials (GCM)



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1. Introduction

The spent nuclear fuel (SNF) reprocessing generates radioactive wastes, including high level radioactive waste (HLW), which is industrially immobilised in the Na-Al-P glass in Russia and A-B-Si glass elsewhere, where A stands for alkaline elements. By 2013, there were about 30,000 accumulated tonnes of vitrified HLW overall in the world [1,2]. Considering the processing rates of vitrification facilities [2–6], the current mass of vitrified HLW can be estimated at about 35,000–36,000 tonnes, of which almost 80% are A-B-Si, and the rest are Na-Al-P glasses. Vitrification of HLW is, however, not the optimal method of immobilisation due to the relative low radionuclide loading of glasses and their susceptibility to crystallisation, which can begin immediately after the melt pouring into canisters due to the residual heat of the melt [6,7]. Partitioning of HLW radionuclides onto groups can provide a better solution for their immobilisation by incorporation within crystalline lattice of silicates, titanates, zirconates, and phosphates. Their natural analogues are minerals zircon, britholite, pyrochlore, zirconolite, murataite, perovskite, monazite, and garnet [8–16]. Fission products (Cs, Sr) can be isolated in both crystalline phases such as hollandite, pollucite, perovskite, langbeinite, and glasses. Glass crystalline materials (GCM) with the same mineral-like phases are optimal for wastes of complex composition. The major component of GCM may be either the crystalline phases with the glass acting as a binding agent or alternatively the vitreous phase may be the major component, with crystalline particles dispersed in the glass matrix [17–21].

The aim of this paper is to highlight the effectiveness of GCM as a universal nuclear wasteform which overcomes limitations of classical vitrification processes related to the low solubility in glasses of some nuclear waste components such as minor actinides (MA) and enhances the waste loading while improving the durability and long-term stability of the wasteform. The review focuses on universality of GCM wasteforms for immobilisation of HLW radionuclides utilizing the fractionation (partitioning) approach when the most dangerous components are immobilized in most durable and most stable crystals whereas the vitreous phase accommodates less dangerous, shorter-lived radionuclides. The vitrification technology currently accepted as baseline for HLW immobilization can be accordingly modified to produce GCM wasteforms.

2. HLW from SNF Reprocessing

The composition of SNF depends on the type of reactor, initial fuel used, the depth of its burnup, and storage time after discharge from reactor [22,23]. HLW radionuclides are fission products, actinides, and activated elements of fuel assemblies. The main fission products are rare earth elements (REE), Zr, Mo, Tc, Ru, Pd, Cs, Sr, Rh, Te, Xe, Kr, and I, with REE accounting for up to 25 wt.%, platinoids—16%, Zr—15%, Mo—12%, Cs—6% [24]. After three years of storage of SNF with a burnup of 33 GW·day (enrichment of 3.5% ^{235}U) it contains in kg/tonne of SNF [19]: Alkalies (Cs, Rb)—3, alkaline earths (Sr, Ba)—2.4, rare earths (mainly light of Ce group)—10.2, transition 4d metals (Mo, Zr, Tc)—7.7, platinoids (Ru, Rh, Pd)—3.9, 0.5 kg Se and Te, 0.2 kg I and Br, 0.1 kg Ag, Cd, Sn, and Sb. These quantities of fission products are determined by their bimodal distribution (yield) which depends on the atomic mass, where the maxima are located in the ranges of 85–105 (Rb, Sr, Zr, Mo, Tc, platinoids, Ag) and 130–150 (Te, I, Xe, Cs, Ba, REE). With the burnup increase the content of fission products in SNF and thus in HLW increases too. Over time, the heat release of SNF decreases and within a few hundred years the main role in heat generation transfers from the short-lived fission products to long-lived actinides.

The SNF reprocessing generates from 1 to 13 m³ of liquid HLW per 1 tonne of SNF [23], although after evaporation its volume is reduced to 250 L [24]. Specific features of the SNF composition are inherited by the HLW; in addition, it contains technological impurities [21,23,24]. In the dry residue of HLW there are [19,25]: 19% of transition metals (Mo, Zr, Tc), 18% of rare earths (La, Ce, Pr, Nd, Sm), 10% alkaline (Cs, Rb) and alkaline earth (Sr, Ba) elements, 7% of platinoids (Ru, Rh, Pd), 2% of minor actinides (Np, Am, Cm), up to 1% Se and Te, and another 43 wt.% belong for Fe, Ni, Cr, Na, P, and less significant elements. Calcined HLW contains (mol.%) [26,27]: Fission products—26.4 REE, 13.2 Zr, 12.2 Mo, 7.6 Ru, 7.0 Cs, 4.1 Pd, 3.5 Sr, 3.5 Ba, 1.3 Rb; 9% of other fission and corrosion products, mainly Tc, Rh, Te, I, Ni, and Cr; actinides: 1.4 (U + Th) and 0.2 (Am + Cm + Pu + Np), impurities—6.4 Fe, 3.2 P, 1.0 Na. According to [28], the HLW calcine after 10 years of storage consists of, wt.%, 6 Cs₂O, 6 TcO₂, 3 SrO, and 6 minor actinides (MA): Np, Am, and Cm, 4 BaO, 10 RuO₂, 15 REE₂O₃, 6 PdO, 15 ZrO₂, 2 Rh₂O₃, 15 MoO₃.

3. HLW Vitrification

Industrial vitrification of liquid HLW from SNF reprocessing is done for more than 50 years. It started in France in 1968–1973 [29] with 12 tonnes of radioactive glass produced by vitrifying 25 m³ of waste. Large-scale vitrification of HLW is done in France since 1978 using A-B-Si glass whereas Russia uses Na-Al-P glass composition since 1987 [2,4,19,21,30–34]. A drawback of glasses is the limited content of nuclear waste which is typically from 3 to 5 wt.% for Na-Al-P glasses and from 5 to 20 wt.% for A-B-Si glasses. This results in a relatively large volume of vitreous product to be disposed of which entails high costs for the construction of underground disposal facilities. Therefore, approximately 1.5–1.8 tonnes of Na-Al-P glass is produced at immobilization of HLW derived at reprocessing of 1 tonne of SNF, while for A-B-Si glasses this value is significantly lower (about 0.4 tonnes only). Low content of radionuclides in the Na-Al-P glass is caused by its lower heat resistance [35]. The temperature of the vitrified waste block is requested to be at least 100 °C lower than the glass transition temperature (T_g) of glass to avoid crystallisation effects [19]. The temperature of the glass block depends on the intensity of radiogenic heat generation. The maximum design HLW radioactivity for Na-Al-P glass is 2500 Ci/L, with practical values being from 60 to 600 Ci/L [24,35]. The intensity of heat generation of vitrified HLW decreases with time from 18 kW/m³ after 5 years to 6 kW/m³ after 25 years, and to 1 kW/m³ after 100 years of storage. Within the first 150 years, the main heat source of HLW is due to the decay of fission products with a dominance of ^{137}Cs and ^{90}Sr , and then due to the MA decay [22,36]. Regulatorily, the heat emission of vitrified HLW in the interim storage should not exceed 5 kW/m³ [24] and 2 kW/m³ on disposal [37]. The last document establishes the requirement for the temperatures up to 450 °C. Glasses are fundamentally metastable and depending on temperature can crystallize over time at elevated temperatures. Cooling of the glass melt on its

draining into the canisters should be fast enough to form a uniform glass. This is achieved by quenching the melt at high cooling rates about 500 °C/h, whereas at cooling rates of 50 °C/h or less, crystalline phases appear [38]. Crystallisation of glass can occur after the melt is drained into canisters due to residual heat [6,7]. Often T_g is taken as the temperature at which the melt viscosity is 10^{12} Pa·s (10^{13} Poise) [39] although the glass transition is a quasi-equilibrium second order phase transformation, and the glassy state of matter differs topologically from that of molten state [40]. The Kauzmann empirical rule $T_g = (2/3) \cdot T_m$ ($T_{g,m}$ values are given in the Kelvin's scale) implies that the T_g increases with the increase of melting temperature (T_m). Heating of glass above T_g accelerates devitrification due to the decrease in glass viscosity and the increase of diffusion rate of elements in it. Na-Al-P glasses have T_g about 400 °C and the crystallization rate maximum is at ~500 °C, whereas A-B-Si glasses with T_g about 550 °C exhibit maximum crystallisation rates at about 650 °C [38,39]. Partial glass devitrification occurred when cooling rates about 30–50 °C/h close to that of HLW vitrification facilities were used [6]. On melt pouring from the EP-500 Joule-heated ceramic melter, the temperature of the container with vitrified HLW decreases within 17 h from 700 to 500 °C [7], that is, the cooling rate was just about 10–15 °C/h. The question therefore remains open about the state of vitrified HLW stored at “Mayak” PA since 1987 as it can be a relative homogeneous glass, although glass with crystalline phases or even a fully crystallized material are also possible variants. A partially crystallized glass in containers with HLW seems more likely and such wastefrom is prone to an accelerated corrosion in the presence of water vapours [41,42].

4. GCM with Mineral-Like Phases

4.1. Importance of Novel Matrices

Much attention is paid to the modernization of existing glass matrices, as well as the search for new types of wasteforms, for example, for HLW radionuclide fractions. Partitioning of HLW and incorporation of the most dangerous long-lived actinides and fission products in a compact and capacious matrix will improve the use of underground repository space. This will reduce the need for the construction of new storage facilities and lead to savings in finances and time for their search and construction. Potential novel matrices for HLW immobilisation are crystalline and GCM which have been studied since the 1970s, almost simultaneously with research of glasses [32,34,43,44].

4.2. Crystalline Matrices

The best known crystalline wasteforms are the Synroc polyphase ceramic and the monophase NZP matrix. In the first, artificial phases of minerals with the structure of perovskite, zirconolite, pyrochlore, and hollandite serve as carriers of radionuclides and the HLW elements are distributed between them in accordance with the radius and charge of cations. The structure of the NZP matrix of the composition $\text{NaZr}_2(\text{PO}_4)_3$ as a natural analogue of the mineral kosnarite is formed by a three-dimensional network of PO_4^{3-} octahedra connected by vertices to ZrO_6 octahedra, and large Na^+ cations occupy voids. The HLW components can enter three positions of the structure: Alkalies, alkaline earths instead of sodium; REE and actinides are in the Zr position, hexavalent Mo replaces phosphorus, etc. Usually, there is an additional phase—REE phosphate with a monazite structure. Kosnarite, $\text{KZr}_2(\text{PO}_4)_3$ is a natural analogue of the NZP matrix, although unlike other phases (pyrochlore, zirconolite, brannerite, monazite, etc.), it does not contain radioactive elements such as U and Th [32]. The waste loading of Synroc and NZP ceramics is about 20 wt.%. Crystalline phases for immobilization of waste have been overviewed in many publications such as [15,16,32,45].

4.3. GCM as an Universal Nuclear Wastefrom

GCM are thermodynamically more stable materials compared with homogeneous glasses. Indeed, the free Gibbs energy G_{GCM} of a GCM containing the volume fraction φ of crystalline phase will be:

$$G_{\text{GCM}} = \varphi G_C + (1 - \varphi) G_G,$$

where the free Gibbs energy of crystalline phase G_C is lower than the free Gibbs energy of glass G_G . Thus, the driving force of crystallization of GCM toward a most stable fully crystalline material (for which $\varphi = 1$) will be smaller.

GCM containing both crystalline and glassy phases are optimal for radioactive waste of complex composition [8,17,19,21,32,38,46–52]. Compared to homogeneous glassy materials, GCMs can incorporate larger amounts of waste elements and they can be produced using lower processing temperatures than those of conventional melting. Indeed, hazardous and nuclear waste constituents can be immobilised both by direct chemical incorporation into the glass structure in a classical vitrification approach and by the physical encapsulation of the waste in a glass matrix, forming a GCM consisting of both vitreous and crystalline phases (Figure 1).

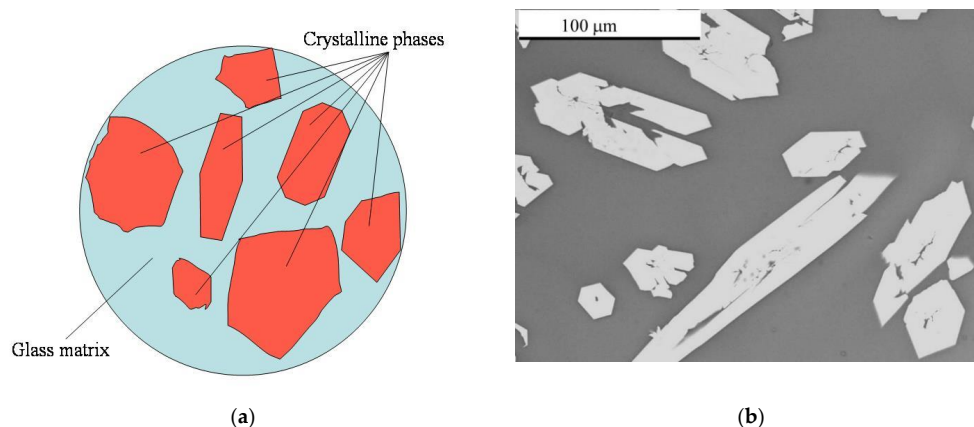


Figure 1. Schematic of a Glass crystalline material (GCM) nuclear wasteform (a) and SEM/BSE image (b) of a real specimen loaded with rare earth elements (REE)-imitator of actinides. Dark areas are composed of glass and light grains are crystals of britholite.

4.4. Examples of GCM Nuclear Wasteforms

GCM include: Glass-ceramics where a glassy wasteform is crystallised using a separate heat treatment schedule, materials in which a refractory crystalline phase is encapsulated in glass, such as hot pressed lead silicate or sodium borosilicate glass matrix encapsulating up to 30 vol.% of $\text{La}_2\text{Zr}_2\text{O}_7$ or $\text{Ga}_2\text{Zr}_2\text{O}_7$ pyrochlore-structure crystals to immobilize actinides [53–57], borosilicate glasses for encapsulation of TRISO- UO_2 particles from pebble bed modular reactor [58], materials in which spent clinoptilolite from aqueous waste reprocessing is immobilised by pressureless sintering [59]; U/Mo-containing materials immobilized in a GCM termed U-Mo, glass formed by cold crucible melting (which partially crystallise on cooling) [60]; yellow phase containing up to 15 vol.% of sulphates, chlorides, and molybdates [61]; and materials to immobilise ashes from incineration of solid radioactive wastes [62]. An example of a recently developed GCM system obtained via sintering is the GCM designed for spent clinoptilolite waste arising from low-level aqueous waste treatment facilities [52,62] where a 2 h pressureless sintering at 750 °C was used. Waste loading ranging from 1:1 up to 1:10 of glass to clinoptilolite volume ratios corresponding to 37–88 mass% were analysed. Water durability of the GCMs assessed by 7 day leaching tests in deionised water at 40 °C based on ASTM C1220-98 standard remained below 6.35×10^{-6} g/(cm² day) in a GCM with 73 mass% waste loading. The sintering process typically takes place at lower temperatures compared to the classical melting route and is of great interest for the immobilization of highly volatile radionuclides such as $^{134,135,137}\text{Cs}$. Crystalline phases within a glassy matrix of GCM can be zirconolite, pyrochlore, brannerite, britholite within a matrix made of a A-B-Si glass, or monazite, or NZP in a Na-Al-P glass. In silicate glass ceramics, radionuclides are incorporated both in the phases of silicates (britholite), titanates, and zirconates (pyrochlore, zirconolite), and molybdates (powellite), and in phosphate glass ceramics—into phosphates with the structure of

monazite, kosnarite, or langbeinite [63–71]. Table 1 outlines various waste types that have been immobilised into GCM both at laboratory and pilot-scale facilities [72,73].

4.5. GCM Phase Assemblage

Generally, host glasses used to develop GCM should have the ability to incorporate various waste constituents, be processed at relatively low processing temperatures, as well as be chemically durable and radiation resistant. High silica-content glasses including borosilicates, alumina silicates, alumina borosilicates, soda-lime silicates, lead silicates, lead borosilicates, phosphates, copper phosphates, silver phosphates, lead-iron phosphates, and soda alumina-phosphate glasses have been examined as host matrices for GCM production [17,18,72,73]. Several processing routes have been examined to produce GCM including controlled crystallisation of a glass, powder methods and sintering, petrological method, and sol-gel precursor glass, which give flexibility in the choice of the optimal immobilisation technology for the target waste as outlined in Table 2.

GCM can be used to immobilise long-lived radionuclides such as MA by incorporating them into the durable crystalline phases, whereas the short-lived radionuclides can readily be accommodated in the less durable glass. Acceptable durability will result if species of concern are locked into the crystal phases that are encapsulated in a durable glass matrix. The processing, compositions, phase assemblages, and microstructures of GCM can be tailored to achieve the necessary properties for improved performance of the wasteform.

4.6. Technology Readiness Level for Industrial-Scale Advanced Wasteforms Fabrication

When choosing a matrix, its hydraulic stability, its capacity for radionuclides, the ability to include other elements of waste, and the availability of industrial production technology play a key role. GCM samples were already obtained in laboratory conditions by viscous- and solid-phase sintering at normal and high pressure; high-speed electro-pulse sintering (SPS); microwave heating or SHS (self-propagating high-temperature synthesis); melting in a resistance furnace or in a “cold” induction heating crucible (CCIM). On an industrial scale, inductance melting in a “hot” or “cold” crucible is already used for the manufacture of A-B-Si glasses to immobilise HLW and intermediate level radioactive waste (ILW) in France and in Russia. The production of highly radioactive wasteforms weighing 10–100 kg corresponds to the value of technology readiness level (TRL) equal to 7, and in the case of their production in an amount of more than 1 tonne—as 8 and 9 [74]. The readiness of the manufacture of radioactive wasteforms via melting or sintering is estimated at TRL values from 7 to 9. These methods are already used in real production, or at semi-industrial and pilot plants. The capabilities of CCIM have been demonstrated in laboratory conditions to obtain blocks of crystalline matrices to 18 kg at TRL 6 [75,76]. The current state of the separation of HLW and methods for obtaining wasteforms with fractionated waste (radionuclide partitioning) envisages a relatively quick transition to the TRL equal to 9, which corresponds to the industrial implementation of this approach to handling HLW and acceptable financial costs [8]. Another way is to separate radionuclides for transmutation although this technique is still at an early stage of development with TRL about 3 to 4. A combined approach uses both options: The utilization of cubic ZrO₂ solid solution with fluorite-type structure, Zr-pyrochlore, or Y-Al garnet as a fuel for actinides (Np, Am) with an inert (composed of non-fertile elements) matrix for a single combustion in a reactor and disposal without reprocessing. The wasteforms to be used for the immobilisation of HLW resulting from SNF reprocessing including the fuel are summarized in Table 3 following the reference [8].

Table 1. Waste streams immobilised into GCM wasteforms.

Waste Type	Waste Description	Waste Loading
LILW	High sulphate, molybdate/noble metal content waste. High concentration of Cl.	30 wt%
Intermediate level radioactive waste (ILW)	High content of Mo, PbO, MnO, and simulated zircaloy chips.	20 wt%
High level radioactive waste (HLW)	Liquid waste arising from reprocessing of natural uranium (UO ₂).	10 wt%
The same	Calcine containing transuranics, fission products, and transition elements.	60–80 wt%
	Acidic HLW with Al, Zr, Na, nitrate, and fluoride ions.	75 wt%
	From reprocessing light water reactor and fast breeder fuel.	5–35 wt%
	Zeolite occluded salt waste (transuranics, fission products, and halides).	75 wt%
	Fission product and transuranic actinides containing salt immobilized in glass bonded sodalite.	75wt%
	Zeolite occluded with molten LiCl-KCl-NaCl and ~6wt% of fission product chlorides.	50–67 wt%
	Simulated waste with spinel forming components.	45 wt%
	Simulated HLW consisting ≤ 35wt% ZrO ₂ .	30–50 wt%
	Plutonium bearing nuclear legacy waste in pyrochlore phases.	30 vol.%
	Containing both actinides and chlorides.	11 wt%
	Simulated HLW waste chemically immobilized in a mixture of chlorapatite, Ca(PO ₄)Cl and spodiosite, Ca ₂ (PO ₄)Cl mineral phase.	65–90 wt%
	Long-lived nuclear simulated waste (actinides).	20 wt%
	Ag ¹²⁹ I	
	TRISO-UO ₂ particles.	16 vol.%
	Actinides surrogate (Ce ₂ O ₃ ,Nd ₂ O ₃ , Eu ₂ O ₃ ,Gd ₂ O ₃ ,Yb ₂ O ₃ ,ThO ₂ in highly durable zirconolite (CaZrTi ₂ O ₇).	4–6wt.%
	Waste fission product and actinides in titanite, CaTiSiO ₅ .	
	Waste ions distributed in sphene, CaTiSiO ₅ phase and glass phase.	5 wt%
	Estimated simulation of HLW from reprocessing of nuclear fuels in Japan Atomic Institute.	25 wt%
	Simulated ⁹⁰ Sr HLW partitioned from of high level liquid waste in China immobilized in apatite glass-ceramic.	35 wt%
Ashes	From incineration of plutonium bearing organics.	50 wt%
	From incineration of solid radioactive waste.	15–40 wt%

Table 2. Processing routes of GCM wasteforms.

Route	Description	Process Parameters
Pressureless sintering	Powder mixing, cold pressing. Relatively low temperature (≤ 1100 K).	Particle size, compacting pressure, temperature and duration of sintering, heating and cooling rate.
Hot Pressing	Pressure and temperature applied during Hot Uniaxial Press (HUP), Hot Isostatic Press (HIP) or Hydrothermal hot-pressing (HHP). Sintering under isostatic pressure by adding amorphous silica. Chemical reaction between waste components and surrounding glass.	Glass composition, particle size, maximum temperature, pressure, soaking time, heating and cooling rate.
Reaction Sintering		Particle size, HIP temperature, pressure and duration of sintering.
Sintering with aerogels	Porous network of silica is soaked in a solution containing the actinide, then dried and fully sintered.	Mechanical properties, capillary forces, permeability of aerogel, sintering temperature.
Cold crucible melting	Electric currents generated inside waste contained in water-cooled crucible, surrounded by an induction coil.	Operating frequency, input vibrating power, operating temperature, melting duration.
Self-sustaining vitrification	Utilises the energy released during exothermic chemical reactions.	Composition of initial waste and Powder Metal Fuel.
In situ sintering	Utilises ambient pressure of a disposal environment, its radiation shielding and extended time of storage.	Disposal environment, ambient pressure and temperature.
Controlled crystallization	Additional heat-treatment on to vitrified glass forming glass-ceramic.	Temperature, duration, heating and cooling rate.
Petrurgic method	Crystals nucleate and grow directly upon cooling glass from the melting temperature.	Cooling rate from melt temperature.
Sol-gel followed by sintering	Allows the formation of a very reactive powder in which components are mixed on a molecular scale.	Calcine temperature, milling media, drying temperature, sintering temperature.

Table 3. Possible wasteforms for HLW fractions. GCM—glass crystalline material, is shown in bold italics.

HLW Fraction	U + Pu	Np	Am	Cm	REE	Cs-Sr	FP ² -UR ³
Methods for managing waste fractions or separate radionuclides	New (fresh) nuclear fuel				Ceramics		Alloy
	Fuel				Ceramics		Alloy
	Fuel				Ceramics		Alloy
	Fuel				Ceramics		Alloy
	Fuel				<i>GCM</i> (An/Ln/TM ¹)		Alloy (UR)
	Fuel				Ceramics		<i>GCM</i>
	Fuel				<i>GCM</i>		

¹ TM—4d transition metals (² FP—fission products: Mo, Zr, Ru, Rh, Pd; corrosion elements—Zr, Fe, Cr, Ni, etc). ³ UR—undissolved SNF residues, composed of Mo-Tc-Ru-Rh-Pd alloy (ϵ -phase).

Although the review did not discuss the economics of immobilisation technologies used, one can note that the SNF reprocessing with fractionation of HLW (radionuclide partitioning) is more expensive than the standard PUREX technology. However, the GCM immobilization option will be cheaper and safer due to the reduced need for expensive deep geological disposal facilities [77,78] and because the dangerous long-lived isotopes are incorporated into the most durable host phases for industrial applying.

5. Conclusions

HLW derived in the close nuclear fuel cycle is currently immobilised into Na-Al-P and A-B-Si glasses using vitrification technology. Waste immobilisation in GCMs has emerged as a versatile technology enabling reliable immobilisation of complex and varying composition waste streams, including both radioactive and hazardous residues, which are otherwise difficult to immobilise using the traditional vitrification technology. The optimisation of the GCM phase assemblages as a function of waste stream composition is important for achieving simultaneously high nuclear waste loadings and corrosion resistance. Future research may focus on practical aspects of GCM utilisation through one or another technological process using either controlled devitrification of synthesized parent glasses or sintering routes using crystalline and vitreous precursors.

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