

Glasses for Nuclear Waste Immobilization

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ABSTRACT

Vitrification of nuclear wastes is attractive because of its flexibility, the large number of elements which can be incorporated in the glass, its high corrosion durability and the reduced volume of the resulting waste form. Vitrification is a mature technology and has been used for high level nuclear waste (HLW) immobilisation for more than 40 years in France, Germany and Belgium, Russia, UK, Japan and the USA. 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. Hazardous waste constituents are immobilised either by direct incorporation into the glass structure or by encapsulation when the final glassy material can be in form of a glass composite material (GCM). Both borosilicate and phosphate glasses are currently used to immobilise nuclear wastes, moreover in addition to relatively homogeneous glasses novel GCM are used to immobilise problematic waste streams. The spectrum of wastes which are currently vitrified increases from HLW to low and intermediate wastes (LILW) such as legacy wastes in Hanford, USA and nuclear power plant operational wastes in Russia and Korea.

INTRODUCTION

The choice of wastefrom to use for nuclear waste immobilisation is a difficult decision and durability is not the sole criterion. In any immobilisation process where radioactive materials are used, the process and operational conditions can become complicated, particularly if operated remotely and equipment maintenance is required. Therefore priority is given to reliable, simple, rugged technologies and equipment, which may have advantages over complex or sensitive equipment. A variety of matrix materials and techniques are available for immobilisation. The choice of the immobilisation technology depends on the physical and chemical nature of the waste and the acceptance criteria for the long term storage and disposal facility to which the waste will be consigned. A host of regulatory, process and product requirements has led to the investigation and adoption of a variety of matrices and technologies for waste immobilisation. The main immobilisation technologies that are available commercially and have been demonstrated to be viable are *cementation*, *bituminisation* and *vitrification* [1]. In most countries HLW has been incorporated into alkali borosilicate or phosphate vitreous waste forms for many years and vitrification is an established technology. Large streams of LILW are planned to be vitrified in the USA, South Korea, Russia. Vitreous waste forms represent one end of the spectrum of HLW waste forms shown in Table I [2, 3].

Table I. Classification of types of glass/ceramic waste forms.

Glasses	Glass Composite Materials (GCM's)	Crystalline Ceramics
Magnox, UK. DWPF* and WVDP**, USA. Alumina phosphate, Russia	Glass Ceramics. Crystal Waste Encapsulated in Glass Matrix.	Single Phase. Multiphase (e.g. Synroc***).

*Defence Waste Processing Facility; **West Valley Demonstration Project; ***Synroc consists of titanates hollandite ($BaAl_2Ti_6O_{16}$), zirconolite ($CaZrTi_2O_7$), perovskite ($CaTiO_3$) and TiO_2 . The hollandite mainly fixes the FP and some process chemicals, whereas actinides and rare earth elements are bound in zirconolite and perovskite.

At the other end of the spectrum shown in Table 1 the use of predominantly crystalline ceramic wasteforms (*ceramication*) has also been proposed including single-phase ceramics such as zircon to accommodate a limited range of active species such as Pu and multiphase systems such as Synroc to accommodate a broader range of active species. To date these systems have not been extensively used to immobilise active waste. Recently, however, there has been a trend to systems intermediate between the “completely” glassy or crystalline materials (Fig. 1).

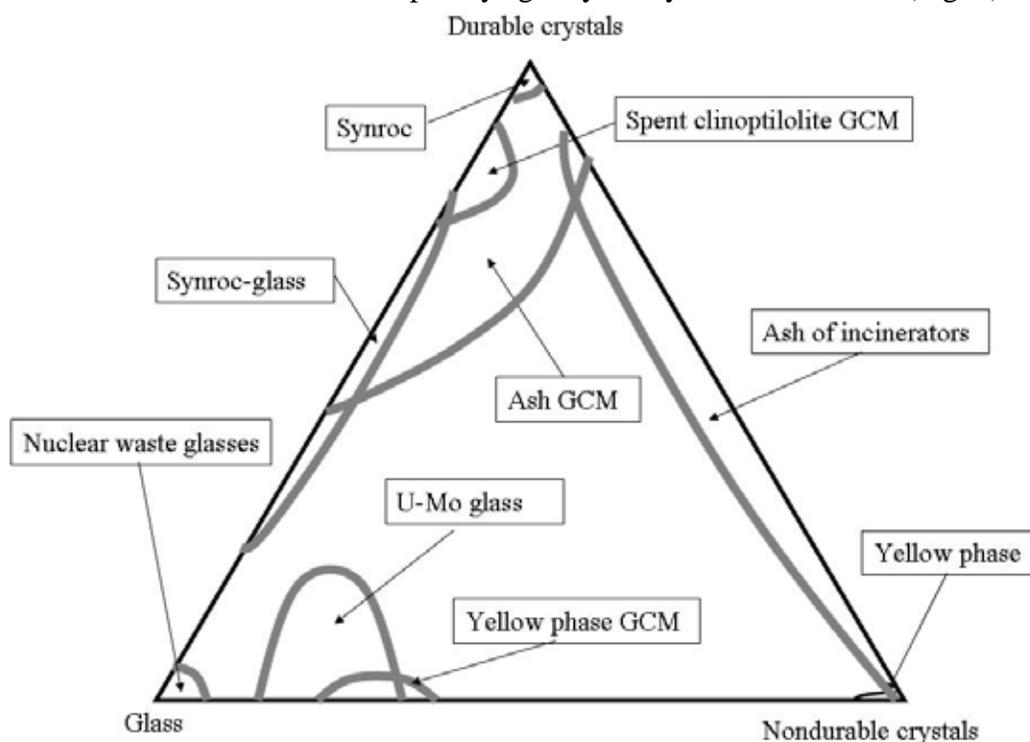


Fig. 1. Illustration of nuclear waste forms used and developed for industrial application. Typically nondurable crystals are such as Na_2SO_4 , $Na_2MoO_4 \cdot 2H_2O$, $CaMoO_4$, NaF , $NaCl$ and durable crystals are such as $BaAl_2Ti_6O_7$, $CaZrTi_2O_7$, $CaTiO_3$, TiO_2 .

GCMs include glass ceramics where a glassy waste form is crystallised in a separate heat treatment [4]; GCM's in which e.g. a refractory waste is encapsulated in glass such as hot pressed lead silicate glass matrix encapsulating up to 30 vol% of $La_2Zr_2O_7$ pyrochlore crystals to immobilise minor actinides [5, 6]; GCM in which spent clinoptilolite from aqueous waste reprocessing is immobilised by a pressureless sintering [7]; Some difficult wastes such as the French HLW U/Mo-containing materials immobilised in a GCM termed U-Mo glass formed by

cold crucible melting (which partly crystallise on cooling) [8]; Yellow phase containing wastes are immobilised in Russia in a yellow phase GCM containing up to 15 vol.% of sulphates, chlorides and molybdates [9], GCM which immobilises ashes from incineration of solid radioactive wastes [10]. Note that alkali-rich wastes at the Hanford site are also immobilised in glassy wastefoms with high crystal contents [11].

GCM's may be used to immobilise long-lived radionuclides (such as actinide species) by incorporating them into the more durable crystalline phases, whereas the short-lived radionuclides may be accommodated in the less durable vitreous phase. Historically, crystallisation of vitreous waste forms has always been regarded as undesirable as it has the potential to alter the composition (and hence durability) of the remaining continuous glass phase which would (eventually) come into contact with water. However, there has been a recent trend towards higher crystallinity in ostensibly vitreous wastefoms so that they are more correctly termed GCM's. This is particularly apparent in the development of hosts for more difficult wastes or where acceptable durability can be demonstrated even where significant quantities of crystals (arising from higher waste loadings) are present such as the high sodium Hanford wastes. Acceptable durability will result if the active species are locked into the crystal phases that are encapsulated in a durable, low activity glass matrix. The GCM option is currently being considered in many countries including Australia, France, UK, USA and Russia. The processing, compositions, phase assemblages and microstructures of GCM's may be tailored to achieve the necessary parameters.

GLASSY STATE

Glasses are among the most abundant materials on the Earth. They have an internal structure made of a more or less well-developed topologically disordered three-dimensional network of interconnected microscopic structural blocks. Glasses are among of the most ancient of all materials known and used by mankind. The geologic glass, obsidian was first used by man thousands of years ago to form knives, arrow tips, jewellery etc. Manmade glass objects appear to be first reported in the Mesopotamian region as early as 4,500 BC glass objects dating as old as 3,000 BC have also been found in Egypt. These glasses have compositions very similar to those of modern soda lime silicate glass as soda ash from fires, limestone from seashells and silica sand from the beaches were long time readily available. Current man-made glasses include a large variety of materials from window panels and cookware to aerospace windows and bulk metallic glasses as well as nuclear waste glassy materials [9, 12-14].

Glasses are typically formed at rapid cooling of melts which allows avoiding crystallisation since little time is allowed for the ordering processes. Whether a crystalline or amorphous solid forms on cooling, depends also on the ease with which a random atomic structure in the liquid can transform to an ordered state. Most of known glassy materials are characterized by atomic or molecular structures that are relatively complex and become ordered only with some difficulty. Therefore a long-term assumption was that the glassy state is characteristic for special glass-forming or network materials such as covalent substances which exhibit a high degree of structure organization at length scales corresponding to several atomic separations. However after the discovery of metallic glasses it was realised that almost any substance, if cooled sufficiently fast, could be obtained in the glassy state [15].

Glasses are amorphous materials with a topologically disordered structure of interconnected structural blocks, which in silicate glasses are SiO_4 tetrahedra. 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 (the melting point). The solid-like behaviour of amorphous materials at low temperatures is separated from liquid-like behaviour at high temperatures by the glass transition temperature, T_g . The glass transition is a kinetically-controlled, fairly sharp change in derivative properties such as thermal expansion coefficient or specific heat. T_g in fact depends on the rate of cooling, although empirically it can be assessed from the Kauzmann's relation:

$$T_g \approx \frac{2}{3}T_L, \quad (\text{Eq. 1})$$

where T_L is the liquidus temperature at which a phase diagram shows a crystal-free melt. The glass transition is a second order phase transition in which a supercooled melt yields, on cooling, a glassy structure and properties similar to those of crystalline materials e.g. of an isotropic solid material [16]. Amorphous materials have internal structure made of a 3-D network of interconnected structural blocks where each broken bond is treated as an elementary configurational excitation - configurons [17]. Configurons motion in the bond network occurs in the form of thermally-activated jumps from site to site. The network is characterised at temperatures below T_g as an ideal disordered structure which is described by a Euclidean 3-D geometry. Its geometry remains 3-D until the concentration of breaking defects is so low that clustering of configurons can be neglected. The higher the temperature the larger are clusters made of configurons in the disordered bond network. Finally at T_g they form a macroscopic so-called percolation cluster, which penetrates the whole volume of the disordered network [18]. The formation of percolation cluster changes the topology of bonds network from the 3-D Euclidean below to the fractal $d_f = 2.55 \pm 0.05$ -dimensional above the percolation threshold. The glass transition temperature depends on thermodynamic parameters e.g. enthalpy (H_d) and entropy (S_d) of broken bonds (configurons) [19, 20]:

$$T_g = \frac{H_d}{S_d + R \ln[(1 - \theta_c) / \theta_c]} \quad (\text{Eq. 2})$$

where for strong melts such as SiO_2 the percolation threshold $\theta_c = \vartheta_c$ where ϑ_c is the Scher-Zallen critical density in the 3-D space $\vartheta_c = 0.15 \pm 0.01$ [18] and for fragile melts the percolation threshold $\theta_c \ll 1$ [20]. Thus the glass-liquid transition can be characterised as a thermodynamic second order phase transition associated with the reduction of the Hausdorff dimension of bonds from the 3-D Euclidean in the glassy state to the fractal $d_f = 2.55 \pm 0.05$ -dimensional in the liquid state. Glasses are amorphous materials, which like crystals have solid like behaviour and the same three dimensional geometry of bonds.

GLASSY WASTE FORMS

Two main glass types have been accepted for nuclear waste immobilisation: Borosilicates and Phosphates. The exact compositions of nuclear waste glasses are tailored for easy preparation and melting, avoidance of phase separation and uncontrolled crystallisation, and acceptable chemical durability, e.g. leaching resistance. Vitrification can be performed efficiently at temperatures below 1200°C because of the volatility of the fission products, notably Cs and Ru,

so avoiding excess radionuclide volatilisation and maintaining viscosities below 10 Pa·s to ensure high throughput and controlled pouring into canisters. A more fluid glass is preferred to minimise blending problems. Phase separation at melting is most important for waste streams containing glass immiscible constituents however these can be immobilized in form of phase separated disperse phase (GCMs). The leaching resistance of nuclear waste glasses is a paramount criterion as it ensures low release rates for radionuclides at potential contact with water.

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. Hazardous waste constituents are immobilised either by direct incorporation into the glass structure or by encapsulation. In the first case, waste constituents are dissolved in the glass melt, some such as Si, B, P being included into the glass network on cooling while others such as Cs, K, Na, Li, Ca, Pb, Mg are confined as modifiers. A number of glass compositions were designed for nuclear waste immobilisation however few were used in practice [1, 7-14]. Table II gives compositions of several nuclear waste glasses.

Table II. Compositions of Some Nuclear Waste Glasses, Mass%.

Glass, Country	SiO₂	P₂O₅	B₂O₃	Al₂O₃	CaO	MgO	Na₂O	Misc	Waste loading
R7/T7, France	47.2	-	14.9	4.4	4.1	-	10.6	18.8	≤28
DWPF, USA	49.8	-	8.0	4.0	1.0	1.4	8.7	27.1	≤33
Magnox Waste, UK	47.2	-	16.9	4.8	-	5.3	8.4	17.4	≤25
PAMELA Germany- Belgium	52.7	-	13.2	2.7	4.6	2.2	5.9	18.7	<30
HLW, Russia	-	52.0	-	19.0	-	-	21.2	7.8	≤10 FP and MA oxides
LILW K26, Russia	43	-	6.6	3.0	13.7	-	23.9	9.8	35

High waste loadings can be achieved both borosilicate and aluminophosphate glasses. Moreover glasses immobilise well large quantities of actinides, for example borosilicate glasses can accommodate up to 7.2, mass% of PuO₂ [21]. In contrast to borosilicate melts molten phosphate glasses are highly corrosive to refractory linings, behaviour which has limited their application. Currently this glass is used only in Russia, which has immobilised HLW from nuclear fuel reprocessing in alumina-phosphate glass since 1987.

It should be emphasized that nuclear waste glasses are never completely homogeneous vitreous materials but contain significant amounts of bubbles, foreign inclusions such as refractory oxides and other immiscible components. Fig. 2 shows an example of SEM characterization of British Magnox Waste glass, which reveals heterogeneities and phase separation characterised by small droplets of 10 to 20 μm sizes, in which further fine segregation on a scale of about 100 nm was observed [22].



Fig.2. British Magnox-waste glass secondary electron image (JEOL 6400 scanning electron microscope operating at 20kV).

Encapsulation is applied to elements and compounds with a reduced solubility in the glass melt and do not fit into the glass microstructure neither as network formers nor modifiers. Immiscible constituents which do not mix easily into the molten glass are typically sulphates, chlorides and molybdates as well as noble metals such as Rh and Pd, refractory oxides with high liquidus temperatures such as PuO_2 , noble metal oxides and spinels.

Encapsulation is carried out either by deliberate dispersion of insoluble compounds into the glass melt, immiscible phase separation at cooling or by sintering of glass and waste powders so that the waste form produced is a GCM. However this requires a more complex melter supplied with a stirrer.

DURABILITY OF GLASSY WASTE FORMS

The reliability of radionuclide immobilisation is characterised by the rate at which radionuclides can be released from the waste form during long-term storage. As the most plausible path for reintroduction of radioactivity into the biosphere is via water, the most important parameters that characterize the ability of glass to hold on to the active species are the leach rates. The leaching behaviour of waste forms containing different amounts of waste radionuclides is compared using

the normalised leaching rates NR_i for each i -th nuclide expressed in $\text{g}/\text{cm}^2\text{day}$. These are determined using a range of approved tests such as the IAEA test protocol ISO 6961-1982. A set of standard tests to determine the water durability of vitrified waste and other wasteforms was developed at the Materials Characterization Centre (MCC) of Pacific Northwest National Laboratory, USA. These MCC tests are now the internationally-approved standards used worldwide. The most important tests are given in Table 3 [23].

Table III. Standard Tests on Immobilisation Reliability.

Test	Conditions	Use
ISO 6961, MCC-1	Deionised water. Static. Monolithic specimen. Sample surface to water volume (S/V) usually 10 m^{-1} . Open to atmosphere. Temperature 25°C (IAEA), $40, 70$ and 90°C (MCC-1)	For comparison of waste forms.
MCC-2	Deionised water. Temperature 90°C . Closed.	Same as MCC-1 but at high temperatures.
PCT (MCC-3)	Product consistency test. Deionised water stirred with glass powder. Various temperatures. Closed.	For durable waste forms to accelerate leaching.
SPFT (MCC-4)	Single pass flow through test. Deionised water. Open to atmosphere.	The most informative test.
VHT	Vapour phase hydration. Monolithic specimen. Closed. High temperatures.	Accelerates alteration product formation.

Vitrified radioactive waste is a chemically durable material which reliably retains radioactive species. Typical normalised leaching rates NR of vitrified waste forms are below $10^{-5} - 10^{-6} \text{ g}/\text{cm}^2 \text{ day}$. Moreover, as glasses and GCM are highly corrosion resistant, their high nuclide retention is expected to last for many millennia. Table IV gives typical data on parameters of HLW borosilicate and phosphate glasses [1, 2, 24].

Table IV. Typical Properties of HLW Glasses.

Glass	Density g/cm^3	Compressive strength, MPa	NR, 28-th day, in $10^{-6} \text{ g}/\text{cm}^2\text{d}$	Thermal stability ¹ , $^\circ\text{C}$	Damaging ¹ dose, Gy
Borosilicate	2.7	22 – 54	0.3 (Cs); 0.2 (Sr).	≥ 550	$>10^9$
Phosphate	2.6	9 – 14	1.1 (Cs); 0.4 (Sr).	≥ 450	$>10^9$

¹The irradiation has a small impact on glasses and the damaging dose is the absorbed dose above which the radionuclide NR's increase several times whereas thermal stability is the temperature above which the radionuclide NR's increase $>10^2$ times.

GLASSES FOR LILW

Although developed initially for HLW vitrification is being currently used for immobilisation of intermediate and low level radioactive wastes (LILW) such as from operation and

decommissioning of nuclear power plants [25, 26]. Vitrification is one of technologies that have been chosen to solidify 18,000 tonnes of geologic mill tailings at the Fernald, Ohio, USA [27]. Plans are in place to vitrify vast volumes of waste; for example the vitrification of the low level radioactive waste at Hanford, USA is expected to produce over 160,000 m³ of glass [28]. The USA Department of Energy (DOE) plans to vitrify 54 million gallons of mixed radioactive waste stored at its Hanford site in eastern Washington State, which represents 60% of the United States' volume of radioactive waste [29]. The largest in the world HLW and LLW vitrification plant (Waste Treatment Project (WTP)) is now under construction at Hanford. Borosilicate glass will be used for immobilization of Hanford's low-activity waste (LAW). The vitrified LAW will be disposed of in a shallow land-burial facility. It was demonstrated that the disposal system will adequately retain the radionuclides and prevent contamination of the surrounding environment. It was found that the release of radionuclides from the waste form via interaction with water is the prime threat to the environment surrounding the disposal site and that the two major dose contributors in Hanford LAW glass that must be retained are ⁹⁹Tc and ¹²⁹I [30]. There were developed a number of glasses to immobilize Hanford low activity wastes with composition range that will meet performance expectations of the Hanford site burial facility [30]. It is planned that the WTP will vitrify 99% of Hanford's waste by 2028. The WTP melter chosen to vitrify HLW is a Joule Heated Ceramic Melter (JHCM). The JHCM has nickel–chromium alloy electrodes which heat the waste and glass-forming additives to ~1150 °C. The glass melt is stirred by convection and by bubbler elements and then poured into carbon steel canisters to cool. Canisters with vitrified HLW are sealed and decontaminated. The vitrified HLW will be disposed of in the Yucca Mountain geological repository. Current plans provide for the vitrified LAW to be stored on site. Moreover at Hanford it is planned to use a Bulk Vitrification process in which liquid waste is mixed with controlled-composition soil in a disposable melter [29]. The process of Bulk Vitrification involves mixing LAW with Hanford's silica-rich soil and surrounding it with sand and insulation in a large steel box. Electrodes are inserted to vitrify the mixture and when cooled the melter, its contents and the embedded electrodes will be buried as LLW in an on-site burial ground.

Vitrification of LLW and ILW was studied intensively in Russia in the middle of 1970's [10]. There were developed a number of glass compositions for immobilization of liquid waste containing mainly sodium nitrate. Various boron-containing minerals as well as sandstone were tested as glass-forming additives. Datolite CaBSiO₄(OH) was found as the most suitable fluxing agent. Partial systems Na₂O (LILW oxides) - 2CaO B₂O₃ - SiO₂ were studied and glass formation regions, melt viscosity and resistivity, leach rate of sodium (and ¹³⁷Cs for actual waste), density, radiation stability, and compressive strength were measured. Suitable glass composition areas were established [10]. The most important properties of these glasses are given in Table V.

Table V. Properties of Vitrified LILW.

Properties	Borosilicate glasses		GCM
	High sodium waste	Operational WWER waste	Glass immiscible (high sulphate) waste
Waste oxide content, mass%	30-35	35-45	30-35 + up to 15vol.% of yellow phase
Viscosity, Pa s, at 1200 °C	3.5-5.0	2.5-4.5	3.0-6.0 (vitreous phase)
Resistivity, Ω m, at 1200 °C	0.03-0.05	0.02-0.04	0.03-0.05*
Density, g/cm ³	2.5-2.7	2.4-2.6	2.4-2.7
Compressive strength, MPa	80-100	70-85	50-70
Leach rate, g/(cm ² day), (28-day IAEA test)	¹³⁷ Cs	10 ⁻⁵ -10 ⁻⁶	~10 ⁻⁵
	⁹⁰ Sr	10 ⁻⁶ -10 ⁻⁷	~10 ⁻⁶
	Cr, Mn, Fe, Co, Ni	~10 ⁻⁷ -10 ⁻⁸	~10 ⁻⁷
	REE, An	~10 ⁻⁸	~10 ⁻⁸
	Na	10 ⁻⁵ -10 ⁻⁶	~10 ⁻⁵
	B	<10 ⁻⁸	<10 ⁻⁸
	SO ₄ ²⁻	~10 ⁻⁶ (if present)	-
			10 ⁻⁴ -10 ⁻⁵ at content <15vol.%

Loam and bentonite clays as glass forming additives were also used. Up to 50% of either loam clay or bentonite in the batch was substituted for sandstone. This substitution increases chemical durability of glass and, moreover, such batch containing 20-25 wt% of water forms stable homogeneous paste being able to be maintained for a long time without segregation and transported in pipes for long distances [10]. Sodium nitrate is the major component of both institutional liquid LILW and nuclear power plant (NPP) operational wastes from RBMK reactor. NPP waste from WWER reactor contains boron and the major components of this waste are sodium nitrate and sodium tetrahydroxyl borate NaB(OH)₄. To vitrify WWER waste there is no need to add boron-containing additives to waste. Silica, loam or bentonite clay or their mixtures are suitable as glass forming additives [10]. Respectively, WWER waste glasses relate to systems Na₂O-(Al₂O₃)-B₂O₃-SiO₂. Glass formation regions in these systems are well-known. Long-term tests of vitrified LILW are carried out in a shallow ground experimental repository since 1987 [31]. These show a quite low and diminishing leaching rate of radionuclides. Aluminosilicate boron free glasses for immobilization of institutional and RBMK wastes were also designed. They are produced from waste, sandstone and loam clay (or bentonite) and relate to Na₂O-(CaO)-Al₂O₃-SiO₂ system.

Some liquid waste streams contain essential content of sulphate and chloride ions. Because of very low sulphate and chloride solubility in silicate and borosilicate melts, waste oxide content is limited by 5-10 wt% and LILW vitrification becomes inefficient. Solubility limit for each sulphate and chloride ions was estimated to be 1%. Excess is segregated as a separate phase floating on the melt surface due to immiscibility of silicate and sulphate (chloride) melts. The same phenomenon occurs at molybdate- and chromate-containing waste vitrification, where separate phase is coloured and named "yellow phase" [32]. Vitrification of this waste can be done by using vigorous melt agitation followed by fast cooling down to upper annealing temperature to fix dispersed sulphate-chloride phase into the host borosilicate glass. Sulphate-chloride-containing GCM (yellow phase GCM in Fig. 1) have only a slightly diminished chemical durability compared to sulphate-chloride free aluminosilicate and borosilicate glasses

(see Table 5) sufficiently high to apply them for waste immobilization. GCM produced using thermochemical technique based on exothermic self-sustaining reactions are also composed of vitreous and crystalline phases, mainly silicates and aluminosilicates [33].

WASTE VITRIFICATION EXPERIENCE

Vitrification is most suitable for aqueous radioactive wastes. Waste vitrification is attractive because of:

- (i) High capability of glass to immobilise various elements,
- (ii) Simple production technology adapted from glass production industry,
- (iii) Small volume of the resulting wasteform,
- (iv) High chemical durability of glasses in natural waters and
- (v) High tolerance of glass to radiation damage.

The high chemical resistance of glass allows it to remain stable in corrosive environments for thousands and even millions of years. Several glasses are found in nature such as obsidians (volcanic glasses), fulgarites (formed by lightning strikes), tektites found on land in Australasia and associated microtektites from the bottom of the Indian Ocean, moldavites from central Europe, and Libyan Desert glass from western Egypt. Some of these glasses have been in the natural environment for about 300 million years with low alteration rates of only tenths of a millimetre per million years.

The excellent durability of vitrified radioactive waste ensures a high degree of environment protection. Waste vitrification enables along with highest waste volume reduction the utilisation of simplest e.g. cheapest disposal facilities. Thus despite of high initial investment and operational costs, accounting for transportation and disposal expenses, the overall cost of vitrified radioactive waste can be smaller comparing non-vitrified options.

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. Self-sustaining vitrification has in contrast to conventional vitrification technologies no such limitations however this technology is limited to calcined waste streams [33].

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 (Fig. 3). In the one stage process both waste calcination and melting occurs 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.

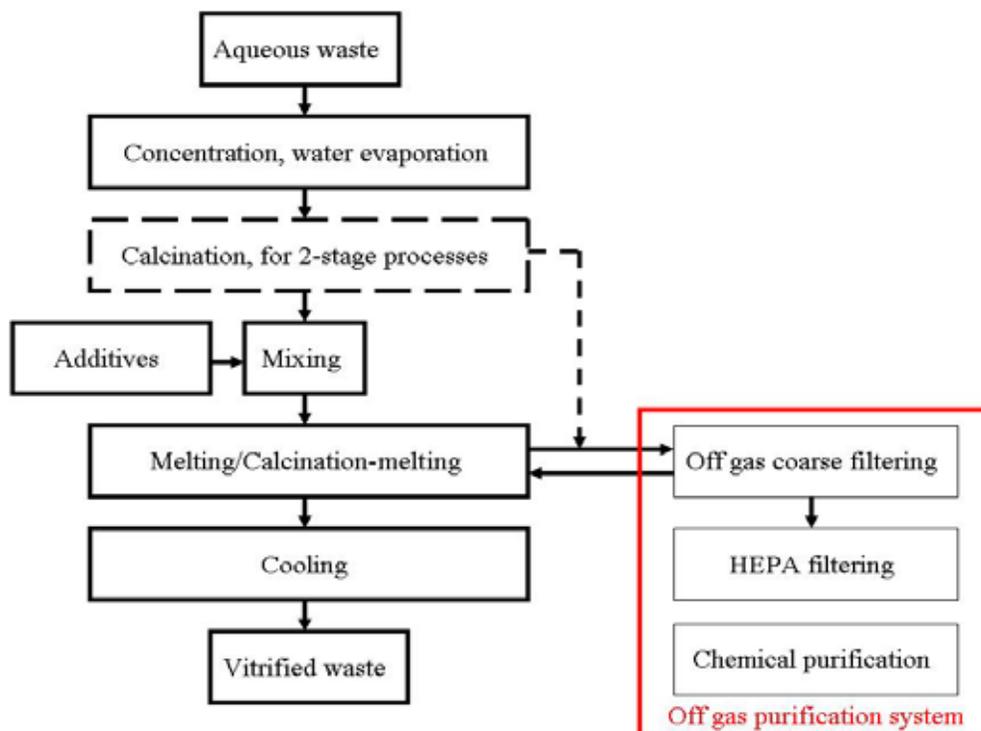


Fig. 3. Schematic of a vitrification process.

In the one-stage vitrification process glass forming additives are mixed with concentrated liquid wastes and so a glass-forming batch is formed (often in the form of a paste). 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 the two-stage vitrification process with separate calcination the waste concentrate is fed into the calciner. After calcination the required glass-forming additives (usually as a glass frit) together with the calcine are fed into the melter. In both cases two streams come from the melter: The glass melt containing most of radioactivity and the off gas flow, which contains off gases and aerosols.

The melt waste glass is poured into containers (canisters) made of stainless or carbon steel. These may be not or may be slowly cooled in an annealing furnace to avoid accumulation of mechanical stresses in the glass. When annealing is not applied, cracking occurs resulting in a large surface area potentially available for attack by water in a repository environment. Despite the higher final surface areas of non annealed glasses these are sufficiently durable to ensure a suitable degree of radionuclide retention. Hence in many cases annealing is not applied in vitrification facilities.

The second stream from the melter goes to the gas purification system, which is usually a complex system that removes from the off gas not only radionuclide but also chemical contaminants [10]. Operation of this purification system leads to generation of a small amount of secondary waste. For example, the distribution of beta gross activity at PAMELA waste vitrification plant was (%): >99.88 in waste glass, and the rest in secondary waste, e.g. <0.1 in medium level waste, <0.01 in cold waste and <0.01 in off gas [34]. Table VI summarises data on radioactive waste vitrification facilities.

Table VI. Operational data of vitrification programmes.

Facility	Waste type	Meting process	Operational period	Performance	References
R7/T7, La Hague, France	HLW	IHC ¹	Since 1989/92	> 4,000 tonnes to 2000 (3.5 10 ⁶ Ci)	[1, 12, 14]
France, La Hague, R7	HLW	CCM ²	Since 2003	GCM: U-Mo glass, ?	[35]
WVP, Sellafield, UK	HLW	IHC	Since 1991	3179 canisters to 2005	[1, 12, 14]
DWPF, Savannah River, USA	HLW	JHCM ³	Since 1996	1500 tonnes to 1999, 1927 canisters to 2005	Ibid
WVDP, West Valley, USA	HLW	JHCM	Since 1996	240 canisters to 1996	Ibid
EP-500, Mayak, Russia	HLW	JHCM	Since 1987	~4000 tonnes to 2006 (450 10 ⁶ Ci)	Ibid
CCM, Mayak, Russia	HLW	CCM	Pilot plant	18 kg/h by phosphate glass	[36]
PAMELA, Mol, Belgium	HLW	JHCM	1985-1991	64 tonnes	[1, 12, 14]
Tokai, Japan	HLW	JHCM	Since 1995	> 100 tonnes	[14, 37]
Radon, Russia	LILW	JHCM	1987-1998	10 tonnes	[10]
Radon, Russia	LILW	CCM	Since 1999	> 30 tonnes to 2001	[10]
Torch, Radon, Russia	LILW	SSV ⁴	Since 2001	10 kg/h, incinerator ash	[33]
WTP, Hanford, USA	LLW	JHCM	Pilot plant since 1998	~ 1000 tonnes to 2000	[14, 29]
Taejon, Korea	LILW	CCM	Pilot plant, planned 2005	?	[26]
Saluggia, Italy	LILW	CCM	Planned	?	[38]

¹IHC - Induction, hot crucible, ²CCM – Cold crucible induction melter, ³JHCM – Joule heated ceramic melter, ⁴SSV - Self-sustaining vitrification.

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