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**Vitrification of Radioactive Wastes – A Current Solution and Enabler for Future Nuclear Technologies**

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## Background

Nuclear energy continues to receive considerable interest as one potential solution to issues such as global warming and a shrinking conventional energy supply. However, nuclear waste management and long-term disposition of current and legacy radioactive wastes remain open issues in the movement to a true "Nuclear Renaissance." Glass is the overwhelming world-wide choice for the immobilization of high level radioactive wastes resulting from nuclear fuel reprocessing due to its tolerance for the myriad of chemical elements found in the waste as well as its inherent stability and durability. Vitrification is a mature technology and has been used for high-level nuclear waste immobilization for more than 50 years. Borosilicate glass is the formulation of choice in most applications; however, phosphate glasses are used to immobilize high level wastes in Russia. Glass has also proven to be a suitable matrix for intermediate and low-level radioactive wastes and is currently used to treat nuclear power plant operational wastes in Russia and South Korea.

## Glassy Materials

Glassy materials in the form of both relatively homogeneous glasses and glass matrices incorporating crystalline dispersed phases are currently the most reliable hosts used for the constituents in nuclear wastes. Glasses are solid state materials which have a topologically-disordered internal structure made of a 3-D network of interconnected structural blocks, thus, are said to exhibit only short-range order within their structural units. Because of disordered arrangement of structural blocks, glasses allow for the accommodation of the wide range of elements that are present in the wastes to be bound within the glass structure. Figure 1 shows the waste elements that are present in US high level radioactive legacy defense wastes that are immobilized in alkali borosilicate glass in the Defense Waste Processing Facility at the Savannah River Site in Aiken, SC.

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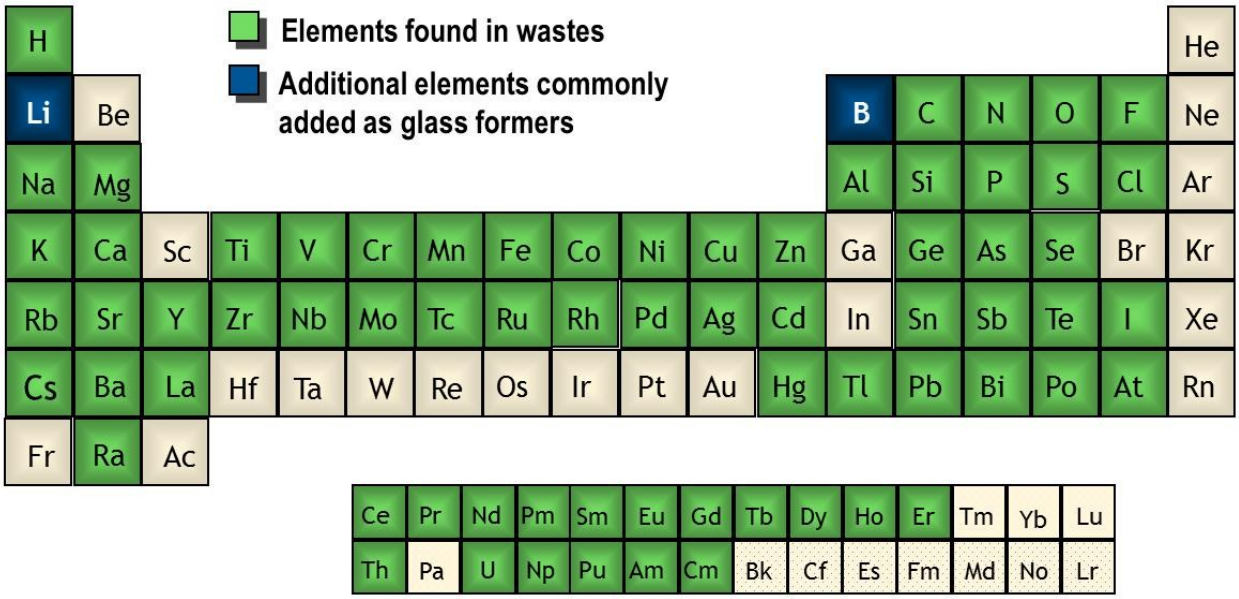


**Figure 1.** Elements present in US high level radioactive defense waste at the Savannah River Site, Aiken, SC, USA.

Glasses are typically formed on rapid cooling of melts and so little crystallization occurs since little time is allowed for the ordering processes of structural blocks. Whether a crystalline or amorphous solid is formed on cooling depends also on the ease with which a random atomic structure in the liquid can transform to an ordered state and is directly related to the glass composition and cooling history of the glass. In industrial nuclear waste vitrification processes, glass is poured into containers to allow for handling and storage of the waste glass (Figure 2).

A B

**Figure 2.** Stainless steel canisters to contain radioactive waste glass. A: R7/T7 Canister at the LaHague Plant in France, [Approximately 0.4 m diameter x 1.3 m tall]; B: Defense Waste Processing Facility Canister at the Savannah River Site in Aiken, SC USA [Approximately 0.6 m diameter x 3.0 m tall].

The glass cooling profile varies with location in the canister with the slowest cooling occurring at the centerline of the canister. The relatively slow cooling within the canister can promote crystallization within the glass. Crystalline phases present in the glass such as spinels and noble metals do not lead to degradation in the aqueous corrosion behavior. However, crystalline species such as nepheline that deplete the matrix of glass forming elements (namely silicon and aluminum) can dramatically decrease glass corrosion performance. Therefore, glass compositions must be carefully formulated to preclude the formation of deleterious crystalline phases. Additionally, the glasses must be formulated to satisfy melter processing constraints associated with viscosity, liquidus temperature, electrical conductivity, thermal conductivity, etc.

**Stability of glasses**

Although compared to crystalline materials of the same composition, glasses are metastable materials, their relaxation to crystalline structures is kinetically impeded so that practically no phase changes such as crystallization can occur within extremely long times which for glasses exceed the lifetime of the universe (~$1.4 \cdot 10^{10}$ years). The high chemical resistance of glasses allows them to remain stable in corrosive environments for many thousands and even millions of years [1]. Several glasses are found in

nature such as obsidians (volcanic glasses), fulgarites (formed by lightning strikes), tektites found on land in Australasia and associated micro-tektites 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 less than a millimeter per million years.

**Nuclear waste vitrification**

Radioactive waste storage and processing varies from country to country depending on how nuclear programs have been initiated and current policies. Most nuclear nations have generated waste from nuclear weapons programs and/or commercial nuclear power generation and store high level radioactive wastes from fuel reprocessing. The wastes are stored either as neutralized nitric acid streams (US and Russia) or acid streams directly stored in stainless steel tanks (France, UK and Japan). The highly radioactive liquid wastes are extracted from the storage tanks for subsequent vitrification [1-4]. Various pretreatment processes are employed on the liquid streams to prepare the feeds for vitrification including evaporation, filtration, chemical addition to adjust rheological properties, etc. Off-gas systems are employed in the vitrification process facilities to remove particulate carryover from the melter and treat gaseous species prior to discharge of the off-gas from the plant.

There are two primary approaches to vitrify the liquid high level waste feeds: 1) a two-step process involving calcination followed by vitrification of the calcined feed, and 2) direct feeding and vitrification of the liquid feed. Both processes operate in a continuous feeding mode.

<u>Calcination and vitrification</u>

Calcination is accomplished in a rotary tube that is heated in a resistance furnace. The high level waste feed is mixed with organic additives prior to introduction into the calciner to minimize calcine agglomeration and control redox conditions. The calcined material drops into the melter simultaneously with glass frit to promote vitrification. A nickel-based superalloy pot is heated inductively to temperatures of approximately 1100° C. The melter can include mechanical stirring or bubbling to promote mixing. Figure 3 shows a schematic of a hot-walled induction melter. The glass is poured in batches into canisters. The canisters are decontaminated and welded closed prior to storage.

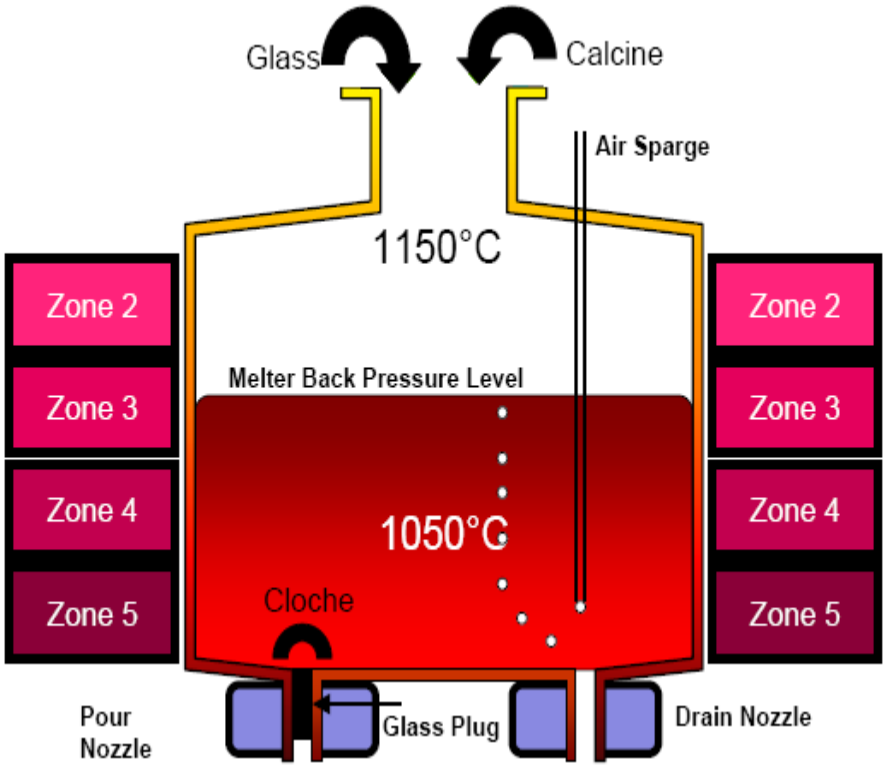


**Figure 3.** Schematic diagram of a hot-walled induction melter for high level radioactive waste vitrification.

Direct vitrification of liquid feed

The liquid high level radioactive waste feed is directly added to the surface of the melter in this approach. The waste solution is either mixed with glass frit or glass forming chemicals in a tank prior to introduction into the melter or is fed to the melter as glass frit is simultaneously fed. Reducing agents are typically added to the feed to control the redox potential within the melt to avoid foaming or precipitation of reduced metal species. The liquid feed forms a “cold cap” on the surface of the melter that assists to minimize constituent volatility. Glass is formed at the bottom of the cold cap. Joule heated ceramic melters are employed in this vitrification approach. These melters consist of a high chromium content refractory lined vessel heated by electric current flowing between paired metal electrodes located at the walls of the melter (Figure 4). Bubbling can be used to assist mixing and homogenization. Glass can be poured continuously via an overflow pour spout or through a thermally operated valve at the bottom of the melter. Filled canisters are decontaminated and welded prior to storage.

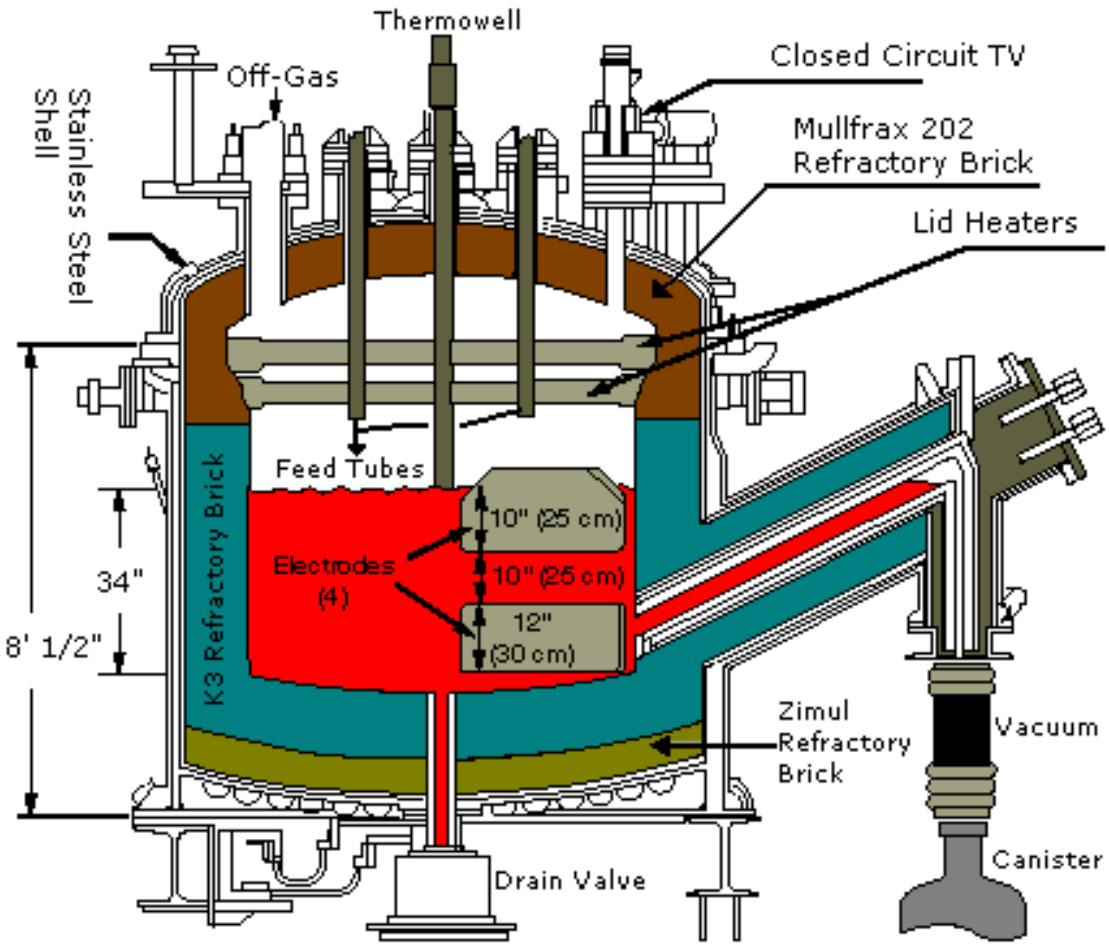


**Figure 4.** Schematic diagram of a Joule heated ceramic melter used for radioactive waste vitrification.

Table I summarises current operational data on radioactive waste vitrification facilities [1].

Table I. Operational data of vitrification programmes.

| **Facility** | **Waste type** | **Melting process** | **Operational period** | **Performance** |
|---|---|---|---|---|
| R7/T7, La Hague, France | HLW | IHC[1] | Since 1989/92 | 5573 tonnes in 14045 canisters to 2008 ($6430 \cdot 10^6$ Ci) |
| AVM, Marcoule, France | HLW | IHC | 1978 – 2008 | 1138 tonnes in 3159 canisters ($45.67 \cdot 10^6$ Ci) |
| R7, La Hague, France | HLW | CCM[2] | Since 2003 | GCM: U-Mo glass |
| WVP, Sellafield, UK | HLW | IHC | Since 1991 | 1800 tonnes in 4319 canisters to 2007 ($513 \cdot 10^6$ Ci) |
| DWPF, Savannah River, USA | HLW | JHCM[3] | Since 1996 | ~ 6500 tonnes in over 3600 canisters ($50 \cdot 10^6$ Ci). |
| WVDP, West Valley, USA | HLW | JHCM | 1996 – 2002 | ~500 tonnes in 275 canisters ($24 \cdot 10^6$ Ci) |
| EP-500, Mayak, Russia | HLW | JHCM | Since 1987 | ~8000 tonnes to 2009 ($900 \cdot 10^6$ Ci) |

| | | | | |
|---|---|---|---|---|
| CCM, Mayak, Russia | HLW | CCM | Pilot plant | 18 kg/h by phosphate glass |
| Pamela, Mol, Belgium | HLW | JHCM | 1985-1991 | ~500 tonnes in 2200 canisters, 12.1 $10^6$ Ci |
| VEK, Karlsruhe, Germany | HLW | JHCM | 2010 – 2011 | ~60 $m^3$ of HLW (24 $10^6$ Ci) |
| Tokai, Japan | HLW | JHCM | Since 1995 | > 100 tonnes in 241 canisters (110 L) to 2007 ($0.4 \cdot 10^6$ Ci). |
| Radon, Russia | LILW | JHCM | 1987-1998 | 10 tonnes |
| Radon, Russia | LILW | CCM | Since 1999 | > 30 tonnes |
| Radon, Russia | ILW | SSV[4] | 2001-2002 | 10 kg/h, incinerator ash |
| VICHR, Bohunice, Slovakia | HLW | IHC | 1997-2001, upgrading work to restart operation | 1.53 $m^3$ in 211 canisters |
| WIP, Trombay, India | HLW | IHPT[5] | Since 2002 | 18 tonnes to 2010 ($110 \cdot 10^3$ Ci) |
| AVS, Tarapur, India | HLW | IHPT | Since 1985 | |
| WIP, Kalpakkam, India | HLW | JHCM | Under testing & commissioning | |
| WTP, Hanford, USA | LLW | JHCM | Pilot plant since 1998 | ~ 1000 tonnes to 2000 |
| Taejon, Korea | LILW | CCM | Pilot plant, planned 2005 | |
| Saluggia, Italy | LILW | CCM | Planned | |

[1]IHC - Induction, hot crucible, [2]CCM – Cold crucible induction melter, [3]JHCM – Joule heated ceramic melter, [4]SSV - Self-sustaining vitrification, [5]IHPT – Induction heated pot type melter. HLW – high level waste, LLW – low level waste, LILW – low and intermediate level waste.

**High Level Waste Glass Storage and Disposal**

Vitrified HLW is currently stored in dedicated storage facilities (Figure 5).

**Figure 5.** Sellafield vitrified product store (UK).

To date no high level radioactive waste glass has been permanently disposed. However, there is world-wide consensus that deep geologic repositories provide the best solution for final disposition of immobilized high level waste. Repository geologies that are deemed suitable include: granite/hard rock, clay/shale or salt. There are currently several national programs evaluating all these candidate geologies for repository applications.

**International Commission on Glass – Technical Committee on Nuclear and Hazardous Waste Vitrification**

The Technical Committee on Nuclear and Hazardous Waste Vitrification (ICG TC05) was established by the International Commission on Glass in 2006 [5]. The vision and mission of the committee are as follows:

- The vision of this committee is to establish a forum to present, discuss and disseminate technical information on waste glass chemistry, vitrification processes, vitrification melter technologies, and waste glass environmental performance.
- The mission and goals of the committee are to facilitate the dissemination of technical information through promoting programming at technical conferences, conducting technical workshops and facilitating publication of information through

established channels. Promoting the exchange of technical data is also a goal of this committee.

The ICG TC05 currently consists of 22 members representing 11 countries [5]. The committee annually conducts technical programming at international conferences and holds committee meetings at these conferences (Figure 6).

**Figure 6.** ICG TC05 Chairman Dr. James Marra (SRNL, USA) and Professor Cristina Leonelli (University of Modena and Reggio Emilia, Italy) lead an International Congress on Glass session in Salvador, Brazil.

The committee completed a round-robin study on liquidus temperature measurement that fostered creation of an ASTM standard. The committee plans to initiate a round-robin study on sample preparation for glass corrosion testing. The technical committee will continue to offer a forum for international collaboration and information sharing.

**Future Outlook**

Vitrification is the world-wide accepted technology for the immobilization of high level radioactive wastes. Glass can accommodate the range of constituents that are present in the waste into the glassy structure. The excellent durability of vitrified radioactive waste ensures a high degree of environmental protection. Waste vitrification is a demonstrated mature technology at the industrial scale. Continued advancements in glass waste forms and nuclear waste vitrification technologies will be keys in enabling widespread deployment of nuclear energy.

Additionally, the pressing issues regarding hazardous domestic disposal may also be effectively solved using vitrification technologies. Stricter regulations regarding waste characterization and land disposal for hazardous wastes will necessitate the need for effective waste treatment methods. The wealth of

knowledge gained in the vitrification of nuclear wastes can be readily extrapolated to treatment of hazardous wastes. The stability and durability of glass waste forms may further provide unique opportunities for recycle or reuse of the immobilized hazardous wastes.

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