Indian Program for Vitrification of High Level Radioactive Liquid Waste

C. P. Kaushik

Waste Management Division, Bhabha Atomic Research Centre, Trombay, Mumbai – 400085, India

Abstract

Nuclear Power Programme in India is based on “closed fuel cycle”. Closed fuel cycle involves reprocessing and recycling of Spent Nuclear Fuel (SNF) coming out of nuclear reactors. During reprocessing, uranium & plutonium, constituting bulk of the SNF are separated and subsequently recycled. The remaining small portion constitutes high level radioactive waste containing most of the fission products and minor actinides. A three-step strategy involving immobilization, interim storage followed by ultimate disposal has been adopted in India for management of High Level Waste (HLW). Borosilicate glass matrix has been identified for immobilization of HLW owing to optimal waste loading, adequate leach resistance and long term stability of the product. Glass formulations are developed by suitable addition of modifiers to accommodate compositional variation in the waste. Detailed characterization studies are carried out to understand the structural modifications in the three dimensional network of incorporation of waste constituents followed by product characterization to ascertain the properties of the conditioned vitrified waste product (VWP). On the strength of these indigenous developments, Indian vitrification facilities are in operation at Trombay, Tarapur and Kalpakkam. Different types of melters like metallic, Joule Heated Ceramic Melter (JHCM) have been successfully deployed on industrial scale for vitrification of HLW. A Cold Crucible Induction Melter (CCIM) has also been developed. An interim storage facility is in operation for storage and surveillance of VWP. A site selection programme has been initiated to identify a few suitable geological domains for identifying a candidate disposal site for high level and long lived radioactive wastes. Presently granites have been studied extensively as a host rock & as a natural barrier. Long term evaluation of vitrified high level waste under geological conditions and its comparison with natural analogues (basaltic & obsidian) is being pursued in India.

Keywords: closed fuel cycle; SNF; HLW; vitrification

* Corresponding author. Tel.: +91-22-25595528; fax: +91-22-2550.
E-mail address: cpk@barc.gov.in
1. Introduction

Majority of radioactivity in the entire nuclear fuel cycle (Figure-1) is concentrated in high level radioactive liquid waste (HLW), which is generated during reprocessing of spent nuclear fuels. HLW is concentrated by evaporation and stored in under-ground stainless steel tanks. These storage tanks require cooling and continuous surveillance. Liquid storage in stainless steel tanks is considered at best, as an interim step. Though it has been practiced safely, on a long term basis, a three step strategy for management of HLW has been adopted in India in line with the internationally adopted practices (Figure-2).

Glass as matrix has been adopted globally for immobilization of HLW [Ojovan et al. (1992), Hench et al. (1984), Freeman et al. (1986)]. Indian waste management facilities are co-located with waste generating facilities, viz., nuclear reactor, reprocessing plant and fuel fabrication facility, so as to avoid any undue radiation exposure during transportation of waste from one place to another. Extensive research and development efforts finally culminated into design and construction of first Indian vitrification facility at Waste Immobilisation Plant (WIP), Tarapur. The second vitrification facility is commissioned at Bhabha Atomic Research Centre (BARC), Trombay to manage HLW generated during reprocessing of spent nuclear fuel from various research reactors [Sunder Rajan et
A third Waste Immobilisation Plant is being set up at Kalpakkam. It has been designed for the treatment and conditioning of HLW generated during reprocessing of irradiated fuel from Pressurized Heavy Water Reactors (PHWR) and Fast Breeder Reactors (FBR).

With respect to second step with regard to management of HLW, a storage facility for interim storage of vitrified waste product at Vitrified Waste Storage Facility (VWSF), Tarapur [Sunder Rajan et al. (1980)] has been commissioned and the same is in operation for last 15 years. As regards the third stage, Indian program on Geological Disposal Facility (GDF) commenced in early eighties with underground experiments (without any radioactivity) in an abandoned section of a gold mine [Mathur et al. (1998)]. The investigations were mainly directed towards development of methodology for in-situ assessment of thermo mechanical behavior of the host rock and to develop and validate the mathematical models associated with it [Bajpai et al. (2008)]. It also addressed the development of associated instrumentation for the measurements and monitoring. Granite as a host rock has been extensively evaluated for emplacement of vitrified waste product. Comprehensive program including identification of candidate site, optimization of back-fill materials and aspects pertaining to societal engineering is on the way for establishing a GDF.

2. Characteristics of high level waste

Composition of HLW depends on various factors including type of fuel, its history in the reactor and the reprocessing chemistry. The waste contains both long and short lived fission products, minor actinides (americium, neptunium & curium), unrecovered Pu/U, processing chemicals like nitric acid, sodium nitrate, dissolved cladding material like aluminum and zirconium and corrosion products of material of construction of storage tanks and piping. HLW being processed at WIP Tarapur is generated from reprocessing of PHWR spent fuel having burn-up of 6000 – 8000 MWd/te. It contains nitric acid (3-3.5M) and has a beta-gamma activity of 1.11 to 1.66 TBq/L. Presently stored high-level liquid waste at Trombay is due to reprocessing of research reactors and is characterized by relatively higher concentration of uranium, sodium and sulphate. This waste is acidic (1-1.5M HNO₃) with average activity of 0.27 to 0.37 TBq/L. The futuristic waste arising from reprocessing of spent fuel from Fast Breeder Reactors and Advanced Heavy Water Reactors will have higher concentration of fission products particularly, belonging to platinum group metals (Ru, Rh &Pd), thorium, aluminum and fluoride in addition to other waste constituents.

3. Desirable characteristics of solidified waste product

The solidified waste form must have certain properties so that its interim and long term storage followed by its ultimate disposal is technologically feasible, safe, economical and environmentally compatible. These desirable properties include: adequate chemical durability i.e. low leachability in ground water, good thermal conductivity, resistance to alpha, beta and gamma radiations, ability to contain high proportion of waste and to have high volume reduction, readily available raw materials at reasonable cost & acceptable processing temperature.

4. Matrix development

In India, borosilicate glass matrix has been adopted for vitrification of HLW [Kanwar Raj et al. (1986), Vaswani et al. (1979)]. Glass formulations were formulated based on glass forming regions of a three component phase diagram. SiO₂, B₂O₃ and Na₂O were taken as components. Large number of glass formulations were made with suitable modifiers and the glass forming region were established. Suitable modifications (Figure-3) have been made in order to accommodate compositional changes in the waste like sulphate, sodium, aluminum, thorium and fluoride [Kaushik et al. (2006), Mishra et al. (2007)]. Waste loading, glass additives and the processing temperature are the essential parameters to be taken into account for development of suitable glass formulation (Figure-4). SiO₂ and B₂O₃ are the basic glass forming oxides while Na₂O, Cs₂O, SrO, BaO and MnO₂ [Soliman et al (2005)] are glass modifiers. In pure silica glass, SiO₄ tetrahedra are linked via bridging oxygen atoms at the vertices so that continuous three dimensional network is established. In case of B₂O₃ glass system, the basic unit is triangular. Thus in borosilicate system, silicon and boron are network formers and are located in the centre of oxygen polyhedral in
configuration of tetrahedral and triangles respectively. However, in sodium borosilicate glass, boron oxide exists in tetrahedral structure also, where sodium ion compensates excess of negative charge. These polyhedra are then connected together by sharing corners, generally in accordance with Zachariasen’s rules [J.E.Shelby (2005)]. Various elements in HLW occupy positions in this three dimensional structure depending on the electro negativity, ionic size and field strength. Compositional details of the glass formulations adopted for vitrification at Tarapur and Trombay are presented in Table-1.

Fig. 3. Development of Glass Formulations for HLW Vitrification

Fig. 4. Basis for development of glass matrices
Table 1. Glass matrix compositions (Wt%) used at WIPs Tarapur and Trombay

| Composition                        | Modified Sodium Borosilicate (IR111 Tarapur) | Lead based borosilicate (WTR-62 Trombay) | Barium based borosilicate (SB-44 Trombay) |
|------------------------------------|---------------------------------------------|-----------------------------------------|-------------------------------------------|
| Glass formers (SiO<sub>2</sub>+B<sub>2</sub>O<sub>3</sub>) | 46                                         | 50                                       | 50.5                                      |
| Glass network intermediate (TiO<sub>2</sub>) | 7                                          | --                                      | --                                        |
| Glass modifiers (Na<sub>2</sub>O+MnO<sub>2</sub>+PbO+BaO) | 16                                         | 30                                       | 28.5                                      |
| Waste Oxide                        | 31                                         | 20                                       | 21                                        |

5. Product characterisation

As a practice, detailed evaluation of Vitrified Waste Product (VWP) is carried out during inactive vitrification runs with simulated waste. Based on the desired product quality, various process parameters are standardized. Conditioned products are evaluated for various properties like product melt temperature, waste loading, homogeneity, thermal stability, radiation stability and chemical durability using advanced analytical instruments, e.g., Scanning Electron Microscope, Electron Microprobe Analyzer, X-ray Diffractometer, Inductively Coupled Plasma Spectrometer and Thermal analysis system. The salient properties of vitrified waste product are presented in Table-2. The properties of vitrified waste products obtained from sodium borosilicate as well as barium borosilicate glass formulations are well in comparison with internationally reported values [Donald et al. (1986)].

Table 2. Salient features of VWP

| Properties                          | Sodium Borosilicate Glass (IR-111) | Lead Borosilicate Glass (WTR-62) | Barium Borosilicate Glass (SB-44) |
|-------------------------------------|------------------------------------|----------------------------------|-----------------------------------|
| Mechanical Properties:             |                                    |                                  |                                   |
| Density (g/cc)                      | 2.99                               | 3.5                              | 3.0                               |
| Impact strength (RIAJ)*             | 1.06                               | 1.12                             | 0.85                              |
| Thermal Properties:                |                                    |                                  |                                   |
| Thermal conductivity,373K (Wm<sup>-1</sup>K<sup>-1</sup>) | 1.045                             | 1.15                             | 0.95                              |
| Co-eff. of thermal expansion (/K)   | 102 x 10<sup>-7</sup>             | 83 x 10<sup>-7</sup>            | 101 x 10<sup>-7</sup>            |
| Viscosity, 1173K (dPa.s)            | 40                                 | 135                              | 70                                |
| Pouring temperature (K)            | 1273                               | 1223                             | 1198                              |
| Softening temperature (K)          | 813                                | 763                              | 809                               |
| Chemical Properties:               |                                    |                                  |                                   |
| Average stabilized leach rate using ASTM C1885-02 procedure (g.m<sup>-2</sup>.d<sup>-1</sup>) | 9.2 x 10<sup>-2</sup>   | 1.8 x 10<sup>-1</sup>           | 4.2 x 10<sup>-2</sup>            |
| Waste Oxides (%)                   | 31                                 | 20                               | 21                                |
| Phase homogeneity                   | Homogeneous                        | Non-homogeneous                  | Homogeneous                       |

*Relative Increase in Area per Joule (RIAJ)

6. Process description

Vitrification process is essentially a batch operation consisting of metering of pre-concentrated waste and glass forming additives in the form of slurry/glass frit into the heated process vessel located in a multi-zone furnace. A simplified flow-sheet of vitrification process adopted at Trombay is presented in Figure-5. The susceptor and the process vessel are made of high Ni-Cr alloy so as to withstand high temperature, oxidizing and corrosive conditions. There is a freeze valve section at the bottom of process pot operable by an independent induction coil. These are heated by induction heating system. With simultaneous concentration and calcinations of waste, solid-liquid interface moves upwards. The level of liquid waste is indicated by the temperatures sensed by the thermocouples
located at different heights. The calcined mass is fused into glass at about 1223K and is soaked at 1223-1273K for eight hours to achieve homogenization. The molten mass is drained into stainless steel AISI 304L canister by operating the freeze valve. The canister filled with VWP is allowed to cool slowly in an insulated assembly. This is then welded remotely by Pulse-TIG method by remote welding machine. Vitrified waste canisters are further enclosed in secondary stainless steel container called overpacks. These overpacks are designed to contain radioactivity of the order of 37000 TBq generating about 3-4 KW of decay heat. An elaborate off-gas cleaning system consisting of condenser, scrubber, chiller, demister and absolute HEPA filter is used to treat the gases before discharge through a tall stack (85-100 m). The plants are provided with central data acquisition and control system to monitor and control the critical process parameters during vitrification operation. The whole operation is carried out in a hot-cell having multiple compartments including concentration operation, furnace operation, welding station and product storage. Remote handling gadgets like servo-manipulator, in-cell cranes etc. have been developed indigenously and deployed to accomplish the entire operation. In view of expanded nuclear energy program and resultant enhancement in waste volume generation JHCM with higher throughput have also been developed & deployed at vitrification facility, BARC, Tarapur. JHCM is developed to facilitate higher throughput during vitrification. Vitrification technology based on cold crucible induction melter has also been developed at research centre to address various requirements such as high temperature availability, high waste loading and compatibility with new matrices like glass-ceramic. An engineering scale cold crucible induction melter has been commissioned and the same is being integrated with other systems like waste feeding, product weighing and draining system with suitable remote handling gadgets to deploy it for industrial scale vitrification of waste.

![Fig. 5. Process schematic for Vitrification of HLW](image)

7. **Study of durability of vitrified waste products**

Studies on long-term evaluation of vitrified waste product under simulated conditions have been conducted in especially designed hot cells at Solid Storage and Surveillance Facility, Tarapur. The studies involve (a) core-drilling of high level waste product from statistically selected canisters, (b) sample preparation from core-drilled pencils, (c) studies for properties like homogeneity, thermal stability and chemical durability and (d) effect of components of repository like granite and back-fill material as well as corrosion products on leach rate of vitrified product. Some of the leach rate experiments are continued for more than 700 days. Presence of secondary phases on the waste product and their effect on chemical durability has also been studied [Vidya Thorat et al (2005)]. It is also planned to compare the chemical durability of waste glasses with natural analogue (basaltic/obsidian) and archeologically available old glasses. The comparison will help to understand the mechanism of leaching in both the types of glasses. The data thus generated will be also useful for modelling to predict release of radionuclide from the nuclear waste glasses over long time durations.
8. Actinide partitioning of HLW

In future, long term management of HLW would involve separation of fission products from long lived minor actinides (MAs) called ‘partitioning’ of HLW. It is planned to burn recovered actinides in fast reactors or in accelerated driven sub-critical systems. It is worth mentioning here, prior to transmutation, lanthanides are separated from actinides. The separated lanthanides are vitrified. Currently, technology for partitioning of HLW with indigenously synthesized amide based extractants is being tested on demonstration scale in India. It is estimated that with adoption of partitioning of HLW, the volume of VWP needing its storage in GDF will be significantly reduced. The VWP without actinides will be stored in stainless steel canisters in interim storage facility for a period of 200 years where most of the fission products would have decayed. Thus closed fuel cycle with partitioning & transmutation offers considerable reduction and optimal use of GDF including radio toxicity reduction.

9. Conclusion

Borosilicate glass has been adopted for immobilization of HLW. India has developed sufficient expertise in this advanced technology with respect to matrix development, process design, construction, commissioning, and operation and remotised maintenance. As far as the technology for waste conditioning is concerned, metallic and ceramic melter technology has been established and demonstrated. Technology has also been developed for the design, construction and operation of interim storage facility for vitrified waste products under surveillance. A large-scale site selection programme has been initiated to identify a few suitable geological domains for identifying a suitable GDF for high and long lived radioactive wastes. Partitioning of actinides from HLW is being studied at industrial scale with HLW. This step will play an important role in having significant reduction in inventory of vitrified waste product awaiting its disposal in GDF. Presently granites have been studied extensively as a natural barrier. Long term evaluation of vitrified high level waste under geological conditions is being pursued in India. This will go a long way in demonstrating safe containment of waste in deep geological repositories, with limited impact on the environment.

Acknowledgement

The experience and expertise gained in the field of Indian Programme for Vitrification of High Level waste is the result of dedicated efforts of a large number of technical and scientific personnel. Author gratefully acknowledges the valuable contribution of his colleagues in Nuclear Recycle Group, BARC, and especially those belonging to Waste Management Division. Special thanks are due to Dr. R.K. Mishra and Ms. Vidya Thorat for their valuable contribution to this paper.

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