

Preparation and characterisation of glass product with modified composition for vitrification of high level radioactive waste

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Abstract During the vitrification of high level radioactive liquid waste (HLW) at advanced vitrification system (AVS) in Tarapur, the glass forming chemicals are introduced into the melter in the form of preformed glass frit, known as base glass. A five component system, $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O-Fe}_2\text{O}_3\text{-TiO}_2$ is presently used as the base glass at AVS. Towards the step to product improvement, a modified base glass composition with seven components, $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O-CaO-Fe}_2\text{O}_3\text{-TiO}_2\text{-K}_2\text{O}$ was formulated with reduced boron content and incorporation of mixed alkali elements Na and K as compared to presently adopted base glass composition. The modification was mainly aimed at reducing boron volatilization during vitrification without affecting the present state of product quality to improve melter life and to some extent take advantage of mixed alkali effect. The modified base glass and product glass based on modified base composition were evaluated for different properties with respect to existing composition. The fusion and pouring temperatures were well with in the range of plant requirement. The glass transition temperature, coefficient of thermal expansion and thermal conductivity were similar or better. The product glass was having good homogeneity and chemical durability.

Keywords Advanced Vitrification system · Base glass · Pouring temperature · Thermal conductivity · Chemical durability

Introduction

Management of radioactive waste is an important aspect in the nuclear fuel cycle. During co-decontamination cum partitioning cycle of reprocessing of spent fuel, high level radioactive liquid waste (HLW) is generated, which contains 99 % radio activity of the spent fuel. Borosilicate glass system has been adopted world wide as a matrix for immobilization of HLW [1, 2]. Vitrification process using induction heated metallic melter was earlier used at Waste Immobilisation Plant, Tarapur [3]. Later on, joule-heated ceramic melter was adopted at AVS Tarapur [4], where the base glass in the form of glass frit is used instead of slurry containing raw glass forming chemicals. A five component base glass composition based on $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O-Fe}_2\text{O}_3\text{-TiO}_2$ system was studied and being used at AVS at Tarapur for ceramic melter [5].

Sodium and boron being more volatile compared to other component of base glass, they are reported in the off gas system and their vapour attacks plenum part of the melter [6]. The attack on the binder used in joints of refractory blocks is a matter of more concern rather than that on refractory itself. The qualitative approach to reduce extent of attack is to reduce either or both components without affecting the product criteria.

It has also been reported that incorporation of modifiers more than limiting concentration is possible to be achieved with use of mixed alkali elements possibly by satisfying the co-ordination number of modifier metal ion in better way because of different ionic radii and stabilising them in the glass network [7]. Most of the waste oxide constituents belonging to alkali metals, alkaline earth metals and transition elements act as modifiers and some belonging to rare earths and transition metals act as intermediates.

In view of the above, a modified seven component composition with $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O-CaO-Fe}_2\text{O}_3\text{-TiO}_2\text{-K}_2\text{O}$

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system was formulated for base glass. Present paper deals with the evaluation of different properties of the vitrified waste product (VWP) prepared using simulated HLW and modified base glass composition.

Experimental

Preparation of glass samples and evaluation of its fusion/pouring temperature

The chemicals used for the preparation of glass samples were of AR grade. Base glass and simulated HLW product glass samples were prepared as per the composition given in Table 1. The waste oxide loading in the VWP was kept 24 % on weight basis. Weighed quantities of different chemicals for modified base glass and known volume of simulated waste were mixed together and dried under IR lamp. The dried raw mixture was charged in quanta into a ceramic crucible placed in the muffle furnace at 700 °C. The temperature of the furnace was gradually increased with an increment of 25 °C up to a temperature at which the completion of fusion reaction was observed visually. The temperature of the furnace was again increased gradually with an increment of 25 °C and in each step pouring of the glass mass from the crucible was tried immediately after removing the crucible from the furnace and tilting it. After ensuring attainment of pouring temperature, the mass was refined by keeping the glass melt at pouring temperature for about 5 h to eliminate the trapped gases to dissolve the crystalline phases and to get homogeneous mass. The refined molten glass was poured on cold SS tray and allowed to cool to room temperature. Fusion and pouring temperatures of the prepared glass samples were noted during preparation. The refined glass sample was used for the characterization of the glass product with respect to density, glass transition temperature, coefficient of thermal expansion, thermal conductivity, homogeneity and chemical durability.

Homogeneity and amorphous nature

To ascertain the amorphous nature of the glass product, optical microscope and XRD analysis were carried out. Microscopic examination of the product glass was carried at maximum magnification of 600 (Fig. 1). XRD patterns of the heat treated VWP samples were taken from 10° to 60° (2θ) by Cu Kα radiation at excitation voltage 40 kV and tube current 30 mA (Fig. 2). Density of the glass samples from different areas of the product glass was determined by water displacement method [8] to ascertain the gross homogeneity.

Table 1 Compositions of base and product glasses of existing and modified

No.	Oxides	Wt% in glass			
		Base glass		Product glass	
		Modified	Existing	Modified	Existing
1	SiO ₂	53.56	48.0	40.71	36.48
2	B ₂ O ₃	11.03	26.2	8.39	19.91
3	Na ₂ O	14.44	11.65	10.97	8.85
4	TiO ₂	9.49	9.5	7.21	7.22
5	CaO	6.14	–	4.67	–
6	K ₂ O	1.21	–	0.92	–
7	Fe ₂ O ₃	4.13	4.65	3.13	3.53
8	Waste oxide	NIL	NIL	24.0	24.0



Fig. 1 Optical micrograph (600×) of modified product glass

Glass transition temperature (T_g)

The glass transition temperature of prepared product glass was determined by Differential thermal analyser (Make, Shimadzu—Model DTA-30). Around 40 mg of powdered glass samples having –25 + 80 ASTM mesh size was used for the study. Heating rate of 20 °C min⁻¹ and sensitivity range ±50 μV were selected. The experiments were carried out in air atmosphere. ΔT between sample and reference was measured as a function of temperature. Curves detailing ΔT (in mV) versus temperature were recorded (Figs. 3, 4).

Coefficient of thermal expansion (α)

Coefficient of thermal expansion of the product glass was determined using Thermomechanical analyser (Make Shimadzu—Model TMA-30). Glass pellet having 10-mm dia

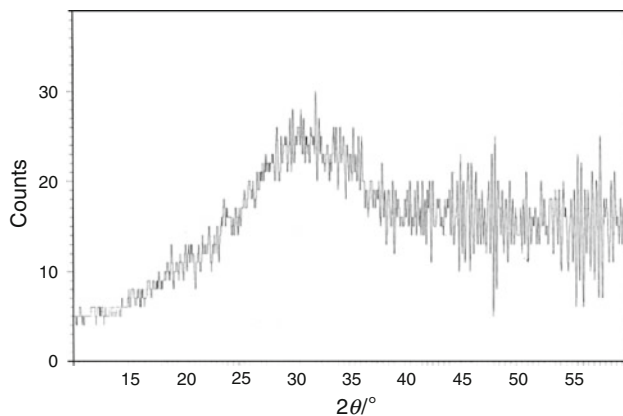


Fig. 2 XRD scan of modified product glass heat treated at 700 °C for 24 h

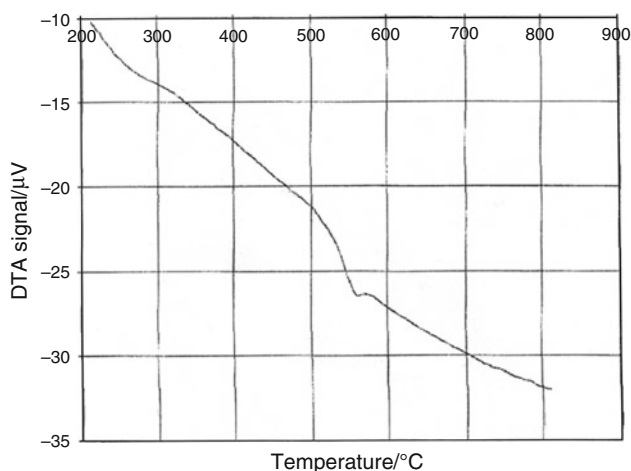


Fig. 3 Glass transition temperature measurement of modified base glass

and 7.22-mm height was used for the study. Heating rate of 10 °C min^{-1} and sensitivity range $\pm 5\text{ }\mu\text{m}$ were selected for the measurement. The experiment was carried out in air atmosphere. Increase in length of the samples was recorded as a function of temperature (Fig. 5).

Thermal conductivity (k)

Thermal conductivity of the product glass sample was determined by comparative method using thermal conductivity instrument (Dynatech R/D Company, Cambridge Make and TCFCM, Model) based on cut bar technique. Cylindrical glass sample having 25-mm dia and 25-mm height and reference standard (Pyrex) having exactly same dimensions were used. Sample was sandwiched between two reference standards. The main heater (heat source) was set at about 20 °C higher than the temperature of measuring (100 °C) and the lower heater (heat sink) was set at a

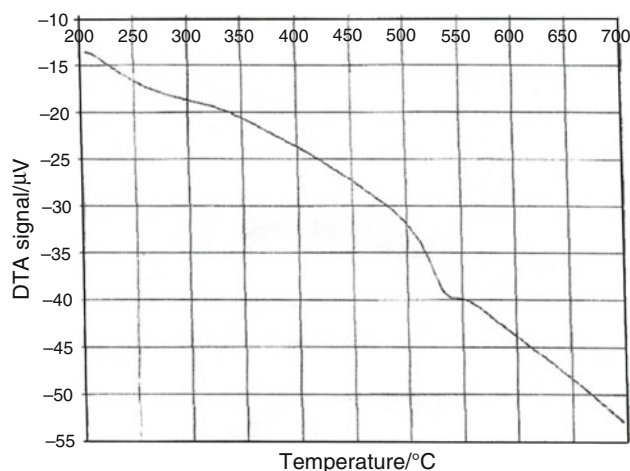


Fig. 4 Glass transition temperature measurement of modified product glass

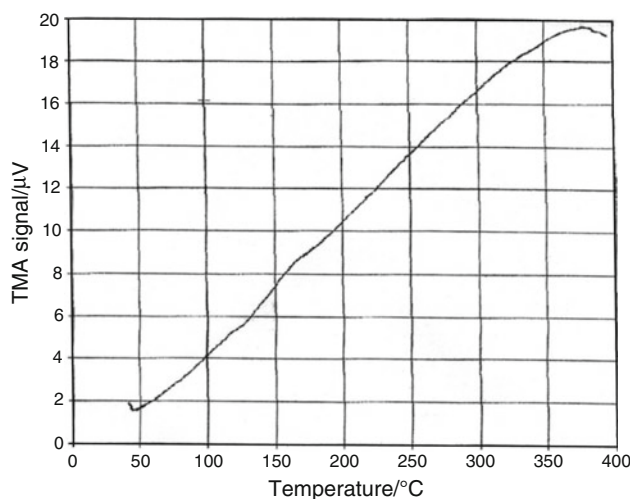


Fig. 5 Coefficient of thermal expansion measurement of modified product glass

about 20 °C lower than the measuring temperature. The temperature gradients in sample and reference standards were measured when steady state was achieved by measuring temperatures at two different locations in sample and references and thermal conductivity was calculated.

Chemical durability

Chemical durability is the most important parameter studied to ascertain the safe containment of the radioactivity inside solid matrices [9]. Accelerated leaching tests were performed by exposing higher surface area of the sample at high temperature to enhance the rate of dissolution and using distilled water as leachant. Powdered sample of product glass having $-16 + 25$ ASTM mesh size ($\sim 800\text{-}\mu\text{m}$ average size with $25\text{ cm}^2\text{ g}^{-1}$ surface area)

Table 2 Properties of existing and modified glasses

No.	Properties	Values			
		Base glass		Product glass	
		Modified	Existing	Modified	Existing
1	Fusion temperature/°C	950	900	875	875
2	Pouring temperature/°C	1050	1000	950	950
3	Density/g cm ⁻³	2.68	2.8	2.78	2.85
4	Homogeneity	Homogeneous		Homogeneous	
5	Glass transition temperature/°C	561	565	542	540
6	Coefficient of thermal expansion/°C	–	–	0.99 × 10 ⁻⁵	1.03 × 10 ⁻⁵
7	Thermal conductivity at 100 °C/w m ⁻¹ K ⁻¹	–	–	0.86	0.96
8	Stabilized leach rate after 77 days/gm cm ⁻² day ⁻¹	–	–	3.4 × 10 ⁻⁵	8.0 × 10 ⁻⁵

was used for the experiment. Leaching studies were carried out by semi static leach tests using a conventional boiling water unit. The water was replaced at regular interval of time as per standard procedure [10] and analysed for the amount of Na leached out during each interval using flame photometer.

Results and discussion

SiO₂ and B₂O₃ are the basic glass forming oxides in both existing and modified glass compositions. Na₂O is used as modifying oxides with the intention to break open the continuous three dimensional glass network by introducing non bridging oxygen atoms so as to bring down the formation temperature to desired range preferably below 1100 °C in view of inconel electrodes used in the furnace. The functions of CaO and K₂O are same as Na₂O in the glass network. However, Ca being divalent in the nature, it is held more tightly in the glass network and hence its effect is less pronounced compared to Na. Difference in the ionic size of Na and K possibly results in the glass network stabilization. TiO₂ was introduced in system as intermediate [8] to suppress the volatility of radioactive caesium from the molten glass during vitrification of HLW. Fe₂O₃ was introduced to moderate the effect of alkali/alkaline earth metal ions on increasing the electrical conductivity due to ionic conduction.

Boron and sodium are predominant as far as volatilisation from glass melt is concerned mainly in the form of sodium tetra borate. For satisfying the need to achieve the desired range of pouring temperature, the particular combination of Na₂O and B₂O₃ are to be maintained. The volatile constituents attack on AZS refractory and binder used for the refractory blocks in plenum area of the melter, where there is no molten glass. The binding material differs significantly from refractory composition. Considering radioactive nature of off gas constituents, integrity of joints

becomes the deciding factor for melter life. Since there is a scope for reduction in the boron content for the presently adopted composition, approach for reducing the boron content was selected.

To reduce boron volatilization, boron oxide content in modified base glass was reduced to 11 % from 26 % with respect to the existing base composition. The reduction of boron oxide alone results in increase in glass formations temperature. The increase in formation temperature was compensated partially with introduction of other modifying oxide like CaO/K₂O and partially by marginal increase in Na₂O content with respect to existing base glass. The comparison of properties of product glasses resulted from existing and modified base glasses with same loading of waste oxide is given in Table 2. The properties evaluated for product glass with modified composition are discussed below.

For plant scale operations, the temperature parameters of the melter are selected based on fusion/pouring temperatures of the glass. When molten mass in the melter is maintained at pouring temperature as determined in laboratory for required time period, homogenization is ensured and draining rate of the product glass from melter is satisfactory. The observed fusion and pouring temperatures (875 and 950 °C, respectively) for modified product glass are well with in the operational range of the melter.

Optical microscope analysis showed homogeneity of the VWP (Fig. 1). No crystalline or liquid phase separations were noticed. The VWP sample was subjected to heat treatment at 700 °C for 24 h to examine the nucleation growth and extent of devitrification, if any. XRD pattern of the VWP sample (Fig. 2) indicates no noticeable devitrification even after heat treatment of the glass sample.

There should be homogeneous distribution of all waste components and glass-forming chemicals in the vitrified waste product. The variation in density of the product glass sampled from different areas reflects the extent of homogeneous distribution of waste oxide in the product. Density of product glass samples varied from 2.76 to 2.78 g mL⁻¹. The very

narrow range of density indicates consistency in the distribution of the constituents in the vitreous melt at gross level.

The minor endothermic base line shifts in the Figs. 3 and 4 (561 and 542 °C) are the glass transition temperature (T_g) of the base glass and product glass samples, respectively, which were identified clearly by derivative signals. The decay heat of radio isotopes present in the active VWP can increase the temperature of VWP above glass transition temperature during disposal conditions and that can result into devitrification of VWP depending on its composition. Therefore, glass transition temperature is one of the important parameters for determination of waste loading into the VWP. The T_g value of 542 °C for the product glass is comparable with the existing glass composition and is well within the acceptable range for optimized waste loading.

Figure 5 shows the thermomechanical graph of the modified glass product. The increase in length of the sample between two temperatures was calculated from the plot. The coefficient of thermal expansion (α) between two points (150 °C and 300 °C) on the plot was calculated using the change in length (Δl) and change in temperature (ΔT) between the two points and the original length (l) of the sample by the equation:

$$\alpha = (\Delta l/l) \times \Delta T \quad (1)$$

Generation of thermal stresses in the VWP depends on the coefficient of thermal expansion. Increase in thermal stresses can produce cracks in VWP which in turn will decrease the chemical durability of the product glass by increasing the surface area. The value of α obtained for the product glass sample is ($0.99 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$) comparable with the existing product glass composition.

From the temperature gradients in the reference standard and sample ($\Delta T/\Delta x$) and the thermal conductivity of reference standard ($k_{\text{reference}}$), thermal conductivity of sample (k_{sample}) is calculated by the equation:

$$k_{\text{sample}} = k_{\text{reference}}(\Delta T/\Delta x)_{\text{reference}} \times (\Delta x/\Delta T)_{\text{sample}} \quad (2)$$

Thermal conductivity of VWP is important from the view point of dissipation of decay heat of the bulk VWP through its surface. Higher value of k is required for ensuring the product central line temperature much below the glass transition temperature during interim storage. Also, it reduces the thermal stresses in VWP, as ΔT between central line and surface of VWP canister will be less for higher k value. Value of thermal conductivity at 100 °C obtained for the modified product glass sample [$0.86 \text{ w m}^{-1} \text{ K}^{-1}$] is within the acceptable range.

Chemical durability is one of the most important properties of the conditioned product indicating proper immobilization of radio nuclides within the glass matrix. Chemical durability of the conditioned products was investigated by studying their

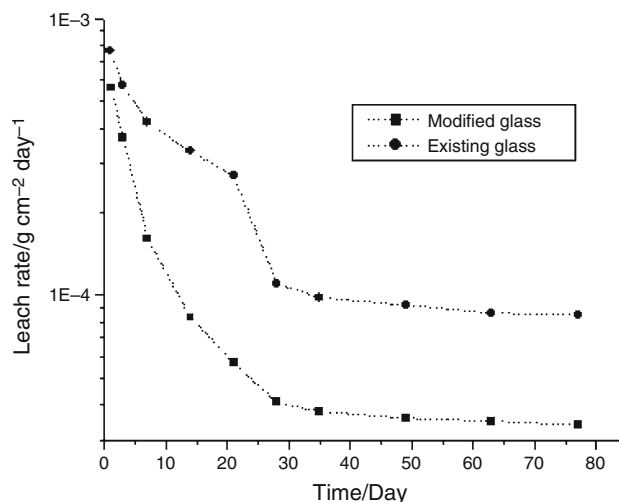


Fig. 6 Leaching pattern of Na from modified and existing product glasses

leaching behaviour. Sodium being monovalent and smaller in ionic size compared to other alkali metals its leach rate can be considered on conservative side, as leaching is diffusion controlled phenomenon. The leach rate with respect to Na leach behaviour was calculated by the standard equation:

$$(\text{LR})_{\text{Na}} = \frac{C_{\text{Na}}}{C_0} \times \frac{W_0}{S \times T} (\text{g cm}^{-2} \text{ day}^{-1}) \quad (3)$$

where $(\text{LR})_{\text{Na}}$ is the Leach rate with respect to the behaviour of Na ($\text{g cm}^{-2} \text{ day}^{-1}$); C_{Na} is the amount of Na leached out (g); C_0 is the amount of Na in the sample (g); W_0 is weight of sample (g); S is the surface area of the sample (cm^2); and T is time interval of leaching (days).

Figure 6 shows the logarithm of normalized leach rate for Na ions as a function of time over a period of 77 days. The average stabilized leach rate has been found to be $3.4 \times 10^{-5} \text{ g cm}^{-2} \text{ day}^{-1}$. This is better than the existing glass composition data and is well within the internationally accepted value of the leach rate for vitrified waste products [11]. The improvement in the leach rate may be due to the mix alkali effect in the system.

Conclusions

The properties of the vitrified waste product prepared using the modified base glass composition are found to be comparable with those of existing vitrified product glass and are well within the acceptable range. From view point of leach rate, the product is comparatively better. The considerable reduction in boron content is expected to result into lesser boron volatilization. This in turn is expected to cause lesser extent of attack of boron on melter refractory and binding material and thereby increase the melter life.

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