GLASS MELTING TECHNIQUES USED IN RADIOACTIVE WASTE IMMOBILIZATION
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Abstract
Development of a homogenous borosilicate glass used for immobilizing sulfur-rich waste at low operating cost is desired. This goal can be achieved by utilizing calcium fluoride (CaF$_2$) as a fining agent without using an external ceramic, platinum stirrer or air purging into melter plenum. The decomposition of CaF$_2$ into fluorine and calcium oxide during the melting improved the bubbling at high temperatures and the chemical durability of the final product respectively. Here we present results regarding the effect of melting duration and fluorine bubbling on foaming and the impact of thermal expansion coefficient (TEC) on the thermal stability of borosilicate glasses. The developed glass (HG-2) with an optimum 2 wt.% CaO in the form of CaF$_2$, was selected as initial frits for vitrification of radio-nuclides captured in the spent ion exchange resins. The residue of spent resin was rich in sulfur and carbon. Bubbling helped in the evolution of SO$_2$ and CO$_2$ gases, with detrimental impact on the glass matrix. On the other hand, foaming can be reduced or even suppressed by sulfate or other salts that do not mix with molten silicates.

Introduction
Species on Earth need to be protected from exposure to radiation from radioactive waste. One of the economically feasible ways to decrease the harm from radioactive waste is to vitrify the waste in a suitable glass composition, to immobilize the radio-nuclides as well as to reduce its volume. Therefore, designing of suitable glass compositions is required to incorporate nuclear waste for long-term safe storage and disposal. Glass melting process consumes large amounts of energy, resulting in gaseous emissions that contribute to the greenhouse effect. The development of glassy materials for a given waste stream is a problem constrained by multi-variant optimizations; for example, viscosity of the melt plays an important role in process-ability. Generally, the most important requirements for accepting the waste form include chemical and thermal stability and fluidity of the glass. The major criteria in preparing new glasses are to optimize their compositions in order to achieve a homogeneous bubble-free chemically and thermally stable final glass. The glass composition is designed to optimize waste loading, homogeneity, redox state and chemical durability [1].

Typical glass compositions used for nuclear waste immobilization comprise two network formers; silica (SiO$_2$) and boron oxide (B$_2$O$_3$). Network formers have strong covalent bonds involving SiO$_4^-$ and BO$_4^-$ tetrahedra and BO$_3^-$ triangles (trihedra). Additionally, such glasses comprise several intermediates such as alumina (Al$_2$O$_3$), iron oxide (Fe$_2$O$_3$) and magnesium oxide (MgO), and network modifiers such as calcium oxide (CaO), lithium oxide...
(Li$_2$O), sodium oxide (Na$_2$O), and sometimes lead oxide (PbO). The intermediates and modifiers have weaker field strength ($F=Z/a^2$) than the network formers, where “$Z$” is the valence charge and “$a$” is the ionic distance; therefore, they can enter into the gaps in network structures, having coordination numbers 6. Modifiers form weaker bonds with oxygen than the network formers and act to balance the negatively charged borosilicate or alumino-borosilicate networks [2]. These modifiers are useful in formulating a glass with potential to incorporate sulphate compounds and high molecular weight of carbon residue arising from thermal treatment of spent organic ion exchange resin (IEX) [2]. High oxidising power of these modifiers balances the reducing strength arising from carbon and sulfur interactions with the glass network during vitrification.

Vitrification can be performed efficiently at relatively low liquidus temperatures ($T_L$) thereby avoiding excess radionuclide volatilisation and maintaining viscosities below 10 Pa.s at 1150°C to ensure high throughput and controlled pouring into canisters [3]. Boron oxide makes glass viscosity sharply dependent upon the temperature as it raises the viscosity of the glass at low temperatures and lowers it at high temperatures, which are beneficial for vitrification. A glass with these properties is called “short glass” [2].

Commercially, borosilicate glasses are prepared with a variety of compositions. Some general compositions and melting temperatures of glasses used for waste immobilization are given in Table 1. Exact details regarding concentration of the modifiers, melting process and heating/cooling schedules are not available in the public domain. These glasses are used for vitrification of high-level waste (HLW), intermediate-level waste (ILW) and low-level waste (LLW) at temperatures ranging from 1000 to 1200°C.

Table 1. The wt.% compositions of glasses used in nuclear waste management [2].

<table>
<thead>
<tr>
<th>Vitrification Plant (Country)</th>
<th>SiO$_2$</th>
<th>P$_2$O$_5$</th>
<th>B$_2$O$_3$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>Others</th>
<th>$T_o$($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&amp;T7 (France)</td>
<td>47.2</td>
<td>14.9</td>
<td>4.4</td>
<td>4.1</td>
<td>-</td>
<td>10.6</td>
<td>18.8</td>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>DWPF (USA)</td>
<td>49.8</td>
<td>8.0</td>
<td>4.0</td>
<td>1.0</td>
<td>1.4</td>
<td>8.7</td>
<td>27.1</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>Magnox (UK)</td>
<td>47.2</td>
<td>16.9</td>
<td>4.8</td>
<td>-</td>
<td>5.3</td>
<td>8.4</td>
<td>17.4</td>
<td>1150</td>
<td></td>
</tr>
<tr>
<td>PAMELA (Germany-Belgium)</td>
<td>52.7</td>
<td>13.2</td>
<td>2.7</td>
<td>4.6</td>
<td>2.2</td>
<td>5.9</td>
<td>18.7</td>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>Defence HLW (Russia)</td>
<td>-</td>
<td>52.0</td>
<td>19.0</td>
<td>-</td>
<td>-</td>
<td>21.2</td>
<td>7.8</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>K-26 LILW (Russia)</td>
<td>48.2</td>
<td>7.5</td>
<td>2.5</td>
<td>15.5</td>
<td>-</td>
<td>16.1</td>
<td>10.2</td>
<td>1150</td>
<td></td>
</tr>
<tr>
<td>P0798 (Japan)</td>
<td>46.6</td>
<td>14.2</td>
<td>5.0</td>
<td>3.0</td>
<td>-</td>
<td>10.0</td>
<td>20.2</td>
<td>1150</td>
<td></td>
</tr>
<tr>
<td>GC-12/9B (China)</td>
<td>46.2</td>
<td>13.4</td>
<td>4.2</td>
<td>2.5</td>
<td>1.5</td>
<td>9.1</td>
<td>23.1</td>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>SL-1 (China)</td>
<td>34.3</td>
<td>2.0</td>
<td>18.0</td>
<td>5.0</td>
<td>10.0</td>
<td>3.0</td>
<td>25.00</td>
<td>2.6</td>
<td>1000</td>
</tr>
</tbody>
</table>

* $T_o$ is the operating temperature at the vitrification plant, it is normally 86°C above the liquidus temperature ($T_L$) of the used glass [4].
The vitrification technology for radioactive waste management commonly favours the use of borosilicate glass.[5]
A low T_L glass (SL-1) was developed in China to vitrify their pressurized water reactor (PWR) borate waste. B and Na, being the dominant components in PWR-borate wastes, the relevant glass formulation with high waste loading can be engineered because only SiO_2 and other glass forming or modifying constituents such as Al_2O_3, MgO and CaO will be needed. PWR-borate glass can incorporate up to 45 wt.% of waste oxides.[6] Glass with appropriate modifiers can incorporate a wide variety of wastes ranging from high level wastes (HLW) to low and intermediate level wastes (LILW). China also developed HLW glass formulation named GC-12/9B and 90-19/U (Table 1), which can incorporate 16–20 wt% HLW at 1100°C or 1150°C; however, the operation temperature of SL-1 glass is 1000°C, which is an advantage for processing. It was also found that high waste loading (Na_2O and B_2O_3>30 wt.%) in SL-1 glass would lead to lower durability and higher corrosion rate in the final glass product.[7].

Previous attempts by Savannah River Technology Centre (SRTC) to immobilise spent ion exchange resin (IRN-77 ang IRN-78) used in Argentina nuclear power plant had shown considerable volatilisation of doped cobalt oxide (11 wt.%) and cesium oxide (29 wt.%) in the resin during vitrification. The operating temperature was 1150°C at around 30 wt.% waste loading. The vitrification process begins with a batch of glass compositions in nitrites aqueous form mixed with wet spent organic resin and heated gradually in platinum crucible (600 ml in experiments) to 1150°C. The reaction of the nitrites solution with the resin caused a sudden forceful gas burst at 300°C, despite that, the experiment was continued and the melting assumed to be corrected. The wt.% composition of the glass used by SRTC was 8.75 B_2O_3-14.23 CaO-21.35 Fe_2O_3-11.63 Na_2O-44.04 SiO_2[8].

The long-term objective of the present work is to increase the waste loading up to 60 wt.%, that will obviously need an increase in the liquidus temperature (T_L) along with the risk of formation of spinel-nepheline crystals and an increase in redox state. Acceptable range of redox according to the operational limits for the US Defense Waste Processing Facility (DWPF) melter is from 0.09 to 0.33 and a higher redox state is considered harmful for the refractory material of the melter.[9].

### Experimental Procedure

Borosilicate glass compositions (given in Table 2) were homogenously melted in high purity alumina crucibles at 1150°C in muffle furnace using the network formers SiO_2, and B_2O_3, intermediate Al_2O_3 and Fe_2O_3, and modifiers CaO (in the form CaF_2), Li_2O, PbO and Na_2O (Alfa Aesar, Purity 99.0 wt.%). It is noticeable that more than 75 wt.% of our glass compositions comprised SiO_2, B_2O_3, Fe_2O_3, Al_2O_3 and CaO, which enhanced the chemical durability of the final product.

The batches of HG-1/hard glass (in high purity alumina crucible, Crucible-A in Figure 1) and UOP-1 soft glass in mullite Crucible-B were placed in a muffle furnace and heated from ambient temperature to 1150°C at 2°C/min for 2 hours. Then, molten glasses were quenched to room
temperature by taking the crucibles out of the heated furnace. Cracks appeared in glass in crucible-B during cooling at ~170°C and the glass in crucible-A was thermally stable; however, both the glasses contained bubbles.

Table 2. The wt.% compositions of glasses melted in this study.

<table>
<thead>
<tr>
<th>Glass ID</th>
<th>SiO₂</th>
<th>Na₂O</th>
<th>B₂O₃</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>PbO</th>
<th>Li₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>UOP-1/soft glass</td>
<td>45</td>
<td>6.5</td>
<td>13.5</td>
<td>11.0</td>
<td>2.0</td>
<td>4.0</td>
<td>10.0</td>
<td>8.0</td>
</tr>
<tr>
<td>UOP-2/soft glass</td>
<td>45</td>
<td>6.5</td>
<td>13.5</td>
<td>11.0</td>
<td>2.0</td>
<td>2.0</td>
<td>10.0</td>
<td>8.0</td>
</tr>
<tr>
<td>HG-1/hard glass</td>
<td>52</td>
<td>5.2</td>
<td>7.8</td>
<td>11.0</td>
<td>2.0</td>
<td>4.0</td>
<td>10.0</td>
<td>8.0</td>
</tr>
<tr>
<td>HG-2/hard glass</td>
<td>52</td>
<td>5.2</td>
<td>7.8</td>
<td>13.0</td>
<td>2.0</td>
<td>2.0</td>
<td>10.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Phase analysis of the glasses was carried out using X-ray Diffraction (JEOL JDX 3532, Japan) with a CuKα source. A JEOL JSM5910 Scanning Electron Microscope (SEM) operating at 30 kV was used to investigate the crystalline inclusions, bubbles and pores within the glass matrix. The final compositions were analyzed using X-ray fluorescence (XRF- Panalytical XIROS, PW-4400124, Netherland). The data are listed in Table 3. In the first stage, the raw glasses HG and UOP (without additives) were analyzed to calculate the concentration of boron oxide (only) in the final glass because boron could not be detected using XRF which was 100 - 91.1 = 8.9 wt.% for HG and 100 - 81.1 = 18.9 wt.% for UOP glass. After calculating the boron concentration, 65 wt.% of HG and UOP each, were independently mixed with 35 wt.% additives to prepare HG-1, UOP-1, HG-2 and UOP-2 glasses to get a rough estimate of lithium oxide (again not detectable with XRF) as 100 minus the rest of the glass composition (e.g. 100 - 91.98 = 8.02 wt% for HG-1 glass) as given in Table 3.
Table 3. XRF results for raw and modified glasses

<table>
<thead>
<tr>
<th>Glass ID</th>
<th>SiO\textsubscript{2}</th>
<th>Fe\textsubscript{2}O\textsubscript{3}</th>
<th>PbO</th>
<th>Na\textsubscript{2}O</th>
<th>CaO</th>
<th>B\textsubscript{2}O\textsubscript{3}</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
<th>Li\textsubscript{2}O</th>
<th>Total</th>
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<tr>
<td>HG</td>
<td>83.5</td>
<td>0</td>
<td>4.5</td>
<td>0</td>
<td>8.9</td>
<td>3.1</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>HG-1</td>
<td>54.3</td>
<td>11.0</td>
<td>10.0</td>
<td>2.9</td>
<td>3.9</td>
<td>5.78</td>
<td>4.1</td>
<td>8.02</td>
<td>100</td>
</tr>
<tr>
<td>HG-2</td>
<td>54.3</td>
<td>12.8</td>
<td>10.2</td>
<td>2.9</td>
<td>1.8</td>
<td>5.78</td>
<td>4.1</td>
<td>8.12</td>
<td>100</td>
</tr>
<tr>
<td>UOP</td>
<td>73.5</td>
<td>0</td>
<td>4.5</td>
<td>0</td>
<td>18.9</td>
<td>3.1</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>UOP-1</td>
<td>46.7</td>
<td>10.6</td>
<td>9.5</td>
<td>2.8</td>
<td>3.8</td>
<td>12.3</td>
<td>7.1</td>
<td>7.2</td>
<td>100</td>
</tr>
<tr>
<td>UOP-2</td>
<td>46.6</td>
<td>12.6</td>
<td>9.6</td>
<td>2.9</td>
<td>1.9</td>
<td>12.3</td>
<td>7.1</td>
<td>7.0</td>
<td>100</td>
</tr>
</tbody>
</table>

\*65% \times 8.9 = 5.78, 65% \times 18.9 = 12.3

A glass Dilatometer (Orton 2010 STD) was used to measure the linear expansion coefficient at 20 to 750°C. Thermal expansion coefficient (TEC) of the melted glasses was also measured to investigate the possible reason of cracking in both the UOP glasses.

Results

The presence of small diffraction peaks on the XRD spectra from HG-1 and UOP-1 glasses (Figure 2) indicated the presence of a small amount of crystalline content. This indicated incomplete or inhomogeneous dissolution of initial ingredients, probably due to the short melting duration (2h). The observed XRD peaks from HG-1 glass matched ICDD card# 300024 for AlFeO\textsubscript{3}, ICDD card# 380471 for Al\textsubscript{2}SiO\textsubscript{5} and ICDD card# 410894 for Al\textsubscript{8}Fe\textsubscript{2}Si labeled as A, B and C respectively in Figure 2. Crystalline phases in UOP-1 glass were identified as Fe\textsubscript{2}SiO\textsubscript{4} (ICDD card# 340178), Al\textsubscript{8}Fe\textsubscript{2}Si (ICDD card# 410894) and Al\textsubscript{3}FeSi\textsubscript{2} (ICDD card# 520917), labeled as D, E and F respectively in Figure 2.

Figure 2. XRD patterns of UOP-1 and HG-1 glasses melted in the first batch showing peaks due to crystalline phases over the amorphous hump.
SEM analysis revealed that both the glasses contained bubbles (Figure 3) due to incomplete refining. These bubbles may be due to fluorine gas evolved as a result of thermal decomposition of calcium fluoride and reaction of other modifiers within the ternary system (Si-Na-B).

The refining process helps to remove the static bubbles and diffuse the emitted gases into the fluorine bubbles \[10\]. Complete refining process can occur by increasing the melting temperature or extending the reaction time in the melter \[11\]. Visual observation of these bubbles during the melting reveals that they were rising up in the molten glass rapidly and accelerated the homogenization of the molten glass. It is obvious that bubbles are extracted faster in glasses having lower viscosities (\(\eta\)) and TEC than those having higher \(\eta\) and TEC. Figure 4 shows the schematic of fining gases (reaction gases) diffusing into the fluorine gas. The glass-forming melt is initially distributed in the form of drops or thin layers coating solid particles. As its amount grows, the islands of melted components join into a connected body with open pores (or vent holes through which gases can easily escape), or closed pores (bubbles that either blow the mixture into a foam or move them upwards due to buoyancy in the case of less viscous melts). The mixture becomes a fluid with suspended refractory grains and bubbles \[12\]. An observation of the melting process of 4 wt.% CaO (in the form of CaF\(_2\)) containing glass batch at 2°C/min ramping rate shows that the mixture blows into foam (Figure 5a). The same procedure was repeated using longer holding time (4 h) at the same temperature (1150°C) with 2 wt.% CaO content. It was observed that the bubbles move upward due to buoyancy (Figure 5b).

Figure 3. Secondary electron SEM micrograph from vertical cross section of HG-1 glass showing the formation of bubbles.
Figure 4. Schematic of the process showing the effect of fluorine gas that causes the bubbles to rise to the surface of the glass.

XRD spectra of the resulting glass (HG-2) showed that the glass was fully amorphous (Figure 6). The three peaks at $\approx 38.49^\circ$ ($d = 2.336\text{Å}$), $44.73^\circ$ ($d = 2.024\text{Å}$) and $65.15^\circ$ ($d = 1.43\text{Å}$) observed on the XRD patterns from HG-2 glass were due to aluminum metal (ICDD# 40787) of the sample holder. It was observed that HG-2 glass was bubble-free with good thermal stability while UOP-1 glass cracked at $\approx 170^\circ\text{C}$. Vertical cross section of HG-2 was taken to analyze its microstructure using SEM analysis (Figure 7).

Figure 5. Ordinary Camera photograph showing a) the molten glasses blowing into foam and b) the blowing of glass foaming within acceptable range.
Analysis of percentage linear coefficient (PLC) of both glasses revealed the presence of boron oxide (13.5 wt.%) in UOP-2 glass, causing a sudden decrease in PLC at 170°C (Figure 8), and consequently, caused cracking upon cooling of the melt. In contrast, the presence of relatively lower (5.78 wt.%) boron oxide content in HG-2 glass resulted in the formation of a thermally stable glass. SEM micrograph of HG-2 glass shows the glass without significant content of crystal formation (Figure 8).

Thermal expansion coefficient (TEC) for UOP-2 glass was higher than that for HG-2 glass due to variations in boron oxide and silica initial concentrations. PLC also showed a decrease in the glass transition temperature ($T_g$) for UOP-2 glass (530°C) in comparison to the HG-2 glass (550°C) which were determined using two
contracted lines drawn on the curves shown in Figure 8.
Assuming $T_L \approx 3/2 T_g$ (empirical Kauzmann rule) \cite{14}, one can roughly assess $T_L$ as

$$T_L = (550+273) \times 3/2 = 1234K = 961°C$$

for HG-2 glass

$$T_L = (530+273) \times 3/2 = 1204K = 931°C$$

for UOP-2 glass

$T_g$ and $T_L$ could be substantially lowered by increasing the amount of fluxing additives \textit{i.e.}, lithium oxide and boron oxide to initial glass compositions. Low $T_g$ and $T_L$ glasses desirably decrease the volatilization of hazardous or radioactive species during vitrification. Volatilization of Cesium-137 and Technitium-99 is an inherent problem during vitrification at temperatures ranging from 1000 to 1200°C; therefore, the melt pool is normally covered by a cold cap generated by heat transfer from the molten glass to the water from the feed (wet feed). High radionuclide volatilization can occur in the days when the cold cap is burned out (dry feed), which decreases the efficiency of radio-nuclides incorporated in the glass and may give rise to the risk of radiation exposure \cite{15}.

Figure 8. Percentage linear coefficients (PLC) for UOP-2 and HG-2 glasses and its relevant glass transition temperatures ($T_g$).

**Conclusions**

Glass melting is a complex process governed by several parameters including initial compositions, melting temperature, heating and cooling rates, and the type of equipment used. The main conclusions of the present study can be summarized as follows:

1. Two types of bubble- and crystal-free novel alkaline borosilicate glasses (UOP-1, HG-1) were melted to assess their melting process, microstructure and thermal coefficient of expansion.

2. Appropriate proportions of boron oxide in the batch lowers the melting point, viscosity and coefficient of thermal expansion, and enhances the thermal stability and chemical durability of the glass; however, high concentrations (13.5 wt.\%) of boron oxide or using mullite crucible (might cause alumina contamination) caused cracking of UOP-1 and UOP-2 glasses upon cooling.

3. The formation of crystal-free glass after 4 h melting at 1150°C (as confirmed by XRD and SEM) indicated that this is the optimal time duration at 1150°C for the dissolution of initial ingredients and formation of a homogeneous glass. Shorter melting duration (2 hours) resulted in an inhomogeneous glass with crystalline inclusions.

4. Microstructural analysis of the final glass (HG-2) and visual examination of the melting process indicated that 2 wt.% CaO (in form of CaF$_2$) is an optimal concentration to refine the glass and avoid foaming.

5. Appropriate concentrations of boron oxide, lithium oxide, lead oxide and...
sodium oxide play a key role in reducing $T_g$ and $T_L$ of the final glass without affecting its thermal stability. The lower $T_L$ for UOP-2 glass (931°C) than HG-2 glass (961°C) is favorable for optimizing a glass used in vitrification; however, that advantage becomes insignificant as the final product cracked upon cooling.

The study is underway to investigate the chemical durability and lower $T_L$ of the new generation of HG glasses. These factors are expected to improve the glass ability for incorporating spent ion exchange resin used in the nuclear industry.

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