Studies on Novel Matrices for High Level Waste from Fast Reactor Fuel Reprocessing

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Abstract

High level waste (HLW) originating from aqueous reprocessing of fast reactor fuels consists mainly of fission products, minor actinides and noble metals which are higher in concentration compared to that from thermal reactors. Borosilicate glass may not be an efficient matrix to fix this waste. Similarly, chloride HLW arising from the pyro-metallurgical reprocessing has poor solubility in borosilicate glass. The present study explores various alternate systems consisting of a glass (iron phosphate glass, IPG), ceramic (monazite) and glass-ceramic (apatite) for the immobilization of such HLW. Studies related to synthesis, thermal stability and waste loading, point to the potential of the three matrices to emerge as viable waste forms for different types of HLW.

1. Introduction

Borosilicate glass [1] is the most acceptable matrix for the immobilization of high level aqueous waste (HLW) arising from reprocessing of thermal reactor nuclear fuel. However, the HLW originating from fast reactor consists of fission products, minor actinides, noble metals and volatile alkali oxides, which are higher in concentration compared to that from thermal reactors. Hence it is essential to investigate alternate matrices suitable for HLW of fast reactor fuels. The present study illustrates the feasibility of iron phosphate glass and monazite as the potential matrices for the incorporation of HLW arising from fast reactors.

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The HLW arising from pyro-metallurgical reprocessing also needs to be immobilized in a suitable matrix. The most widely reported waste form in this regard is a glass-bonded sodalite [2]. However the waste loading is low. We report here the immobilization of 20 wt% LiCl-KCl eutectic mixture and 20 wt% oxide waste of fast reactor origin in IPG. Chlorapatite, a naturally occurring mineral, is capable of incorporating chloride in its crystal structure and can be a promising alternate matrix for the immobilization of pyro-metallurgical waste. The present work demonstrates the feasibility of a chlorapatite waste form suitable for the pyrometallurgical waste.

2. Iron phosphate glass

Iron phosphate glass is considered as an alternate glass for the immobilization of HLW due to its salient features like good glass forming ability, very high waste loading and favourable chemical stability [3,4]. Among the various compositions of IPG, the glass with Fe/P ratio of 0.67 is found to be chemically the most durable [5].

![Fig. 1 XRD pattern of the IPG and its waste form](image1)

Iron phosphate glass waste form containing 20 wt % simulated waste (Table 1) was prepared by homogenizing waste oxides with reagent grade Fe$_2$O$_3$ and NH$_4$H$_2$PO$_4$ maintaining Fe/P ratio as 0.67. The mixture was heated to 1323 K.
Table 1. Simulated HLW composition

<table>
<thead>
<tr>
<th>HLW Oxide</th>
<th>Wt.%</th>
<th>HLW Oxide</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag₂O</td>
<td>0.73</td>
<td>TiO₂</td>
<td>0.10</td>
</tr>
<tr>
<td>BaO</td>
<td>3.75</td>
<td>NiO</td>
<td>0.77</td>
</tr>
<tr>
<td>CdO</td>
<td>0.33</td>
<td>Fe₂O₃</td>
<td>2.78</td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>6.27</td>
<td>Eu₂O₃ (Eu+Am)</td>
<td>1.54</td>
</tr>
<tr>
<td>Cs₂O</td>
<td>10.41</td>
<td>Gd₂O₃ (Gd+Pr+Nd+Sm)</td>
<td>0.84</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.38</td>
<td>Nd₂O₃</td>
<td>9.66</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>3.42</td>
<td>PdO</td>
<td>6.86</td>
</tr>
<tr>
<td>MoO₃ (Mo+Tc)</td>
<td>14.73</td>
<td>Pr₂O₁₁</td>
<td>3.45</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.15</td>
<td>Rh₂O₃</td>
<td>2.99</td>
</tr>
<tr>
<td>Rb₂O</td>
<td>0.49</td>
<td>Ru₂O₂</td>
<td>9.97</td>
</tr>
<tr>
<td>SnO₂</td>
<td>0.41</td>
<td>Sm₃O₃</td>
<td>2.73</td>
</tr>
<tr>
<td>SrO</td>
<td>1.19</td>
<td>TeO₂</td>
<td>1.38</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>8.49</td>
<td>Y₂O₃</td>
<td>0.73</td>
</tr>
<tr>
<td>U₃O₈ (U+Pu)</td>
<td>5.47</td>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>

by melt-quench technique. The molten mixture was air quenched in a graphite mold. Similarly, binary IPG was also prepared by melt–quench technique by heating the glass formers to 1423 K. The air quenched products were characterized by XRD. Density of the IPG and IPG waste form was measured at room temperature by Archimedes method using dibutyl phthalate as the medium of suspension. The glass transition temperature (T_g) was measured by using Differential Scanning Calorimeter (DSC) (M/s. Mettler Toledo DSC 821e/700). Thermal stability was determined by a simultaneous TGA/DTA (M/s. Setaram) system. All these thermal characterizations were carried out at 10 K/min in flowing Ar (50 ml/min) atmosphere. Pt crucibles were used as sample containers. The error in the temperature measurement was ± 1K.

Surface morphology was examined by Scanning Electron Microscopy (SEM). Thermal expansion was measured by a home built push rod dilatometer in air up to 750 K at a heating rate of 2 K/min. High density thoria pellets were used as standards. The amorphous nature of the IPG and IPG waste form were confirmed by XRD as shown in Fig. The density of IPG waste form was 3.1 g/cc, whereas that of IPG was 2.9 g/cc. The higher density indicates the effect of waste loading in the matrix. SEM (Fig 2) showed the homogeneous nature of the glass and its waste form. Glass transition temperature of the IPG was 783 K, whereas that of IPG waste form was 785 K. It is well known that addition of alkali and alkaline earth oxides reduces the thermal stability of the glass and addition of heavy metal oxides in turn increases the thermal stability. Since the waste oxides contain both types of oxides, the T_g of the waste form is not altered and it is similar to that of IPG. No detectable weight loss was observed from TGA curve (Fig. 3). The liquidus temperature (T_L), crystallization temperature (T_c) and T_g are shown in Fig. 3. Two stage crystallization was observed for IPG whereas IPG waste form undergoes single stage crystallization as observed from the DTA curve. Thermal expansion behaviours of IPG and its
waste form are shown in Fig. 4. Thermal expansion of the waste loaded iron phosphate glass is similar to that of IPG which reveals that the expansion behavior is not altered by waste loading. Thus the thermal stability of the waste loaded IPG is found to be similar to that of pristine IPG.

![Graph showing thermal expansion of IPG and waste form](image)

Fig. 4 Thermal expansion behaviour of IPG and its waste form

The feasibility of immobilizing pyrometallurgical chloride waste in IPG was studied by incorporating 20 wt% LiCl-KCl eutectic. IPG glass formers and the eutectic salt were together melted at 1223 K and air quenched. XRD showed the air quenched melt to be amorphous. XRF analysis of the eutectic salt loaded glass showed the absence of chloride in the sample. The chloride salts might have decomposed. The glass transition temperature was found to be 768 K (Fig. 5). These initial results show that if IPG is to be a host for pyro-metallurgical chloride waste, the chlorine gas evolved during processing must be treated separately.

![Graph showing DSC curve](image)

Fig. 5 DSC curve showing the glass transition temperature of eutectic salt loaded IPG

3. Monazite

Monazites are mixed rare-earth orthophosphate minerals. The fact that natural monazites exist for billions of years with appreciable amounts of thorium and uranium has led to the suggestions [6] that analogs of these minerals would be ideal hosts for the immobilization of HLW. The advantage of monazite as the ceramic host is that it is single phase and accommodates all the elements of the HLW as solid solution in its crystal lattice. A monazite waste form based on CePO₄ was fabricated by synthesizing the powders by a solution chemistry route. High density monoliths were made by cold pressing and sintering in air at 1473 K. Simulated FBTR waste composition (Table 1) with up to 30 wt% loading was prepared. The XRD characterization showed the formation of single phase monazite as given in Fig. 6. The linear thermal expansion of 10 wt % simulated waste-loaded CePO₄ monazite was measured in air up to 900 K using a home-built quartz push-rod dilatometer and by high temperature XRD. Fig. 7 compares the dilatometric results with the HTXRD measurement [7].
4. Apatite

Apatites are another class of naturally occurring phosphate minerals with the general formula $M_{10}(PO_4)_6X_2$, where $M = Ca, Sr, Ba$, $X = OH^-, Cl^-, F^-, CO_3^{2-}$ [8]. Apatites can tolerate non-stoichiometry in their cation and anion sub-lattices; thus they can incorporate cations and anions from the waste solutions to a large extent in the structure without collapsing the crystal structure. Further, apatites are highly resistant to leaching and can be easily prepared by low temperature ($773-1073$ K) methods of synthesis, which is a pre-requisite to avoid loss of volatile fission products from the HLW while processing. Ca-chloroapatite matrices were prepared by mixing $Ca(OH)_2$, $NH_4H_2PO_4$ and $NH_4Cl$ in a stoichiometric proportion and heat-treating the reaction mixture within $773-1073$ K/4 h in air. Phase pure $Ca_{10}(PO_4)_6Cl_2$ was obtained. The waste loading of the Ca-chloroapatite was carried out by adding simulated chloride waste (LiCl, KCl, NaCl, CsCl, BaCl$_2$, NdCl$_3$, CeCl$_3$) to the Ca-chloroapatite forming agents (i.e $Ca(OH)_2$ and $NH_4H_2PO_4$) and glass forming reagents (SiO$_2$, B$_2$O$_3$ and Na$_2$O). The mixture was thoroughly mixed and ground and heat-treated at $773-1073$ K/4h in air. The formation of Ca-chloroapatite and waste loaded (16-32 wt. %) glass-ceramic was examined by XRD and various other techniques.
The XRD patterns in Fig. 8 confirm the formation of phase pure Ca-chloroapatite and apatite glass-ceramics. 16 wt. % waste loading is feasible based on the preliminary leaching studies, XRD and SEM-EDAX examination of the matrices. In Fig. 8, even though 32 wt. % waste loaded Ca-chloroapatite-glass ceramic showed only the presence of Ca-chloroapatite crystalline phase, it showed higher leaching of Cl\(^-\) with deionized water. The thermal expansion characteristics of Ca\(_{10}(PO_4)\)_6Cl\(_2\) and 16 wt. % waste loaded pellets (10 mm dia and 10 mm height) were found to be nearly the same indicating 16 wt. % waste loading did not significantly affect the thermal expansion behavior of the Ca-chloroapatite matrix (Fig.9).

**Fig. 8** The XRD pattern of Ca\(_{10}(PO_4)\)_6Cl\(_2\) and 16-32 wt. % waste loaded apatite glass-ceramics

**Fig. 9** Percentage thermal expansion of Ca\(_{10}(PO_4)\)_6Cl\(_2\) and 16 wt. % waste loaded Ca-chloroapatite glass-ceramics by dilatometry

**References**