Glass waste forms for heat-generating Cs$^+$ and Sr^{2+} wastes from pyro-processing

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1. Introduction

Pyro-processing is one of the promising recycling technologies for spent nuclear fuel (SNF) from Light Water Reactors (LWR) in Korea [1]. This processing is able to separate radioactive waste nuclei and reduce heat loading in storage site by extraction of heat-generating radioactive nuclei (e.g. Cs$^+$, Sr^{2+}). During the pyro-processing, radioactive Cs$^+$ and Sr^{2+} ions are generated. Cs$^+$ will be captured by fly ash filter in an oxide form during the off-gas treatment. On the other hand, radioactive Sr^{2+} will be removed during the salt waste treatment in the chemical forms SrCO$_3$ mixed with BaCO$_3$. After decomposition of carbonate under high temperature, remaining oxide forms of Sr^{2+} and Ba^{2+} are to be immobilized. Up to present, several aluminosilicate and borosilicate glasses were investigated as potential hosts for Cs$^+$ and Sr^{2+} ions [2, 3]. In this study, we used alumino-borosilicate glasses for the immobilization of Cs$_2$O and SrO wastes. Glasses were prepared and their important properties including chemical durability were analyzed. In addition, heat generation and its effect on thermal stability of glasses was examined.

2. Experimental procedures

2.1. Glass preparation

Glass samples were produced by melting the mixture of surrogated non-radioactive waste components with glass frit powders. 2/3 of the final glass weight was made of fly ash filter containing captured Cs$^+$ with a final composition of 60SiO$_2$-25Al$_2$O$_3$-15Cs$_2$O (wt.%). Remaining 1/3 was composed of B$_2$O$_3$, CaO, Na$_2$O powders added to decrease the melting temperature. Final nominal composition (wt.%) of glass was 40SiO$_2$-16.67Al$_2$O$_3$-10B$_2$O$_3$-15.83Na$_2$O-7.5CaO-10Cs$_2$O that is equivalent of 66.7wt.% waste loading. Melting was done at 1200℃ for 45 minutes using an alumina crucible.

Sr^{2+} waste glass was prepared directly from the oxides and carbonates. Weight ratio of BaO/SrO = 5:12 was used based on the ratio normally found from the wastes. Overall glass composition (wt.%) was 40SiO$_2$-

8.3Al$_2$O$_3$-18.5B$_2$O$_3$-6Na$_2$O-19.2BaO-8SrO with the waste loading of 27.2wt.%. Powders were melted at 1200℃ for one hour in a platinum crucible to avoid alumina contamination. All glass specimens were annealed at 400℃ for one hour to remove the residual thermal stress.

2.2. Characterization

Densities of glasses were measured at room temperature using the Archimedes method with DI water as immersion fluid. DTA (Differential Thermal Analyzer) was used to record the glass transition temperatures. Approximately 25mg of glass powder was placed in platinum pans under N$_2$ condition and heated from room temperature to 700℃ with a 10℃/min heating rate. TMA (Thermomechanical Analyzer) was used to measure the linear expansion coefficient with 2×2×10mm rectangular parallelepiped bulk specimens. Specimens were heated from room temperature to the softening temperature with 10℃/min heating rate under N$_2$ atmosphere. X-ray diffraction patterns of fine glass powders were recorded X-ray diffractometer Cu-Kα radiation at 40kV and a current of 100mA.

2.3. Chemical durability

Product consistency test (PCT) was conducted to examine the chemical durability of waste glasses. Glass powders with 75~150μm in diameter were mixed with de-ionized (DI) water and placed in a Teflon container at 90℃ for seven days. Concentrations of dissolved elements in the solution were measured by ICP-AES or ICP-MS. Normalized elemental mass release (g/m^2) was calculated from following equation (1).

$$r_i = \frac{c_i}{f_i\left(S/V\right)} \quad (1)$$

c$_i$ corresponds to a concentration of certain element "i" in the leachate(μg/cm^3). f$_i$ is the elemental mass fraction of certain element "i" in glass (unitless). S is the overall surface area of particles which is assumed to be

spherical shape with an average diameter of 112μm. V is the volume of DI water used as leachate.

3. Results

3.1. Compositions and properties

Glasses prepared were bubble free and visually transparent. XRD patterns of both Cs_2O and SrO waste glasses proved non-crystalline nature of the glasses (Fig.1). Retention of of Cs_2O in the Cs^+-waste glass after melting was about 89.1% and Sr^{2+} volatilization did not occur from SrO waste glass (Table I). Densities of Cs_2O and SrO waste glasses were $2.611g/cm^3$, $3.070g/cm^3$ and glass transition temperatures (T_g) were 535℃ and 587℃, respectively. Linear expansion coefficients of Cs_2O and SrO waste glasses were $9.97\times10^{-6}/℃$, $7.78\times10^{-6}/℃$. All these properties were comparable to those of the typical high level waste borosilicate glass [4] of which density, T_g and a linear expansion coefficient are $\sim2.7g/cm^3$, $<550℃$ and $8.0\times10^{-6}/℃$, respectively.
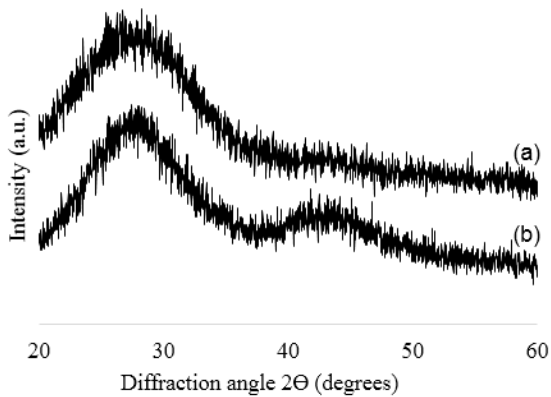

Fig. 1. XRD patterns of (a) Cs_2O waste glass and (b) SrO waste glass.

Table I: Analysis of glass compositions by ICP-AES, ICP-MS and XRF.

Compositions (oxide form)	Cs^+-glass (wt.%)		Sr^{2+}-glass (wt.%)	
	Nominal	Analyzed	Nominal	Analyzed
SiO_2	40	38.36	40	34.52
Al_2O_3	16.67	17.57	8.3	8.78
B_2O_3	10	10.24	18.5	18.05
Na_2O	15.83	17.48	6	7.50
CaO	7.5	7.44	-	-
Cs_2O	10	8.91	-	-
BaO	-		19.2	22.91
SrO	-		8	8.23

3.2. Chemical durability

Results of normalized elemental mass release from Cs_2O and SrO waste glasses are in Table II. Values of all elements from both glasses were well below the reference value of $2.0g/m^2$ for Low-Activity Waste (LAW) glass of the United States Department of Energy (DoE) regulation.

Table I: Normalized elemental mass release (g/m^2) values of Cs_2O glass and SrO glasses obtained from PCT.

Elements	Normalized elemental release (g/m^2)	
	Cs^+-glass	Sr^{2+}-glass
Si	0.100	0.133
Al	0.099	0.003
B	0.207	0.637
Na	0.399	0.693
Ca	0.016	-
Cs	0.137	-
Ba	-	0.296
Sr	-	0.388

4. Simulation on heat generation during the storage

4.1. Assumptions and conditions

It is assumed that pyro-processing was done using the spent nuclear fuel. 4.5% enriched, 55,000MWd/TU, 1MTU PWR after ten years of cooling. It is known that specific elemental thermal power in this spent fuel for Cs^+ and Sr^{2+} are 262W/4070g, 110W/1230g, respectively. Under the normal operation, cylindrical canisters containing radioactive waste glasses inside a long-term storage facility will be under the well-controlled cooling system. However, in case of unexpected failure of the cooling system, temperature inside the canister may rise due to the heat generated from the Cs^+ and Sr^{2+} wastes. Therefore, it is necessary to anticipate the temperature of glass and canisters under the conditions when cooling is entirely dependent on the natural convection of air.

4.2. Governing equations

The dominant heat transfer mechanisms considered are conduction of glass and stainless steel cask with convection of surrounding air. Conductive heat transfer of the cylindrical coordination follows the relationship in equation (2). While, Newton's law of cooling in equation (3) shows the convective heat transfer. Upon the failure of the cooling system, temperature of glass will asymptotically approach to the thermally steady-state for a short period (~a week) compared to the half-life of ^{137}Cs (~30.17 years) and ^{90}Sr (~28.90 years). At this steady-state, right hand side of equation (2) becomes negligible and the relationship can be expressed using equation (4).

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{1}{r^2}\frac{\partial^2 T}{\partial \phi^2} + \frac{\partial^2 T}{\partial z^2} + \frac{q}{k} = \frac{1}{\alpha}\frac{\partial T}{\partial t} \quad (2)$$

$$q = hA(T_s - T_\infty) \quad (3)$$

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{1}{r^2}\frac{\partial^2 T}{\partial \phi^2} + \frac{\partial^2 T}{\partial z^2} + \frac{q}{k} = 0 \quad (4)$$

Variables in equations are q: specific thermal power, k: thermal conductivity of glass, α: thermal diffusivity (m^2/s), h: convective heat transfer coefficient (W/m²℃), A: surface area (m^2) T_s: surface temperature of canister (℃), T_∞: surrounding temperature (℃).

4.3. Computational analysis

ANSYS Workbench 16.2 was used to obtain the temperature gradient inside the canisters. Natural convection was applied to all surfaces of canister except for the bottom face. Total number of 13299 nodes and 7779 elements were used to cover the canister geometry. All properties used in simulation are presented in Table III.

Table IIII: Parameters and the specification of the canister used for simulation

Properties	Cs⁺-canister	Sr²⁺-canister
Specific thermal power (q)	$15836W/m^3$	$18570W/m^3$
Thermal conductivity of glass (k)	0.75W/m℃	
Thermal conductivity of stainless steel	14.8W/m℃	
Surrounding temperature (T_∞)	27℃	
Convective heat transfer coefficient (h)	5W/m²℃	
Effective surface area (A)	$1.2421m^2$	
Thickness of canister	6mm	

4.3. Temperature gradients of canister and h-k-T diagram

Fig. 2 shows the images of the cross sectional temperature gradient inside the canisters. Red region refers to the high temperature area with its highest value of 442.9℃ for Cs⁺-canister and 514.8℃ for Sr²⁺-canister. The maximum temperatures anticipated in the middle of the canisters are lower than T_g of both glasses. In addition, convective heat transfer coefficient and thermal conductivity may change during storage. Fig. 3 shows h-k-T diagram of two canisters and two curves are correspond to the possible combinations that will

increase the temperature up to the value of Tg. Thermal conductivity and convective heat transfer of normal atmosphere is show as a dot in Fig 3 and it is located at T<T_g. Therefore, glasses appear to be stable enough from self-heating issues even under the failure of cooling systems inside the depository.
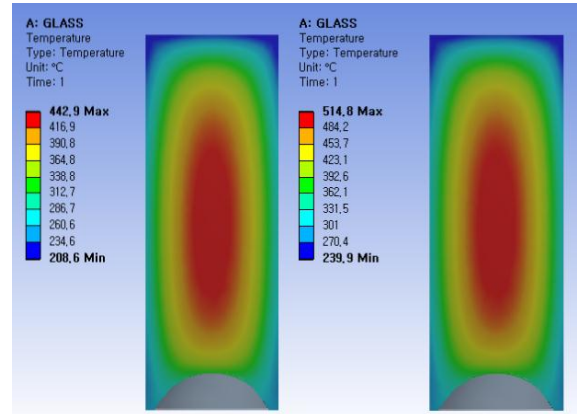

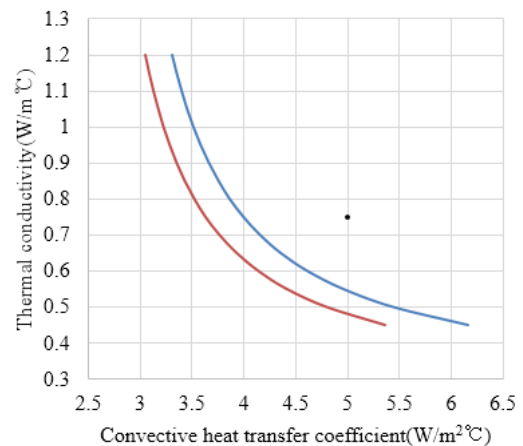Fig. 2. Cross sectional view of temperature gradient of the Cs⁺-canister (left) and Sr²⁺-canister (right).

Fig. 3. Convective heat transfer coefficient (h) – Thermal conductivity (k) – Maximum temperature (T) diagram. T=Tg lines of the Cs⁺-canister (Red curve) and Sr²⁺-canister (Blue curve). Simulated value are presented as a black dot.

4. Conclusions

Glass waste forms that contain heat-generating Cs⁺ and Sr²⁺ from pyro-processing were synthesized. Basic properties of glasses such as densities, linear expansion coefficients and glass-transition temperatures were similar to those of industrial radioactive waste glass. Analysis on the heat load simulation under the failure of the cooling system indicated that maximum temperature inside the canisters are well below the glass-transition temperature of each glass.

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