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

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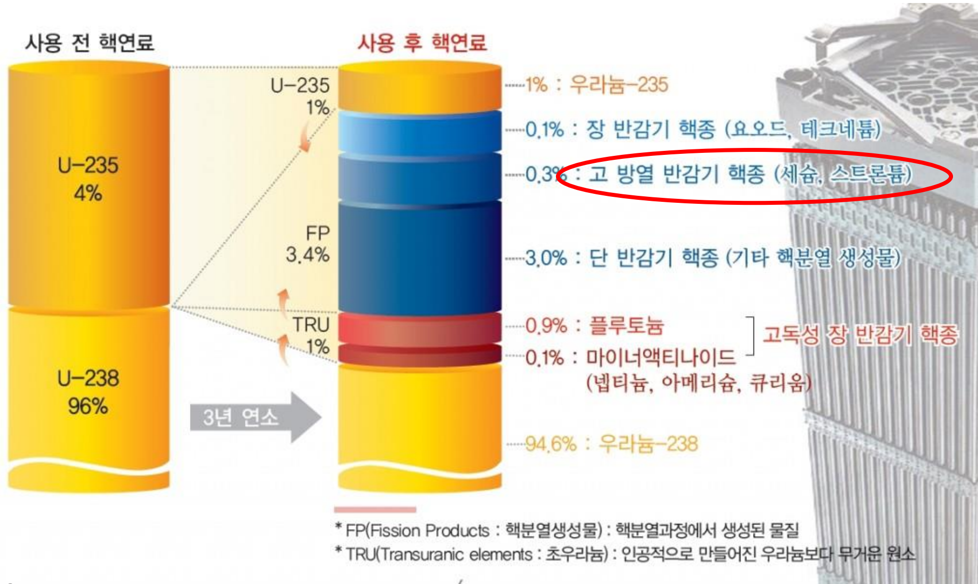
Contents

Introduction

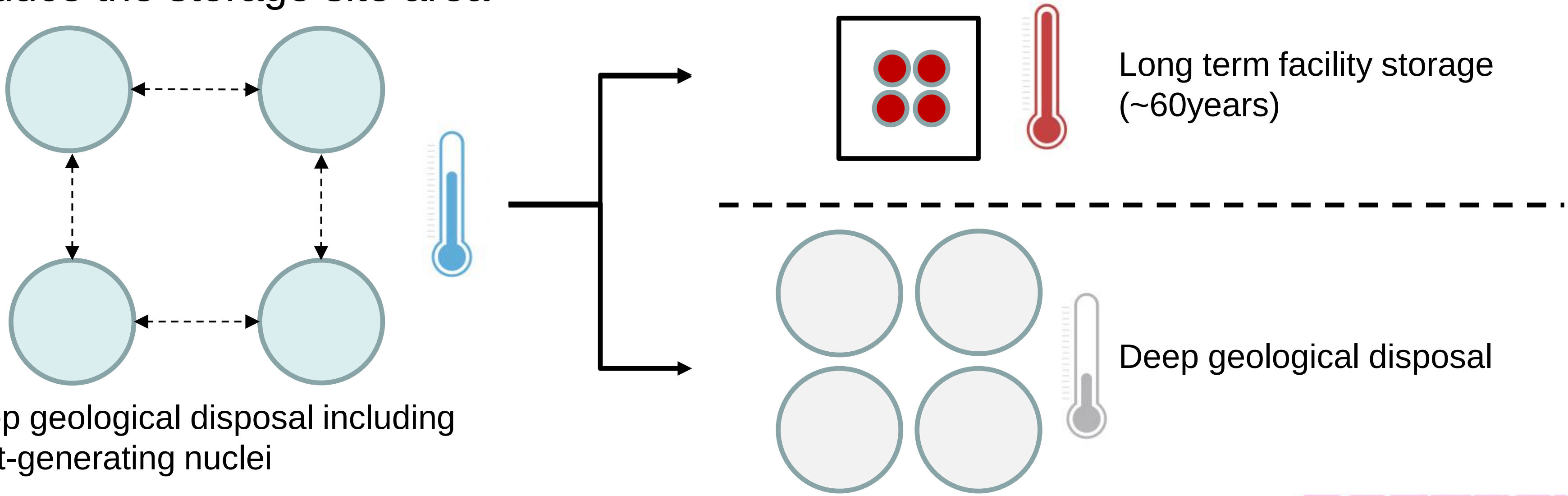
Spent nuclear fuel

We are considering spent nuclear fuel from 4.5%, 55,000MWd/TU, 1MTU PWR after ten years of cooling

Highly radioactive and short lived nuclei(e.g. ^{134}Cs) will decay during the cooling



Separation of heat-generating nuclei(^{137}Cs, ^{90}Sr: $t_{1/2}$~30years) from the rest of wastes can reduce the storage site area



Long term facility storage (~60years)

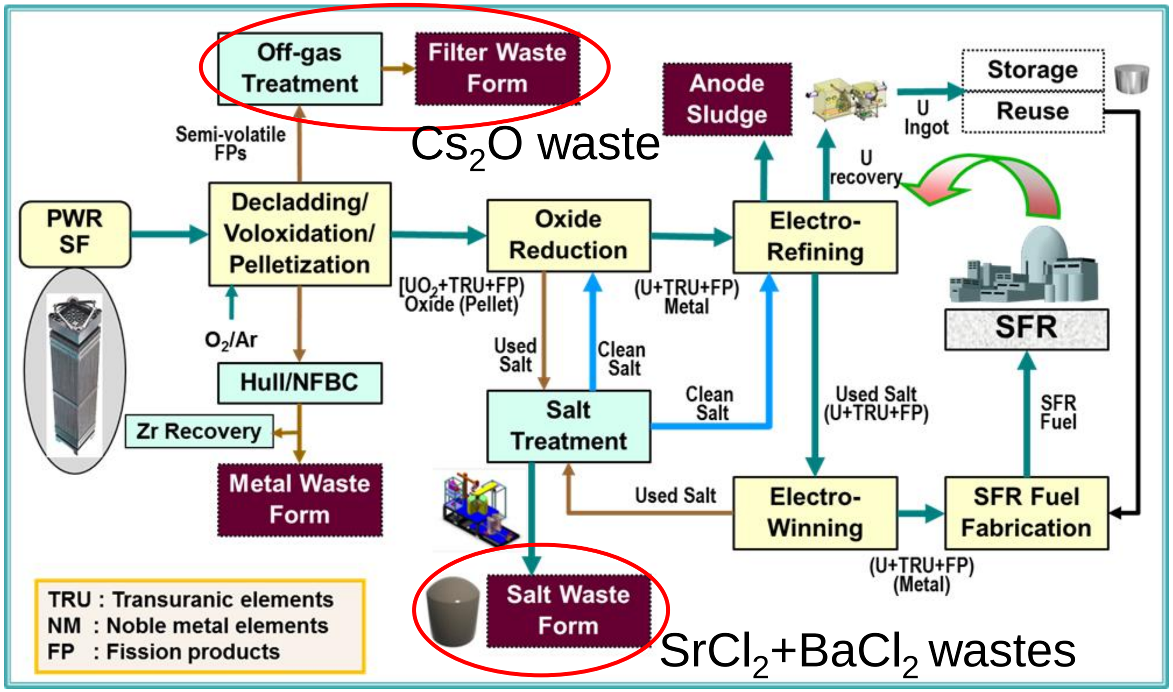
Deep geological disposal

Deep geological disposal including heat-generating nuclei

Figure: https://atomstory.or.kr/p/43773/

Introduction

Pyro-processing



Cs_2O waste

$SrCl_2$+$BaCl_2$ wastes

Elements	Concentrations [1]
Cs	4070g/t
Sr	1230g/t
Ba	3050g/t

Heat-generating(radioactive) Cs^+ and Sr^{2+} should be immobilize safely

Waste loading $\propto$ Heat load

Glass waste forms were used world wide for many years to immobilize heat-generating HLW since easy production, good chemical durability and thermal stability

Figure & 1) KAERI

Introduction

Cs^+ glass selection

(1) Given waste form

Cs^+ will be captured by fly ash filter[2] in an oxide form during the off-gas treatment (~1000℃)

$Cs_2O(g) + Al_2O_3 \cdot 4SiO_2(s) \rightarrow 2CsAlSi_2O_6(s)$

Compositions	Concentration (wt.%)
SiO_2	60
Al_2O_3	25
Cs_2O	15

(2) Glass design

Wastes
- Increasing melting temperature
- Increasing heat load

Glass frits
- B_2O_3, Na_2O, CaO were added to decrease the melting temperature

Cs_2O waste loading: 10wt.%
Melting temperature: ≤1200℃
(reduce volatilization of Cs_2O)
Chemical durability: <$2 g/m^2$

In previous research[3], 9.6wt.% loaded Cs containing borosilicate glass with CaO addition which improved the chemical durability of waste glass up to $1 g/m^2$ of B, Na, Cs PCT ri values

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2) 공개특허 10-2014-0052541
3) Banerjee, D., et al. "Physicochemical properties of Cs borosilicate glasses containing CaO." *Journal of Nuclear Materials* 413.3 (2011): 177-182.

Experiments & Results

Cs^+ glass preparation

Cs^+ contained fly ash filter waste + Glass frits

$^2/_3$ $^1/_3$

~18g mixed powder, alumina crucible

1200℃ 45m melt

Fast quenching

500℃ 2h annealing

Compositional analysis by ICP-AES, ICP-MS

Compositions	Cs^+ glass(wt.%)	
	nominal	analyzed
SiO_2	40	38.36
Al_2O_3	16.67	17.57
B_2O_3	10	10.24
Na_2O	15.83	17.48
CaO	7.5	7.44
Cs_2O	10	8.91

Volatilization of Cs_2O: 10.9%
Waste loading: 64.84 wt.%

Introduction

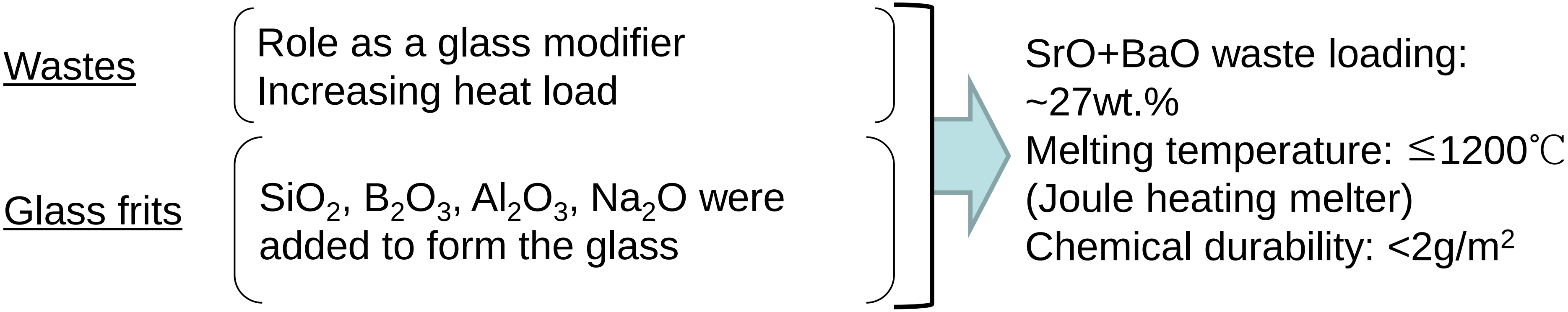
Sr^{2+} glass selection

(1) Given waste form

$SrCl_2$+$BaCl_2$ → $SrCO_3$, $BaCO_3$ wastes[3], exchanged chlorides (e.g. LiCl) can recycle into pyro-processing.

Residual SrO and BaO have 5:12 weight ratio after pyro-processing.

(2) Glass design



Wastes

Role as a glass modifier
Increasing heat load

Glass frits

SiO_2, B_2O_3, Al_2O_3, Na_2O were added to form the glass

SrO+BaO waste loading: ~27wt.%
Melting temperature: ≤1200℃ (Joule heating melter)
Chemical durability: <2g/m^2

30wt.% loaded Sr containing calcium aluminosilicate glass with 0.06g/m^2 of Sr PCT r_i value was produced from 1350℃ melting condition[4]

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[3] Cho, Yung-Zun, et al. "Carbonate reaction of alkaline-earth element by carbonate agent injection method." *Journal of nuclear science and technology*45.5 (2008): 459-463.

[4] Sengupta, Pranesh, Sara Fanara, and Sumit Chakraborty. "Preliminary study on calcium aluminosilicate glass as a potential host matrix for radioactive 90 Sr—An approach based on natural analogue study." *Journal of hazardous materials* 190.1 (2011): 229-239.

Experiments & Results

Sr^{2+} glass preparation

$SrCO_3$, $BaCO_3$ mixed wastes + Glass frits

~10g mixed powder, platinum crucible

1200℃ 1h melt

Fast quenching

500℃ 2h annealing

Compositional analysis by ICP-AES, ICP-MS, XRF

Compositions	Sr^{2+} glass(wt.%)	
	nominal	analyzed
SiO_2	40	34.52
Al_2O_3	8.3	8.78
B_2O_3	18.5	18.05
Na_2O	6	7.50
BaO	19.2	22.91
SrO	8	8.23

Volatilization of SrO: none
Waste loading: 31.14wt.%

Experiments & Results

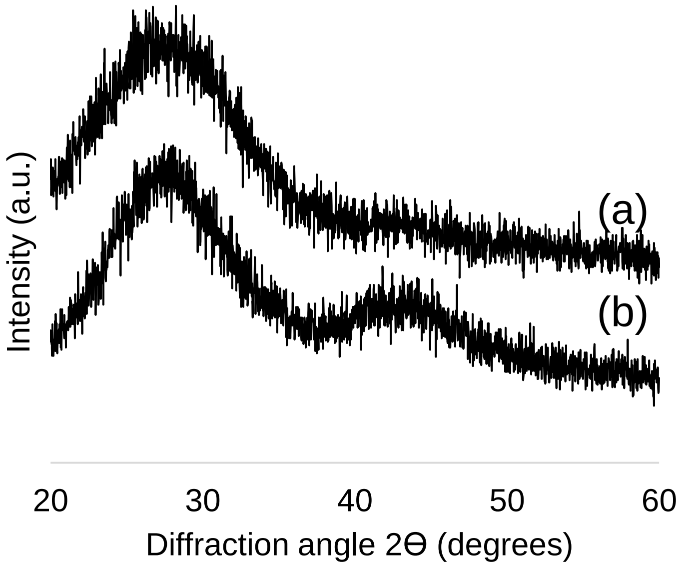
Characterization

XRD patterns of both Cs_2O (a) and SrO (b) waste glasses proved non-crystalline nature of the glasses

Density was measured by Archimedes method and DEP (Diethyl Phthalate, ρ=1.120g/cm^3) was used

Glass transition temperature(T_g) was measured by DTA (10℃/min heating rate)

Linear thermal expansion coefficient was measured by TMA (10℃/min heating rate) from RT to 500℃



Properties	Cs^+ glass	Sr^{2+} glass	HLW borosilicate glass$^{5)}$
Density	2.646g/cm^3	3.030g/cm^3	~2.7g/cm^3
Glass transition temperature	518℃	587℃	>550℃
Linear thermal expansion coefficient	9.97×10^{-6}/℃	7.78×10^{-6}/℃	8.1×10^{-6}/℃

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5) Ojovan, Michael I., and William E. Lee. *An introduction to nuclear waste immobilisation*. Newnes, 2013.

Experiments & Results

Chemical durability

PCT(Product Consistency Test)[6], which was developed specifically to measure the chemical durability of radioactive glass waste forms.

10ml DI water/g of 75μm~150μm(r_{avg}=56μm) powder in Teflon container in 90℃ for 7days.

$$\frac{SA}{V} = \frac{3w}{\rho r_{avg} V}$$

SA/V: Cs^+ glass=2051m^{-1}, Sr^{2+} glass=1798m^{-1}

Normalized elemental release(g/m^2) ⇒ $NL_i = \frac{c_i(\text{sample})}{(f_i) \cdot (SA/V)}$

Values of all elements from both glasses were well below the reference value of 2.0g/m^2 [7]

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

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6) ASTM C1285-14, Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT), ASTM International, West Conshohocken, PA, 2014

7) *Secondary Waste Form Down-selection Data Package: Fluidized Bed Steam Reforming Waste Form*. Pacific Northwest National Laboratory, 2011.

Thermal stability

Assumptions & conditions

Normal condition
(forced convection)

Accident
(cooling system failure)

Accident condition
(natural convection & thermal steady state)

(1) Canister

Material: stainless steel STS-304
Geometry: hollow cylindrical shape with concave bottom
In France and Japan[8], this kind of canister was successfully used for several decades.
We used diameter of 0.35m and 1m height canister.

(2) Thermal power

1) Elemental power density(W/g)[9]
Cs: 262W/4070g, Sr: 110W/1230g
2) Elemental concentration in glass(g/g)
3) Density of glass(g/cm^3)

Multiplication & unit conversion

Specific thermal power(W/m^3)

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[8] http://www.jnfl.co.jp/business-cycle/hlw/return-vitrified-object.html
[9] KAERI

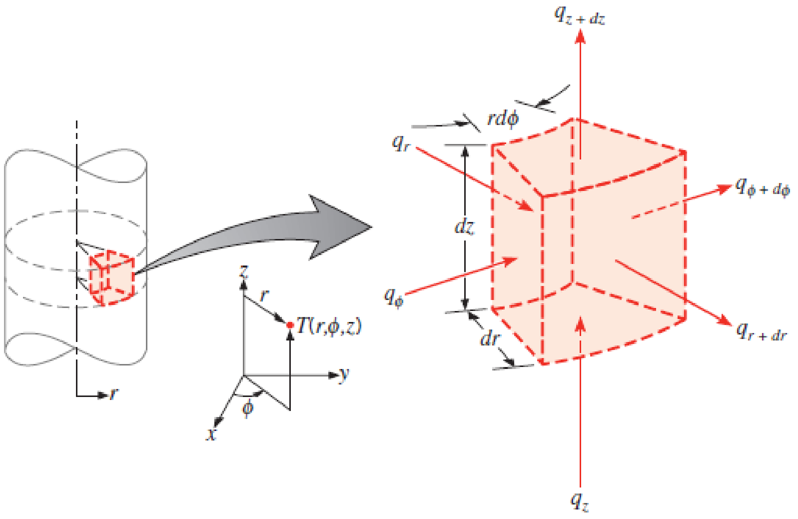
Thermal stability

Governing equations[10)]

(1) Conduction

Cylindrical coordination of heat conduction equation (1) governs the heat transfer of heat-generating glass.

$$\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}+\frac{1}{r^2}\frac{\partial^2 T}{\partial \phi^2}+\frac{\partial^2 T}{\partial z^2}+\frac{q}{k}=\cancelto{0}{\frac{1}{\alpha}\frac{\partial T}{\partial t}} \qquad (1)$$



q: specific thermal power (W/m³) ,k: thermal conductivity (W/m℃)
α: thermal diffusivity (m²/s)

Steady state, equation (1) → (2).

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

(2) Convection

Newtonian cooling equation (3) of ambient RT air will transfer heat from the canister surface to surrounding

$$q = hA(Ts - T_\infty) \qquad (3)$$

T_s: temperature of canister surface(℃) A: surface area(m²) T: surrounding temperature(℃)
h: convective heat transfer coefficient (W/m²℃)

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10) Bergman, Theodore L., Frank P. Incropera, and Adrienne S. Lavine. *Fundamentals of heat and mass transfer*. John Wiley & Sons, 2011.

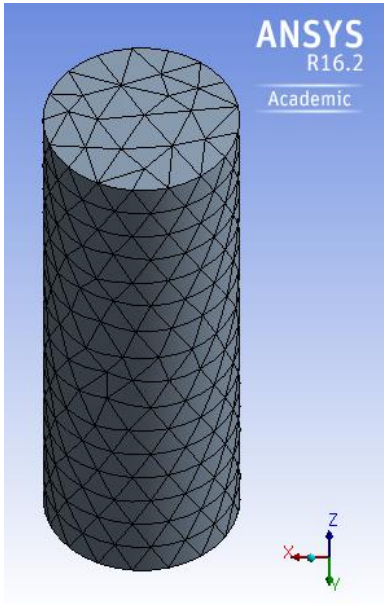
Thermal stability

Computational analysis[11)]

ANSYS 16.2 Workbench (Mechanical APDL) steady state thermal

Geometry of canister was meshed by 13299 nodes and 7779 elements
Volumetric heat-generation was applied to entire glass matrix.
Natural convection was applied to all surfaces of canister except for the bottom face.

Properties	Cs^+ glass	Sr^{2+} glass
Specific thermal power (q)	15.835kW/m^3	18.570kW/m^3
Thermal conductivity of glass (k)[12)]	0.75W/m℃	
Thermal conductivity of stainless steel	14.8W/m℃	
Surrounding temperature (T_∞)	27℃	
Natural convective heat transfer coefficient (h)[13)]	5W/m^2℃	
Effective surface area (A)	1.2421m^2	
Thickness of canister	6mm	



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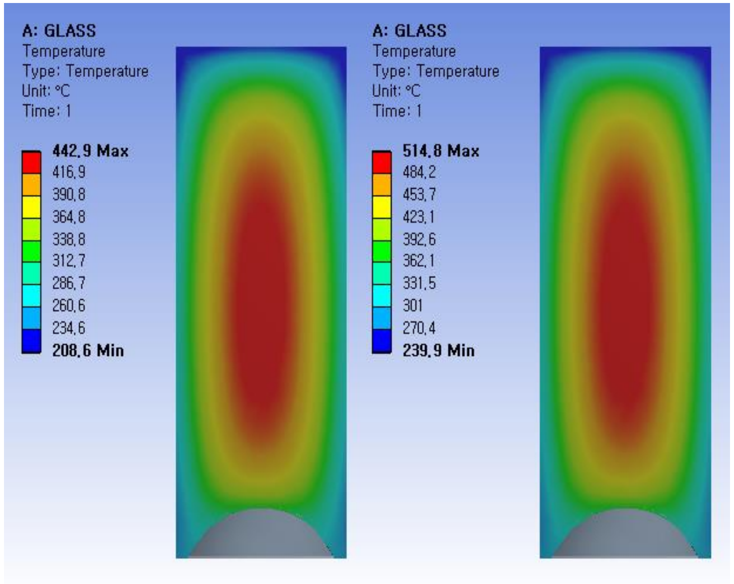
11) http://148.204.81.206/Ansys/150/ANSYS%20Mechanical%20APDL%20Thermal%20Analysis%20Guide.pdf
12) http://glassproperties.com/thermal-conductivity
13) https://www.ansys.kr/Uploaded_Files/2014Icepak/1_Management_of_Electronics_r1.0.pdf

Thermal stability

Graphical results

(1) Cross sectional temperature gradient

T_g of Cs^+ glass(518℃) > T_{Max} of Cs^+ glass(442.9℃)
T_g of Sr^+ glass(587℃) > T_{Max} of Sr^{2+} glass(514.8℃)

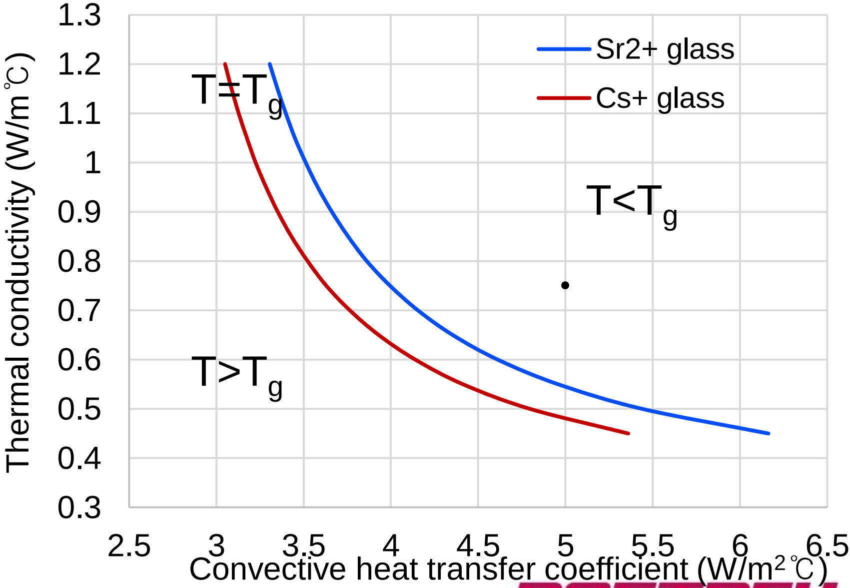


(1) h-k-T diagram

Two curves are correspond to the possible combinations that will increase the temperature up to the value of T_g.

Simulated accident condition was located at $T<T_g$ region

Glasses appear to be stable enough from self-heating issues even under the failure of cooling system



Conclusions

- We synthesized alumino-borosilicate glasses for heat-generating cesium and strontium

- Density, glass transition temperature, linear thermal expansion coefficient were measured and results were comparable to typical HLW glass

- Cs^+ and Sr^{2+} glasses were chemically durable

- 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.