A Study on Vitrification for LLW Radioactive Wastes - 16235

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ABSTRACT

Ash and ion exchange resin wastes to be vitrified were considered among various radioactive wastes in the Japanese nuclear industry. The appropriate glass composition for the waste is calculated using the computer program. The glass composition is systematically studied using a ternary diagram, considering viscosity, electrical conductivity, and durability. The optimized glass composition based on calculated parameters of vitrification process and the convenience of mixing wastes is selected for crucible experiment. Since differences between calculated values and measured values may occur upon evaluation of glass formulations using glass formulation computer simulation program, the calculated glass formulations should be verified through experiments on a laboratory scale for more meticulous development of glass formulations. For the follow-up development of glass formulations, several glass formulations are planned to be developed. The candidate glasses for treatment of ash and ion exchange resin were melted and fabricated using reagents, respectively. The chemicals were weighed out to produce the desired batch compositions and mixed thoroughly and then put into clay crucibles for melting. Next, the crucibles were introduced into an electric furnace at 1,150 ℃ in the ambient atmosphere and pressure with occasional stirring by a quartz rod. A hold time of 1 hour was introduced to promote homogenization. Finally, the melted material was poured on a graphite plate to be rapidly cooled. The viscosities of all fabricated glasses were in the desired range. After rapid cooling, the micro-structure of the glasses was analyzed using the SEM. They exhibited amorphous structure with good homogeneity.

INTRODUCTION

Since various types of Low-Level Waste (LLW) have been generated from the Japanese nuclear industry, various treatment methods, such as incineration, compaction, polymerization, and cementation, have been applied. Vitrification, converting nuclear wastes into a glass or glass-like substances through thermal process, is being actively considered as an efficient and reliable technology for treatment of LLW [1,2]. The vitrification starts with the base glass melting. After sufficient melting of base glass at certain temperature, usually 1,100 ~ 1,200 ℃, the target waste is introduced into the melted glass. The throughput and feeding rate is determined by the condition of the melted glass including glass composition, status of target waste, etc. The vitrification of the radioactive waste is completed with pouring of melted glass, consists of base glass and wastes. The vitrification offers various advantages such as simple and fast process, good physical and chemical durability of resulting glass, flexibility of the waste and glass composition, and high volume reduction effect [3,4].

RESULT AND DISCUSSION

In this paper, vitrification of ash and ion exchange resin (IER) are studied. The chemical composition of ash and IER, selected for the present study, is shown in Table 1 and 2. For the vitrification of the wastes, development of optimum glass composition is essential using the specific physicochemical characteristics of the wastes. The optimum glass composition satisfies the requirements of chemical durability like leach rate, mechanical durability of compressive strength, and processability such as electrical conductivity and viscosity with maximum waste loading.

The chemical composition of ash, selected for the present study, is shown in Table 1. The majority elements of ash are SiO_2, CaO, and Al_2O_3. The SiO_2, more than 40 wt% of the waste, is an important element to construct the structure of the borosilicate glass. The Al_2O_3 increases the viscosity and chemical durability. The CaO also affects the viscosity and generation of secondary phase of the glass.

Table1. Chemical composition for Ash

Oxide elements	Composition (wt%)
SiO_2	42.73
CaO	20.23
Al_2O_3	18.74
MgO	2.72
Na_2O	4.85
K_2O	1.61
Fe_2O_3	9.12
Total	100

The chemical composition of IER, selected for the present study, is shown in Table 2. The primary element of IER is Fe_2O_3. More than 85 wt% of IER is consists of Fe_2O_3. It is well known that Fe_2O_3 reduces the viscosity and increases the chemical durability of the glass.

Table 2. Chemical composition for IER

Oxide elements	**Composition (wt%)**
Fe_2O_3	89.1
Cr_2O_3	2.1
NiO	1.8
CoO	1.8
CuO	1.8
ZnO	1.8
Cs_2O	0.8
SrO	0.8
Total	100.0

The development procedure of optimum glass composition for vitrification is shown in Figure 1. Above all, the accurate characterization of target waste comes first. The computer simulation using program, Glass Form 1.1, follows to achieve the maximum waste loading with minimum additive glass. The lab scale glass melting test is implemented to observe the feasibility and physicochemical property of the candidate glass. The candidate glass is qualified as a final glass composition after the lab test. In development of candidate glasses for vitrification, inorganic materials composition affects the process variables such as viscosity and electrical conductivity, etc.

The computer simulation using program, Glass Form 1.1, enables development of chemically stable glass composition, in terms of phase stability and leach rate, with viscosity of ≤ 70 poise and electrical conductivity of ≥0.4 S/cm at a CCIM operation temperature of 1,150 ℃ using inorganic materials composition, waste loading, etc.

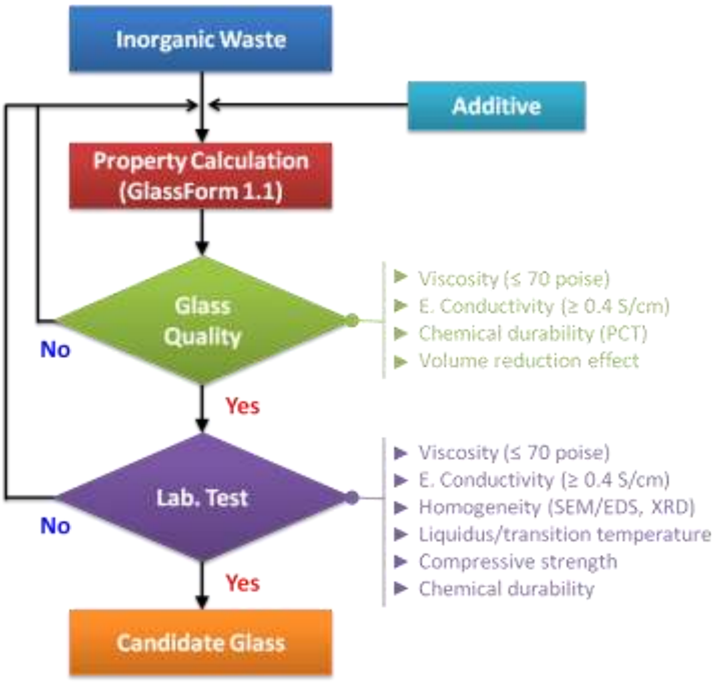


Figure 1. Procedure for development of candidate glass

In vitrification processes, amounts and chemical compositions capable of vitrifying wastes are determined by contents of inorganic materials contained in the wastes. Since the chemical compositions of a glass determine materials properties such as melting point, viscosity, compressive strength, and electrical conductivity of glass, selection of a suitable glass composition for a given radioactive waste can be considered to be the same as optimization of several variables under limiting conditions. Here, the limiting conditions include operation ease of the molten glass (viscosity, electrical conductivity, etc.) and characteristics of the vitrified form (chemical durability, compressive strength, etc.). In general, operation ease of the molten glass and characteristics of the vitrified form are known to have a trade-off relationship.

Chemical composition of the wastes produced in a nuclear power plant (NPP) can be largely divided into organic materials and inorganic materials. In vitrification processes, organic materials are processed mainly by an off-gas treatment system through thermal decomposition, while inorganic materials affect characteristics of the vitrified form. In the present study, computer simulation has been carried out based on inorganic oxide compositions of the wastes to conduct a study on glass compositions. Therefore, there can be a difference between the volume reduction ratio of the actual waste and the presented waste loading.

The glass composition for vitrification of ash is simulated based on the chemical composition of ash. The waste loading is controlled from 40 to 75 wt% with balancing SiO_2+B_2O_3 and other inorganic elements such as Li_2O, CaO, etc. In order to analyze the chemical durability of the resulting glass, 7-days PCT of Si, B, Li, and Na is calculated. For the operational aspect, viscosity and electrical conductivity are considered.

For the vitrification of ash, the optimization range of glass composition was derived using a ternary diagram with SiO_2 and B_2O_3, composing the glass structure of borosilicate glass, on the bottom, waste on the right and other components (alkali and alkaline earth oxides) on the left as shown in Figure 2. Each axis of the Ternary diagram has been set with the references as follows.

- SiO_2 + B_2O_3: The composition constituting the basic structure of glasses is denoted on the bottom side of the ternary diagram triangle.
- Waste (SiO_2, CaO, Al_2O_3, MgO, Na_2O, K_2O, Fe_2O_3): The sum of compositions of the waste contained in ash is denoted on the right side of the ternary diagram triangle.
- Others (Oxides: Li, Na, etc.): The sum of compositions of oxide as an additive to improve the glass quality upon glass manufacturing is denoted on the right side of the ternary diagram triangle.

In order to determine the appropriate glass composition range for ash, the scope of change of the modeling input values for viscosity, electrical conductivity and leaching rate was determined in the following manner:

- Waste: the sum of the waste components if at least one of the modeling values (viscosity, electrical conductivity, leaching rate) was lower or higher than the reference value when waste loading was varied by 5 wt% per time
- SiO_2 + B_2O_3 and other components: sum of the corresponding components when the waste content varied according to waste.
- The initial variation range of the components was set when the physiochemical property value for at least one of the values (viscosity, electrical conductivity, leaching rate) was lower or higher than the reference value.

The contents of SiO_2 + B_2O_3 was changed within the range of 40-75 wt% by 5 wt%. The waste and other components were controlled to balance total amount. The conformities of the viscosity, electrical conductivity, and leaching rate were assessed according to the corresponding compositions. As the waste loading changed, chemical compositions were generated in the horizontal direction and the glass former and glass modifier contents were adjusted to derive the glass compositions.

The results of ash glass composition assessment using a ternary diagram showed that the viscosities and electrical conductivity of the points in the overlapped area of Figure 2 were in the range of 11.4-76.5 poise and 0.56-0.74 S/cm, respectively. Viscosity has an effect in the processes of discharging glass and mixing glass with waste as well as the corrosion in the melting furnace. The higher or lower viscosity, compared to reference value, has a negative effect on the vitrification process. On the other hand, the left side in the diagram showed a high leaching rate (over 2 g/m^2) and was determined to have low chemical durability.

The optimal glass composition range with considerations of processability and glass quality was indicated as the optimized area in Figure 2, and the optimized glasses were selected for lab scale tests.

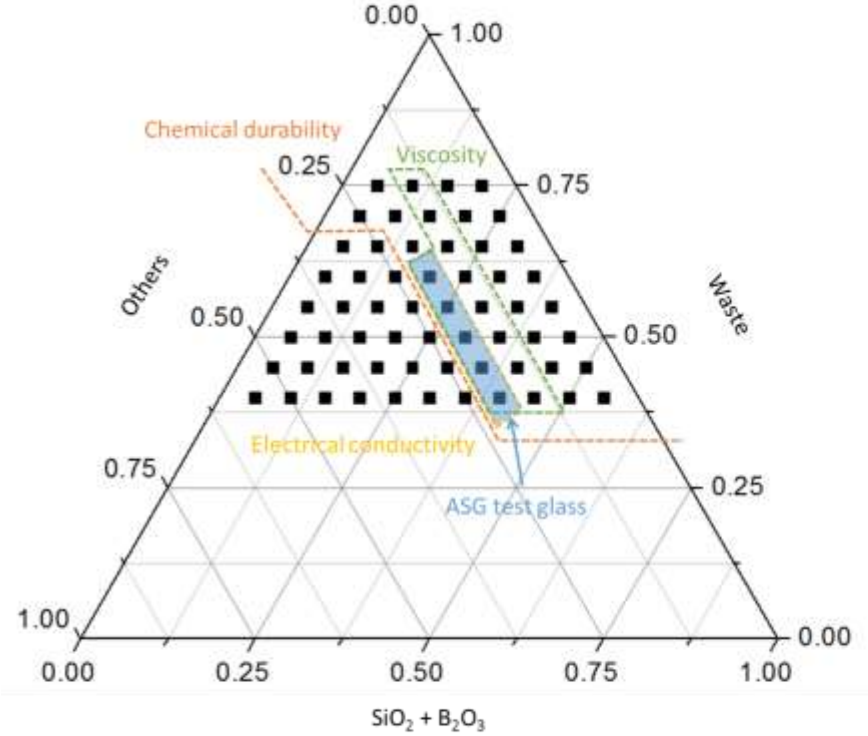


Figure 2. Ternary diagram for vitrification of ash

For the vitrification of ash, the optimization range of glass composition was derived using a ternary diagram with SiO_2 and B_2O_3, composing the glass structure of borosilicate glass, on the bottom, waste on the right and other components (alkali and alkaline earth oxides) on the left as shown in Figure 3. Each axis of the Ternary diagram has been set with the references as follows.

- SiO_2 + B_2O_3: The composition constituting the basic structure of glasses is denoted on the bottom side of the ternary diagram triangle.
- Waste (Fe_2O_3, Cr_2O_3, NiO, CoO, CuO, ZnO, Cs_2O, SrO): The sum of compositions of the waste contained in ash is denoted on the right side of the ternary diagram triangle.
- Others (Oxides: Li, Na, etc.): The sum of compositions of oxide as an additive to improve the glass quality upon glass manufacturing is denoted on the right side of the ternary diagram triangle.

The contents of SiO_2 + B_2O_3 was changed within the range of 20-35 wt% by 5 wt%. The waste and other components were controlled to balance total amount.

The conformities of the viscosity, electrical conductivity, and leaching rate were assessed according to the corresponding compositions. As the waste loading changed, chemical compositions were generated in the horizontal direction and the glass former and glass modifier contents were adjusted to derive the glass compositions.

The Fe_2O_3 is hard to be dissolved into the glass matrix. Since the IER has large amount of Fe_2O_3, the waste loading of the waste need to be carefully controlled, considering solubility. In this calculation, the concentration of the Fe_2O_3 is limited to 32 wt% of the total chemical composition of the glass. It is generally known that the dissolution concentration of the Fe_2O_3 is lower than that. However, the wide range of the Fe_2O_3 concentration is considered in this study for understanding of general behavior of the glass formation and chemistry. The strict analysis will be followed for the clear understanding of this type of glass, in terms of phase separation and homogeneity.

The results of the ash glass composition assessment using a ternary diagram showed that the viscosities and electrical conductivity of the points in the overlapped area of Figure 3 were in the range of 12.2-60.9 poise and 0.42-0.78 S/cm, respectively. Viscosity has an effect in the processes of discharging glass and mixing glass with waste as well as the corrosion in the melting furnace. The higher or lower viscosity, compared to reference value, has a negative effect on the vitrification process. On the other hand, the left side in the diagram showed a high leaching rate (over 2 g/m^2) and was determined to have low chemical durability.

The optimal glass composition range with considerations of processability and glass quality was indicated as the optimized area in Figure 3, and the optimized glasses were selected for lab scale tests.

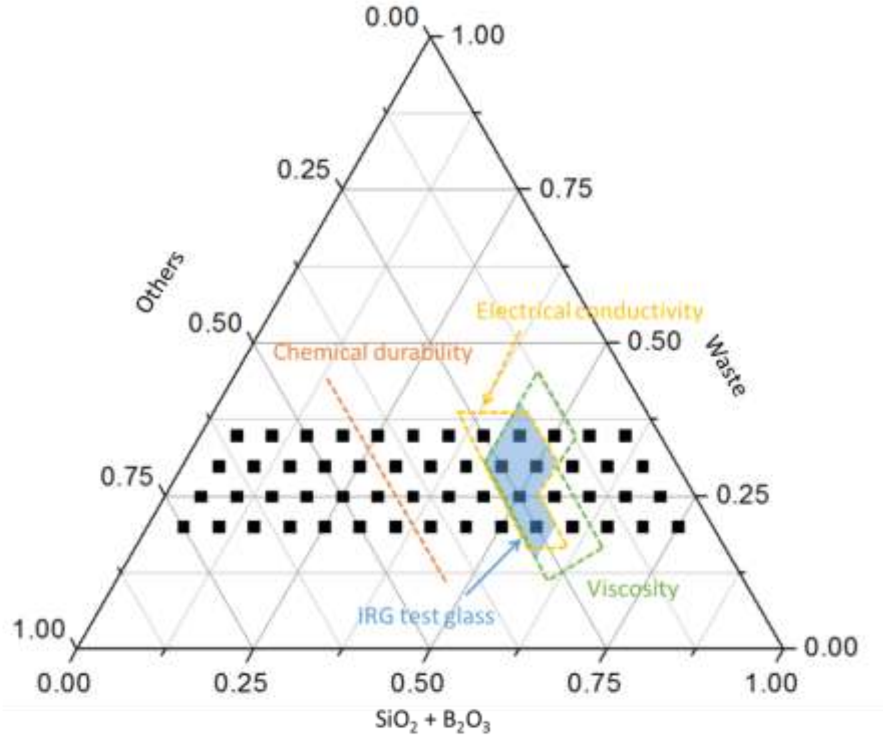


Figure 3. Ternary diagram for vitrification of IER

The laboratory test was followed to verify the suitable glass formulation for vitrification of ash. Clay crucibles and 200-300 g of batch chemicals were prepared for lab test. The batch of chemicals, made according to the glass formulations, was transferred into a clay crucible and was melted at a temperature of 1,150 °C with heating rate of 3 °C/min in $MoSi_2$ electrically heated furnace. When the temperature reached 1,150 °C, the clay crucible was taken out and the molten glass was mixed homogeneously using a quartz rod. It was then inserted into the electrically heated furnace again to be melted at 1,150 °C for 15 minutes before being poured into a graphite mold to be cooled and manufactured into glass.

When tracing the metal precipitate phenomena during the glass fabrication process, in situ observation with naked eye has resolution limit. However, the method offers quick analysis with reasonable accuracy for certain amount of precipitation, especially at the interface between glass and crucible.

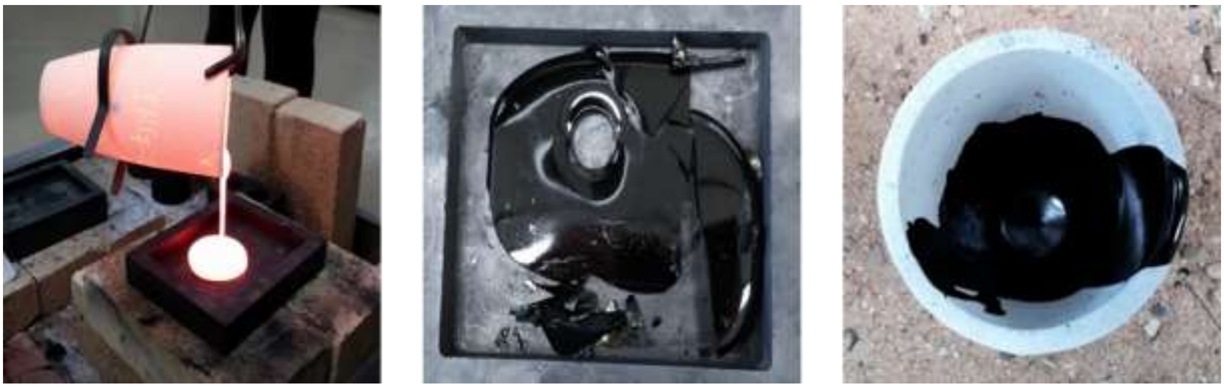
The Figure 4, 5, 6, and 7 shows that the fabricated ASG_45_35, ASG_50_30, IRG_25_55, and IRG_30_50 glass. Respectively. The fabricated glass exhibited reasonable viscosity and good homogeneity, without any precipitation. According to the in situ evaluation, it is found that the chemicals were sufficiently dissolved without any un-melted lumps around the clay crucible.

(a) (b) (c)

Figure 4. Fabrication of ASG_45_35 glass: (a) melting and pouring of glass, (b) cooled glass, and (c) clay crucible after glass fabrication

(a) (b) (c)

Figure 5. Fabrication of ASG_50_30 glass: (a) melting and pouring of glass, (b) cooled glass, and (c) clay crucible after glass fabrication



(a) (b) (c)

Figure 6. Fabrication of IRG_25_55 glass: (a) melting and pouring of glass, (b) cooled glass, and (c) clay crucible after glass fabrication

(a) (b) (c)

Figure 7. Fabrication of IRG_30_50 glass: (a) melting and pouring of glass, (b) cooled glass, and (c) clay crucible after glass fabrication

The detailed homogeneity of the glass surface was evaluated through an observation using the SEM. The surface of glasses, which were fabricated using the optimized glass composition, is analyzed with the 1,000 times magnified SEM images. When the backscattering mode is used during the SEM analysis, the presence of heterogeneous particles, i.e. crystal, is indicated as a white spot. According to the SEM images, shown in Figure 8, it suggests that the fabricated glass is homogeneous.

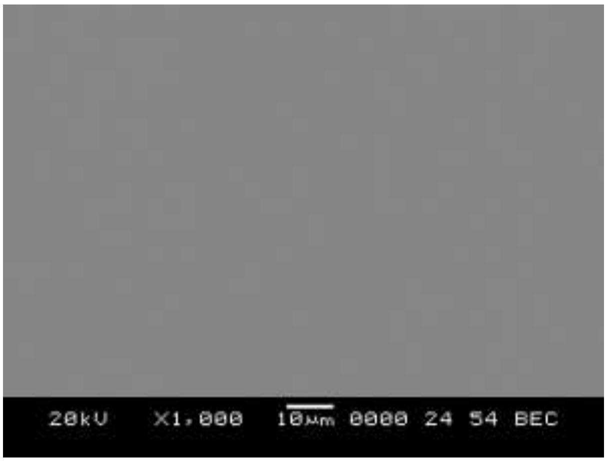


Figure 8. SEM image for ASG_45_35 (representatively shown)

CONCLUSION

The chemical compositions of target wastes, ash and IER are investigated and quantitatively evaluated. The glass composition is calculated using the obtained waste composition. The viscosity, electrical conductivity, and chemical durability of the calculated glasses are studied using ternary diagram. The systematic ternary diagram study offers the optimized chemical composition. The lab test is followed using the optimized chemical composition for vitrification of ash and IER, respectively. During lab test, the viscosity, homogeneity, and solubility are studied. For the detailed analysis of the glass structure, SEM analysis is followed. The results indicate that the fabricated glass exhibits reasonable viscosity and good homogeneity without any precipitation.

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