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Characteristics of Vitrification Process and Vitrified Form for Radioactive Waste

방사성폐기물 유리화 공정 및 유리고화체 특성

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Abstract

In order to vitrify the combustible dry active waste (DAW) generated from Korean Nuclear Power Plants, a glass formulation development based on waste composition was performed. A borosilicate glass, DG-2, was formulated to vitrify the DAW in an induction cold crucible melter (CCM). The processability, product performance, and volume reduction effect of the candidate glass were evaluated using a computer code and were measured experimentally in the laboratory and CCM. The glass viscosity and electrical conductivity as the process parameters were in the desired ranges. Start-up and maintaining glass melt of the candidate glass were favorable in the CCM. The product of the glass product such as chemical durability, phase stability, and density was satisfactory. The vitrification process using the candidate glass was also evaluated assuming that it was operated as economically as possible.

Key Words : dry active waste (DAW), glass formulation, CCM, viscosity and electrical conductivity

I. Introduction

Conversion of hazardous and radioactive wastes into a stable glass through vitrification processes, with a typical thermal process, is increasingly being considered for treating various wastes and an appealing technology for waste treatment because it is the flexibility of the process in treating a wide variety of waste streams and contaminants, can achieve large waste volume reductions with about more than 1/20, can create a durable waste form, and can destroy organic compounds more effectively than other competing technologies such as polymerization, cementation, and ceramic formation. Vitrification in borosilicate glass was selected as the best technology because of the high durability and ease of processing of the wasteform[1].

In order to vitrify the combustible dry active waste (DAW) such as working clothes, cotton gloves, working shoes, decontamination paper, plastic bag, rubber shoes, etc. generated from Korean Nuclear Power Plants, the study on optimized glass formulation development based on waste composition was performed at NETEC, KHNP. The optimization of constrained multivariables in this process is the key in developing the viable glass formulation technology. As such, it is therefore essential to recognize and state clearly both the imposed constraints and the key variables in the work. The constraints can usually be summarized in three categories: processability, product performance, and volume reduction effect[2]. As shown in Fig. 1, a candidate glass formulation to treat the DAW was formulated through the property calculation using a computer code, laboratory test, and pilot test using the CCM. Process parameters such as viscosity and electrical conductivity, product quality such as leach rate and microstructure of the glass, and volume reduction effect were evaluated as the major considerations for formulating the candidate glass.

II. Computer Modeling for Glass Formulation

In order to formulate the candidate glass for the DAW, the following oxides were selected as the major components to form the borosilicate glass matrix: SiO_2, B_2O_3, Na_2O, Li_2O, CaO, MgO, Fe_2O_3, and Al_2O_3. Each of the oxides may be melted with a second oxide or mixture of oxides and the melt cooled to form a glass, but there are usually limits to percentages of other oxides which may be added. The properties of candidate glass compositions were calculated using property models embedded within a computer code (GlassForm 1.1)[3]. Since the property models are linear, the waste glass composition must fall within the bounds over which the models were developed. Extrapolation of the models to glass compositions that fall outside the bounds of the model will produce inaccurate results. To extend the bounds

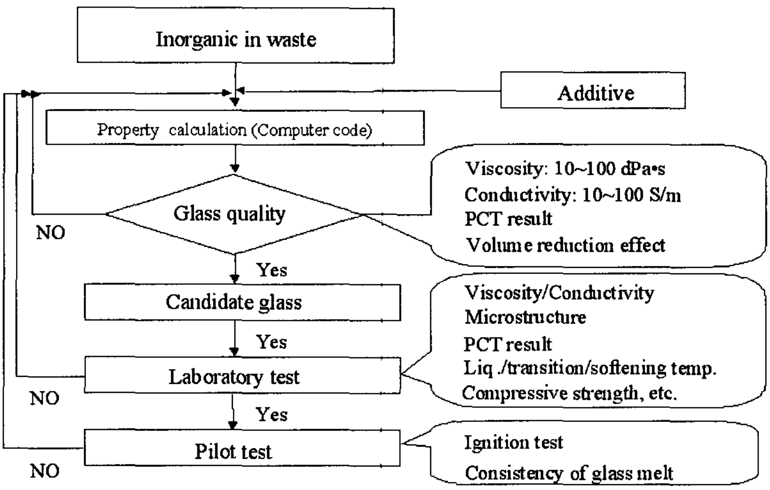

Fig. 1. Flow diagram for formulation and test of candidate glass

Table 1. Composition range of linear glass composition property models

Model Bounds	SiO_2	B_2O_3	Na_2O	Li_2O	CaO	MgO	Fe_2O_3	Al_2O_3	Others
Lower	37%	5%	5%	0%	0%	0%	0%	0%	0%
Upper	57%	25%	25%	8%	13%	2%	5%	16%	10%

of the model, a composition variation study is required. The composition range of the linear glass property models is in Table 1.

III. Experimental Methods

There are several experimental methods, procedures and techniques that were used to obtain data in this study. The bulk glass which was used in this experiment was made by weighing out raw chemicals and by mixing and melting together. And then, a pilot scale test using the CCM was conducted to evaluate its workability and reliability.

In preparing the glasses for the laboratory test, the chemicals were weighed out to produce the desired batch compositions and mixed thoroughly, put into clay crucible, and then thrown into a high temperature furnace of 1,423K(1,150 ℃) in air at ambient pressure for 1 hour. The melt was stirred manually to ensure homogeneous chemical mixture. Finally, the glass melt was poured on to a graphite plate to obtain a rapid cooling rate, and a glass sample was taken to examine its property.

In order to evaluate the ignition and consistency of glass melt of the DG-2 glass in the CCM, 70kg of DG-2 glass frit was loaded inside of the CCM. The high frequency generator supplied the energy to 0.07kg of Ti-ring inside the DG-2 glass to ignite it and maintain the glass melt after ignition completed. The DAW and DG-2Base frit were simultaneously fed into the CCM with 20 and 25kg/h at a nominal and maximum feed rates, respectively. Three glass samples, i.e., initial, middle and final glass samples, were taken during the pilot test to analyze their physico-chemical properties.

Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) was used for microstructural evaluation in this study. The SEM was equipped with an Oxford energy dispersive x-ray spectrometer (INCA energy) and digital image acquisition and analysis system. The US DOE product consistency test (PCT) was used to evaluate the relative chemical durability of the glass by measuring the concentrations of the chemical species released from crushed glass (75-149㎛) to the test solution (deionized water). PCT test of the candidate glass was performed at 363K(90 ℃). The ratio of the glass surface area to the solution volume for this test is about $2000m^{-1}$. The test was conducted for 7 days[4]. 1 ml of leachate was mixed with 20 ml of 1M HNO_3 and the resulting solution was analyzed by ICP-AES. Sample of glass was subjected to total acid dissolution in mixture of HF and HNO_3, and the resulting solution analyzed by ICP-AES for all constituents.

IV. Results and Discussion

The properties of glass formulation for vitrification of low-and intermediate-level radioactive waste (LILW) were calculated using the modeling program. As a result of the efforts to glass formulation development, DG-2Base as an additive and DG-2 as a candidate glass were obtained using the computer code[3], laboratory and pilot test as shown in Table 2.

1. Processability

Data on melt viscosity and electrical conductivity, that is key processing parameters, are summarized in Table 3. There was in good agreement between the values of viscosity and electrical conductivity obtained by the computer code[3] and those of viscosity and electrical conductivity evaluated by oxygen bubbling method and impedance value of the pilot facility, respectively. It is shown that a relationship between glass properties and glass composition was able to be reliable. Thus, the model what we made was acceptable to predict these process parameters. The viscosity and electrical conductivity of the melt are of considerable importance if the induction CCM technology is used. For the purpose of the study, we have considered a process which requires melt viscosity of 10-100dPa · s(poise) and electrical conductivity of 10-100S/m at processing temperature of 1,423K(1,150°C)[5]. Consequently, two major process parameters for the DG-2 glass were in the desired ranges.

In order to evaluate the ignition and consistency of glass melt of the DG-2 glass in the CCM, 70kg of DG-2 glass frit was loaded inside of the CCM. Next, the high frequency generator (HFG) supplied the energy to ignite the Ti-ring(0.07kg) and maintain the glass melt in the CCM. It was easy to ignite the Ti-ring and to propagate the ignition energy into the DG-2 glass. The Ti-ring was uniformly energized up by the HFG as shown in Fig. 2(a). The DG-2 glass frit was initially melted by the combination energy of the ignition and the HFG. After the ignition completed, it was easy to maintain the glass melt as shown in Fig. 2(b) since the glass is electrically conductive at the operating temperature.

2. Product Performance

The estimated density of the DG-2 glass through the 1st order computer code[3] was to be 2.65g/cm³ and met the constraint. To get a favorable waste with density above 2.5g/cm³[1],

Table 2. Additive (DG-2Base) and candidate glass (DG-2) for vitrification of the DAW

	DG-2Base	DG-2
SiO_2	55.00	41.25
Alkali oxides	20.00	19.78
B_2O_3	15.00	11.29
Al_2O_3	8.00	7.07
Alkali-earth oxides	0.50	14.40
Transition metal oxides	0.00	5.09
Others	1.50	1.10

Table 3. Physico-chemical properties of the candidate glass (DG-2), † @ 1,423K

		DG-2
Computer coding & Lab. test	Density (g/cm³)	2.65
	Viscosity (dPa · s) †	10
	E. conductivity (S/m) †	46
	Mineral loading(%)	25
	Volume Reduction Factor (= vol. of initial waste/vol. of vitrified form)	175
	SEM/EDS observation	Final waste glass @ 1,423K: Homogeneous
	PCT	Leach rates below benchmark glass
Pilot test	Ignition	Favorable in CCM
	Consistency of glass melt †	Easy to control

innocuous components (e.g., water, carbon dioxide, etc.) in the waste form should be removed.

SEM/EDS was used to examine the final waste glass. According to the SEM/EDS observation, there was no secondary phase formation in the DG-2 glass matrix as shown in SEM micrograph (Fig. 3).

The standard leaching test for radioactive waste glass, the US DOE Product Consistency Test (PCT), was used to evaluate the leach resistance of the poured glasses during the initial, middle and final stage of the pilot test. The results used computer calculation and obtained after the nominal 7-day leaching period were in good agreement. The PCT data for four elements showed very small changes in the glass composition compared to the benchmark glass (SRL-EA). There is a good reason to believe that this behavior is related to the addition of additives such as ZrO_2, Al_2O_3, and B_2O_3. It has a stabilizing effect on the leaching behavior and suppresses, or at least delays, or the rise in the leach rate. Leach rates, in grams per square meter of glass are shown in Fig. 4.

3. Volume Reduction Effect

A minimum additive waste stabilization (MAWS) approach was used to achieve high waste loading to the extent of 25% in terms of inorganic mineral basis. Thus, only 75% of additive would be sufficient to vitrify the DAW at 1,423K(1,150°C). And the volume reduction factor was evaluated to be 175. Additive impacts the overall volume reduction effect from several perspectives. First is the direct cost of the additive itself. Second is the cost associated with using the non-waste additive into the process, which will include a combination of additional operating costs (labor, utilities, etc.) and increased capital costs, depending on whether the additive is accommodated by increasing the size of the process or the length of the production run. Third is the increased disposal costs since a certain fraction of the volume of the waste form is composed of purchased additive, but not waste. Since disposal of the final stabilized waste form

(a) (b)

Fig. 2. Ignition of Ti-ring(a) and maintaining glass melt(b) of DG-2 glass in the CCM

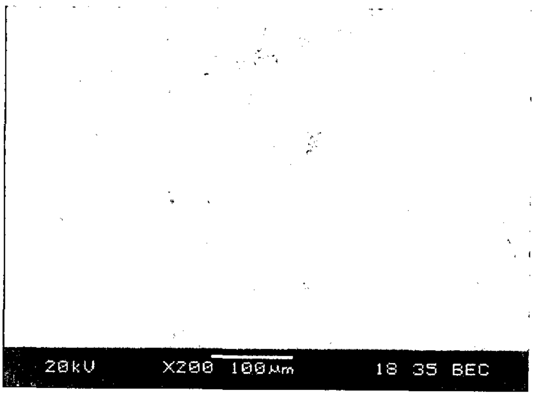

Fig. 3. SEM micrograph of final waste glass matrix

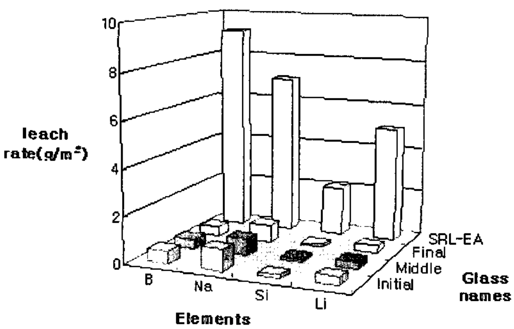

Fig. 4. 7-day PCT leach rates for B, Na, Si, & Li of initial, middle and final poured glasses compared to benchmark glass (SRL-EA)

invariably incurs a per-unit-volume disposal cost, the volume change upon stabilization is an important economic factor. Processes in which the volume is decreased upon stabilization are therefore favorable over those in which the volume is increased.

V. Conclusions

The candidate glass, DG-2, for the DAW met all of the KHNP's glass property constraints. Use of this glass formulation on the pilot scale melter, i.e., induction cold crucible melter (CCM), was satisfactory. Linear property model was able to be used to predict the properties of LILW glass as a function of composition. Based on the observed results, the models for viscosity, electrical conductivity, and PCT elemental release were able to accurately predict the actual properties. Consequently, the candidate glass for vitrifying DAW was evaluated to be a competitive alternatives.

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