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■ 論 文 ■

Studies on the Physico-chemical Properties of Mixed Radioactive Waste Glass

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Abstract - In order to vitrify the W1 waste (ion-exchange resin(IER), zeolite, and dry active waste(DAW)) generated from Korean Nuclear Power Plants, a glass formulation development based on waste compositions and production rates was performed. A aluminoborosilicate glass, AG8W1, was formulated to vitrify the W1 waste in an induction cold crucible melter(CCM). The processability, product performance, and economics of the candidate glass were calculated 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 quality of the glass such as chemical durability, phase stability, etc. was satisfactory. The vitrification process using the candidate glass was also evaluated to be operated as economically as possible.

Key words : glass formulation, CCM, viscosity and electrical conductivity

INTRODUCTION

In the mid 1950's, there was a realization of the need for long-term planing regarding the handling and ultimate disposal of radioactive waste. Wastes from nuclear power plants and military programs were the most obvious problem, and other industrial uses of radioactive materials also created large volumes of low-level radioactive wastes. Conversion of hazardous and radioactive wastes into a stable glass through vitrification, typically through a 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 and can achieve large waste volume reductions with about more than 1/20 rates, create a durable waste form and destroy organic compounds more effectively than 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 W1 waste(mixture of ion-exchange resin(IER), zeolite, and dry active waste(DAW)) generated from Korean Nuclear Power Plants, a glass formulation development based on waste compositions and production rates was performed at NETEC, KHNP. Development of viable glass formulation for any given waste stream is basically a problem in constrained multivariate optimization. As such, it is therefore essential to recognize and state clearly both the imposed constraints and the key variables in the problem. The constraints can usually be summarized in three categories: Processability, Product Performance, and Economics.[2] As shown in Fig. 1, a candidate glass formulation to treat the W1 waste was formulated through the property calculation using a computer code, laboratory test, and pilot test using the CCM. Process parameters such as

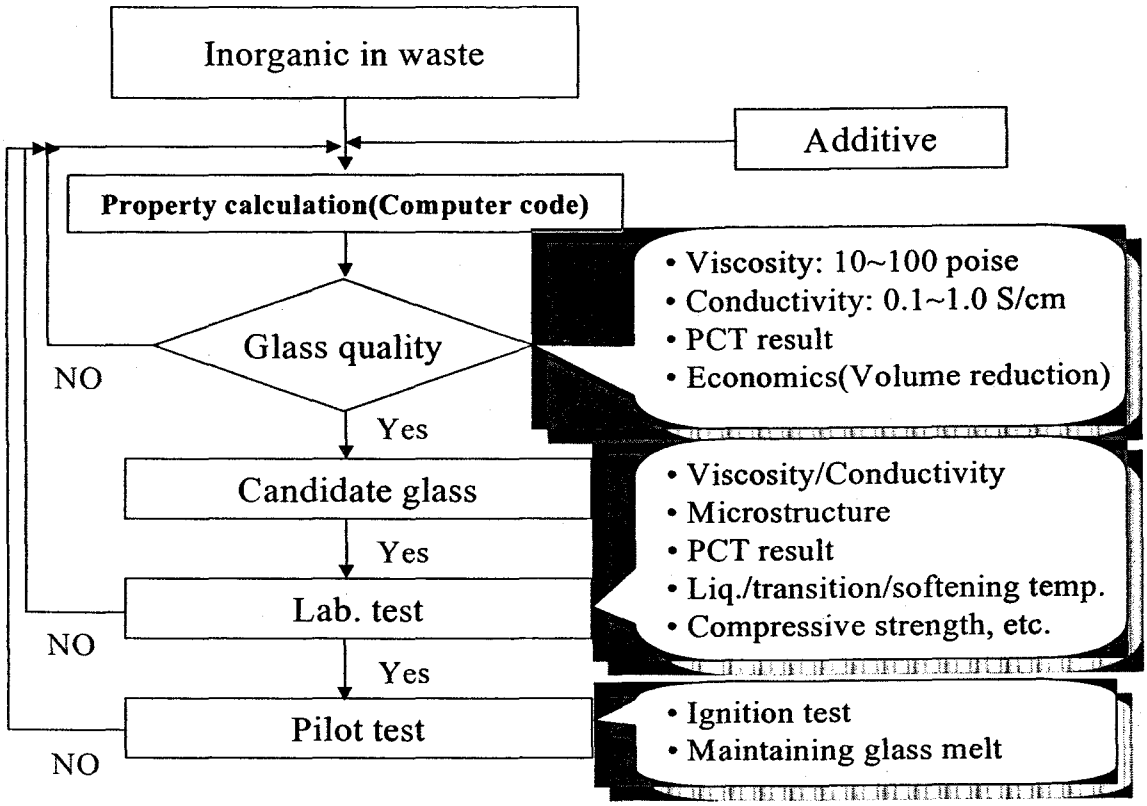

Fig. 1. Flow diagram for formulation and test of candidate glass.

viscosity and electrical conductivity, product quality such as leach rate and microstructure of the glass, and economics such as volume reduction were evaluated as the major considerations for formulating the candidate glass.

COMPUTER MODELING FOR GLASS FORMULATION

In order to formulate the candidate glass for the W1 waste, 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 the 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 of the model, a composition variation study is required. The composition range of the linear glass property models is in Table 1.

The linear glass property models for viscosity and elemental leach response were used to identify candidate glass compositions that would meet the glass property constraints. The models include a linear coefficient for each silicon dioxide, boron oxide, sodium oxide, lithium oxide,

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%

calcium oxide, magnesium oxide, iron oxide, aluminum oxide, and others (including trace elements). Some of the components present in KHNP waste were not included in the original linear property models. In order to model KHNP compositions, the coefficients of glass formers and modifiers present in KHNP formulations were assumed to be equal to the chemically similar compounds for which coefficients were available in the model. The coefficients for titanium dioxide, potassium oxide, nickel oxide, phosphate, and manganese dioxide were assumed to be equal to the coefficients for silicon dioxide, sodium oxide, calcium oxide, silicon dioxide, and silicon dioxide respectively.

EXPERIMENTAL METHODS

There are several experimental methods, procedures and techniques that were used to obtain data in this study. Generally, raw chemicals were weighed out, mixed and melted to make bulk glass which was used in study to determine various physical properties. And then, a pilot scale test using the CCM was conducted to evaluate its workability and reliability.

In making glasses for the laboratory test, raw materials used were K_2CO_3, Na_2CO_3, $CaCO_3$, Li_2CO_3, $MgCO_3$, $NaH_2PO_4H_2O$, Al_2O_3, CeO_2, CoO, Cr_2O_3, MnO_2, Fe_2O_3, NiO, Sb_2O_3, SiO_2, TiO_2, ZrO_2, and VO_2. The chemicals were weighed out to produce the desired batch compositions and mixed thoroughly, put into clay crucible, and then introduced into a high temperature furnace at 1,150°C in air at ambient pressure for 1 hour. The melt was stirred manually at half way through the melting process to ensure adequate mixing of chemicals. Finally, the melt was poured on to a graphite plate to obtain a rapid cooling rate.

The melt viscosity was obtained from measurement of the torque at various rotation speeds using a spindle attached to a viscometer. The electrical conductivity of the glass was determined by measuring the resistance of the glass melt as a function of frequency using a platinum/rhodium electrode probe attached to a impedance analyzer. In order to evaluate the ignition and maintaining glass melt of the AG8W1 glass in the CCM, 70 kg of AG8W1 glass was loaded inside of the CCM. And then, the high frequency generator supplied the energy to the Ti-ring inside of the AG8W1 glass to ignite it and maintain the glass melt after ignition completed.

Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) has been used for microstructural evaluation in this study. Sample of glass was prepared for observation in a JEOL SEM (JSM-5600) by embedding them in epoxy metalographic mounts and polishing them on a sequence of metal bonded diamond abrasive grids. The SEM was equipped with an Oxford energy dispersive x-ray spectrometer(INCA energy) and digital image acquisition and analysis system. The liquidus temperature of the glass was obtained by heat treatments followed by analysis using optical and/or electron microscopy. Sample of about 3g was heat heated in a platinum/gold crucible at a pre-melt temperature of 1,150°C for one hour to destroy any pre-existing nuclei followed by a 20-hours at several temperature points. The 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 μm) to the test solution(deionized water). PCT test conducted on the candidate

glass was performed at 90°C. The ratio of the glass surface area to the solution volume for this test is about 2000m^{-1}. The test was conducted for 7, 30, 60, and 120 days.[4] One milliliter of leachate was mixed with 20 ml of 1M HNO_3 and the resulting solution was analyzed by ICP-AES. A compressive strength measurement on the as-prepared glass was performed. The compressive strength test necessitates the use of glass sample having regular and well-defined geometry. Cylinder of the glass was cast, annealed, and the top and the bottoms cut parallel and polished.

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.

RESULTS AND DISCUSSION

Properties of glass formulation developed for vitrification of KHNP LLW were calculated using the modeling program, then measured. Each of the properties calculated and measured is discussed separately in the following paragraphs. As a result of the efforts for glass formulation development, AG8 as an additive and AG8W1 as a candidate glass were formulated using the computer coding, laboratory and pilot tests as shown in Table 2.

Table 2. Additive(AG8) and candidate glass(AG8W1) for vitrification of the W1 waste.

	AG8	AG8W1
SiO_2	44.52	43.41
Alkali oxides	26.24	20.44
B_2O_3	8.57	9.97
Al_2O_3	14.42	12.30
Alkali-earth oxides	0.00	6.94
Transition metal oxides	4.17	5.57
Others	2.08	1.64

Processability

Data on melt viscosity and electrical conductivity, both 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 coding and those of viscosity and electrical conductivity obtained by the laboratory measurements. 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 a melt viscosity of 10-100 poise and an electrical conductivity of 0.1-1.0 S/cm at the processing temperature, 1,150°C.[5] Consequently, two major process parameters for the AG8W1 glass were in the desired ranges.

In order to evaluate the ignition and maintaining glass melt of the AG8W1 glass in the CCM, 70 kg of AG8W1 glass frit was loaded inside of the CCM. And then, the high frequency generator(HFG) supplied the energy to ignite the Ti-ring and maintain the glass melt in the CCM. It was easy to ignite the Ti-ring and to propagate the ignition energy into the AG8W1 glass. The Ti-ring was uniformly energized up by the HFG as shown in Fig. 2(a). And then, the AG8W1 glass 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.

Product Performance

The density of the AG8W1 glass was needed for evaluating the volume reduction of the W1 waste after completion of the vitrification. The density model was based on a linear relation of the type: Density = ΣD_iM_i, (i = 1, 2, 3···n component oxides), where D_i = the density of a component i in the glass system and M_i = the

Table 3. Physico-chemical properties of the candidate glass(AG8W1), † @ 1,150 °C.

		AG8W1
Computer coding	Density (g/cm^3)	2.67
	Viscosity (poise)†	67
	E. conductivity (S/cm)†	0.31
	Mineral loading(%)	40
	VRF	84
Lab. test	Viscosity (poise)†	62
	E. conductivity (S/cm)†	0.33
	SEM/EDS observation	As melted glass @ 1,150°C: Homogeneous
	PCT	Leach rates below benchmark glass
	Liquidus temp.(°C)	950
	Compressive strength(psi)	2,146
Pilot test	Ignition	Favorable in CCM
	Maintaining glass melt†	Easy to control

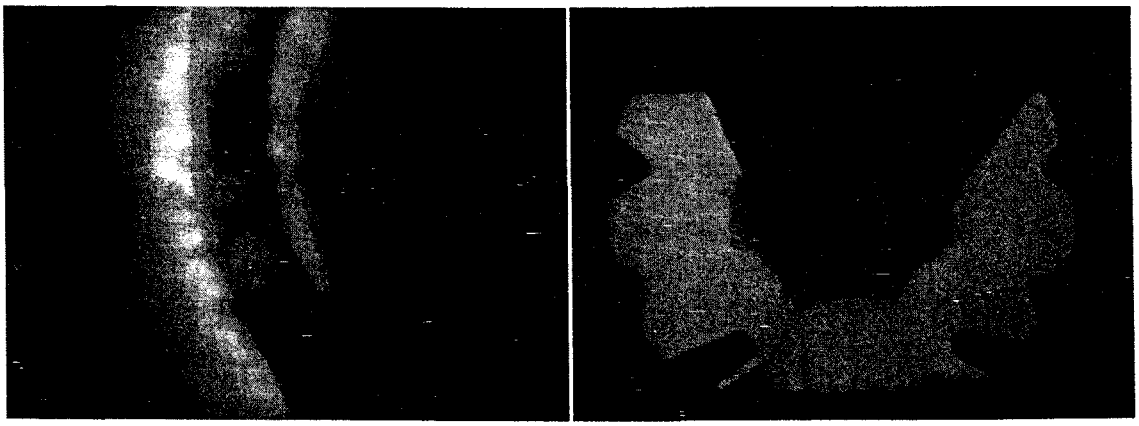

Fig. 2. Ignition of Ti-ring(a) and maintaining glass melt(b) of AG8W1 glass in the CCM.

mole fraction of the component i. The computer code converts oxide weight percents into mole fractions. Once the density of each component is input, the algorithm calculates the fractional density of each component and sums the fractions. Consequently, the density of the AG8W1 glass was evaluated as high as 2.67 g/cm^3 and met the constraint. In order to remove the innocuous components (e.g., water, carbon dioxide, etc.) rather than contained within the waste form, high density (lager than 2.5 g/cm^3) waste form is favored.

SEM/EDS was used to examine the as-melted glass. According to the SEM/EDS observation,

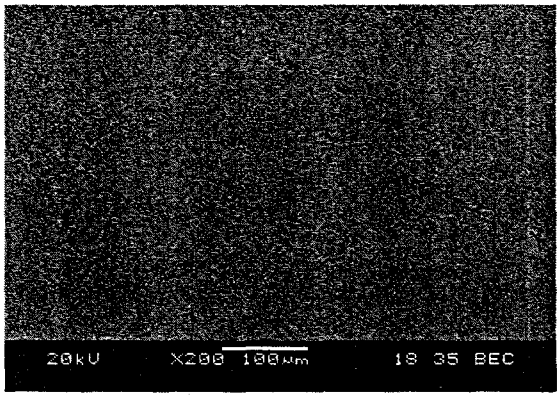

Fig. 3. SEM micrograph of as-melted AG8W1 glass matrix.

there was no secondary phase formation in the AG8W1 glass matrix as shown in SEM micrograph(Fig. 3). In order to determine a bound on the liquidus temperature, the glass sample was heat treated for 20 hours in the temperature range of 900-1050°C after a 1 hour pre-melt at 1,150°C. Crystallization of Sb-Ce-Zr combination on the order of trace (less than 0.1 vol%) was found in the AG8W1 glass that was heat treated for 20 hours at 900°C. Thus, the liquidus temperature was estimated as about 950°C.

The standard radioactive waste glass procedure, the Product Consistency Test (PCT), was used to evaluate the leach resistance of the AG8W1 glass. The results used computer calculation and obtained after the nominal 7-day leaching period were in good agreement. The long-term PCT data for four elements showed very small changes in the glass composition compared to the benchmark glass (SRL-EA). There is 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 long-term behavior and suppresses, or at least delays, the rise in the leach rate. Leach rates, in grams per square meter of glass exposed per day over the 120-day test duration, are shown in Fig. 4. In general, the leaching process of four elements in the AG8W1 was saturated after 60-day test, although those elements in the benchmark glass are leached out continuously.

A compressive strength measurement on the as-prepared glass (cylinder type) was performed. The compressive strength was measured as high as 2,146 psi and exceeded the requirement (500 psi) by a considerable margin.[6]

Economics

A minimum additive waste stabilization (MAWS) approach was used to achieve high waste loading as high as 40% in terms of inorganic mineral basis. Thus, only 60% of additive would be sufficient to vitrify the W1 waste at 1,150°C. And the volume reduction factor was evaluated as high as 84. Additive impacts the overall economics from several perspectives. First, is the direct cost of the additive itself. Second, is the cost associated with running the non-waste additive through 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 not of waste but of purchased additive. Since disposal of the final stabilized waste form 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 favored over those in which the volume is increased.

CONCLUSIONS

The candidate glass, AG8W1, for the W1 waste met all of the KHNP glass property constraints. Use of this glass formulation on the pilot scale melter, i.e., induction cold crucible melter(CCM), was satisfactory. Linear property models were able to be used to predict the properties of LLW glass as a function of composition. Based on the observed results, the

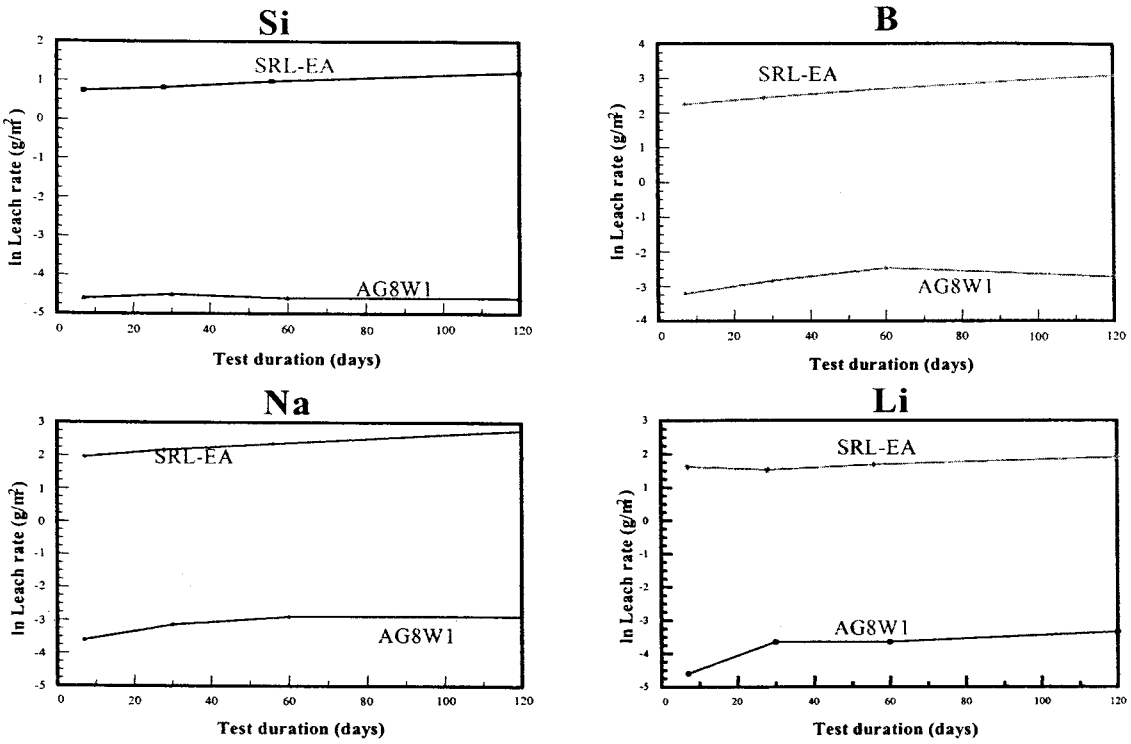

Fig. 4. PCT data for AG8W1 glass leach rates of Si, B, Na, & Li vs. time compared to benchmark glass(SRL-EA).

models for viscosity, electrical conductivity, PCT elemental release were able to accurately predict the actual properties. Also, it was evaluated that the candidate glass can be operated for the W1 waste as economically as possible.

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