

## Glass Formulations for Vitrification of Low-and Intermediate-level Waste

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### ABSTRACT

In order to develop glass formulations for vitrifying Low-and Intermediate-Level radioactive Wastes (LILW) from nuclear power plants of Korea Hydro & Nuclear Power (KHNP) Co., Ltd., promising glass formulations were selected based on glass property model predictions for viscosity, electrical conductivity and leach resistance. Laboratory measurements were conducted to verify the model predictions. Based on the results, the models for electrical conductivity, US DOE 7-day Product Consistency Test (PCT) elemental release, and pH of PCT leachate are accurate for the LILW glass formulations. However, the model for viscosity was able to provide only qualitative results. A leachate conductivity test was conducted on several samples to estimate glass leach resistance. Test results from the leachate conductivity test were useful for comparison before PCT elemental release results were available. A glass formulation K11A meets all the KHNP glass property constraints, and use of this glass formulation on the pilot scale is recommended. Glass formulations K12A, K12B, and K12E meet nearly all of the processing constraints and may be suitable for additional testing. Based on the comparison between the measured and predicted glass properties, existing glass property models may be used to assist with the LILW glass formulation development.

**Key words :** Low-and Intermediate-Level radioactive Waste (LILW), Glass formulation, Viscosity, Electrical conductivity, PCT

### 1. Introduction

In Korea, Low-and Intermediate-Level radioactive Wastes (LILW) generated from nuclear power plants has been stored in on-site storage buildings after being super compacted, dried or solidified. Such on-site storage capacity is almost exhausted. If a permanent repository for the LILW is not available in the near future, current on-site storage capability should be expanded to accept the waste drums from further operations. Thus, it is important to develop a technology that will significantly reduce the volume of the LILW and enhance their disposal stability. In the meantime, Nuclear Environment Technology Institute (NETEC), a division of Korea Hydro & Nuclear Power (KHNP) Co., Ltd, has investigated and evaluated various thermal treatment technologies for the LILW. NETEC has focused on a treatment technology that will result in a large reduction of volume, enhance the stability of the waste form, and can treat all waste streams generated from Korean nuclear power plants. It was decided in early 1994 that vitrification technology to treat the LILW was the most promising technology. The vitrified radioactive waste is expected to remain stable in the repository environment for over one

million years. In addition, vitrification technology contributes to a waste volume reduction factor of greater than 50.<sup>1,2)</sup>

Idaho National Engineering and Environmental Laboratory (INEEL) and NETEC researchers have collaborated to develop borosilicate glass formulations for the LILW generated at commercial nuclear power plants operated by KHNP. The composition of major LILW, on an organic-free basis, is shown in Table 1. The LILW consists of two waste types, Dry Active Waste (DAW) and resin waste, that are blended during the vitrification process. DAW comprises blotter paper, packing material, contaminated clothing, disposable shoe covers, plastic bags, and plastic sheet, while resin waste consists mainly of spent ion exchange resins from plant demineralizers.<sup>3,4)</sup> It has been assumed that these waste streams may be blended at a ratio of 93 : 7 DAW to resin waste, 4 : 1 DAW to resin waste, and 2 : 1 DAW to resin waste during processing. The waste loading of the vitrified product has been assumed to be 20 wt%.

### 2. Glass Formulation Development Approach

The purpose of the work has been to develop acceptable glass formulations to vitrify the LILW. It has been assumed that acceptable glass formulations would meet the glass property constraints as shown in Table 2.<sup>5)</sup> To develop glass formulations, the following approach was used. First, the

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**Table 1.** Chemical Composition of the LILW and Three Blends for which Glass Formulations were Developed

Component	DAW	Resin	93 : 7 DAW : Resin	4 : 1 DAW : Resin	2 : 1 DAW : Resin
SiO <sub>2</sub>	15.1		14.0	12.1	10.1
B <sub>2</sub> O <sub>3</sub>		18.9	1.3	3.8	6.3
Na <sub>2</sub> O	1.6		1.5	1.3	1.0
Li <sub>2</sub> O		16.8	1.2	3.4	5.6
CaO	51.1		47.5	40.9	34.1
MgO	6.4		6.0	5.1	4.3
Fe <sub>2</sub> O <sub>3</sub>	0.6	6.3	1.0	1.7	2.5
Al <sub>2</sub> O <sub>3</sub>	1.4		1.3	1.1	0.9
TiO <sub>2</sub>	15.7		14.6	12.6	10.5
K <sub>2</sub> O	3.7		3.4	3.0	2.5
NiO		13.1	0.9	2.6	4.4
MnO <sub>2</sub>	0.2	0.3	0.2	0.2	0.2
P <sub>2</sub> O <sub>5</sub>	2.4		2.2	1.9	1.6
SO <sub>3</sub>	1.8	44.5	4.8	10.3	16.0

**Table 2.** Glass Property Constraints Used to Develop Candidate Glass Formulations

Glass property	Constraint
Waste loading	20 wt% minimum
Electrical conductivity	0.2 to 0.6 S/cm
Viscosity	Between 10 and 100 dPa·s (Poise)
Product Consistency Test (PCT) leach response	95% (1.5 orders of magnitude) lower than EA glass
Processing temperature	About 1423 K (1150°C)
Radiation field strength of glass canister	Less than 10 mSv/h at a distance of 10 cm

properties of candidate glass compositions were estimated using linear glass property models. These models were originally developed at Pacific Northwest National Laboratories (PNNL)<sup>6,8)</sup> and have been modified by INEEL for the purposes of this work. Second, the predicted properties of the candidate glasses were sorted based on their predicted properties. Third, glass compositions that were predicted to have acceptable properties (see Table 2) were subjected to laboratory testing. A glass composition was acceptable if the measured properties met the glass property constraints (see Table 2). Acceptable glass compositions are recommended for additional testing or for application in a pilot scale vitrification plant. The following sections describe the glass property models, laboratory measurements used to verify the model predictions, and calculation of the radiation field strength.

### 2.1. Glass Property Models

The properties of candidate glass formulations were estimated using linear glass property models developed by PNNL and modified by INEEL. The original glass property models have been shown to be accurate for the glass composition range shown in Table 3. The accuracy of the original PNNL models has been reported in terms of correlation coefficients. For example, the reported correlation coefficients for the leach response model vary from 0.86 to 0.95 (Square of the correlation coefficients,  $R^2=0.74$  to 0.91).<sup>6)</sup>

For molten glass properties the correlation coefficient varies from 0.94 to 0.97 (Square of the correlation coefficients,  $R^2=0.89$  to 0.94)<sup>6)</sup> for glasses whose compositions fall within the glass composition range (see Table 3). The concentration of all major chemical components found in KHNP wastes fall within the bounds of the model with the exception of calcium oxide. Other minor components found in KHNP waste such as titanium dioxide, potassium oxide, nickel oxide, manganese dioxide, phosphate, and sulfate are found in higher concentrations than in the bounds of the model and may adversely impact the accuracy of the glass property models. This issue will be discussed later in this paper.

Linear glass property models have been developed for glass transition temperature and pH of the US DOE Product Consistency Test (PCT)<sup>9)</sup> leachate. These linear models are expressed as

$$L_{\alpha} = \sum_{i=1}^n b_{\alpha i} g_{\alpha i} \quad (1)$$

where  $L_{\alpha}$  = property of interest,  $b_{\alpha i}$  = linear property coefficient of component  $i$ ,  $g_{\alpha i}$  = mass fraction of chemical component  $i$ .

Similarly, logarithmic glass property models developed for viscosity, electrical conductivity, and elemental leach rate as measured by the PCT are of the form

$$M_{\alpha} = \ln \left( \sum_{i=1}^n b_{\alpha i} g_{\alpha i} \right) \quad (2)$$

**Table 3.** Composition Range of Glass Property Models

Model bounds	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Li <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	Others
Lower	37%	5%	5%	1%	1%	0%	6%	0%	3%	5%
Upper	57%	20%	20%	7%	2%	2%	10%	15%	5%	8%

**Table 4.** Glass Property Model Coefficients (Mass Basis)

	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Li <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	Others
Si	-2.97	-0.61	10.7	19.7	-6.04	2.93	-4.23	-17.34	-10.81	-0.73
B	-4.32	12.00	17.6	22.6	-8.71	10.90	-3.20	-25.41	-10.56	0.16
Li	-3.23	10.2	14	18.4	-5.35	7.12	-4.51	-22.31	-10.06	0.62
Na	-4.41	9.41	19.4	19.1	-1.96	11.80	-4.10	-25.43	-11.42	-0.66
pH	8.19	3.33	23.6	31.2	17.2	15.30	8.59	5.36	7.61	9.27
ln $\eta$	9.0	-6.2	-11.0	-34.2	-7.5	-2.8	0.0	11.3	7.4	-0.2
ln $\sigma$	0.9	2.3	11.0	23.5	1.4	1.1	2.6	1.3	1.1	3.5

Note) ln  $\eta$  = Viscosity at 1423 K (Pa · s), ln  $\sigma$  = Electrical Conductivity at 1423 K (S/cm)

where  $M_\alpha$  = property of interest.

The original PNNL glass property model coefficients are shown in Table 4. Coefficients for components that were not present in the original property model were added to the model by INEEL. These added coefficients are shown in Table 5. These additional coefficients were selected based on the expected behavior of these components in a borosilicate glass. For example, sodium oxide is expected to act as a glass modifier. Potassium oxide also acts as a glass modifier, but coefficients for this component were not included in the original glass property models. In order to calculate the effect of potassium oxide on the properties of KHNP glasses, the coefficients for sodium oxide were used for potassium oxide. The properties of KHNP waste glass formulations were calculated using Eqs. (1) and (2) with the coefficients shown in both Tables 4 and 5.

## 2.2. Laboratory Measurements

Laboratory measurements of selected glass properties were conducted to verify glass-modeling results. The properties measured in the laboratory included molten glass viscosity, molten glass electrical conductivity, conductivity of

**Table 5.** Glass Property Model Coefficients Assumed for Components of KHNP Waste that were not Included with Original Glass Property Model Coefficients

	TiO <sub>2</sub>	K <sub>2</sub> O	NiO	MnO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>
PCT leach response					
Si	-2.97	10.7	-6.04	-2.97	-2.97
B	-4.32	17.6	-8.71	-4.32	-4.32
Li	-3.23	14	-5.35	-3.23	-3.23
Na	-4.41	19.4	-1.96	-4.41	-4.41
pH	8.19	23.6	17.2	8.19	8.19
ln $\eta$	9.0	-11.0	-7.5	9.0	9.0
ln $\sigma$	0.9	11.0	1.4	0.9	0.9

Note) ln  $\eta$  = Viscosity at 1423 K (Pa · s), ln  $\sigma$  = Electrical Conductivity at 1423 K (S/cm)

PCT leachate solutions, and PCT elemental leach response. The molten glass viscosity was measured in a rotating spindle viscometer (Brookfield Digital Viscometer, Model DV-III) at 1223, 1273, 1323, 1373, 1423, 1473, and 1523 K. To conduct the viscosity measurements, the Pt-20%Rh spindle with 1.4 cm in diameter was submerged in molten glass contained in a small Pt crucible with 50 mm in diameter. The data were interpolated to standard temperatures using the Vogel-Fulcher equation:  $\ln \eta = A/(T - T_0) + B$ , where A, B, and  $T_0$  are fitting parameters. Electrical conductivity was measured with a Pt-20% Rh probe with 7 × 38-mm blades set 9 mm apart at 1223, 1323, 1423, and 1523 K, 1 kHz frequency AC current, and a HP 4262A LCR meter. The electrical conductivity data were interpolated to standard temperatures using the Arrhenius equation:  $\ln \sigma = A/T + B$ , where A and B are fitting parameters. Scanning Electron Microscopy (SEM) analysis of prepared waste forms was completed with a Phillips Model XL30ESEM. X-Ray Diffraction (XRD) was completed using a Siemens D5000 equipped with a Bruker defrac and software.

The US DOE PCT procedure<sup>9)</sup> was performed to determine the relative leach resistance of the waste glasses at 90°C. The concentrations of the chemical species released from crushed (75–149  $\mu\text{m}$ ) to the test solution (deionized water) were measured. The ratio of the glass surface area to the solution volume was about 2000  $\text{m}^{-1}$ . Prior to the elemental analyses of the PCT leachates, the conductivities of the leachates were measured with an Orion Model 126 conductivity probe and to arrive at a preliminary indication of the leach resistance of the glasses. This technique which was developed at INEEL<sup>10)</sup> is described below. The leachate conductivity test protocol is similar to that of the PCT except the conductivity of the PCT leachate is measured for the leachate conductivity test, with the total mass loss calculated from the leachate conductivity assuming a linear correlation. If the relationship between the leachate conductivity and total mass loss is assumed to be linear, the total mass loss of candidate glass formulas can be estimated as follows:

$$Estimated\ Total\ Mass\ Loss = \frac{LC}{LC_{STD}} \tag{3}$$

where  $LC$  is the leachate conductivity of the candidate formulation and  $LC_{STD}$  is the leachate conductivity of Environmental Assessment (EA) glass which is a benchmark glass. The leachate conductivity test has been used at INEEL for several years to compare the leach response of glass waste forms. The method has proven to be quick, reliable, and inexpensive. This estimation represents a conservative estimate of the total mass loss. The estimated total mass loss becomes more accurate as the composition of the glass used as a reference approaches the composition of interest.

In order to compare the measured total mass loss (as estimated by the leachate conductivity test) to the predicted total mass loss, the total mass loss was calculated from the predicted elemental leach response as follows:

$$Predicted\ Total\ Mass\ Loss = \frac{\sum NL_i \times f_i}{\sum f_i} \tag{4}$$

where  $NL_i$  = predicted elemental leach response of compo-

nent  $i$  ( $g/m^2$ ) and  $f_i$  = mass fraction of component  $i$  in the glass specimen before leaching.

**2.3. Calculation of the Radiation Field Strength**

The magnitude of the radiation field strength surrounding a canister of vitrified LILW was calculated for a 4 : 1 resin waste blend at a waste loading of 20 wt%. This calculation was completed to verify that vitrified KHNP LILW would meet the external radiation field strength constraint for the LILW; that is, 10 mSv/h at a distance of 10 cm from the canister. Calculations were completed using MicroShield Version 5.03a.<sup>11)</sup>

**3. Results and Discussion**

The composition of promising glass formulations developed using the linear glass property models is shown in Table 6. The predicted viscosity and electrical conductivity of these glasses are shown with the measured properties and their respective  $R^2$  in Table 7. The predicted and measured total mass loss rate as approximated by the leachate

**Table 6.** Compositions of Candidate KHNP Glasses that were Developed Using Glass Property Models

Component	Glass formulas for 93 : 7 DAW : Resin			Glass formulas for 4 : 1 DAW : Resin waste blends				Glass formulas for 2 : 1 DAW : Resin waste blends			
	K1	K2	K3	K4	K5	K6	K7	K11A	K12A	K12B	K12E
S <sub>2</sub> O <sub>2</sub>	42.1	44.3	43.9	41.1	39.6	38.6	42.0	41.2	40.4	47.2	39.5
B <sub>2</sub> O <sub>3</sub>	7.5	8.0	7.7	8.0	7.5	7.2	7.3	14.1	19.9	19.7	18.9
N <sub>2</sub> O	14.9	15.7	6.3	9.5	9.1	10.4	6.0	5.1	5.5	5.1	6.1
L <sub>2</sub> O	1.7	1.8	6.2	7.2	6.6	4.2	5.9	5.5	4.0	3.8	3.7
CaO	9.5	9.5	9.5	9.5	9.5	9.5	9.5	8.2	8.1	8.1	8.1
MgO	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.0	1.0	1.0	1.0
Fe <sub>2</sub> O <sub>3</sub>	8.9	4.8	6.2	6.7	6.6	9.5	5.9	2.8	1.9	1.8	2.9
Al <sub>2</sub> O <sub>3</sub>	9.0	9.5	13.7	11.5	14.7	14.3	17.0	16.0	14.6	8.7	15.3
TiO <sub>2</sub>	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.5	2.5	2.5	0.0
K <sub>2</sub> O	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.6	0.6	0.6	2.5
NiO	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.5	1.0	1.0	0.6
P <sub>2</sub> O <sub>5</sub>	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
SiO <sub>3</sub>	1.0	1.0	1.0	1.0	1.0	1.0	1.0	2.1	0.0	0.0	0.0

**Table 7.** Predicted and Measured Viscosities and Electrical Conductivities for KHNP LILW Glass Formulations

Glass	Predicted viscosity (dPa·s)	Measured viscosity (dPa·s)	R <sup>2</sup>	Predicted electrical conductivity (S/cm)	Measured electrical conductivity (S/cm)	R <sup>2</sup>
K1	54	49		0.26	-	
K2	51	40		0.26	0.28	
K3	53	36		0.29	-	
K4	50	15	0.38	0.50	0.48	0.96
K5	42	21		0.42	-	
K6	46	33		0.29	-	
K7	76	47		0.26	0.26	
K11A	55.5	35		0.23	0.28	
K12A	47.9	38		0.17	-	
K12B	51.4	40	ND	0.15	-	ND
K12E	52.8	40		0.17	-	

**Table 8.** Measured Values of Selected Glass Properties for EA Glass and Six Candidate KHNP Glass Compositions

Glass	PCT Leachate conductivity ( $\mu\text{S}/\text{cm}$ )	Predicted conductivity ratio	Measured conductivity ratio	$R^2$
EA glass	3970 (3940)	1.00	1.00	
K1	790 (830)	0.21	0.20	
K2	830 (815)	0.21	0.21	
K3	575 (585)	0.05	0.15	0.19
K4	1891 (1866)	0.05	0.47	
K5	1144	0.06	0.29	
K6	887 (877)	0.05	0.22	
K12A	217 (209)	-	0.05	
K12B	289 (298)	-	0.07	ND
K12E	184.8 (187.1)	-	0.05	

Note) Values in Parenthesis are Duplicate Samples.

conductivity is shown together with the respective correlation coefficients in Table 8. Lastly, the predicted and measured normalized PCT elemental release values are shown in Table 9. A discussion of the results obtained is presented in the following section.

### 3.1. Glass Modeling and Laboratory Measurements

Properties of glass formulations developed for vitrification of KHNP LILW were modeled, then measured. Each of the properties measured is discussed separately in the following paragraphs. Glass K11A appears to be the best formulation developed for vitrification of KHNP waste. This glass met all of the processing and property constraints for KHNP waste glasses. This glass formulation is recommended for additional testing or for direct application on the pilot scale. Glass formulations K12A, K12B, and K12E met all glass constraints with the exception of the boron PCT elemental leach response. These formulations may merit additional study also. All of the candidate KHNP compositions contain

10% calcium oxide, outside the models bounds of 1 to 2% calcium oxide (see Table 2). Since calcium oxide is a waste component, its concentration cannot be reduced unless it is blended with another waste or the waste loading is decreased significantly. Better predictions for glass viscosity and leach response would be possible if the composition range of the linear models were extended to include the expected range of KHNP compositions. To extend the range of the models, a composition variation study is needed.

#### 3.1.1. Glass Viscosity and Electrical Conductivity

Based on the results, all of the formulations developed met the glass processing constraint for viscosity. Also, all of the formulations tested met the constraint for electrical conductivity. Based on the comparison of the predicted and measured glass electrical conductivity, the glass property models were able to predict the electrical conductivity fairly well. The correlation coefficient and  $R^2$  values for this property were 0.98 and 0.96 respectively. Hence, the electrical conductivity may be accurately predicted for the glass compositions studied. The property model for viscosity did not predict the measured values as well as the electrical conductivity model. The correlation coefficient for the glass viscosity suggests that the model does not predict the viscosity for KHNP glass compositions very well. Based on the comparison of the predicted and measured glass viscosity, the glass viscosity correlation coefficient was 0.62 ( $R^2=0.38$ ). This is less than the correlation coefficient reported for glass compositions that fall within the bounds of the model ( $R^2=0.89$  to 0.94). The lower correlation coefficient observed for the viscosity model is caused by the relatively high calcium oxide concentrations in KHNP waste as compared to the bounds of the glass property model (see Table 2). At a waste loading of 10%, KHNP glass formulations contain approximately 10% calcium oxide whereas the bounds of the model are 1 to 2% calcium oxide (see Table 2). Since calcium oxide is a waste component, its concentration cannot be reduced unless another waste that does not contain calcium oxide is

**Table 9.** Predicted and Measured Normalized PCT Elemental Release Values. Bolding Indicates the Measured Values Met the Processing Constraint

Glass	Si ( $\text{g}/\text{m}^2$ )			B ( $\text{g}/\text{m}^2$ )			Li ( $\text{g}/\text{m}^2$ )			Na ( $\text{g}/\text{m}^2$ )			pH PCT leachate		
	P	M	$R^2$	P	M	$R^2$	P	M	$R^2$	P	M	$R^2$	P	M	$R^2$
EA	-	2.21	ND	-	10.0	ND	-	5.22	ND	-	8.10	ND	-	11.4	ND
K3	0.07	0.16	0.88	0.06	<b>0.31</b>	0.71	0.09	0.68	0.63	0.07	<b>0.37</b>	0.72	10.9	10.8	0.95
K4	0.18	0.32		0.25	0.68		0.31	1.39		0.33	1.10		11.7	11.4	
K5	0.09	0.17		0.09	<b>0.37</b>		0.13	0.78		0.12	0.57		11.4	11.0	
K6	0.07	0.20		0.07	<b>0.48</b>		0.10	0.92		0.10	0.83		11.1	11.1	
K7	0.04	0.12		0.02	<b>0.24</b>		0.04	0.54		0.03	<b>0.29</b>		10.7	10.5	
K11A	0.04	<b>0.07</b>		0.06	<b>0.15</b>		0.11	<b>0.25</b>		0.07	<b>0.18</b>		10.1	10.1	
K12A	0.05	<b>0.066</b>	ND	0.14	<b>0.26</b>	ND	0.21	0.39	ND	0.14	<b>0.20</b>	ND	9.6	9.1	ND
K12B	0.10	<b>0.103</b>		0.41	<b>0.44</b>		0.58	0.58		0.42	<b>0.34</b>		9.3	9.0	
K12E	0.04	<b>0.064</b>		0.11	<b>0.22</b>		0.17	0.36		0.12	<b>0.18</b>		9.6	9.0	
Const.	-	<b>0.11</b>	-	-	0.48	-	-	0.25	-	-	<b>0.37</b>	-	-	-	-

Note) P=Predicted leach response; M=Measured leach response;  $R^2$ =Square of the correlation coefficient; EA=Environmental assessment glass; Const.=KHNP Constraint on leach resistance (95% lower than EA glass)

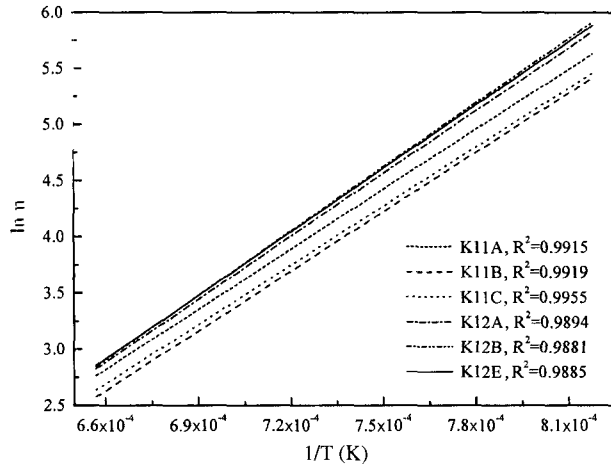


Fig. 1. Experimental plots of logarithm viscosity as a function of temperature.

adled for the waste loading is decreased below 20%.

Plots of logarithm viscosity ( $\ln \eta$ ) versus reciprocal absolute temperature ( $1/T$ ) are in Fig. 1. The straight lines were obtained by using least squares curve fit method applying to the data points between 1223 and 1523 K. The slope of the line yields a value of  $\Delta E_\eta/R$ . Activation energies ( $\Delta E_\eta$ ) for viscosity of K11A, K11B, K11C, K12A, K12B, and K12E were determined to be 147.92, 146.26, 145.43, 154.57, 157.89, and 156.23 kJ/mol, respectively. According to the literature,  $\Delta E_\eta$  values for alkali borate and silicate melts at different temperature vary from 83.74 to 649.40 kJ/mol, and are, for pure  $\text{SiO}_2$  glass melt, as high as 712.21 kJ/mol. Even though the glass formulations used in this study were fairly complicated, its activation energies were of the same order of magnitude as those determined by other researchers who used simpler systems.<sup>12)</sup> Plots of logarithm electrical conductivity ( $\ln \sigma$ ) versus reciprocal absolute temperature ( $1/T$ ) are in Fig. 2. The straight lines were also obtained by using squares curve fit method. The slope of the line yields a value of  $-\Delta E_\sigma/R$ . Activation Energies ( $\Delta E_\sigma$ ) for electrical conductivity of K2, K4, K7, and K11A were determined to be 71.88,

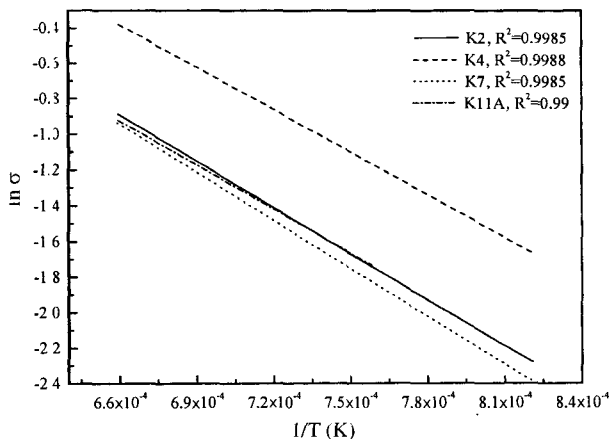


Fig. 2. Experimental plots of logarithm electrical conductivity as a function of temperature.

66.31, 74.71, and 68.23 kJ/mol, respectively. These activation energies that 1 mole of charge carriers need to overcome in order to jump out of their sites were of the same order of magnitude as those determined by other researchers who have researched the vitrification for high-level radioactive waste.<sup>13,14)</sup> The viscosity and electrical conductivity of glasses seem unlikely that there is any quantitative relation between these properties because their temperature dependence is very different.

**3.1.2. Glass Leach Resistance**

Glass leach resistance was measured by two methods: PCT leachate conductivity and PCT elemental release. Both measurements were conducted on the leachate from the PCT test, but the leachate conductivity test is accomplished much more quickly. The results of the leachate conductivity test showed that glasses K12A and K12E were the only two formulations that met the leach resistance constraint (see Table 2). This result compares favorably with the more expensive PCT elemental release values. Only the K11A glass met the leach resistance constraint for PCT elemental release values. Several of the other glasses, such as K12A, K12B, and K12E, met the constraint for all elements with the exception of Li. Several other formulations met one or two of the elemental leach release constraints, but they did not appear to be as leach resistant as the K11A, K12A, K12B, and K12E formulations. The leachate conductivity measurements predicted the same glasses to be the most durable as the PCT elemental release. This is important, since the leachate conductivity test is much less expensive than measurement of the PCT elemental leach response, so it can provide a quick and simple method to test the relative leach resistance of candidate waste forms. In order to complete the leachate conductivity measurement, a simple conductivity meter is all that is required. On the other hand, measurement of the elemental leach response requires the use of Inductively Coupled Plasma equipped with a Mass Spectrometer (ICP-MS). Hence, use of the PCT leachate conductivity test during scoping glass formulation studies is recommended. The predicted leach resistance of the formulations tested matched the measured values fairly well. For example, the correlation coefficient associated with the pH of the PCT leachate measurements was 0.97 ( $R^2 = 0.95$ ). The correlation coefficient for the elemental leach response of KHNP glass formulations ranged from 0.79 to 0.94 ( $R^2 = 0.63$  to 0.88). The correlation coefficient was lowest for Li and highest for Si. These correlation coefficients reported here are slightly lower than those reported in the literature.<sup>15)</sup> This is because the concentration of calcium oxide and other trace constituents in these formulations is outside the bounds of the model. It is recommended that a dedicated composition variation study be completed to develop property models specific to KHNP waste formulations.

**3.2. XRD and SEM/EDS Observations**

Glass samples with the compositions shown in Table 6 also were analyzed by XRD and SEM/EDS. The XRD

results showed that the borosilicate glass formulations developed were amorphous. The SEM/EDS results showed that there were no crystalline phases in the glass matrix.

### 3.3. Radiation Field Strength

The results of the radiation field strength calculations showed that vitrified LILW would meet the applicable field strength constraint. Based on the result of the radiation field strength calculations, a waste loading of 20 wt% may be used to vitrify KHNP LILW without exceeding the constraint of 10 mSv/h at a distance of 10 cm.

## 4. Conclusions

Glass formulation K11A meets all of the KHNP glass property constraints. Use of this glass formulation on the pilot scale is recommended. Glass formulations K12A, K12B, and K12E meet nearly all of the processing constraints and may be suitable for additional testing. Linear glass property models may be used to predict the properties of KHNP LILW as a function of composition. Based on the observed results, the models for electrical conductivity, PCT elemental release, and pH of PCT leachate are able to accurately predict the actual values. However, the model for viscosity was able to provide only qualitative results. In order to develop a more accurate model for KHNP wastes, a composition variation study is recommended. This study and associated model development would improve the ability of a model to accurately predict candidate KHNP LILW glass properties. The model could be extended to support operations once a waste blend and base waste-glass formula are developed.

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