Proceedings of the Korean Nuclear Society Spring Meeting
Kori, Korea, May 2000

Viscosity Calculations of Simulated Ion-exchange Resin Waste Glasses

Cheon-Woo Kim, Jong-Kil Park, Kyung-Ho Lee, Myung-Chan Lee
and Myung-Jae Song
Nuclear Environment Technology Institute - KEPCO
P. O. Box 149, Yusung, Taejon 305-600, South Korea

Pierre BRUNELOT
SGN
1, rue des Herons Montigny le Bretonneux 78182 St Quentin Yvelines Cedex, France

Abstract

An induction cold crucible melter (CCM) located in the NETEC-KEPCO has been used to vitrify simulated ion-exchange resin. During vitrification, the CCM operations were tightly constrained by glass viscosity as an important process parameter. Understanding the role of viscosity and quantifying viscosity is highly required in the determination of optimized feed formulations and in the selection of the processing temperature. Therefore, existing process models of glass viscosity based on a relationship between the glass composition, its structure polymerization, and the temperature were searched and adapted to our borosilicate glass systems. Calculated data using a viscosity model based on calculation of non-bridging oxygen (NBO) were in good agreement with the measured viscosity data of benchmark glasses.

1. Introduction

As a result of more than 20 years of activities of the nuclear power plants in Korea, a safe and inexpensive treatment and disposal problems of low- and intermediate-level radioactive wastes exist. Radioactive waste materials such as ion-exchange resin, borate concentrate, and Dry Active Waste (DAW) are generated and stored in the interim storage building on site. Therefore, the key to achieve environmental restoration is to develop proper technologies for radioactive waste stabilization. Conversion of radioactive wastes into a stable glass through vitrification technology is an appealing technology for waste treatment because it can achieve large waste volume reductions, create a durable waste form and destroy organic compounds more effectively than competing technologies such as polymerization, cementation and ceramic formation [1].

Technically, many challenging problems related to physics, chemistry and engineering need

to be solved to make vitrification a mature technology in radioactive waste remediation. The processability of a waste melt and the chemical durability of the produced glass are the main concerns. The processability includes the viscosity of a melt, the conductivity of a melt and liquidus temperature of a melt. Melt viscosity is the single most important processing property; it determines the rate of melting of the raw feed, the rate of glass bubbles release due to foaming and fining, the rate of homogenization, the pourability of the glass, and the heat transfer within the molten glass. It exerts this control primarily by impacting convection currents. The melt viscosity is strongly dependent on the melt composition and temperature. Understanding and quantifying this dependence is an important factor in the determination of optimized feed formulations and also plays a role in the selection of the processing temperature through the interplay between system constraints and glass formulation constraints. A desirable viscosity range is 20-100 dPa sec (poise) at an operating temperature. If the viscosity is too low, excessive convection current can occur, and viscosity melts may speed up the corrosion/erosion of the melter components (refractories and metals) and also may decrease the chemical durability of the waste glasses. High viscosity melts may slow down the processing rates because the interaction between feed and glass is slowed and may even block the melter' s discharging system [2].

The purpose of this study is to obtain an information whether the existing viscosity model can be used as a useful tool for NETEC-KEPCO waste glasses or not. If an appropriate viscosity model can be adapted and applicable to predict the glass viscosity within the reasonable error range, the time to know the glass viscosity may be saved and this technique will be an economic tool.

2. Theory and model

2.1. Viscosity theory and measurement

When a shearing force is applied to a liquid, a displacement results and with continued application of the force, flow takes place. The ratio of force to displacement is the measure of the viscosity. If two parallel planes of area A, and distance d apart, are subject to a tangential force difference F, the viscosity η is defined as [3]:

$$\eta = Fd/(A\ \Delta v) \tag{1}$$

where Δv is the relative velocity of the two planes. The unit of dynamic viscosity in SI system is pascal second, a tenth of which has been commonly known as a poise (P). The term Fd/A is called the stress applied by force F, and usually written as $\tau = Fd/A$. So equation (1) can be rewritten as:

$$\tau = \eta \Delta v \tag{2}$$

for a more complicated heterogeneous liquid, the equation (2) can be rewritten as:

$$\vec{t} = h \vec{\nabla} \vec{n} \tag{3}$$

where $\vec{\tau}$ is the stress tensor and linearly proportional to the velocity gradient perpendicular to the shear and $\vec{n}$ is the velocity vector. This is the general equation describing the viscous flow of liquids. This equation can be directly derived from the Navier-Stokes equation, which is the most important equation governing the state of a viscous fluid in the field of hydrodynamics [4]. Using Newton's second law of dynamics for the incompressible flow, we have the following equation using equation (3)

$$\rho \frac{d\vec{n}}{dt} = -\vec{\nabla} p + \vec{\nabla} \cdot \vec{\tau} = -\vec{\nabla} p + \eta \vec{\nabla}^2 \vec{n} \tag{4}$$

where ρ is the density of the liquid and p is the pressure including the hydrostatic pressure the liquid is subject to.

There is a technique available to measure the viscosity of glass, among which are the capillary method, the falling sphere method, the high-temperature torsion method, the low-temperature torsion method, the rotating cylinder method, the rod elongation method, the penetration method, and the bending methods, and each technique is appropriate at a different viscosity range. Most common method frequently used to measure viscosity of glass and glass-forming melts is the rotating cylinder method that consists of a rotating spindle viscometer [5]. In the experiment, the viscosity measurement system consists of a cylindrical platinum crucible held stable inside a tube furnace, a cylindrical spindle hung on a viscometer and able to rotate concentrically inside the crucible. If using cylindrical coordinates, in the z (vertical) direction the flow inside the crucible is subject to gravity ρ**g** only. In the horizontal (r, θ) plane, the flow is confined in the cylinder by the centrifugal force

$$(\vec{\nabla} p)_r = \rho \frac{n_q^2}{r} \vec{e}_r \tag{5}$$

and zero drag force in θ direction

$$(\vec{\nabla}^2 \vec{n})_q = (\frac{\partial^2 n_q}{\partial r} + \frac{1}{r}\frac{\partial n_q}{\partial r} - \frac{1}{r^2} n_q)\vec{e}_q = 0 \tag{6}$$

Together with the boundary conditions: a) r_1 being the inner spindle radius and Ω being its rotation rate in units of angular velocity or revolutions per minutes (rpm); b) r_2 being the radius of outer crucible cylinder without rotation, Equation (6) for the velocity can be solved as a function of r, i.e.,

$$\vec{n}_q = \frac{r_1^2}{r_2^2 - r_1^2}(\frac{r_2^2}{r} - r)\vec{e}_q \tag{7}$$

Since the angular momentum should be conserved, the torque to the rotating spindle $\vec{T}_{in}$ and the torque to the outer crucible cylinder $\vec{T}_{out}$ are equal in amount but opposite in direction,

$$\vec{T}_{in} = -\vec{T}_{out} = 2\pi\eta \text{ x } [\vec{r}_2 \cdot (\vec{\nabla}\vec{n})_q \Big|_{\vec{r}_2}] = 4\pi\eta \frac{r_1^2 r_2^2}{r_2^2 - r_1^2} \tag{8}$$

The torque to the spindle $\vec{T}_{in}$ is the torque recorded by the viscometer.

According to Equation (8), the calculation of viscosity of glass melt is proportional to the slope of the torque-angular velocity curve by the following equation:

$$\eta = \frac{r_2^2 - r_1^2}{4\pi r_2^2 r_1^2}\frac{T}{\Omega} = \text{constant x}\ \frac{\Delta T}{\Delta\Omega} \tag{9}$$

Changing T/Ω to ΔT/ΔΩ (their ratios are equal) is for the measurement's convenience, namely, to avoid using the absolute values of the torques and rotation rates. The proportionality constant is determined by measuring the torques for a standard viscosity oil at several different rotation rates (rpm), then fitting the torque versus the rotation to a straight line to determine the slope which is the constant in Equation (9).

Viscosities of glass melt are measured at several different temperatures usually between 900°C to 1400°C. The relationship of viscosity to determine follows the Vogel-Fulcher-Tammann equation [6]:

$$\ln \eta(T) = A + \frac{B}{(T - T_o)} \tag{10}$$

where

$$A = \frac{1}{\Delta}\left[\sum_{i=1}^{N}\frac{1}{\sigma_i^2}\left(\frac{1}{T_i - T_o}\right)^2 \sum_{i=1}^{n}\frac{\ln \eta_i}{\sigma_i^2} - \sum_{i=1}^{N}\frac{1}{\sigma_i^2}\left(\frac{1}{T_i - T_o}\right)\sum_{i=1}^{N}\frac{\ln \eta_i}{\sigma_i^2}\left(\frac{1}{T_i - T_o}\right)\right] \tag{11}$$

and

$$\Delta = \sum_{i=1}^{N}\frac{1}{\sigma_i^2}\sum_{i=1}^{N}\frac{1}{\sigma_i^2}\left(\frac{1}{T_i - T_o}\right)^2 - \left[\sum_{i=1}^{N}\frac{1}{\sigma_i^2}\left(\frac{1}{T_i - T_o}\right)\right]^2 \tag{12}$$

The standard deviation of A is

$$\sigma_A \approx \sqrt{\frac{1}{\Delta}\sum_{i=1}^{N}\frac{1}{\sigma_i^2}\left(\frac{1}{T_i - T_o}\right)^2} \tag{13}$$

The slope B is, according to linear fit method

$$B = \frac{1}{\Delta}\left[\sum_{i=1}^{N}\frac{1}{\sigma_i^2}\sum_{i=1}^{N}\frac{\ln \eta_i}{\sigma_i^2}\left(\frac{1}{T_i - T_o}\right) - \sum_{i=1}^{N}\frac{1}{\sigma_i^2}\left(\frac{1}{T_i - T_o}\right)\sum_{i=1}^{N}\frac{\ln \eta_i}{\sigma_i^2}\right] \tag{14}$$

and its standard deviation is

$$\sigma_B \approx \sqrt{\frac{1}{\Delta}\sum_{i=1}^{N}\frac{1}{\sigma_i^2}} \tag{15}$$

Various values of T_o in the range of about –273 to -300°C are tried, and least square fit method is used to find values for A and B. The set of T_o, A and B data with the best linear fit are taken as final fitting parameters. Once T_o, A and B have been determined, the viscosity values at standard temperatures can be calculated.

2.2. Selection of appropriate viscosity model

The approach taken in the development of the viscosity process model was a first principles approach based on glass structural considerations, expressed as a calculated non-bridging oxygen (NBO) term. Calculation of the NBO term from the glass composition was combined with quantitative statistical analyses of response surfaces to express glass viscosity as a function of melt temperature and glass composition. Silicon was considered to be coordinated by 4 oxygen atoms in tetrahedral arrangements. The SiO_4 tetrahedra link continuously into a three-dimensional network. When alkali is present it depolymerizes the SiO_4 linkages, thus reducing the melt viscosity. Therefore, in the viscosity process model every mole of alkali was assumed to create 2 NBO bonds to form. Al_2O_3 forms AlO_4 tetrahedral linkage and forms 2 bridging oxygen (BO) bonds per Al_2O_3 present. Fe_2O_3 can form bridging or non-bridging oxygen bonds depending on the amount of alkali and Al_2O_3 present. B_2O_3 is an important glass forming oxide that is known to affect viscosity. At low concentrations of B_2O_3 enter the glass network as BO_4 tetrahedra, while at higher concentrations these tetrahedra are converted into planar BO_3 groups containing one non-bridging oxygen atom. A non-bridging oxygen (NBO) term is given by the expression [7]:

$$NBO = 2(Na_2O+K_2O+Cs_2O+Li_2O+Fe_2O_3-Al_2O_3)+B_2O_3/SiO_2 \quad (16)$$

This NBO parameter is representative of the amount of structural depolymerization in the glasses studied. At a temperature of 1150^{o}C as a suitable operation temperature, the lowest and the highest viscosity in a NETEC-KEPCO's induction cold crucible (CCM) melter is 20 and 100 dPa sec. The melt viscosity is calculated by several codes using a viscosity prediction model developed using the concepts of glass structure. The following empirical correlation is to be used in the algorithm to predict reasonably the viscosity.

$$\text{Log } \eta \text{ (dPa sec)} = -0.61 + 4472.45/[T(^oC)] - 1.534*NBO \quad (17)$$

There has been a variety of similar ongoing viscosity model developments for waste glasses at the U.S. Department of Energy (DOE) sites such as PNNL, SRL, INEEL, etc. We evaluated all the available models and determined that the empirical models developed by DOE. Equation (17) developed by U.S. DOE Savannah River Lab. (SRL) is the viscosity process model currently being used at DOE sites [8].

3. Results

3.1.Viscosity measurement for benchmark glasses

Our primary interest is the viscosity of benchmark glasses at a temperature range between 900^{o}C to 1400^{o}C. At this temperature range, the viscosity of the glass melt is well within the range of the rotating spindle viscometer that was used to measure the viscosity of the benchmark glass melts. The precision and accuracy of the viscosity measurements are estimated to be within ±10%. Table 1 represents the compositions of three benchmark glasses, FA/MA, KG-SRM, and NET-A based on mole % as analyzed. All glasses are borosilicate

glasses similar to our glass systems containing Al_2O_3, B_2O_3, Fe_2O_3, Na_2O_3, and SiO_2 as major constituents. Table 2 shows the measured and calculated viscosity data for FA/MA and KG-SRM glasses. Figure 1 shows the plots of viscosity versus temperature for FA/MA glass. Bold curve represents a measured viscosity whereas dotted curve represents a calculated viscosity. The measured viscosity at the lower temperature region (below 1050°C) was increased rapidly compared to the calculated data. It was assumed that the glass as a Newtonian fluid had a phase transition to Non-Newtonian at below the liquidus temperature. According to the measured viscosity, the liquidus temperature was defined as at around 1050°C because the relationship between the melting temperature (T_M) at 50 dPa sec and the liquidus temperature (T_L) difference ($\Delta = T_M - T_L$) must not exceed a certain minimum value, typically 100°C [9]. Figure 2 shows the plots of viscosity versus temperature for KG-SRM glass. Measured and calculated data are almost the same and overlapped each other as shown in the Figure. As another example of use, glass was made having NET-A constituents in the molar amounts listed in Table 1. The calculated value of NBO is 0.9397. At a temperature of 1160°C, the calculated viscosity is 63.6 dPa sec. The measured viscosity was 61 dPa sec.

Table 1. Compositions of three benchmark glasses (all numbers are mole % as analyzed)

Oxides (mole %)	FA/MA	KG-SRM	NET-A
Al_2O_3	6.58	13.32	2.9
B_2O_3	17.81	16.70	6.77
BaO		0.02	
CaO		0.42	1.06
Cr_2O_3		0.01	
Fe_2O_3	2.10	0.69	4.76
K_2O		2.21	0.02
Li_2O		3.20	11.04
MgO		0.12	1.2
MnO_2		0.05	2.42
Na_2O	21.63	16.03	10.83
NiO		0.24	
P_2O_5		3.98	0.86
SiO_2	51.88	40.95	57.75
TiO_2		0.07	
ZrO_2		1.99	0.38
SUM	100.00	100.00	99.99

Table 3 shows six calculated NBO and viscosity data for NETEC-KEPCO glasses between 1000°C and 1400°C. An induction cold crucible melter (CCM) has been used to vitrify simulated ion-exchange resin of the NETEC-KEPCO. All bottom glasses of NET-R01, NET-R02, and NET-R03 were added simulated ion-exchange resin on each base glasses. There are six calculated data plots in Figure 3. The viscosity of a waste glass should remain below 100 dPa sec to be operated in a CCM successfully and a desirable melting temperature (T_M) is defined as a temperature at which the melt viscosity is 50 dPa sec. Consequently, all glasses,

except NET-R02-Bottom is highly viscose at below about 1250°C, can be operated at around 1150°C or higher temperature. If the most restrictive limit on melter operation is the upper temperature limit of 1150°C in order to lead to decreased cesium volatility, our glass compositions need to be modified.

Table 2. Measured and calculated viscosity data for FA/MA and KG-SRM glasses

	FA/MA		KG-SRM	
Temperature (°C)	**Measured (dPa sec)**	**Calculated (dPa sec)**	**Measured (dPa sec)**	**Calculated (dPa sec)**
903			417.6	415.6
1000		209.7		
1003			137.9	133.3
1006	234.8	197.0		
1055	136.5	122.4		
1100	89.0	82.2		
1104	86.1	79.4	54.5	52.5
1153	58.0	53.4		
1200	40.0	37.7		
1204			27.3	24.2
1300		19.5		
1400		11.1		

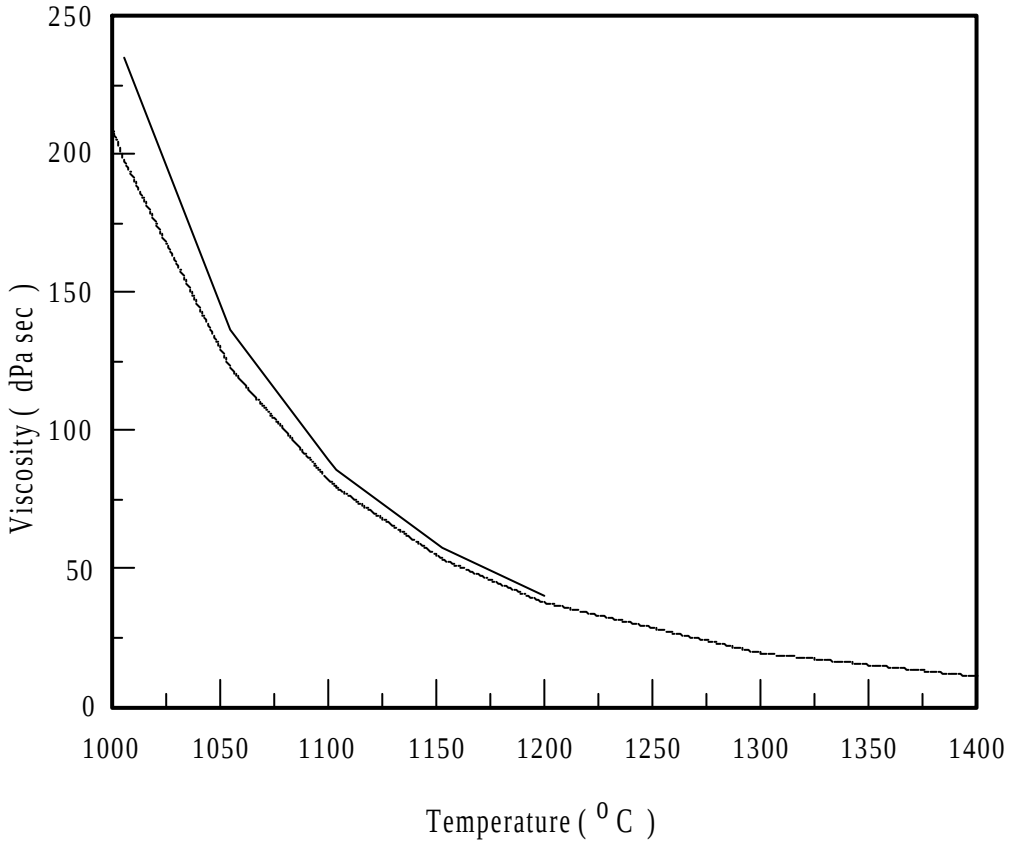

Figure 1. Plots of viscosity versus temperature for FA/MA glass. Bold curve represents a measured viscosity whereas dotted curve represents a calculated viscosity.

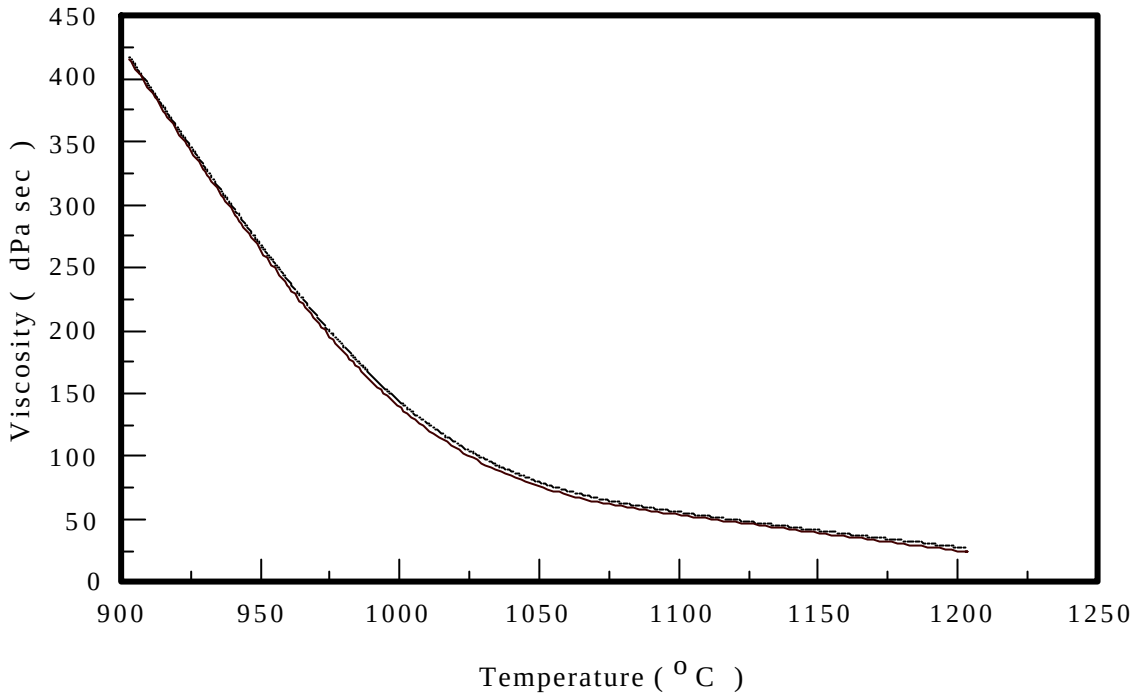

Figure 2. Plots of viscosity versus temperature for KG-SRM benchmark glass. Measured and calculated viscosities are overlapped.

Table 3. Calculated NBO and viscosity data for NETEC-KEPCO glasses between 1000°C and 1400°C

	NET-R01		NET-R02		NET-R03	
Oxides (mole %)	Base (Before resin feeding)	Bottom (After 128kg resin feeding)	Base (Before resin feeding)	Bottom (After 182kg resin feeding)	Base (Before resin feeding)	Bottom (After 106kg resin feeding)
Al_2O_3	8.69	10.41	10.36	10.77	10.40	9.95
B_2O_3	10.28	9.80	9.91	8.09	9.53	10.21
BaO		0.04		0.07		0.06
CaO		0.14		0.15		0.12
Cr_2O_3		0.03		0.01		
CuO		0.01		0.01		
Fe_2O_3	1.21	1.13	0.54	0.43	0.52	0.41
K_2O		0.09		0.06		0.13
MgO		0.05		0.05		0.05
MnO_2		0.02				
MoO_3		0.01				
Na_2O	25.0	26.42	26.49	24.45	26.61	26.30
NiO						
P_2O_5						
SiO_2	54.83	51.28	52.70	55.47	52.94	52.39
TiO_2		0.50		0.33		0.27
ZnO		0.01				
ZrO_2		0.07		0.10		0.09
NBO	**0.8267**	**0.8629**	**0.8211**	**0.6570**	**0.8120**	**0.8398**
Viscosity (dPa sec) at temp. (°C)	1000: 393.0 1100: 154.1 1150: 102.6 1200: 70.6 1250: 50.1 1300: 36.5 1400: 20.7	1000: 345.8 1100: 135.6 1150: 90.2 1200: 62.1 1250: 44.1 1300: 32.1 1400: 18.2	1000: 400.8 1100: 157.2 1150: 104.6 1200: 72.0 1250: 51.1 1300: 37.2 1400: 21.1	1000: 715.4 1100: 280.5 1150: 186.7 1200: 128.6 1250: 91.2 1300: 66.4 1400: 37.7	1000: 413.8 1100: 162.3 1150: 108.0 1200: 74.4 1250: 52.8 1300: 38.4 1400: 21.8	1000: 375.1 1100: 147.1 1150: 97.9 1200: 67.4 1250: 47.8 1300: 34.8 1400: 19.8

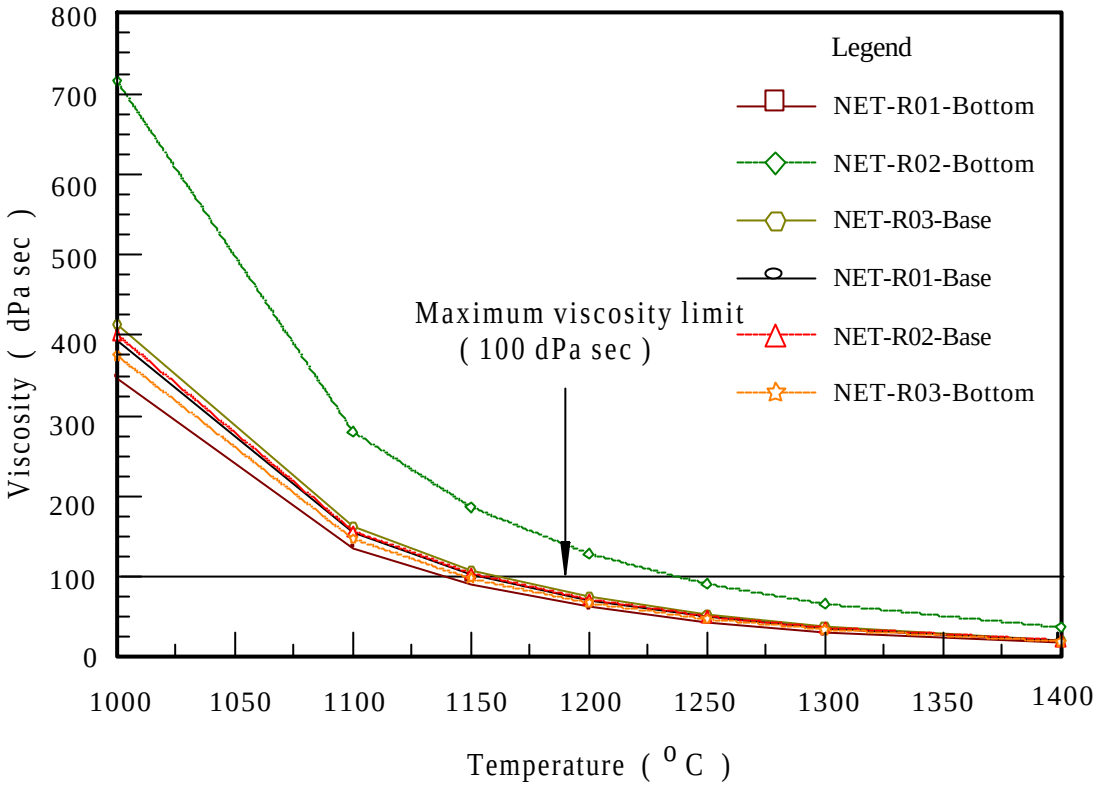

Figure 3. Plots of viscosities versus temperature for all NET glasses.

4. Conclusions

During vitrification using an induction cold crucible melter (CCM), the glass viscosity was required as an important process parameter. Express quantifying the viscosity through the feed formulations will provide useful information in the melter operation. An application of the first principles for glass viscosity model developed for the waste vitrification has been incorporated into the NETEC-KEPCO's ion-exchange resin treatment project. Existing process models of glass viscosity based on a relationship between the glass composition, its structure polymerization, and the temperature were searched and adapted to our borosilicate glass systems. Calculated data using a viscosity model based on calculation of non-bridging oxygen (NBO) were in good agreement with the measured viscosity data of benchmark glasses. Therefore, the NETEC-KEPCO has used the existing viscosity model and considered it as a reasonable quantitative predictors for glass viscosity with the range of waste glass compositions upon which they have been based (interpolative use). The existing viscosity model is useful for rough composition screening purposes and general trends guidance on NETEC-KEPCO's waste glass viscosity, but to obtain confident predictions requires additional data to validate and/or modify the model for the appropriate NETEC-KEPCO's waste compositions.

References

[1] I. L. Pegg, "Basic Consideration in the Application of Vitrification Technologies," a special report, 1994.

[2] C. M. Jantzen, "First Principle Process-Product Models for Vitrification of Nuclear Waste: Relationship of Glass Composition to Glass Viscosity, Resistivity, Liquidus Temperature, and Durability," *Ceramic Transactions*, **23**, pp. 37-51, 1991.

[3] R. M. Christensen, Theory of Viscoelasticity, 2nd ed., Academic Press, Inc., New York, 1982.

[4] K. Huang, Statistical mechanics, John Wiley & Sons, Inc., 1987.

[5] D. R. Uhlmann and N.J. Kreidl, Eds, "Viscosity and Relaxation," **3**, pp.233-236, in *Glass: Science and Technology*, Academic Press, Inc., New York, 1986.

[6] G. S. Fulcher, "Analysis of Recent Measurements of the Viscosity of Glasses," *J. Am. Ceram. Soc.*, **75**[5], pp.1043-1059, 1992.

[7] C. M. Jantzen, "Methods for melting glass by measurement of non-bridging oxygen," US Patent, 5,102,439, April, 1992.

[8] K. Vinjamuri, GLASSFORM-Version1: An Algorithm for Generating Preliminary Glass Formulations for Waste Streams, INEEL/EXT-98-00269, March, 1998.

[9] P. Hrma, J. D. Vienna, and M. J. Schweiger, "Liquidus Temperature Limited Waste Loading Maximization for Vitrified HLW," *Ceramic Transactions*, **72**, pp. 449-456, 1996.