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Utilizing the non-bridge oxygen model to predict the glass viscosity

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ABSTRACT

Viscosity is the most important process property of waste glass. Viscosity measurement is difficult and costs much. Non-bridging Oxygen (NBO) model which relates glass composition to viscosity had been developed for high level waste at the Savannah River Site (SRS). This research utilized this NBO model to predict the viscosity of KEPRI's 55 glasses. It was found that there was a linear relationship between the measured viscosity and the predicted viscosity. The NBO model could be used to predict glass viscosity in glass formulation development. However the precision of predicted viscosity is out of satisfaction because the composition ranges are very different between the SRS and KEPRI glasses. The modification of NBO calculation, which included modification of alkaline earth elements and TiO_2, could not strikingly improve the precision of predicted values.

INTRODUCTION

Vitrification is the process of converting materials into a glass or glassy substance, typically through a thermal process. It has been selected as the Best Demonstrated Available Technology (BDAT) for the treatment of high-level radioactive waste in USA. With the high concern of environment protection and the rapid increase of disposal cost, vitrification is becoming an attractive technology for low and intermediate level radioactive waste treatment. The treatment and disposal of the low and intermediate level radioactive wastes is increasingly becoming a major operating expense to the Korean nuclear power plants (NPPs). Volume reduction has become one of the most important issues of radioactive management in Korean NPPs. Korea Electric Power Research Institute (KEPRI) has been developing the vitrification technology for treatment low and intermediate radioactive from NPPs, the wastes include combustible dry active waste, borate waste, spent resin, et al. More than 50 glass formulations have been developed to solidify different waste sources.

Viscosity is the most important process property of waste glass. To pour satisfactorily glass it should have a viscosity of 20 - 100 poise. Increasing the melting temperature will decrease the melt viscosity. In order to decrease the waste volatile and increase the melter life, the melting temperature should be about 1150 ^{o}C.

Measurement of glass viscosity is difficult and lengthy. Routine measurement of glass viscosity during glass production, under hazardous circumstance of fabricating radioactive glasses, would be impossible in a remote environment. Processing algorithm which relate glass composition to glass viscosity has been developed for the high level radioactive waste to be processed in the Defense Waste Processing Facility (DWPF) at the Savannah River Site in USA. This model is based on mechanistic arguments, rather than being strictly empirical, in order to increase confidence in their predictive ability. This model has been successfully used to control several scale melter campaigns at SRS. These campaigns involved both simulated and actual radioactive waste glass. Kielpinski [2] has extended this model to alkaline earth low level mixed wastes.

KEPRI has developed the vitrification technology for several years. Glass viscosity at high temperature is an important process parameter, but viscosity measurement is difficult and costs much. If any model could be used to predict the viscosity according to it's composition, it would be helpful in glass formulation study and would save time and cost. Because the KEPRI's waste sources are different from DWPF, it should be checked how well the Jantzen's NBO model also predicts the viscosity of KEPRI's glasses. KEPRI has developed more than 70 glass formulations. This model has been applied to KEPRI's 55 glasses, which viscosity data have been measured.

DESCRIPTION OF VISCOSITY MODEL

Processing algorithm which relate glass composition to glass viscosity has been developed for the high level radioactive waste to be processed in the Defense Waste Processing Facility (DWPF) at the Savannah River Site in USA. This viscosity model is based on a relationship between the glass composition and its structural polymerization. Here called Jantzen's Model. It is based on the well-established concept of a silicate glass as a network of SiO_4 tetrahedra. Bonds between tetrahedra are broken by the presence of alkaline cations, i.e., bridging oxygens are converted to non-bridging oxygens (NBO). The NBO parameter indicates the degree to which the network has been interrupted, and can be correlated with the amount of cation present. Similarly, the NBO is affected by the amount of other components which may act to build the NBO, rather than interrupt the network. The model was a first principles approach based on the calculated NBO term. The NBO was calculated as the following equation in Jantzen's model:

$$NBO = \frac{2(\Sigma(M_2O) + \Sigma(M'O) + Fe_2O_3 - Al_2O_3) + B_2O_3}{SiO_2} \quad (1)$$

where M is an alkaline element, and M' is an alkaline earth element. The NBO is taken as the number of non-bridge oxygen per Si atom in the glass. Two oxygen bridges are broken for every additional molecule of M_2O, $M'O$, or Fe_2O_3; one bridge is broken for every B_2O_3 molecule, and two oxygen bridges are created for every Al_2O_3 molecule.

In Jantzen's Model, the viscosity is predicted as a function of both temperature and composition as follows:

$$\log_{10} \eta = -0.61 + 4472.45/ T[^oC] - 1.534NBO \quad (2)$$

If the melting temperature is 1150 ^{o}C, then equation (2) changed to the follows:

$$\log_{10} \eta = 3.279 - 1.534NBO \quad (3)$$

Equation (3) could be used to predict the viscosity of a known composition glass.

Kielpinski [2] found that Jantzen's Model was not very suitable for the alkali silicate systems. He found that a simple adjustment of the NBO calculation would improve the agreement with experimental data. He considered that an atom of alkaline earth cation provided 1.5 NBO, so the calculation of NBO was calculated as the following equation:

$$NBO = \frac{2(\Sigma(M_2O) + Fe_2O_3 - Al_2O_3) + \Sigma 1.5 \times (M'O) + B_2O_3}{SiO_2} \quad (4)$$

THE COMPOSITION OF DEVELOPED GLASS FORMULATIONS

Korea Electric Power Research Institute (KEPRI) has developed the vitrification technology to treat low and intermediate level radioactive waste from NPPs. Some glass formulations have been selected. Table 1 provided the composition of some glass formulations.

TABLE 1: Composition of glass formulations

Glass No.	Composition, wt%									
	SiO2	B2O3	Na2O	Al2O3	Fe2O3	CaO	MgO	Li2O	TiO2	others
1	59.92	11.59	15.57	12.50	0.00	0.42	0.00	0.00	0.00	0.00
2	47.17	9.55	20.71	5.07	9.75	7.76	0.00	0.00	0.00	0.00
3	36.59	23.57	11.68	8.48	19.44	0.24	0.00	0.00	0.00	0.00
4	35.59	19.85	28.81	8.28	0.00	7.47	0.00	0.00	0.00	0.00
5	35.17	19.80	30.91	4.52	9.35	0.25	0.00	0.00	0.00	0.00
6	58.87	19.45	20.95	0.44	0.00	0.25	0.00	0.00	0.00	0.04
7	60.73	0.00	17.36	5.03	0.00	16.87	0.00	0.00	0.00	0.01
8	52.96	0.00	17.33	4.30	0.13	15.31	0.09	0.00	9.24	0.64
9	34.77	18.88	18.26	2.86	0.13	15.13	0.09	0.00	9.24	0.64
10	36.58	7.17	18.11	1.01	11.99	15.17	0.09	0.00	9.24	0.64
11	38.35	11.11	11.81	3.02	0.17	19.12	0.12	0.00	11.88	4.42
12	30.41	10.82	12.84	2.46	1.36	19.27	2.30	7.92	11.97	0.65
13	45.35	1.82	1.82	3.17	1.75	19.82	2.96	10.18	12.32	0.81
14	49.29	6.40	8.00	0.95	0.00	21.80	0.00	0.00	13.55	0.01
15	37.87	10.00	15.00	0.97	0.00	22.30	0.00	0.00	13.86	0.00
16	35.86	7.74	11.61	7.46	0.00	23.02	0.00	0.00	14.31	0.00
17	33.74	10.00	15.00	1.08	0.00	24.78	0.00	0.00	15.40	0.00
18	56.36	14.54	21.09	5.45	2.47	0.00	0.00	0.00	0.00	0.09
19	43.77	10.18	14.83	4.46	1.86	14.87	0.09	0.00	9.24	0.70
20	41.67	9.45	13.79	4.30	1.76	17.34	0.11	0.00	10.78	0.80
21	39.58	8.72	12.74	4.13	1.66	19.82	0.12	0.00	12.32	0.91
22	37.48	8.00	11.70	3.97	1.56	22.30	0.14	0.00	13.86	0.99

23	35.38	7.27	10.66	3.81	1.46	24.78	0.16	0.00	15.40	1.08
24	47.91	25.30	19.60	4.63	2.10	0.13	0.26	0.00	0.00	0.07
25	45.09	28.89	19.10	4.36	1.98	0.17	0.35	0.00	0.00	0.06
26	39.45	36.07	18.11	3.82	1.73	0.25	0.52	0.00	0.00	0.05
27	42.88	9.45	13.89	4.62	1.90	16.19	0.17	0.00	10.02	0.88
28	40.96	8.72	12.86	4.50	1.82	18.51	0.19	0.00	11.46	0.98
29	39.03	8.00	11.83	4.38	1.74	20.82	0.22	0.00	12.89	1.09
30	39.89	8.73	12.80	4.21	1.71	19.40	0.20	0.00	12.06	1.00
31	43.43	8.72	13.07	5.16	2.11	16.15	0.31	0.00	9.90	1.15
32	43.00	8.06	12.70	5.28	2.41	16.77	1.46	0.00	10.35	0.00
33	41.39	7.29	11.70	5.25	2.39	18.75	1.63	0.00	11.57	0.00
34	39.90	6.56	10.75	5.22	2.37	20.67	1.80	0.00	12.76	0.00
35	47.91	18.62	17.93	4.63	3.54	0.00	0.00	4.23	0.00	3.14
36	45.09	19.98	16.87	4.36	3.89	0.00	0.00	5.64	0.00	4.17
37	39.45	22.70	14.76	3.82	4.61	0.00	0.00	8.47	0.00	6.19
38	33.82	25.42	12.65	3.27	5.32	0.00	0.00	11.29	0.00	8.23
39	58.24	10.18	16.05	8.33	3.55	1.12	0.79	0.00	0.16	1.58
40	59.50	7.27	12.69	10.25	4.28	1.86	1.32	0.00	0.27	2.56
41	50.20	10.24	16.06	6.03	2.92	6.33	1.76	0.00	3.84	2.62
42	46.10	7.38	12.70	6.42	3.22	10.55	2.93	0.00	6.41	4.29
43	42.00	4.52	9.34	6.81	3.51	14.76	4.10	0.00	8.97	5.99
44	54.07	10.21	16.05	7.14	3.22	3.82	1.29	0.00	2.07	2.13
45	52.54	7.33	12.69	8.26	3.73	6.37	2.16	0.00	3.46	3.46
46	46.30	10.90	16.30	3.20	8.70	1.00	1.60	4.20	0.70	7.10
47	48.95	11.12	16.71	3.67	8.97	1.13	1.66	4.28	0.71	2.80
48	48.95	11.12	16.71	3.67	8.97	1.13	1.66	4.28	0.71	2.80
49	47.61	10.00	15.56	20.03	2.32	1.49	0.66	0.00	0.92	1.41
50	44.44	25.46	5.06	18.69	2.16	1.39	0.62	0.00	0.85	1.33
51	38.09	25.00	15.44	16.02	1.85	1.19	0.53	0.00	0.73	1.15
52	38.09	33.95	6.49	16.02	1.85	1.19	0.53	0.00	0.73	1.15
53	31.75	42.44	7.93	13.35	1.55	0.99	0.44	0.00	0.61	0.94
54	41.27	25.00	9.98	17.36	2.01	1.29	0.57	0.00	0.79	1.73
55	41.27	21.22	14.26	17.36	2.01	1.29	0.57	0.00	0.79	1.23

RESULTS

Predicted results by Jantzen's Equation

According the equation (1), we calculated the NBO values of glasses. The comparison between the model and experiment is shown in Fig.1. It is found that there is a linear relationship between the measured and predicted viscosity. Jantzen's Model predicts the viscosities of our developed glasses in less accuracy, when compared to the literature results. It is because, in the different glass composition range, the Jantzen's Model had been developed on the basis of the experiment data of DWPF glasses.

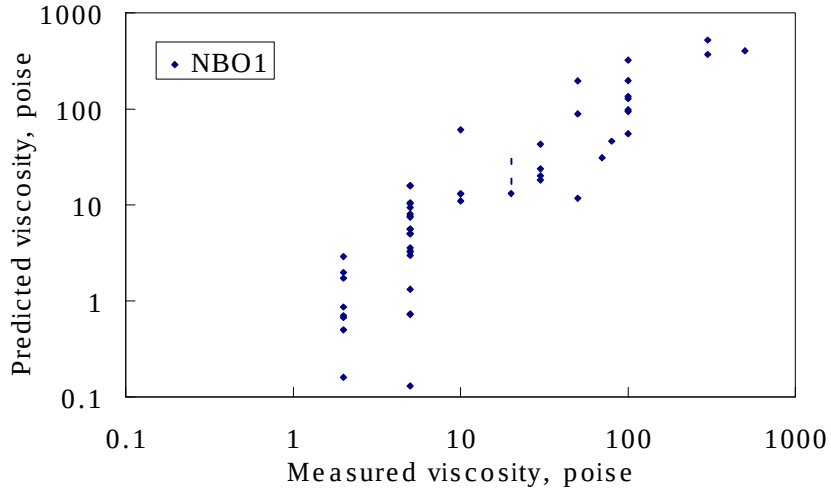


Fig.1 Comparison of measured and predicted viscosity
(Jantzen's Model)

Predicted results by Kielpinski's Equation

Fig.2 shows the glass viscosity predicted using the Kielpinski's equation (4). The results are similar to Fig.1, and there is no great improvement.

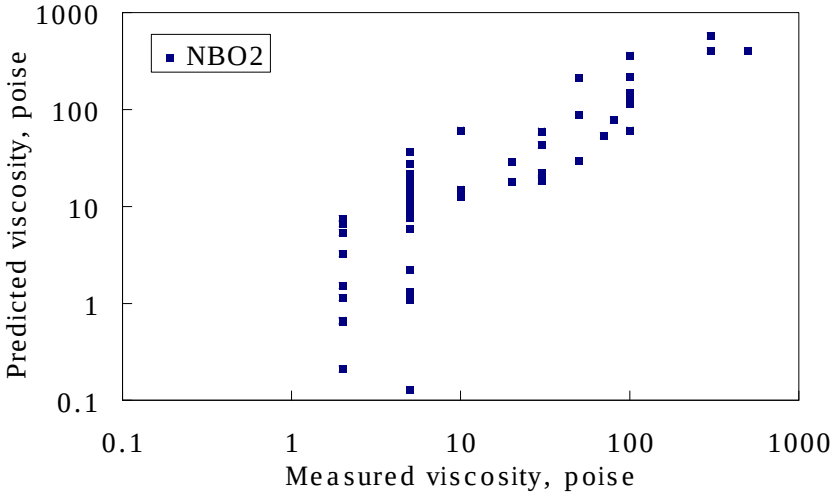
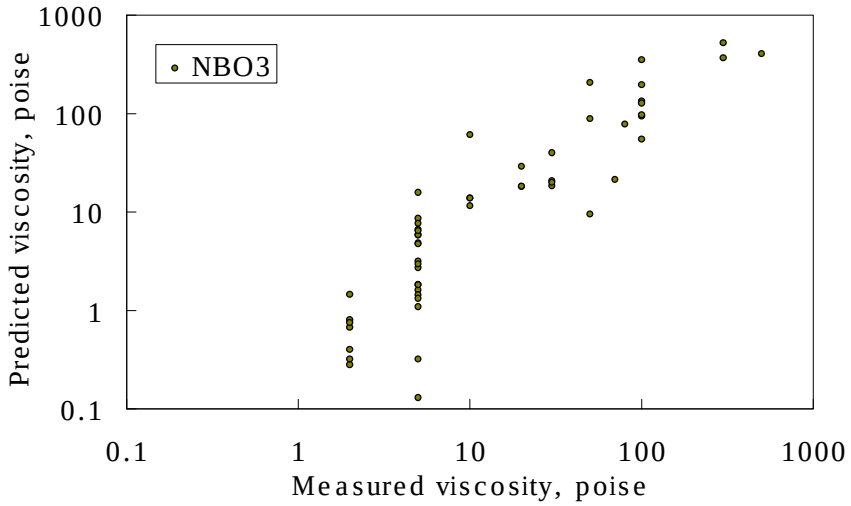


Fig.2 Comparison of measured and predicted viscosity
(Kielpinski's Equation)

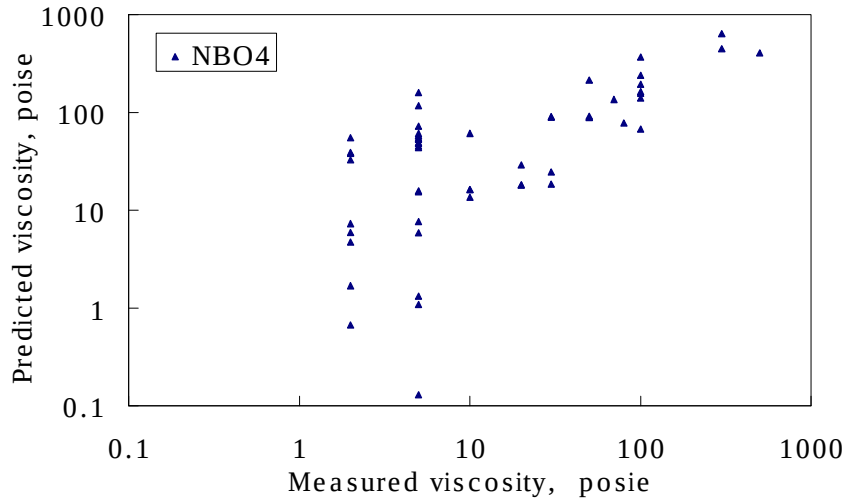
Adjustment of TiO_2 effects

The glasses developed in KEPRI have relatively high content of TiO_2. The above models have not considered the effects of TiO_2. Usually the TiO_2 content in glasses is low. However, some glasses in this study have high content of TiO_2. The effect of TiO_2 on glass durability is complex. Some research found

that TiO_2 would slightly decrease viscosity, and the effect is a little similar to Fe_2O_3. It is assumed that TiO_2 provides same number of NBO as provided by Fe_2O_3. The result was shown in Fig.3 (a). Compared to Fig.1 or Fig.2, there is a little improvement, but no striking improvement. Also, considering TiO_2 as making bridge oxygen as Al_2O_3, Fig.3 (b) gave the results. It is found that TiO_2 could not be considered as a network component.



(a)



(b)

Fig.3 Comparison of measured and predicted viscosity
(Adjustment of TiO_2)
(a) as 2 NBO per TiO_2 ; (b) TiO_2 provides bridge oxygen

SUMMARY

The Jantzen's NBO model has been developed for the high level radioactive waste to be processed in the Defense Waste Processing Facility (DWPF) at the Savannah River Site. This model is simple and based on mechanistic arguments. The result is good for the DWPF composition range. Kielpinski's work has modified this model to alkaline earth low level mixed wastes. The NBO calculation treats all NBO equivalently, regardless of what cation creates the NBO.

This project utilizes the model to predict the viscosity of glasses which have been developed to vitrify low and intermediate level wastes from NPPs. It was found that this model could be applied to our research. There has a linear relationship between the measured viscosity and predicted data. However, the modification of NBO calculation has no significant improvement of the results. Because of the different composition range, it is not very suitable to directly utilize this model to predict glass viscosity in our research. In our future research, we could primarily apply this model to predict glass viscosity. Also, this model could be improved in our glass composition range.

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