**The Influence of Waste Variability on the Properties and
Phase Stability of the West Valley Reference Glass**

Topical Report

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Abstract

A year long study of the effects of waste variability on properties and phase stability of the West Valley reference glass has been conducted. Viscosity, electrical conductivity, glass transition temperature, density, and liquidus temperature have been measured for a series of glasses where the weight fraction of Al_2O_3 , Fe_2O_3 , NiO , MnO_2 , Cr_2O_3 , and P_2O_5 was varied systematically around the reference glass composition. A computer program for predicting melt viscosity has been developed. A preliminary Time-Temperature-Transformation diagram was also determined for the reference composition. It is concluded that the system, "Glass Formers-Zeolite-Waste Mix," is a forgiving one in the sense that considerable variation of waste composition can be tolerated without substantially affecting the melting and phase behavior of the reference glass.

Contents

ACKNOWLEDGEMENTS	1
EXECUTIVE SUMMARY	2
1.0 INTRODUCTION/OVERVIEW	3
2.0 COMPOSITIONS STUDIED	4
2.1 Introduction	4
2.2 Starting Compositions	4
2.3 Components Varied	6
3.0 PREPARATION AND CHARACTERIZATION OF GLASSES	8
3.1 Batching and Melting	8
3.1.1 Batching	8
3.1.2 Melting	11
3.2 Chemical Analysis	11
3.3 Petrography	12
3.4 X-Ray/Energy Dispersive Spectroscopy	13
3.4.1 X-Ray Analysis	13
3.4.2 Energy-Dispersive Spectroscopy (EDS)	23
3.5 Thermal Analysis	24
3.5.1 Procedure- DSC	24
3.5.2 Procedure- Dilatometry	27
3.5.3 Results	27
3.5.4 Analysis	29
4.0 PROPERTY MEASUREMENTS	31
4.1 Density	31
4.2 Viscosity Measurements	31
4.2.1 Low-Temperature Viscosity Measurements	31
4.2.1.1 Sample Preparation	31
4.2.1.2 Experimental Procedure	32
4.2.1.3 Calibration	32
4.2.1.4 Data Collection	32
4.2.2 High-Temperature Viscosity Measurements	32
4.2.2.1 Sample Preparation	32
4.2.2.2 Experimental Procedure	33
4.2.2.3 Calibration	33
4.2.2.4 Data Collection	37
4.2.2.5 Viscosity Data Analysis	37
4.3 Electrical Conductivity	45
4.3.1 Experimental Apparatus	45
4.3.2 Calibration of the Conductivity Cell	45
4.3.3 Comparison to Previous Work	46
4.3.4 Present Work	46
4.4 Spider Diagrams	58
4.4.1 Single Variations	58
4.4.2 Double Variation	64

5.0 PHASE STABILITY STUDIES	68
5.1 Glass Formation Region	68
5.1.1 Starting Components	68
5.1.2 Compositions Studied	69
5.1.3 Experimental Procedure	69
5.1.4 Results	70
5.2 Determination of the Origin of the Dark Phase Observed in WV-205 Glass	70
5.2.1 Starting Components	77
5.2.2 Compositions Studied	77
5.2.3 Experimental Procedure	77
5.2.4 Results	77
5.3 Liquidus Temperature	78
5.3.1 Starting Components	80
5.3.2 Compositions Studied	80
5.3.3 Experimental Procedure	80
5.3.4 Results	80
5.3.5 Analysis	82
5.4 Time -Temperature-Transformation (TTT) Diagram	82
5.4.1 Starting Components	82
5.4.2 Compositions Studied	82
5.4.3 Experimental Procedure	82
5.4.4 Results	84
 6.0 DISCUSSION/RECOMMENDATIONS FOR FUTURE WORK	 115

Figures

3.3.1: Optical micrographs of the Aluminum Oxide Variation Series	14
3.3.2: Optical Micrographs of the Chromium Oxide Variation Series	15
3.3.3: Optical Micrographs of the Iron Oxide Variation Series	16
3.3.4: Optical Micrographs of the Manganese Oxide Variation Series	17
3.3.5: Optical Micrographs of the Nickel Oxide Variation Series	18
3.3.6: Optical Micrographs of the Phosphorous Oxide Variation Series	19
3.3.7: Optical Micrograph of the Centroid Composition	20
3.3.8: Optical Micrograph of Double Variation Glass	21
3.3.9: Optical Micrographs of Double Variation Glasses	22
3.4.2.1: EDS Spectrum of a Dark Phase in WV-205 Glass	25
3.5.1.1: Typical DSC Data For Glass P-004	26
3.5.2.1: Typical Dilatometry Data for Sample FE-002	28
3.5.4.1: Comparison of the Glass Transition Temperature Between DSC and Dilatometry Methods	30
4.2.1.3.1: Low Temperature Viscosity Calibration	34
4.2.1.4.1: Low and High Temperature Viscosity Data for Centroid Glass	35
4.2.2.3.1: High Temperature Viscosity Calibration	36
4.2.2.5.1: High Temperature Viscosity Data for All Glasses	38
4.2.2.5.2: Viscosity of Al ₂ O ₃ series glasses at 1000, 1050, 1100 AND 1150°C	39
4.2.2.5.3: Viscosity of Cr ₂ O ₃ Series Glasses at 1000, 1050 1100 and 1150°C	40
4.2.2.5.4: Viscosity of Fe ₂ O ₃ Series Glasses at 1000, 1050 1100 and 1150°C	41
4.2.2.5.5: Viscosity of MnO ₂ Series Glasses at 1000, 1050 1100 and 1150°C	42
4.2.2.5.6: Viscosity of NiO Series Glasses at 1000, 1050 1100 and 1150°C	43
4.2.2.5.7: Viscosity of P ₂ O ₅ Series Glasses at 1000, 1050 1100 and 1150°C	44
4.3.1.1: Schematic Drawing of Electrical Conductivity Apparatus	47
4.3.3.1: Resistivity Data for SRM 711 Glass	48
4.3.4.1: Resistivity Data for the Centroid Composition	49
4.3.4.2: Imaginary Versus Real Resistivity as a Function of Frequency for the Centroid Composition Glass Melt ..	50
4.3.4.3: Resistivity of All the Glasses Used in this Study	51
4.3.4.4: Change in Resistivity as a Function of Mole Percent Al ₂ O ₃	52
4.3.4.5: Electrical Resistivity as a Function of Mole Percent Cr ₂ O ₃	53
4.3.4.6: Electrical Resistivity as a Function of Mole Percent Fe ₂ O ₃	54
4.3.4.7: Electrical Resistivity as a Function of Mole Percent MnO ₃	55
4.3.4.8: Electrical Resistivity as a Function of Mole Percent NiO	56
4.3.4.9: Electrical Resistivity as a Function of Mole Percent P ₂ O ₅	57
4.4.1.1: Spider Diagram for Viscosity at 1000°C	60
4.4.1.2: Spider Diagram for Viscosity at 1050°C	61
4.4.1.3: Spider Diagram for Viscosity at 1100°C	62
4.4.1.4: Spider Diagram for Viscosity at 1150°C	63
4.4.2.1: Viscosity Data for High Al ₂ O ₃ High P ₂ O ₅ Glass	65
4.4.2.2: Viscosity Data for High Al ₂ O ₃ Low P ₂ O ₅ Glass	66
4.4.2.3: Viscosity Data for High Al ₂ O ₃ High P ₂ O ₅ Glass	67
5.1.4.1: Glass Formation Region - One Hour Melts in Porcelain Crucibles at 1000°C	71
5.1.4.2: Glass Formation Region - One Hour Melts in Porcelain Crucibles at 1100°C	72
5.1.4.3: Glass Formation Region - One Hour Melts in Porcelain Crucibles at 1200°C	73
5.1.4.4: Glass Formation Region - 22-Hour Melts in Porcelain Crucibles at 1000°C	74
5.1.4.5: Glass Formation Region - 22-Hour Melts in Porcelain Crucibles at 1100°C	75
5.1.4.6: Glass Formation Region - 22-Hour Melts in Porcelain Crucibles at 1200°C	76
5.2.4.1: WV-205 Untreated Glass (250X)	79
5.2.4.2: WV-205S Untreated Glass (250X)	79
5.2.4.3: WV-205R Glass without RuO ₂ and RhO ₂ (250X)	79
5.4.4.1: Optical Micrograph of WV-205 Glass Heat Treated for 12 Hours at 500°C	85
5.4.4.2: Optical Micrograph of WV-205 Glass Heat Treated for 24 Hours at 500°C	85
5.4.4.3: Optical Micrograph of WV-205 Glass Heat Treated for 48 Hours at 500°C	86

(Figures)

5.4.4.4:	Optical Micrograph of WV-205 Glass Heat Treated for 72 Hours at 500°C	86
5.4.4.5:	Optical Micrograph of WV-205 Glass Heat Treated for 6 Hours at 600°C	87
5.4.4.6:	Optical Micrograph of WV-205 Glass Heat Treated for 24 Hours at 600°C	87
5.4.4.7:	Optical Micrograph of WV-205 Glass Heat Treated for 48 Hours at 600°C	88
5.4.4.8:	Optical Micrograph of WV-205 Glass Heat Treated for 72 Hours at 600°C	88
5.4.4.9:	Optical Micrograph of WV-205 Glass Heat Treated for 1 Hour at 650°C (250X)	89
5.4.4.10:	Optical Micrograph of WV-205 Glass Heat Treated for 2 Hours at 650°C (250X)	89
5.4.4.11:	Optical Micrograph of WV-205 Glass Heat Treated for 3 Hours at 650°C (250X)	89
5.4.4.12:	Optical Micrograph of WV-205 Glass Heat Treated for 6 Hours at 650°C	90
5.4.4.13:	Optical Micrograph of WV-205 Glass Heat Treated for 12 Hours at 650°C	90
5.4.4.14:	Optical Micrograph of WV-205 Glass Heat Treated for 30 Minutes at 700°C	91
5.4.4.15:	Optical Micrograph of WV-205 Glass Heat Treated for 1 Hour at 700°C	91
5.4.4.16:	Optical Micrograph of WV-205 Glass Heat Treated for 2 Hours at 700°C	92
5.4.4.17:	Optical Micrograph of WV-205 Glass Heat Treated for 3 Hours at 700°C	92
5.4.4.18:	Optical Micrograph of WV-205 Glass Heat Treated for 6 Hours at 700°C	93
5.4.4.19:	Optical Micrograph of WV-205 Glass Heat Treated for 12 Hours at 700°C	93
5.4.4.20:	Optical Micrograph of WV-205 Glass Heat Treated for 24 Hours at 700°C	94
5.4.4.21:	Optical Micrograph of WV-205 Glass Heat Treated for 48 Hours at 700°C	94
5.4.4.22:	Optical Micrograph of WV-205 Glass Heat Treated for 1 Hour at 750°C	95
5.4.4.23:	Optical Micrograph of WV-205 Glass Heat Treated for 2 Hours at 750°C	95
5.4.4.24:	Optical Micrograph of WV-205 Glass Heat Treated for 3 Hours at 750°C	96
5.4.4.25:	Optical Micrograph of WV-205 Glass Heat Treated for 6 Hours at 750°C	96
5.4.4.26:	Optical Micrograph of WV-205 Glass Heat Treated for 12 Hours at 750°C (250X)	97
5.4.4.27:	Optical Micrograph of WV-205 Glass Heat Treated for 12 Hours at 750°C (400X)	97
5.4.4.28:	Optical Micrograph of WV-205 Glass Heat Treated for 6 Hours at 800°C	98
5.4.4.29:	Optical Micrograph of WV-205 Glass Heat Treated for 12 Hours at 800°C	98
5.4.4.30:	Optical Micrograph of WV-205 Glass Heat Treated for 48 Hours at 800°C	99
5.4.4.31:	Optical Micrograph of WV-205 Glass Heat Treated for 72 Hours at 800°C	99
5.4.4.32:	Optical Micrograph of WV-205 Glass Heat Treated for 6 Hours at 900°C	100
5.4.4.33:	Optical Micrograph of WV-205 Glass Heat Treated for 10 Hours at 900°C	100
5.4.4.34:	Optical Micrograph of WV-205 Glass Heat Treated for 48 Hours at 900°C	101
5.4.4.35:	Optical Micrograph of WV-205 Glass Heat Treated for 72 Hours at 900°C	101
5.4.4.36:	Optical Micrograph of WV-205 Glass Heat Treated for 24 Hours at 1000°C	102
5.4.4.37:	Optical Micrograph of WV-205 Glass Heat Treated for 48 Hours at 1000°C	102
5.4.4.38:	Optical Micrograph of WV-205 Glass Heat Treated for 72 Hours at 1000°C	103
5.4.4.39:	Optical Micrograph of WV-205 Glass Heat Treated for 96 Hours at 1000°C	103
5.4.4.40:	Optical Micrograph of WV-205 Glass Heat Treated for 12 Hours at 1100°C	104
5.4.4.41:	Optical Micrograph of WV-205 Glass Heat Treated for 48 Hours at 1100°C	104
5.4.4.42:	T T T Diagram for WV-205 Glass	106
5.4.4.43:	EDS Spectrum of a Particle in WV-205 Glass Heat-Treated for 72 Hours at 500°	107
5.4.4.44:	EDS Spectrum of a Particle in WV-205 Glass Heat-Treated for 72 Hours at 500°C	108
5.4.4.45:	EDS Spectrum of a Particle in WV-205 Glass	109
5.4.4.46:	EDS Spectrum of a Particle in WV-205 Glass	110
5.4.4.47:	EDS Spectrum of a Dark Crystal in WV-205 Glass	111
5.4.4.48:	EDS Spectrum of Part of a Crystal in WV-205 Glass	112
5.4.4.49:	EDS Spectrum of a Center of a Crystal in WV-205 Glass	113

Tables

2.2.1: Unsubstituted Waste Mix	5
2.2.2: Substituted Waste Mix	5
2.2.3: Nominal Oxide Composition of IE-96+	6
2.3.1: Composition Ranges Studied (in wt. %)	7
2.3.2: Centroid Composition	7
3.1.1.1: Master Waste Mix	8
3.1.1.2: Master Batch Subset (Oxide Wt. %)	9
3.1.1.3: Al ₂ O ₃ Series Master Recipe (Wt. %) Batch Designation	9
3.1.1.4: Cr ₂ O ₃ Series Master Recipe (Wt. %)	10
3.1.1.5: Fe ₂ O ₃ Series Master Recipe (Wt. %)	10
3.1.1.6: MnO ₂ Series Master Recipe (Wt. %)	10
3.1.1.7: NiO Series Master Recipe (Wt. %)	10
3.1.1.8: P ₂ O ₅ Series Master Recipe (Wt. %)	11
3.2.1: Target and Analyzed Compositions	12
3.4.1.1: Observed and Reported peak 2θ Values and Relative Intensities for NBS Standard Silicon (SRM 640a)	23
3.5.3.1: Glass Transition Temperature (T _g) Data Obtained By the DSC Method	29
4.4.1.1: Actual and Adjusted Viscosity Values for the Centroid Composition	58
4.4.1.2: Spider Diagram Coefficients	59
4.4.2.1 Measured Versus Calculated Viscosity Data for the Double-Variation Glass	64
5.1.2.1: WV-205 Glass Former (Oxide) Composition	69
5.4.4.1: Average Size of Crystals and Volume Fraction of Crystals in Heat-Treated Glass	105

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EXECUTIVE SUMMARY

A year-long study was conducted at the Institute of Glass Science and Engineering on behalf of West Valley Nuclear Services Co., Inc. for the West Valley Demonstration Project (WVDP). This study involved: (1) a determination of property composition relations where six components of the waste, Al_2O_3 , Fe_2O_3 , MnO_2 , NiO , P_2O_5 , and Cr_2O_3 were varied systematically around a centroid composition (WV-205); (2) a determination of the region of glass formation in the system, "Glass Formers-Zeolite-Waste Mix"; (3) a determination of a TIME-TEMPERATURE-TRANSFORMATION diagram for the composition WV-205; (4) measurement of the glass transition temperature of all glasses melted in this work; and (5) an investigation of microstructure of all glasses prepared by optical microscopy, scanning electron microscopy, and X-ray diffraction. The properties of interest in number one were viscosity, electrical conductivity, density, and liquidus temperature.

It was found that all glasses prepared contained a dispersed, undissolved phase which was identified as RuO_2 . Removal of this compound from the simulated waste mix resulted in single-phased, homogenous glasses. Crystal growth was seen to occur around RuO_2 particles during isothermal crystallization studies.

Very little dependence of density, liquidus temperature, and electrical conductivity (in the liquid state) on composition was observed. Viscosity increased substantially with increasing Al_2O_3 , and only slightly with P_2O_5 and NiO additions. Addition of Cr_2O_3 lowered viscosity slightly; at higher temperatures, MnO_2 and Fe_2O_3 additions caused a substantial reduction of viscosity. From the data obtained in this work, a computer program was developed which allows the calculation of viscosity when one, two, or more components are varied.

The rate of crystallization was a maximum in the temperature range of 700° to 750°C. Above 800°C, only spinel was found. In the temperature range of 700° to 800°C, two phases -- spinel and sodium iron-silicate -- were observed. Three crystalline phases developed in the range of 600° to 700°C; two of the phases were spinel and sodium iron-silicate. The third phase (not definitively identified) is probably a sodium aluminosilicate or sodium potassium aluminosilicate.

The main conclusion of this investigation was that for the composition ranges studied, the resulting system, "Glass Formers-Zeolite-Waste Mix," is a forgiving one, that is, considerable variations of these components can be allowed without significantly affecting the properties measured.

1.0 INTRODUCTION/OVERVIEW

The following pages summarize recent West Valley Demonstration Project (WVDP) waste glass processability testing and characterization performed from November 1, 1985 to September 30, 1986. A major portion of this investigation was concerned with measuring the effect of waste variations on properties such as electrical conductivity, viscosity, density, glass transition temperature, and liquidus temperature. Another portion was concerned with constructing a TIME-TEMPERATURE-TRANSFORMATION (TTT) diagram for WV-205, the present West Valley reference borosilicate glass. Additionally, the region of glass formation in the system, "Glass Formers-Zeolite-Waste Mix," was determined.

This report is organized around five main sections. Following the introduction, the second section deals with compositions studied and the method by which target compositions were calculated. The third part deals with the preparation and characterization of glasses prepared in this work (for example, melting, chemical analysis, petrographic examination, and X-ray diffraction studies), energy-dispersive spectroscopy and thermal analysis. The fourth section describes the measurement of viscosity, electrical conductivity, and density, all as a function of composition, and the results we obtained. Also included in this section is a description of a computer program for calculating viscosity as a function of composition.

The final portion of this report concentrates on phase stability studies in the system, "Glass Formers-Zeolite-Waste Mix."

2.0 COMPOSITIONS STUDIED

2.1 Introduction

A portion of this work involved a determining the effect of varying certain components in the simulated waste mix on the physical properties of a glass-forming melt containing this mix at a loading level of 23.0 weight percent. In accordance with the vitrification flow sheet now planned for the WVDP, the other components of this melt were "glass formers" (67.0 percent) and zeolite (10.0 percent). The following components in the waste mix were selected to be varied: Fe_2O_3 , Al_2O_3 , MnO_2 , Cr_2O_3 , P_2O_5 , and NiO . In selecting these components and in establishing the ranges of variations to be examined for each, the following factors were considered:

Some of the major components in the waste mix, for example, SiO_2 , Na_2O , K_2O , and MgO , also comprise a portion of the glass formers used to create the melt which will dissolve the waste mix. Since the composition of the glass formers can be adjusted prior to mixing (within reasonable limits) to reflect variation of components in the waste mix, it was not believed necessary to assess their influence on the above properties. Thus, the components selected for study cannot readily be adjusted in the resulting glass-forming melts, that is, excess Fe_2O_3 , Cr_2O_3 , NiO , etc., cannot be extracted. Rather, it should be determined whether or not these excesses (or deficiencies) can be accommodated by a centroid glass melt defined by 23 percent waste, 67 percent glass formers, and 10 percent zeolite.

Many different approaches can be used in designing a systematic study of the effect of composition on properties. For the West Valley vitrification process, it was preferable to start this study by first varying only one component at a time over the range of interest and then proceeding to examine the effects of varying two components. In this way, the effect of each component on the properties of interest can be determined unambiguously. A single-component variation is essential for understanding the relationship between properties and composition. This is especially true when determining the influence of single-component variations on microstructure. This influence cannot be modeled, that is, one must physically prepare the series in question and proceed to analyze them. Thus, the required series was melted, the properties of interest were measured, the microstructure was determined, and the effect of multicomponent variations on properties such as viscosity and electrical conductivity was predicted. It will be seen that this procedure proved to be quite satisfactory and substantially reduced the number of glasses that were needed for this work scope.

The procedures that were employed to obtain the calculated compositions of the waste and the resulting glasses are discussed below. In Section 3.0, the batching, mixing and melting procedures employed in this work are discussed.

2.2 Starting Compositions

The unsubstituted waste mix calculated in this work is presented in Table 2.2.1. The substituted waste mix used for the centroid composition is given in Table 2.2.2. The glass formers are those specified for WV-205 (for example, SiO_2 -57.29 percent, K_2O -5.28 percent, Li_2O -4.68 percent, MgO -1.77 percent, B_2O_3 -15.29 percent, TiO_2 -1.48 percent, and Na_2O -14.21 percent). The zeolite used in this study was IE-96 (Union Carbide) and has the nominal composition given in Table 2.2.3.

Table 2.2.1: Unsubstituted Waste Mix

Oxide	wt. %	Oxide	wt. %
Ag ₂ O	0.001	Nd ₂ O ₃	0.544
Al ₂ O ₃	5.017	NiO	1.178
AmO ₂	0.034	NpO ₂	0.105
B ₂ O ₃	0.289	P ₂ O ₅	2.859
BaO	0.209	PdO ₂	0.033
CaO	1.723	Pm ₂ O ₃	0.001
CdO	0.001	Pr ₂ O ₃	0.145
CeO ₂	0.313	PuO ₂	0.036
CmO ₂	trace	Rb ₂ O	0.002
CoO	0.001	RhO ₂	0.063
Cr ₂ O ₃	0.713	RuO ₂	0.355
Cs ₂ O	0.020	SO ₃	1.403
CuO	0.292	Sb ₂ O ₃	0.001
Eu ₂ O ₃	0.007	SeO ₂	0.002
Fe ₂ O ₃	53.182	SiO ₂	1.270
Gd ₂ O ₃	0.002	Sm ₂ O ₃	0.125
HgO	0.020	SnO ₂	0.003
In ₂ O ₃	trace	SrO	0.126
K ₂ O	0.276	TeO ₂	0.013
La ₂ O ₃	0.157	Tc ₂ O ₇	0.008
Li ₂ O	--	ThO ₂	16.742
MgO	0.393	UO ₂	2.619
MnO ₂	4.421	Y ₂ O ₃	0.082
MoO ₃	0.041	ZnO	0.104
Na ₂ O	4.355	ZrO ₂	<u>0.715</u>
			100.000

Table 2.2.2: Substituted Waste Mix

Oxide	wt. %	Oxide	wt. %
Al ₂ O ₃	5.61	NiO	1.62
B ₂ O ₃	0.32	P ₂ O ₅	3.20
BaO	0.23	Pr ₂ O ₃	0.16
CaO	1.93	RhO ₂	0.12
CeO ₂	0.35	RuO ₂	0.40
Cr ₂ O ₃	0.80	SO ₃	1.60
Fe ₂ O ₃	59.44	SiO ₂	1.42
K ₂ O	0.32	Sm ₂ O ₃	0.15
La ₂ O ₃	0.18	SrO	0.14
MgO	0.44	Y ₂ O ₃	0.09
MnO ₂	4.94	ZnO	0.12
Na ₂ O	4.87	ZrO ₂	<u>10.96</u>
Nd ₂ O ₃	0.61	Total	100.02

Table 2.2.3: Nominal Oxide Composition of IE-96⁺

Oxide	wt. %
Al ₂ O ₃	16.81
BaO	0.18
CaO	1.03
CdO	<0.07
Cr ₂ O ₃	<0.05
CuO	<0.07
Fe ₂ O ₃	3.93
K ₂ O	0.64
La ₂ O ₃	<0.03
MgO	0.87
MnO ₂	0.08
MoO ₃	<0.05
Na ₂ O	7.68
NiO	<0.08
P ₂ O ₅	<0.26
PbO	<0.06
Sb ₂ O ₃	<0.07
SiO ₂	67.49
SrO	0.05
TiO ₂	0.32
V ₂ O ₅	<0.10
ZnO	<0.04
ZrO ₂	<0.05
	100.01

⁺ Union Carbide Corporation Central Scientific Laboratories Analysis No. 008501, Sample 50-1

2.3 Components Varied

As previously mentioned, we selected the following waste oxides to be varied: Al₂O₃, Cr₂O₃, Fe₂O₃, MnO₂, NiO, and P₂O₅. The variation range of each of these oxides was chosen to insure that the centroid composition of that component in the final glass was bracketed. The ranges for the components to be studied (in both the final glass and waste) are tabulated in Table 2.3.1. Based on the results obtained for these studies in which only single components were varied, melts were made in which two components were changed simultaneously (see Section 4.4.2). The calculated centroid composition (67 percent glass formers, 23 percent substituted waste mix, and 10 percent zeolite) is given in Table 2.3.2.

Table 2.3.1: Composition Ranges Studied (in wt. %)

Waste Mix

<u>Oxide</u>	<u>001</u>	<u>002</u>	<u>003</u>	<u>004</u>	<u>005</u>
Al ₂ O ₃	0.00	2.80	5.61	9.611	5.22
Cr ₂ O ₃	0.00	0.40	0.80	2.14	3.48
Fe ₂ O ₃	43.48	51.46	59.44	67.42	75.40
MnO ₂	0.00	2.47	4.94	8.99	13.04
NiO	0.00	0.81	1.62	2.99	4.35
P ₂ O ₅	0.00	1.60	3.20	7.91	12.61

Final Glass

<u>Oxide</u>	<u>001</u>	<u>002</u>	<u>003</u>	<u>004</u>	<u>005</u>
Al ₂ O ₃	1.68	2.32	2.97	3.89	5.18
Cr ₂ O ₃	0.00	0.10	0.19	0.50	0.80
Fe ₂ O ₃	10.39	12.23	14.06	15.90	17.74
MnO ₂	0.01	0.58	1.14	2.08	3.01
NiO	0.01	0.19	0.38	0.70	1.01
P ₂ O ₅	0.03	0.39	0.76	1.84	2.93

Table 2.3.2: Centroid Composition

<u>Oxide</u>	<u>wt. %</u>	<u>Mol %</u>	<u>Oxide</u>	<u>wt. %</u>	<u>Mol %</u>
Al ₂ O ₃	2.97	1.99	NiO	0.38	0.35
B ₂ O ₃	10.31	10.14	P ₂ O ₅	0.76	0.37
BaO	0.07	0.03	PbO	0.01	0.00
CaO	0.54	0.66	Pr ₂ O ₃	0.04	0.01
CdO	0.01	0.01	RhO ₂	0.03	0.02
CeO ₂	0.08	0.03	RuO ₂	0.09	0.05
Cr ₂ O ₃	0.19	0.09	SO ₃	0.37	0.32
CuO	0.01	0.01	Sb ₂ O ₃	0.01	0.00
Fe ₂ O ₃	14.06	6.03	SiO ₂	45.46	51.86
K ₂ O	3.67	2.67	Sm ₂ O ₃	0.04	0.01
La ₂ O ₃	0.04	0.01	SrO	0.04	0.03
Li ₂ O	3.14	7.19	TiO ₂	1.02	0.87
MgO	1.37	2.33	V ₂ O ₅	0.01	0.00
MnO ₂	1.14	0.90	Y ₂ O ₃	0.01	0.00
MoO ₃	0.01	0.00	ZnO	0.03	0.03
Na ₂ O	11.41	12.60	ZrO ₂	2.53	1.41
Nd ₂ O ₃	0.14	0.03			

3.0 PREPARATION AND CHARACTERIZATION OF GLASSES

This section discusses the way in which the glasses and melts used in this study were prepared. Also discussed are the various characterizations undertaken for most of these glasses.

3.1 Batching and Melting

3.1.1 Batching

One of the major errors in composition -- properties studies of the type conducted here -- involves the homogeneity of the resulting batch and glasses. Poor mixing or melting procedures may contribute to composition fluctuations which are undesirable. For these reasons, melting, crushing and remelting of the batches is preferred. Chemical analysis of the resulting glasses is also helpful to establish the correlations between properties and composition. Finally, mixing of the batches is greatly facilitated by considering a series of subsets derived from master mixes of the components of interest, a procedure which was adopted in the present work. The procedures we have employed to obtain the calculated compositions of the waste and the resulting glasses are outlined below.

A Master Waste Mix (MWM) was computed and prepared to facilitate the accurate preparation of the batches to be used in this study. The oxide composition of this MWM is given in Table 3.1.1.1, and is composed of the components to be varied (at their minimal weight percentages) and the remaining fixed oxides. Preparation of the batches for each series were made by the addition of the desired component in a specified amount to the MWM. In this way, the total number of weighings required for each mixture was greatly reduced.

Table 3.1.1.1: Master Waste Mix

Oxide	wt. %	Oxide	wt. %	Oxide	wt. %
B ₂ O ₃	0.58	MgO	0.79	SiO ₂	2.56
BaO	0.41	Na ₂ O	8.76	Sm ₂ O ₃	0.27
CaO	3.47	Nd ₂ O ₃	1.10	SrO	0.26
CeO ₂	0.63	Pr ₂ O ₃	0.28	Y ₂ O ₃	0.17
Fe ₂ O ₃	56.13	RhO ₂	0.22	ZnO	0.22
K ₂ O	0.58	RuO ₂	0.72	ZrO ₂	19.71
La ₂ O ₃	0.32	SO ₃	2.88	TOTAL	100.06

Preparation of the batches was further simplified by the compilation of Variable Master Batch Subsets (VMBS) for each component to be studied. These compositions are given in Table 3.1.1.2 where it is seen that the VMBSs are devoid of the particular oxide of that series. The quantities in this table were calculated by normalizing the remaining oxides to be varied following subtraction of the variable oxide of interest.

Table 3.1.1.2: Master Batch Subset (Oxide Wt. %)

Oxide	AMBS ⁺	CMBS ⁺	FMBS ⁺	MMBS ⁺	NMBS ⁺	PMBS ⁺
Al ₂ O ₃	-	36.50	34.69	49.96	38.56	43.25
Cr ₂ O ₃	7.58	-	4.95	7.12	5.50	6.17
MnO ₂	46.78	32.14	30.55	-	33.95	12.49
NiO	15.34	10.54	10.02	14.43	-	38.09
P ₂ O ₅	<u>30.30</u>	<u>20.82</u>	<u>19.79</u>	<u>28.50</u>	<u>21.99</u>	=
	100%	100%	100%	100%	100%	100%

⁺ AMBS - Al₂O₃ Master Batch Subset
 CMBS - Cr₂O₃ Master Batch Subset
 FMBS - Fe₂O₃ Master Batch Subset
 MMBS - MnO₂ Master Batch Subset
 NMBS - NiO Master Batch Subset
 PMBS - P₂O₅ Master Batch Subset

The composition of the batches in the variation series can be calculated using Tables 2.3.1 and 2.3.2. A change in the weight percent of a variable oxide should be reflected by a proportional change in all the remaining oxides (variable and nonvariable). Table 2.3.1 specifies the target values of the variable components within the variation series. From the centroid composition in Table 2.3.2, adjustment of the oxides to the values specified for the variation series is arrived at by the following procedure: If 'C' represents the centroid value of the variable component in Table 2.3.2 and 'T' represents the target value of the variable component in the variation series (Table 2.3.1), then all the other oxides (variable and nonvariable) are multiplied by $(100-T)/(100-C)$.

By multiplying the resulting weight percent component oxide by the loading factor for the waste and adding in the contribution of each component from the glass formers and zeolite, the total composition of the oxides in the variation series is obtained.

To facilitate the preparation of the actual batches, master recipe tables are constructed. These are given in Tables 3.1.1.3 to 3.1.1.8. Here it is seen that the correct batching of the variation series is easily done by the addition of the four components listed (variable oxide, VMBS, Fe₂O₃, and MWM), in the specified weight percent.

Table 3.1.1.3: Al₂O₃ Series Master Recipe (Wt. %) Batch Designation

	AL-001	AL-002	AL-003	AL-004	AL-005
Al ₂ O ₃	0.00	2.80	5.61	9.61	15.22
AMBS	11.19	10.87	10.56	11.11	9.48
Fe ₂ O ₃	26.10	25.36	24.63	23.58	22.13
MWM	<u>58.90</u>	<u>57.26</u>	<u>55.60</u>	<u>53.25</u>	<u>49.94</u>
TOTAL	100.00	100.00	100.00	100.00	100.00

Table 3.1.1.4: Cr₂O₃ Series Master Recipe (Wt. %)

Batch Designation

	CR-001	CR-002	CR-003	CR-004	CR-005
Cr ₂ O ₃	0.00	0.40	0.80	2.14	3.48
CMBS	15.50	15.43	15.37	15.16	14.97
Fe ₂ O ₃	28.47	28.35	28.23	27.86	27.47
MWM	<u>56.03</u>	<u>55.82</u>	<u>55.60</u>	<u>54.84</u>	<u>54.09</u>
TOTAL	100.00	100.00	100.00	100.00	100.00

Table 3.1.1.5: Fe₂O₃ Series Master Recipe (Wt. %)

Batch Designation

	FE-001	FE-002	FE-003	FE-004	FE-005
FMBS	*	19.31	16.17	12.99	9.81
Fe ₂ O ₃	0.00	14.06	28.23	42.36	56.54
MWM	<u>77.47</u>	<u>66.63</u>	<u>55.60</u>	<u>44.65</u>	<u>33.65</u>
TOTAL	100.00	100.00	100.00	100.00	100.00

Table 3.1.1.6: MnO₂ Series Master Recipe (Wt. %)

Batch Designation

	MN-001	MN-002	MN-003	MN-004	MN-005
MnO ₂	0.00	2.47	4.94	8.99	13.04
MMBS	11.81	11.52	11.23	10.75	10.27
Fe ₂ O ₃	29.70	28.96	28.23	27.03	25.84
MWM	<u>58.49</u>	<u>57.05</u>	<u>55.60</u>	<u>53.23</u>	<u>50.85</u>
TOTAL	100.00	100.00	100.00	100.00	100.00

Table 3.1.1.7: NiO Series Master Recipe (Wt. %)

Batch Designation

	NI-001	NI-002	NI-003	NI-004	NI-005
NiO ₂	0.00	0.81	1.62	2.99	4.35
NMBS	14.79	14.67	14.55	14.35	14.15
Fe ₂ O ₃	28.70	28.47	28.23	27.84	27.45
MWM	<u>56.51</u>	<u>56.05</u>	<u>55.60</u>	<u>54.82</u>	<u>54.05</u>
TOTAL	100.00	100.00	100.00	100.00	100.00

* In the case of FE-001, the other vairable components were added individually.

Table 3.1.1.8: P₂O₅ Series Master Recipe (Wt. %)

Batch Designation	P-001	P-002	P-003	P-004	P-005
PMBS	16.52	16.25	15.99	15.21	14.44
FePO ₄ •2H ₂ O	0.00	4.48	8.90	21.99	35.05
Fe ₂ O ₃	29.18	26.37	23.58	15.38	7.17
MWM	<u>57.43</u>	<u>56.53</u>	<u>55.60</u>	<u>14.24</u>	<u>50.19</u>
TOTAL	103.13	102.63	104.07	66.82	106.85

3.1.2 Melting

The initial melting studies concentrated on verifying the batching procedure, specifically the concept of combining sets of prebatched components (for example, MWM, VMBSs, Glass Former (GF) WV-205) which, when done properly, should greatly improve precision in both the trace elemental composition and in overall weight percentages of all the oxides in the final glass. In addition, it was desired to examine in more detail the melting procedure used at Alfred University for the WVDP. The batch designated AL-001 was chosen for this preliminary study. A 500-g (oxide weight) batch was prepared using the master recipe. After melting for two hours with a lid at 1150°C, the cool glass was weighed. The glass weighed 500 g, which was the target value. This implies that the concept of batching from prebatched subsets is valid. A 1000-g (oxide weight) batch of designation AL-003 produced glass (two hours at 1150°C) weighing 999.8 g, a further confirmation of the batching procedure. The piece of glass (AL-001) was subsequently annealed at 460°C for two hours, and after cooling to room temperature, core drilled to provide a cylinder from which four thin sections were taken. The remaining portion of the boule of AL-001 was remelted at 1150°C for 12 hours. The weight loss due to volatilization was determined by weighing the boule before and after the second melt. A weight loss of 0.17 weight percent occurred. The boule was annealed in the same manner as before and thin sections were prepared. All thin sections were examined for melt homogeneity.

Sample AL-001, after a two-hour melt at 1150°C, shows some evidence of unreacted batch. Sample AL-001, after an additional 12 hour-melt at 1150°C, shows a marked improvement in homogeneity. Present in this glass is a dark phase which Energy-Dispersive Spectroscopy (EDS) shows to be RuO₂. This phase is present in melts of 22-hour duration. Therefore, no benefit is gained from a further melting of the master glass melts beyond 12 hours. All batches used in the variation series were prepared from the master recipes using the master subsets. Batches of 750 g each were prepared in all cases except the centroid composition for which a 1000-g batch was melted.

3.2 Chemical Analysis

It was judged important to characterize these glasses by measuring their chemical composition. Accordingly, an analysis of the targeted waste component variations was conducted. To this end, about 80 g of sample, randomly selected from fragments of each melt, were ground in a tungsten ball mill and submitted for analysis.*

* By X-ray fluorescence and atomic absorption spectroscopy.

The results obtained from this analysis and the targeted compositions are presented in Table 3.2.1. Excellent agreement was obtained between measured and calculated values. The concept of subbatching and remelting to produce homogeneous glasses was valid for the present work. Subsequently, more credence can be placed upon the composition-property studies discussed in Section 4.0.

3.3 Petrography

Thin sections of each glass within the variation series were prepared, viewed and photographed at 200X magnification with a Leitz Laborlux II POL petrographic microscope with a polaroid camera attachment. The photographs were mounted in series, for example, 001 through 005, in order to compare variations within and between the individual compositional series (Figures 3.3.1 to 3.3.6). A micrograph of the centroid composition is given in Figure 3.3.7. It was found that there were slight variations in the microstructure within and between the individual glass series. A slight preference pattern for larger crystal masses (that is, clumps, and increased crystal growth) in the 001 and 002 compositions was seen throughout the variation series. Some color banding was also noted and may be caused by oxidation-reduction differences in the melt. No change in microstructure was noted within these bands.

Table 3.2.1: Target and Analyzed Compositions*

Sample Series	Al ₂ O ₃	Fe ₂ O ₃	NiO	MnO ₂	Cr ₂ O ₃	P ₂ O ₅
001 (1.83)	1.68 (10.44)	10.39 (0.0033)	0.01 (0.015)	0.01 (0.0039)	0.00 (0.08)	0.03
002	2.32 (2.45)	12.2 (12.16)	0.19 (0.18)	0.58 (0.59)	0.10 (0.09)	0.39 (0.37)
003	2.97 (3.09)	14.06 (14.03)	0.38 (0.35)	1.14 (1.14)	0.19 (0.21)	0.76 (0.89)
004	3.89 (4.06)	5.09 (14.05)	0.70 (0.67)	2.08 (2.10)	0.5 (0.47)	1.84 (1.82)
005	5.18 (5.32)	17.74 (17.67)	1.01 (0.78)	3.01 (2.95)	0.8 (0.7)	2.93 (2.93)

In addition, micrographs of double-component variation glasses are included (Figures 3.3.8 to 3.3.9). A full description of these glasses is given in Section 4.4.2.

As discussed below, the dark crystals in these micrographs are most likely undissolved RuO₂ (see Section 5.2.4). Evidently, the insolubility of RuO₂ in the glasses prepared in this study was independent of composition.

* Analyzed compositions are in parentheses.

3.4 X-Ray/Energy Dispersive Spectroscopy

3.4.1 X-Ray Analysis

Sample Preparation

X-ray Diffraction (XRD) spectra were collected from glasses which were heat treated for different periods of time. The heat-treated glass samples were crushed and ground to obtain a fine powder. The powder was sieved through a U.S. Standard Series 100 mesh sieve to obtain samples for XRD. An XRD spectrum was collected for the untreated glass.

Calibration of XRD Unit

The XRD spectra were collected on an automated Philips Norelco XRD unit. The calibration of the unit was checked using a National Bureau of Standard (NBS) reference material (SRM 640a) silicon. The data were collected from values of 10 to 90 degrees at a step width of 0.02 degree and count time of one second. Peak locations were obtained using a data reduction program "IDR." The observed peak locations were in excellent agreement with the reported values. The reported and observed 2 θ values are given in Table 3.4.1.1.

AL001 (200X)

AL002 (200X)

AL004 (200X)

AL005 (200X)

Figure 3.3.1: Optical micrographs of the Aluminum Oxide Variation Series

CR001 (200X)

CR002 (200X)

CR004 (200X)

CR005 (200X)

Figure 3.3.2: Optical Micrographs of the Chromium Oxide Variation Series

FEO01 (200X)

FEO02 (200X)

FEO04 (200X)

FEO05 (200X)

Figure 3.3.3: Optical Micrographs of the Iron Oxide Variation Series

MNOO1 (200X)

MNOO2 (200X)

MNOO4 (200X)

MNOO5 (200X)

Figure 3.3.4: Optical Micrographs of the Manganese Oxide Variation Series

NI001 (200X)

NI002 (200X)

NI004 (200X)

NI005 (200X)

Figure 3.3.5: Optical Micrographs of the Nickel Oxide Variation Series

Figure 3.3.6: Optical Micrographs of the Phosphorous Oxide Variation Series

ALPHA CENTROID COMPOSITION (200X)

Figure 3.3.7: Optical Micrograph of the Centroid Composition

HAHP (200X)

Figure 3.3.8: Optical Micrograph of Double Variation Glass HAHP

Figure 3.3.9: Optical Micrographs of Double Variation Glasses (Top: HAHP, Bottom: HALF)

Table 3.4.1.1: Observed and Reported peak 2θ Values and Relative Intensities for
NBS Standard Silicon (SRM 640a)

Observed		Reported	
<u>2θ Peak</u>	<u>Relative Intensity</u>	<u>2θ Peak</u>	<u>Relative Intensity</u>
28.452	100.0	28.443	100.0
47.300	64.2	47.304	55.0
56.113	33.6	56.124	30.0
69.102	7.5	69.132	6.0
76.352	7.4	76.378	11.0
87.999	17.3	88.033	12.0

Results

The centroid glass did not show any crystalline phases as determined by XRD. Analysis of the XRD spectra collected from heat-treated glasses is discussed in Section 5.4.4 (Phase Stability Studies).

3.4.2 Energy-Dispersive Spectroscopy (EDS)

Energy-Dispersive Spectroscopy (EDS) was performed on annealed samples of the heat-treated glasses in order to determine the elemental composition of the crystalline phases observed in the glasses.

Sample Preparation

Annealed samples of the heat-treated glasses were cut using a Buehler low-speed diamond saw to obtain a small sample (-1 cm by 1 cm by 3 mm) for EDS. The samples were mounted on SEM sample holders and coated with gold palladium to a thickness of -200 Å. The metal samples which were used to check the calibration of the instrument were not coated with gold palladium.

Calibration of EDS Unit

EDS was performed using a Princeton Gamma Tech Energy-Dispersive Spectrometer along with an ETEC Autoscan Scanning Electron Microscope. The accuracy of the data obtained from the unit was checked by collecting spectra from samples of pure metals which were 99.99 percent pure. The metals used were aluminum, indium and silver. The observed peak locations were in good agreement with the reported values.

Data Collection

The glass sample was examined for the presence of crystalline phases using an ETEC Scanning Electron Microscope. After a crystalline phase (a well-defined particle) was observed, the crystal was examined at a high magnification. EDS analysis was done on crystalline phases located in this manner.

Results

WV-205 glass used in the TTT study was analyzed using EDS. EDS data were collected from two dark particles observed in the glass. One particle contained ruthenium with very minor amounts of silicon and iron. A second particle contained silicon, potassium, iron, calcium, manganese, titanium, and minor amounts of aluminum.

EDS data for ruthenium-rich particles are given in Figure 3.4.2.1. Analyses of the EDS data obtained from heat-treated glasses are given in Section 5.0 (Phase Stability Studies). As mentioned previously, elimination of RuO_2 from the batch resulted in an ostensibly particle-free WV-205 (see Section 5.2).

3.5 Thermal Analysis

The glass transition temperature, T_g , was measured by Differential Scanning Calorimetry (DSC)* and was independently confirmed by dilatometry.**Two methods were used due to the lack of a standard reference material to which T_g data by either method could be compared. The dilatometric softening point, T_D , was also measured.

3.5.1 Procedure- DSC

Sample preparation for DSC consisted of breaking a piece of the quenched glass into small fragments weighing 10 mg, and placing the sample in a covered aluminum sample pan. The DSC measurement was performed according to the procedures outlined in the Perkin-Elmer instructional booklet for this instrument. The purge gas used was compressed air. The Al_2O_3 series was run three times at a heating rate of $10^\circ\text{C}/\text{minute}$. All other samples were run once at $10^\circ\text{C}/\text{minute}$. In addition, the centroid composition was run at heating rates of 3, 5, 10, and $15^\circ\text{C}/\text{minute}$.

Data were collected and analyzed using the "TADS, DSC Standard Program."*** The T_g was calculated by rescaling the temperature axes to a range of 300° to 510°C , selecting the lower and upper limits (lower = 412°C ; upper = 488° to 497°C), and having the program calculate T_g . Figure 3.5.1.1 illustrates typical DSC data obtained.

* Perkin Elmer, DSC, Model 4

** Theta Dilamatic II

*** Perkin Elmer

AL FROM ALFA

ALUMINUM METAL

Figure 3.4.2.1: EDS Spectrum of a Dark Phase in WV-205 Glass

CAPOZZI FILE: P004.D4

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Figure 3.5.1.1 Typical DSC Data For Glass P-004

3.5.2 Procedure- Dilatometry

Sample preparation for dilatometry consisted of annealing* (~4 by 4 by 0.5 cm) of the quenched glass at ~10 to 20°C above T_g for two hours. The sample (~3.0 by 0.5 by 0.5 cm) was then cut using a low-speed diamond saw. The length of the sample was measured to ± 0.05 mm using a vernier caliper. The dilatometer was operated according to the "Thermal Expansion Data Collection" procedure. The heating rate used for all samples was 3°C/minute. The centroid composition was run four times; all other samples were run once. Data were collected using the COLLEX** program and analyzed using the ANALEX** program. The T_g was estimated by mechanical construction; the T_D was determined by the program as being the maximum point on the curve. Figure 3.5.2.1 illustrates typical data obtained. Because of the small sample lengths (~3.0 cm), expansivities are accurate to only ± 15 percent; for this reason, the coefficients of thermal expansion were not calculated. Sample length, of course, does not influence measured values of T_g or T_D .

3.5.3 Results

To determine the reproducibility of the T_g values as measured by DSC, the Al_2O_3 series was run in triplicate. It was found that each T_g measurement was within $\pm 5^\circ C$ of the average value. The data are given in Table 3.5.3.1.

* Thermolyne Type 200 Furnace

** Developed at the Institute of Glass Science and Engineering

Figure 3.5.2.1: Typical Dilatometry Data for Sample FE-002

Table 3.5.3.1: Glass Transition Temperature (T_g) Data Obtained By the DSC Method

Sample	Trial:	T_g (C)			Average T_g (°C)
		1	2	3	
Al-001		467	474	467	469
Al-002		462	464	465	465
Al-003		465	462	466	464
Al-004		464	464	468	465
Al-005		470	466	464	467

To determine the reproducibility of T_g and T_D as determined by dilatometry, the centroid composition was measured four times. The average T_g value was $461^\circ\text{C} \pm 3^\circ\text{C}$. The average T_D value was $498^\circ\text{C} \pm 2^\circ\text{C}$.

3.5.4 Analysis

A plot of T_g by dilatometry versus T_g by DSC is given in Figure 3.5.4.1. This plot illustrates two major conclusions of this study. First, the glass transition temperature is not markedly affected by changes in composition within the ranges studied. All the points are clustered randomly about the centroid composition. Second, T_g as determined by DSC is in excellent agreement with T_g determined by dilatometry. All the points cluster along the 45-degree line with a general tendency to be slightly below the line.

This might be due to the different heating rates used for the two methods, that is, $3^\circ\text{C}/\text{minute}$ for dilatometry and $10^\circ\text{C}/\text{minute}$ for DSC. Again, it is noted that the average difference between each method is 3°C and, on balance, indicates excellent correlation. In addition, the data for each method are very reproducible.

The reproducibility for T_g by DSC was $\pm 5^\circ\text{C}$, T_g by dilatometry $\pm 3^\circ\text{C}$, and for T_D by dilatometry $\pm 2^\circ\text{C}$.

Figure 3.5.4.1: Comparison of the Glass Transition Temperature Between DSC and Dilatometry Methods

4.0 PROPERTY MEASUREMENTS

In this section, the measurement of several properties carried out in this investigation is discussed. Among these are density, viscosity, and electrical conductivity. The development of property-composition diagrams (commonly referred to as spider diagrams) is also discussed. From these diagrams, a computer program was developed which allows a reasonable estimation of viscosity from composition. Finally, data sheets for each glass studied are presented.

4.1 Density

The density was measured by the pycnometer method using annealed samples of the glass. The density values ranged from 2.69 to 2.78 g/cm³ with an average value of 2.72 g/cm³. There were no obvious trends between the density and percent variable component for any of the variation series. Measurement of the silver standard density indicated a difference between the measured and reported value of ± 2.5 percent.

4.2 Viscosity Measurements

Both low- and high-temperature viscosities were measured during the course of this work. Low-temperature viscosity was measured using the beam bending method and high-temperature viscosity was measured using a rotating viscometer. Both methods are discussed below.

4.2.1 Low-Temperature Viscosity Measurements

Low-temperature viscosity of WV-205 glass (centroid) was measured by the isothermal beam bending method.

4.2.1.1 Sample Preparation

Pieces of glass were annealed for two hours at a temperature 10°C higher than the glass transition temperature. Samples (3.0 cm by 5.0 mm by 3.0 mm) were cut from the annealed glass sample for measurement of viscosity.

4.2.1.2 Experimental Procedure

The sample beam was kept in the furnace and a load was applied at the midpoint of the sample. Using a Linear Variable Differential Transformer (LVDT) and a strip chart recorder, the number of divisions of pen movement on the recorder per unit deflection was measured. The furnace was heated until the sample beam showed some deflection. The temperature was allowed to equilibrate and data were collected as temperature and rate of deflection. Viscosities were calculated at each temperature using the following equations.

$$\eta = \frac{g L^3 M}{2.4 I_c v}$$

g = acceleration of gravity (980 cm/sec²)

L = support span of the beam (cm)

M = centrally applied load on the beam (gm)

I_c = cross-section moment of inertia of the beam (cm⁴)

v = midpoint deflection rate of beam (cm/minute)

$$I_c = \frac{WT^3}{12}$$

where W = width of the beam (cm)

and T = thickness of the beam (cm)

4.2.1.3 Calibration

Calibration of the beam bending viscometer was checked using NBS reference lead silicate glass (SRM 711). Twelve measurements were made in the temperature range of 462° to 506°C. The viscosities were calculated and compared to the reported values. Good agreement was obtained between the reported values and those obtained in this study as can be seen in Figure 4.2.1.3.1.

4.2.1.4 Data Collection

Low-temperature viscosity data for the centroid composition (WV-205) were measured using the beam bending method. Data were collected in the temperature range of 477° to 499°C. A plot of both low- and high-temperature viscosity (see below) is given for WV-205 glass in Figure 4.2.1.4.1.

4.2.2 High-Temperature Viscosity Measurements

High-temperature viscosities were measured using a Theta Rheotronic 11S rotating viscometer. Viscosities were measured for the centroid composition and all the variation series glasses.

4.2.2.1 Sample Preparation

Approximately 100 g to 120 g of glass were crushed and placed in the platinum-rhodium viscometer crucible. The glass was melted in a Lindberg electric furnace for 30 minutes with the furnace controller set at 1150°C. The crucible with the glass was subsequently transferred to the viscometer.

4.2.2.2 Experimental Procedure

The glass sample (~100 g to 120 g) was melted in the viscometer crucible, and the crucible with glass was placed in the viscometer furnace. Viscosities were measured in the temperature range of 1000° to 1150°C. The isothermal method was used in the collection of viscosity data where sufficient time was given for the furnace and the crucible to come to equilibrium. Raw viscosity data were collected as the spindle speed (N) and the torque (S). Viscosities were calculated using the following equation.

$$\eta = \frac{G \cdot S}{N}$$

S = torque

N = spindle speed

G = geometric constant which depends on the measuring system and

η = viscosity

4.2.2.3 Calibration

The geometric constant (G) was determined using Brookfield Standard viscosity oils of known viscosity. The G was determined as a function of the bob-depth in the oil. After G was determined, the unit was calibrated using NBS reference lead silicate glass (SRM 711). Data (S and N) were collected in the temperature range of 1000° to 1250°C. The viscosities were calculated and compared to the reported values. The values obtained in the initial part of this study were uniformly higher by 10°C as compared to the reported values. Subsequent calibrations did not show this difference between measured and reported values. The data for pre-, mid-, and post-study calibrations along with the reported values are given in Figure 4.2.2.3.1. The 10°C factor was applied only to those melts studied in the first part of this work, since later calibrations did not indicate the need for this factor.

LOW TEMPERATURE VISCOSITY CALIBRATION FIT TO NBS REPORTED DATA

Figure 4.2.1.3.1: Low Temperature Viscosity Calibration

LOW & HIGH TEMPERATURE VISCOSITY DATA FOR CENTROID, FIT TO A FULCHER EQ.

Figure 4.2.1.4.1: Low and High Temperature Viscosity Data for Centroid Glass

PRE, MID, AND POST VISCOSITY CALIBRATION, USING NBS711 GLASS STANDARD

Figure 4.2.2.3.1: High Temperature Viscosity Calibration

4.2.2.4 Data Collection

Viscosity data were collected for the centroid and each of the glasses in the variation series. Data were collected in the temperature range of 1000° to 1150°C.

Measurements were made isothermally on all melts by heating the sample to the required temperatures (ramp up). For some melts, a hysteresis effect (0 to 25 percent at low temperatures) was observed for isothermal measurements taken during cooling (ramp down). Since the standard glass showed the same behavior, and whereas good correlation with the standard was obtained during isothermal ramp-up measurements, the data reported in this work are those obtained during ramp-up isothermal measurements only.

4.2.2.5 Viscosity Data Analysis

The viscosity data, temperature (°C) versus log viscosity in poise, were fitted to a polynomial by least-square regression. The coefficients of the polynomial obtained by this technique were used to calculate the viscosity of the glasses at different temperatures using the following equation:

$$\log \text{ viscosity} = A + BT = CT^2 + DT^3$$

Variables A, B, C, and D are the coefficients of the polynomial from the least-square regression and T is temperature (°C). The coefficients of the polynomial are given for each composition in the corresponding data sheet (Section 4.5).

Viscosities of all the glasses measured in this study are compiled in Figure 4.2.2.5.1, where an acceptable "window" of viscosity versus temperature, defined as a viscosity less than 100 poise at 1100°C, is seen to enclose the glasses used in this study. Viscosity at four temperatures (1000°, 1050°, 1100°, and 1150°C) as a function of weight percent of the variable oxide is given in Figures 4.2.2.5.2 to 4.2.2.5.7.

COMPILATION OF RAMP UP VISCOSITY DATA

Figure 4.2.2.5.1: High Temperature Viscosity Data for All Glasses

WT. % AL2O3 vs VISCOSITY @ 1000, 1050, 1100 AND 1150 (C).

Figure 4.2.2.5.2: Viscosity of Al₂O₃ series glasses at 1000, 1050, 1100 AND 1150°C

WT. % CR2O3 vs VISCOSITY @ 1000, 1050, 1100 AND 1150 (C).

Figure 4.2.2.5.3 Viscosity of Cr_2O_3 Series Glasses at 1000, 1050 1100 and 1150°C

WT. % FE2O3 vs VISCOSITY @ 1000, 1050, 1100 AND 1150 (C).

Figure 4.2.2.5.4 Viscosity of Fe_2O_3 Series Glasses at 1000, 1050 1100 and 1150°C

WT. % MnO₂ vs VISCOSITY @ 1000, 1050, 1100 AND 1150 (C).

Figure 4.2.2.5.5 Viscosity of MnO₂ Series Glasses at 1000, 1050 1100 and 1150°C

WT. % NiO vs VISCOSITY @ 1000, 1050, 1100 AND 1150 (C).

Figure 4.2.2.5.6 Viscosity of NiO Series Glasses at 1000, 1050 1100 and 1150°C

WT. % P2O5 vs VISCOSITY @ 1000, 1050, 1100 AND 1150 (C).

Figure 4.2.2.5.7 Viscosity of P₂O₅ Series Glasses at 1000, 1050 1100 and 1150°C

4.3 Electrical Conductivity

Electrical conductivity measurements were carried out in a specially constructed, high-temperature conductivity cell. Our procedure for measuring melt resistivity has been found to be very accurate and provides reproducible results.

4.3.1 Experimental Apparatus

The resistivity cell shown in Figure 4.3.1.1 is similar in design to that of Boulos et al.¹

The melt was contained in a Pt-Rh crucible which rests on the base of a vertical furnace.* The electrical resistance was measured between two Pt-Rh electrodes, which dip about 0.75 cm below the melt surface. The electrodes could be lowered into the melt to a prescribed level by use of a micrometer device located above the furnace. The melt temperature was measured with a platinum-sheathed, type S thermocouple which was in contact with the melt surface.

Measurements of impedance values (both real and imaginary parts) were made with a digital LCR meter** over the frequency range 0.1 to 100.0 KHz. Contributions from lead resistance were eliminated by zeroing the instrument.

4.3.2 Calibration of the Conductivity Cell

Resistivity values were calculated through the following equation:

$$\rho = R(L/A)$$

Where ρ is resistivity, R is the measured resistance and the quantity (L/A) is an effective cell constant. This quantity was determined by measuring the resistance of solutions of known resistivity, which in the present work were 0.1 N and 1.0 N KCl. The cell constant was determined for three different volumes of solution at three different electrode immersion depths. It was determined that for a given immersion depth, the quantity (L/A) was constant to within ± 2.0 percent for melt volumes between 85 to 88 mL. Accordingly, from known room temperature densities, the quantity of glass needed to provide 85 to 88 mL of melt was determined. Upon melting this quantity in the cell, the electrodes were lowered to a predetermined depth and the resistance of the melt was measured. Thus the resistivity of the melts was determined as a function of temperature and frequency. All measurements were done isothermally.

* Lindberg Model 56622

** Hewlett Packard Model 4272A

4.3.3 Comparison to Previous Work

In order to verify the experimental methods used, the resistance of a lead silicate glass (SRM 711), a glass whose melt resistivity had been previously reported,* was measured first. This comparison was made at the beginning, midpoint, and conclusion of the measurements. The results obtained are presented in Figure 4.3.3.1. It is shown that the agreement with published values is excellent.

4.3.4 Present Work

In Figures 4.3.4.1 and 4.3.4.2, the resistivity of melt AL003 (the centroid composition) and its frequency dependence at three different temperatures are presented, respectively. It is seen that at the temperatures cited, there is no demonstrable frequency dependence.

In Figure 4.3.4.3, the data obtained for all glasses studied are presented. The figure shows that only a small dependence of resistivity on composition exists. Figures 4.3.4.4 to 4.3.4.9 further demonstrate insensitivity of resistivity with composition.

* E. Boulos, J. Smith, C. Moynihan, "Rapid and Accurate Measurements of Electrical Resistivity on Glass Melts," Proceeding, I.C.G. XIII, Glastechn, Ber. 56 K (1983), p. 509.

Figure 4.3.1.1 Schematic Drawing of Electrical Conductivity Apparatus

48

Resistivity versus temperature for SRM 711 glass melts.

Figure 4.3.3.1 Resistivity Data for SRM 711 Glass

Temperature versus resistivity for Al₀₀₃ glass melt.

Figure 4.3.4.1 Resistivity Data for the Centroid Composition

Plot showing independence of resistivity from frequency effects for Al003

Figure 4.3.4.2 Imaginary Versus Real Resistivity as a Function of Frequency for the Centroid Composition Glass Melt

Figure 4.3.4.3 Resistivity of All the Glasses Used in this Study

Change in resistivity with varying amounts of Al₂O₃.

Figure 4.3.4.4 Change in Resistivity as a Function of Mole Percent Al₂O₃

Change in resistivity with varying amounts of Cr2O3.

Figure 4.3.4.5 Electrical Resistivity as a Function of Mole Percent Cr_2O_3

Change in resistivity with change in Fe2O3 content.

Figure 4.3.4.6 Electrical Resistivity as a Function of Mole Percent Fe_2O_3

Change in resistivity with varying amounts of MnO_2 .

Figure 4.3.4.7 Electrical Resistivity as a Function of Mole Percent MnO_3

Variation in resistivity with changing NiO content.

Figure 4.3.4.8 Electrical Resistivity as a Function of Mole Percent NiO

Variation of resistivity with change in P₂O₅ content.
Figure 4.3.4.9 Electrical Resistivity as a Function of Mole Percent P₂O₅

4.4 Spider Diagrams

4.4.1 Single Variations

Data were represented in several ways in preparation of property versus composition or "spider" diagrams. First, the property-temperature data were collected and plotted for each glass. By best-fitting a polynomial of the form $P = A + BT + CT^2 + DT^3$ (P =property) to the data, the coefficients of the curve were determined, allowing the accurate calculation of the property at specific reference temperatures, namely 1000°, 1050°, 1100°, and 1150°C. Compiling the fitted data from the five single-component variations within a series allowed the presentation of the data as property versus mole percent variable oxide at a given reference temperature, as in Figures 4.2.2.5.2 to 4.2.2.5.7 (Section 4.2.2.5).*

It was recognized after representing the data in this fashion, that data accuracy decreased with decreasing temperature. (This may be due to microstructural effects such as incipient crystallization, which we noted in the phase stability study of Section 5.0.) These data were then further adjusted by fitting them to a first-degree polynomial of the form $Y = mX + b$ (Y = property, m = slope = dY/dX , X = weight-percent variable oxide, b = Y -axis intercept). In addition, the viscosity values of the centroid composition at the four reference temperatures were normalized in the following manner: First, it was recognized that the first-degree, polynomial-fitted viscosity versus weight-percent variable oxide data curves will not all intersect the viscosity value of the centroid composition. This is a result of the small errors in the viscosity measurements and melt composition, and possible nonlinear dependence of viscosity on weight percent of variable oxide.

Second, if the curves were forced to intersect the viscosity value of the centroid composition, too much weight would be given to the data at the centroid composition, and the adjustment in the vertical intercepts of the viscosity versus weight-percent curves would necessarily be large. Therefore, it was decided to adjust the viscosity value of the centroid composition to a new value chosen to minimize the required adjustment in the vertical intercept of the viscosity versus weight-percent curve. The adjustment in the viscosity value for the centroid composition was done by treating Al_2O_3 and Fe_2O_3 , the two variable oxides with the greatest effect on viscosity as variables in the program DBLVAR. With these two oxides as variables and their values set to that of their centroid composition values, the program calculated the new viscosity value: the adjusted centroid composition viscosity value. It should be noted that the change in viscosity at the centroid was only a few percent of the actual viscosity value. Table 4.4.1.1 presents the actual and adjusted viscosity versus temperature data for the centroid composition at the four reference temperatures.

Table 4.4.1.1: Actual and Adjusted Viscosity Values for the Centroid Composition

Viscosity (Poise)			
Temperature (C)	Actual	Adjusted	Change
1000.0°	136.1	131.8	4.3
1050.0°	83.0	81.0	2.0
1100.0°	52.5	52.1	0.4
1150.0°	34.6	35.7	1.1

In Table 4.4.1.2, the coefficients of the first-degree polynomial fit of log viscosity versus weight-percent variable oxide curves are given. Table 4.4.1.2 also gives the adjusted intercept values.

* All compositions used in these calculations were target and not analyzed.

Table 4.4.1.2: Spider Diagram Coefficients

Temperature = 1150°C

Variable Oxide	Slope	Intercept		
		Actual	Adjusted	Change (Poise)
Al ₂ O ₃	0.0589946	1.37299	1.37601	0.2
Cr ₂ O ₃	0.004093	1.51466	1.54074	2.0
Fe ₂ O ₃	-0.013572	1.59906	1.59373	0.5
MnO ₂	-0.017443	1.60025	1.60532	0.5
NiO	-0.010497	1.55364	1.58453	2.6
P ₂ O ₅	0.007878	1.51744	1.52964	0.9

Temperature = 1100°C

Variable Oxide	Slope	Intercept		
		Actual	Adjusted	Change (Poise)
Al ₂ O ₃	0.064039	1.53558	1.52388	0.9
Cr ₂ O ₃	0.005523	1.67892	1.69943	2.3
Fe ₂ O ₃	-0.017722	1.77996	1.76767	1.7
MnO ₂	-0.016442	1.76336	1.76533	0.3
NiO	-0.008653	1.70996	1.74196	3.9
P ₂ O ₅	0.008003	1.67997	1.69199	1.3

Temperature = 1050°C

Variable Oxide	Slope	Intercept		
		Actual	Adjusted	Change (Poise)
Al ₂ O ₃	0.062651	1.73604	1.72105	1.8
Cr ₂ O ₃	0.005374	1.86865	1.89288	4.2
Fe ₂ O ₃	-0.022251	1.98384	1.97575	1.8
MnO ₂	-0.016674	1.94852	1.95902	2.2
NiO	-0.008071	1.89263	1.93321	7.6
P ₂ O ₅	0.003266	1.88188	1.89920	3.1

Temperature = 1000°C

Variable Oxide	Slope	Intercept		
		Actual	Adjusted	Change (Poise)
Al ₂ O ₃	0.063078	1.94847	1.93077	3.5
Cr ₂ O ₃	0.007140	2.07150	2.09858	7.6
Fe ₂ O ₃	-0.027344	2.20653	2.20203	1.7
MnO ₂	-0.010375	2.12365	2.15113	8.7
NiO	-0.008185	2.08821	2.14456	17.0
P ₂ O ₅	0.004276	2.07131	2.10717	10.1

In this manner, spider diagrams for viscosity were generated at the four reference temperatures for the six, single-variation component series. These are shown in Figures 4.4.1.1 to 4.4.1.4. The other physical properties measured during this work did not exhibit an appreciable change as a function of the glass composition. In effect, spider diagrams for the other physical properties will be flat, that is, the curves will have no appreciable slope.

SPIDER DIAGRAM FOR VISCOSITY AT 1000°C

Figure 4.4.1.1 Spider Diagram for Viscosity at 1000°C

SPIDER DIAGRAM FOR VISCOSITY AT 1050°C

Figure 4.4.1.2 Spider Diagram for Viscosity at 1050°C

SPIDER DIAGRAM FOR VISCOSITY AT 1100°C

Figure 4.4.1.3 Spider Diagram for Viscosity at 1100°C

SPIDER DIAGRAM FOR VISCOSITY AT 1150°C

Figure 4.4.1.4 Spider Diagram for Viscosity at 1150°C

4.4.2 Double Variation

As a test of the additivity of the property-composition curves, double-variation glasses were prepared using the procedure outlined in the section on melting and batching (Section 3.1). Batches of 500 g (oxide weight) were prepared and the viscosity was measured. To facilitate this study, a program was written to calculate the total glass composition (weight-percent oxide) for a multiple-variation glass. The above program also calculates the property value (viscosity) as a function of temperature by an interpolation of the data collected during the single-variation studies. The program uses the adjusted viscosity value (adjusted as discussed in Section 4.4.1) for the centroid composition. Within the program, the oxides to be varied are selected and their values input. The total glass composition is calculated from this inputted data. The program vectorially sums, in a linear fashion, the contribution of the variable components taken separately and adds them to the viscosity value of the centroid composition. Since the program relies heavily on the measured data which exhibits its highest reliability at the higher temperatures, the measured data are weighted accordingly. For example, the data for Cr_2O_3 , MnO_2 , NiO , and P_2O_5 were multiplied by the following temperature-dependent factor:

$$\text{TFACT} = \frac{T - 1000.0}{150.0}$$

This leaves the data at the higher temperatures virtually unadjusted, and in the other extreme, ignores the contribution of the particular variable oxide at 1000°C. Three double-variation glasses were prepared. The first glass, designated HAHP, contained high Al_2O_3 (6.5 weight percent in the final glass) and high P_2O_5 (2.5 weight percent in the final glass). The second glass, designated HAHF, contained high Al_2O_3 (5.18 weight percent) and high Fe_2O_3 (17.74 weight percent). The third glass, designated HALF, contained high Al_2O_3 (5.18 weight percent) and low Fe_2O_3 (10.39 weight percent).

The viscosity versus temperature profiles for the double-variation glasses all followed the expected trends. The fitted data are presented in Figures 4.4.2.1 to 4.4.2.3, and tabulated in Table 4.4.2.1. From these plots it can readily be seen that the measured data for the double-variation glasses are accurately calculated from the single-component variation glasses. The error between the calculated and measured viscosity values at the four reference temperatures is given in Table 4.4.2.1.

Table 4.4.2.1 Measured Versus Calculated Viscosity Data for the Double-Variation Glass

Glass Designation	Temperature (°C)	Viscosity (Poise)		
		Measured	Calculated	Difference
HAHP	1000.0	226.5	220.6	5.9
	1050.0	138.7	132.4	6.3
	1100.0	89.5	85.4	4.1
	1150.0	61.2	54.2	7.0
HAHF	1000.0	147.9	156.1	8.2
	1050.0	93.3	99.7	6.4
	1100.0	63.1	66.1	3.0
	1150.0	43.7	43.3	0.4
HALF	1000.0	179.1	183.8	4.7
	1050.0	107.9	117.5	9.6
	1100.0	70.1	77.2	7.1
	1150.0	47.9	50.0	2.1

HIGH Al₂O₃-HIGH P₂O₅ DOUBLE VARIATION

Figure 4.4.2.1 Viscosity Data for High Al₂O₃ High P₂O₅ Glass

HIGH Al_2O_3 -LOW Fe_2O_3 DOUBLE VARIATION

Figure 4.4.2.2 Viscosity Data for High Al_2O_3 Low P_2O_5 Glass

HIGH Al_2O_3 -HIGH Fe_2O_3 DOUBLE VARIATION

Figure 4.4.2.3 Viscosity Data for High Al_2O_3 High P_2O_5 Glass

5.0 PHASE STABILITY STUDIES

Phase stability studies on the West Valley reference glass WV-205 involved four different parts:

- Determination of the region of glass formation in the system, "Glass Formers-Zeolite-Waste."
- Determination of the dark phase origin observed in WV-205 glass.
- Determination of the liquidus temperature of WV-205 glass and the variation series glasses used in the composition-property studies.
- Determination of the region of glass formation in the system, "Glass Formers-Zeolite-Waste."
- Determination of the dark phase origin observed in WV-205 glass.
- Determination of the liquidus temperature of WV-205 glass and the variation series glasses used in the composition-property studies.
- Determination of the TTT diagram for WV-205 glass.

Each part is discussed separately below.

5.1 Glass Formation Region

This part of the study was concerned with the determination of the glass formation region in the system, "Glass Formers-Zeolite-Waste," when compositions were melted at 1000°, 1100°, or 1200°C.

5.1.1 Starting Components

The starting components and their respective raw materials are given below:

Zeolite IE-96 unexchanged zeolite from Union Carbide.

Glass Formers:

SiO₂ (SiO₂)
Li₂O (Li₂CO₃)
Na₂O (Na₂CO₃)
B₂O₃ (Na₂B₄O₇ · 10 H₂O)
MgO (MgO)
K₂O (K₂CO₃)
TiO₂ (TiO₂)

The raw materials used to introduce each oxide component are given in parentheses.

Waste Mix

Oxide composition of the waste mix used in this study is given in Table 2.2.2.

5.1.2 Compositions Studied

The composition of the glass former oxides used in this study is given in Table 5.1.2.1. The composition of the glass-former oxides used in this part of the study was slightly different from the composition of the WV-205 glass-former oxides. Waste and zeolite were prepared to determine the approximate boundary of the glass-forming region, 10-g batches of glass with varying composition of glass former. Glasses were made along lines with constant ratio of zeolite to waste. The zeolite-to-waste ratios used in this study were 2:1, 1:1, 1:2, 1:2.3, and 1:3.

One set of glasses was made with no zeolite. Six glasses were melted in each set. Glasses with the same composition were melted at 1000°, 1100°, or 1200°C.

After the approximate boundary of the glass formation region was determined, 50-g batches of glass were prepared for detailed studies. The composition of these glasses lies just inside the boundary of glass formation which was determined using 10-g batches.

Table 5.1.2.1: WV-205 Glass Former (Oxide) Composition

<u>Oxide</u>	<u>Composition Used in the Study</u>	<u>Actual WV-205 Composition</u>
K ₂ O	5.20	5.28
Li ₂ O	4.62	4.68
MgO	1.75	1.77
Na ₂ O	15.42	14.21
B ₂ O ₃	15.07	15.29
SiO ₂	56.48	57.29
TiO ₂	1.46	1.48

5.1.3 Experimental Procedure

Batching and Melting

For the preliminary studies, glass former, waste, and zeolite were weighed and mixed with a mortar and pestle to obtain 10g of glass. The glasses were melted in porcelain crucibles for one hour each at 1000°, 1100°, or 1200°C in a SiC-resistant heated furnace. The glasses were cooled in the crucible with no annealing. For the detailed studies, 50-g glasses were prepared. The glasses were melted in covered platinum-gold crucibles at 1000°, 1100°, or 1200°C in an electric furnace. The glasses were cooled in the crucible, removed, and annealed at 460°C for two hours.

Optical Microscopy

For the scouting studies, crush-mounted samples of the glasses were examined using a Leitz Laborlux 11 Pol optical microscope. For detailed studies, polished thin sections of the annealed glass samples were examined using the optical microscope. A uniformly dispersed dark phase was observed in varying amounts in all the glass samples. Depending on the amount and the type of phases observed, the glasses were classified as good, marginal or bad.

5.1.4 Results

The approximate boundary of the range of glass formation obtained from the preliminary studies using 10-g glasses is given in Figures 5.1.4.1 to 5.1.4.3 for 1000°, 1100°, and 1200°C, respectively. The boundary of the glass formation region for the system, "Glass Formers-Zeolite-Waste," which was obtained from the detailed studies on 50-g glass melts is given in Figures 5.1.4.4 to 5.1.4.6, respectively for 1000°, 1100°, and 1200°C. The range of glass formation depends on the melting temperature of the glasses. At lower temperatures, the range of glass formation is reduced due to the increase in the amount of unmelted batch. All the glasses prepared in this part of the study contained varying amounts of a dark phase. The amount of this phase increased with increase in the waste content of the glass. The elemental composition of this phase was determined by energy-dispersive spectroscopy. The main component of this phase was found to be ruthenium; small amounts of silicon and iron also were found.

5.2 Determination of the Origin of the Dark Phase Observed in WV-205 Glass

This part of the study was aimed at determining the origin of a dark phase observed in WV-205 glass, and also in assessing the effect of batch size on the amount of this phase in the final glass.

Figure 5.1.4.1 Glass Formation Region - One Hour Melts in Porcelain Crucibles at 1000°C

Figure 5.1.4.2 Glass Formation Region - One Hour Melts in Porcelain Crucibles at 1100°C

Figure 5.1.4.3 Glass Formation Region - One Hour Melts in Porcelain Crucibles at 1200°C

Figure 5.1.4.4 Glass Formation Region - 22-Hour Melts in Porcelain Crucibles at 1000°C

Figure 5.1.4.5 Glass Formation Region - 22-Hour Melts in Porcelain Crucibles at 1100°C

Figure 5.1.4.6 Glass Formation Region - 22-Hour Melts in Porcelain Crucibles at 1200°C

5.2.1 Starting Components

The starting components for this study are given in Section 5.1.1.

5.2.2 Compositions Studied

The basic glass composition used in this study was WV-205 (the final glass composition of WV-205 is given in Table 2.3.2). One glass was prepared without any ruthenium or rhodium.

5.2.3 Experimental Procedure

Batching and Melting

Glass formers (WV-205), waste mix, and zeolite were weighed and mixed using a mortar and pestle to yield 500 g of glass. The batches were melted in covered platinum-gold crucibles in a SiC electric furnace with the furnace controller set to 1150°C. The batches were initially melted for two hours, then poured, crushed, and remelted for an additional 20 hours to obtain a homogeneous glass. The glasses were annealed in a Thermolyne annealer with the controller set at 460°C. This melt was called WV-205.

A second melt of the same composition was made as described above, but only 50 g of the glass was prepared in one crucible. This melt was designated as WV-205S.

Fifty grams of the glass with the same composition as WV-205 was prepared without any ruthenium or rhodium. For the preparation of this glass batch, 200 g of waste mix oxides was prepared without ruthenium or rhodium. The melting and annealing procedure was the same as described above. The melt was designated as WV-205R.

Optical Microscopy

Small samples of the glass were obtained by cutting the glass samples using a low-speed diamond saw. These samples were ground and polished using a Buehler Ecomet with whirlimet attachment. The thin sections were examined using an optical microscope. Photographs of the thin sections were taken at 250X in transmitted light.

5.2.4 Results

Optical micrographs of the glasses WV-205, WV-205S, and WV-205R are given in Figures 5.2.4.1, 5.2.4.2, and 5.2.4.3, respectively. Where 150 g of the glass was prepared at one time, WV-205 contained the maximum amount of crystals. Where only 50 g of the glass was prepared at a time, WV-205S, the glass with the same composition as WV-205, contained a lesser number of crystals. WV-205R, the glass without ruthenium and rhodium, was practically free of the dark crystal phase. The size of the batch does affect the amount of the dark phase. Ruthenium or rhodium seems to be

the major cause for the appearance of crystals/inclusions in WV-205 glass. This is supported by energy-dispersive spectroscopy which indicates that ruthenium is the major element in the dark phase observed in WV-205 glass.

5.3 Liquidus Temperature

In this part of the study, the liquidus temperatures were determined for the centroid composition and each one of the glasses in the waste variation series. Since the glasses had some crystalline phase present at all temperatures, liquidus temperature was determined as the temperature at which the heat-treated glass had the same amount of crystals as the untreated glass sample.

Figure 5.2.4.1
WV-205 Untreated Glass (250X)

Figure 5.2.4.2
WV-205S Untreated Glass (250X)

Figure 5.2.4.3
WV-205R Glass without RuO_2 and RhO_2 (250X)

5.3.1 Starting Components

The starting components are given in Section 5.1.1.

5.3.2 Compositions Studied

Composition ranges used in this study are given in Table 2.3.1.

5.3.3 Experimental Procedure

Batching and Melting

The procedures for batching and melting the glass are given in Section 3.1.

Heat Treatment

A small sample of the glass (~1.0 by 1.0 by 0.5 cm) was heat treated in a Thermolyne furnace at 700°C for 17 hours to promote crystallization. The sample was heat treated in a platinum-gold foil crucible. The furnace temperature was calibrated prior to heat-treatment studies. The crystallized glass sample was cooled to room temperature and removed from the crucible. The surfaces and edges of the sample were removed using a 120-grit SiC paper. The crystallized glass was crushed into small fragments to obtain samples for further heat treatment.

In order to determine the liquidus temperature, ~100 mg of crystallized glass fragments were placed in a platinum-gold foil crucible and heat treated. For most of the samples, heat treatment was done for two hours at 900°, 950°, and 975°C. The Al_2O_3 series was heat treated at 1000°, 1025°, 1050°, and 1070°C for two hours. CR-004 and CR-005 were heat treated at 1000°C for two hours. In addition, AL-003, FE-005, CR-001, AND P-005 were heat treated at 950°C for four hours.

Optical Microscopy

Samples of the crystallized, heat-treated and untreated glasses were crushed and mounted on petrographic slides using Canada balsam. The samples were examined using a Leitz Laborlux 11 Pol optical microscope. Optical micrographs of some of the heat-treated glass samples were made to compare the extent of crystallization.

5.3.4 Results

A description of samples crystallized at 700°C for 17 hours follows:

Al_2O_3 Series

All glasses in this series contained small black crystals (spinel). Some had planes of a yellow-brown crystal attached to the faces of this crystal. The crystals were surrounded by a colorless glassy matrix. The amount of crystals increased with increasing Al_2O_3 content.

Fe_2O_3 Series

FE-001 and FE-002 contained the black crystals. The amount of black crystals was much greater in FE-002 than in FE-001. FE-004 and FE-005 contained both types of crystals. FE-005 had the most

amount of crystallization of any iron series samples. There was almost no glass phase detectable.

MnO₂ Series

MN-001 and MN-004 were similar to AL-003 in the type and degree of crystallization. MN-004 had mostly black crystals with a few yellow-brown crystals. MN-005 had only black crystals.

P₂O₅ Series

P-001 contained only black crystals and was similar to FE-001. P-002 contained both types of crystals and was similar to AL-003. P-004 contained distinct regions of black crystals and regions where the yellow-brown crystals also were present. This was different from the other samples in that the crystals were not uniformly distributed through the sample. P-005 was totally different from all other samples. The black crystals were present, but most of the fragments had a green tint and there were a few fragments which had a yellow-brown tint. These fragments did not show any distinct crystalline structure.

NiO Series

The NiO series was very similar to the MnO₂ series.

Cr₂O₃ Series

The Cr₂O₃ series was similar to the Al₂O₃ series in that both types of crystals were present and their amount increased with increase in Cr₂O₃ content. The only difference was that the amount and size of the yellow-brown crystals were smaller.

Description of Heat-Treated Samples

Heat Treatments = 900°C for two hours (all samples)

All samples contained only black crystals in amounts much greater than the glass that was not heat treated. The glass phase had a dark brown tint.

Heat Treatment = 950°C for two hours (all samples)

All samples contained only black crystals in amounts much less than the corresponding sample heated at 900°C for two hours, but still more than the glass that was not heat treated. The glassy phase had a light brown tint.

Heat Treatment = 975°C for two hours (all samples)

All samples, except for CR-004 and CR-005, had the same crystalline content as the untreated glass. The glassy phase for samples not heat treated was amber; the heat-treated glass was a light brown. CR-004 and CR-005 both had greater crystalline content than the corresponding unheat-treated glass.

Heat Treatment = 1000°C for two hours (CR-004 and CR-005)

Both samples contained the same crystalline content as the glass that was not heat treated.

Heat Treatment = 950°C for four hours (FE-005, P-001, CR-001)

All three samples contained the same crystalline content as the corresponding sample heated at 975°C for two hours which is also equivalent to the untreated glass.

Heat Treatment = 1000°, 1025°, 1050°, and 1075°C for two hours (Al₂O₃ Series)

The crystalline content continued to decrease slightly with each increase in temperature. There were crystals present, even at 1075°C, but the amount was less than the glass that was not heat treated.

The color of the glassy matrix became lighter with increasing temperature.

5.3.5 Analysis

All of the crystallized samples contained spinel crystals in a colorless glass matrix in amounts much greater than the glass that was not heat treated. In addition to the black crystals, yellow-brown crystals were present in various amounts and sizes in all the samples except FE-001, FE-002, MN-005, NI-005, P-001, and P-005. For each variation series, the degree of crystallization increased with increasing variable oxide.

Subsequent to heat treatment at 900°C for two hours, the amount of black crystals was not significantly reduced, but yellow-brown crystals were eliminated. After heat treatment at 950°C for two hours, the crystalline content was substantially reduced. After heat treatment at 975°C for two hours, the crystalline content (for all samples except CR-004 and CR-005) was the same as the untreated glasses. After heat treatment at 1000°C for two hours, the crystalline content of CR-004 and CR-005 were the same as the glass that was not heat treated. Heat treating the Al_2O_3 series at 1000°, 1025°, 1050°, and 1075°C for two hours resulted in a continual decrease in crystalline content. Heat treating AL-003, FE-005, P-001, and CR-001 at 950°C for four hours resulted in glasses with the same crystalline content as the corresponding untreated glass.

The liquidus temperature for this study was defined to be the temperature at which the heat-treated glass had the same crystalline content as the untreated glass. According to this criterion, the liquidus temperatures for CR-004 and CR-005 were determined to be between 975° and 1000°C; for all other samples it was determined to be between 950° and 975°C. These temperature ranges were shown to be valid for a two-hour heat treatment only. It is possible that with longer heat treatments, the liquidus temperature range may be slightly reduced.

5.4 Time -Temperature-Transformation (TTT) Diagram

5.4.1 Starting Components

The starting components are given in Section 5.1.1.

5.4.2 Compositions Studied

A TTT diagram was determined for the West Valley reference glass composition WV-205. The final glass composition is given in Table 2.3.2.

5.4.3 Experimental Procedure

Batching and Melting

The procedures for batching and melting the glass were discussed in Section 5.2.3.

Heat Treatment of the Glasses

For each heat treatment, approximately 2.3 g of the glass were weighed, kept in crucibles (1 cm by 1 cm by 1 cm) made of platinum-gold foil, and melted in a Lindberg SiC furnace for 10 minutes with the furnace controller set at 1150°C. The crucibles were taken out of the furnace, cooled to room temperature, and put into tube furnaces maintained at the desired temperature. The glasses were heat treated at temperatures in the range of 500° to 1100°C for time periods varying from 30 minutes to 96 hours. The temperature of the tube furnaces (Lindberg Kanthal tube furnaces) was measured using calibrated thermocouples. The temperature inside the furnaces was maintained to within $\pm 1^\circ\text{C}$ over a 96-hour period. On introduction of the sample, the temperature in the tube furnace dropped by about 20°C, but returned to the target temperature in less than three minutes. Heat-treated glasses were taken out, cooled, removed from the crucible, and annealed for one hour with the furnace controller set at 460°C.

Optical Microscopy

Portions of the heat-treated glasses were cut using a diamond saw. These sections were ground and polished to obtain thin sections. The thin sections were examined using a Leitz Laborlux 11 Pol microscope. Optical micrographs of the thin sections were made in transmitted light using a Leitz Panphot optical microscope.

To determine the volume fraction of the crystalline phase, the thin sections were studied in reflected light using a Leitz Panphot optical microscope. In order to determine the volume fraction of the crystalline phase, the crystals in a known area were counted. Also, the average size of the crystals was determined using a filar eyepiece. Prior to the determination of the crystal size, the filar eyepiece was calibrated at different magnifications. To determine the size of the crystals, the size of 40 crystals was measured and the average was computed. Approximately 350 to 500 crystals were counted to obtain the number of crystals in a known area.

X-ray Diffraction (XRD)

Section 3.4.1 discusses the details about the calibration, sample preparation, and data collection for XRD. The XRD spectra were collected for a number of heat-treated glasses.

Energy-Dispersive Spectroscopy (EDS)

Section 3.4.2 discusses the details about calibration, sample preparation, and data collection for EDS. EDS data were collected from the untreated glass used for TTT studies and also from one glass each for every temperature of heat treatment.

5.4.4 Results

Optical Microscopy

Optical micrographs of the heat-treated glasses are given in Figures 5.4.4.1 to 5.4.4.41. As shown in the micrographs, WV-205 glass crystallizes extensively in the temperature range of 600° to 800°C. Rate of crystallization is maximum from 700° to 750°C. At least two different phases can be seen in the glasses heat treated at 700° to 750°C. At 800°C and above, only one dark phase is observed. Appreciable crystallization is not observed at or below 500°C. At 1000°C, the glass has approximately the same amount of crystalline phase as the starting glass. On heat treatment for long periods of time at 1100°C, the dark phase observed in the untreated glass slowly disappears.

The volume fraction of the crystalline phase in three of the heat-treated glasses was determined by optical microscopy in reflected light. The crystallites were assumed to be spherical in the calculation of crystal volume. Since the actual crystal shapes were not spherical, some error can be found in the calculations and the volume fractions obtained should be considered approximate. The number of crystals per unit volume was determined by the following equation.

$$N = n/Ad$$

N = Number of Crystals per Unit Volume
 n = Number of Crystals in A
and d = Average Diameter of the Crystals

By multiplying the number of crystals per unit volume by the average volume of the crystals, volume fraction of the crystalline phase was calculated. The volume fraction of the crystalline phase and the average size of the crystals for three of the heat-treated glasses are given in Table 5.4.4.1.

500°C 12h (250X)

Figure 5.4.4.1 Optical Micrograph of WV-205 Glass Heat Treated for 12 Hours at 500°C

500°C 24h (250X)

Figure 5.4.4.2 Optical Micrograph of WV-205 Glass Heat Treated for 24 Hours at 500°C

500°C 48h (250X)

Figure 5.4.4.3 Optical Micrograph of WV-205 Glass Heat Treated for 48 Hours at 500°C

500°C 72h (250X)

Figure 5.4.4.4 Optical Micrograph of WV-205 Glass Heat Treated for 72 Hours at 500°C

600°C - 6h (250X)

Figure 5.4.4.5 Optical Micrograph of WV-205 Glass Heat Treated for 6 Hours at 600°C

600°C - 24h (250X)

Figure 5.4.4.6 Optical Micrograph of WV-205 Glass Heat Treated for 24 Hours at 600°C

600°C 48h (250X)

Figure 5.4.4.7 Optical Micrograph of WV-205 Glass Heat Treated for 48 Hours at 600°C

600°C 72h (250X)

Figure 5.4.4.8 Optical Micrograph of WV-205 Glass Heat Treated for 72 Hours at 600°C

Figure 5.4.4.9:
Optical Micrograph of WV-205 Glass
Treated for 1 Hour at 650°C (250X)

Figure 5.4.4.10:
Optical Micrograph of WV-205 Glass
Treated for 2 Hours at 650°C (250X)

Figure 5.4.4.11:
Optical Micrograph of WV-205 Glass
Treated for 3 Hours at 650°C (250X)

650°C 6h (250X)

Figure 5.4.4.12 Optical Micrograph of WV-205 Glass Heat Treated for 6 Hours at 650°C

650°C 12h (250X)

Figure 5.4.4.13 Optical Micrograph of WV-205 Glass Heat Treated for 12 Hours at 650°C

700°C 30 min. (250X)

Figure 5.4.4.14 Optical Micrograph of WV-205 Glass Heat Treated for 30 Minutes at 700°C

700°C 1h (250X)

Figure 5.4.4.15 Optical Micrograph of WV-205 Glass Heat Treated for 1 Hour at 700°C

700°C 2h (250X)

Figure 5.4.4.16 Optical Micrograph of WV-205 Glass Heat Treated for 2 Hours at 700°C

700°C 3h (250X)

Figure 5.4.4.17 Optical Micrograph of WV-205 Glass Heat Treated for 3 Hours at 700°C

700°C 6h (250X)

Figure 5.4.4.18 Optical Micrograph of WV-205 Glass Heat Treated for 6 Hours at 700°C

700°C 12h (250X)

Figure 5.4.4.19 Optical Micrograph of WV-205 Glass Heat Treated for 12 Hours at 700°C

700°C 24h (250X)

Figure 5.4.4.20 Optical Micrograph of WV-205 Glass Heat Treated for 24 Hours at 700°C

700°C 48h (250X)

Figure 5.4.4.21 Optical Micrograph of WV-205 Glass Heat Treated for 48 Hours at 700°C

750°C 1h (250X)

Figure 5.4.4.22 Optical Micrograph of WV-205 Glass Heat Treated for 1 Hour at 750°C

750°C 2h (250X)

Figure 5.4.4.23 Optical Micrograph of WV-205 Glass Heat Treated for 2 Hours at 750°C

750°C 3h (250X)

Figure 5.4.4.24 Optical Micrograph of WV-205 Glass Heat Treated for 3 Hours at 750°C

750°C 6h (250X)

Figure 5.4.4.25 Optical Micrograph of WV-205 Glass Heat Treated for 6 Hours at 750°C

750°C 12h (250X)

Figure 5.4.4.26 Optical Micrograph of WV-205 Glass Heat Treated for 12 Hours at 750°C (250X)

750°C 12h (400X)

Figure 5.4.4.27 Optical Micrograph of WV-205 Glass Heat Treated for 12 Hours at 750°C (400X)

800°C 6h (250X)

Figure 5.4.4.28 Optical Micrograph of WV-205 Glass Heat Treated for 6 Hours at 800°C

800°C 12h (250X)

Figure 5.4.4.29 Optical Micrograph of WV-205 Glass Heat Treated for 12 Hours at 800°C

800°C 24h (250X)

Figure 5.4.4.30 Optical Micrograph of WV-205 Glass Heat Treated for 48 Hours at 800°C

800°C 72h (250X)

Figure 5.4.4.31 Optical Micrograph of WV-205 Glass Heat Treated for 72 Hours at 800°C

900°C 6h (250X)

Figure 5.4.4.32 Optical Micrograph of WV-205 Glass Heat Treated for 6 Hours at 900°C

900°C 10h (250X)

Figure 5.4.4.33 Optical Micrograph of WV-205 Glass Heat Treated for 10 Hours at 900°C

Figure 5.4.4.34 Optical Micrograph of WV-205 Glass Heat Treated for 48 Hours at 900°C

900°C 72h (250X)

Figure 5.4.4.35 Optical Micrograph of WV-205 Glass Heat Treated for 72 Hours at 900°C

1000°C 24h (250X)

Figure 5.4.4.36 Optical Micrograph of WV-205 Glass Heat Treated for 24 Hours at 1000°C

1000°C 48h (250X)

Figure 5.4.4.37 Optical Micrograph of WV-205 Glass Heat Treated for 48 Hours at 1000°C

1000°C 72h (250X)

Figure 5.4.4.38 Optical Micrograph of WV-205 Glass Heat Treated for 72 Hours at 1000°C

1000°C 96h (250X)

Figure 5.4.4.39 Optical Micrograph of WV-205 Glass Heat Treated for 96 Hours at 1000°C

1100°C 12h (250X)

Figure 5.4.4.40 Optical Micrograph of WV-205 Glass Heat Treated for 12 Hours at 1100°C

1100°C 48h (250X)

Figure 5.4.4.41 Optical Micrograph of WV-205 Glass Heat Treated for 48 Hours at 1100°C

Table 5.4.4.1: Average Size of Crystals and Volume Fraction of Crystals in Heat-Treated Glass

Temperature of Heat Treatment (Celsius)	Time of Heat Treatment (Hours)	Average Crystal Diameter (microns)	Volume of Crystal Phase (percent)
800°	12	4.75	0.77
800	72	5.35	1.54
900	10	3.29	0.40

The TTT diagram for the glass WV-205 is given in Figure 5.4.4.42. This diagram is based mainly on the results of the optical microscopy study. The dotted line in Figure 5.4.4.42 corresponds to less than one volume percent of crystalline phase.

X-ray Diffraction (XRD)

XRD spectra were collected from the heat-treated glasses in order to identify the crystalline phases present in these samples. According to these data, at least two phases are formed in the glasses during heat treatment. At high temperatures (800°C and above), the main crystalline phase is spinel of the Fe_3O_4 type. Some of the iron in the spinel is replaced by one or more other transition metals (Ni, Cr, Mn). In the temperature range of 650° to 750°C, other crystalline phases are observed along with lesser amounts of spinel. From 700° to 800°C, other phases are present in addition to the spinel. Two types of sodium iron silicates are present: $\text{NaFeSi}_2\text{O}_6$ (acmite) and $\text{Na}_3\text{Fe}(\text{SiO}_3)_4$. Since the peaks in the XRD data were not very strong, only the strongest peaks were matched with the JCPDS data for sodium iron silicates.

In the temperature range of 600° To 700°C, yet another phase was observed along with the spinel and sodium iron silicates. Due to the low intensity of the peaks, this phase could not be identified positively. This phase is probably a sodium aluminosilicate or a sodium potassium aluminosilicate. One of the phases observed at 750°C (Figure 5.4.4.27) visually appears very similar to a $(\text{Cr}, \text{Fe})_2\text{O}_3$ structure reported for West Valley glasses. This could not be confirmed by XRD.

Energy Dispersive Spectroscopy (EDS)

EDS data for the glasses heat treated at different temperatures are given in Figures 5.4.4.43 to 5.4.4.49. The temperature and time of heat treatment are given at the top left corner of the plots. The untreated glass which was used in the study is termed as ITT glass in the figures.

At 800°C, the dark crystalline phase is a spinel. The XRD data indicate the presence of a spinel, and EDS data show that this spinel contains Cr, Mn, and Ni in addition to Fe (Figure 5.4.4.47). The center of a spinel phase at 700°C is composed mainly of ruthenium (Ru) (Figure 5.4.4.45). EDS data on the crystal surrounding the ruthenium show the presence of Fe, Mn, Ni, Cr, Si, Ti, and K (Figure 5.4.4.46). The presence of Si and K could possibly be from the matrix. A dark particle which was observed in a sample heat treated at 1000°C is composed almost entirely of Ru (Figure 5.4.4.49). Ruthenium particles exist in the glass at all the temperatures studied. EDS data indicate the presence of ruthenium in most of the crystalline particles, especially towards the center of the particle. Ruthenium seems to act as a nucleation site for the crystallization of other phases.

Figure 5.4.4.42 T T T Diagram for WV-205 Glass

500C 72H

A DARK PARTICLE

Figure 5.4.4.43 EDS Spectrum of a Particle in WV-205 Glass Heat-Treated for 72 Hours at 500°

652C 6HRS

A DARK CRYSTAL

Figure 5.4.4.44 EDS Spectrum of a Dark Crystal in Wv-205 Glass

700C 12H

CENTER OF CRYSTAL

Figure 5.4.4.45 EDS Spectrum of a Center of a Crystal in WV-205 Glass

7080 12H

PHASE AROUND RU

Figure 5.4.4.46 EDS Spectrum of the Phase Around Ruthenium in WV-205 Glass

Figure 5.4.4.47 EDS Spectrum of a Crystal in WV-205 Glass

CRYSTAL

800C 48H

900C 48H

DARK PHASE

Figure 5.4.4.48 EDS Spectrum of Part of a Dark Phase in WV-205 Glass

1000C 24H

A DARK PARTICLE

Figure 5.4.4.49 EDS Spectrum Part of a Dark Particle in WV-205 Glass

6.0 DISCUSSION/RECOMMENDATIONS FOR FUTURE WORK

From the results presented throughout this report, it is apparent that the system, "Glass Formers-Zeolite-Waste Mix," can accommodate considerable variation of the waste mix loading and still remain within the glass-forming region of this system. Moreover, variations in the waste composition itself (over the ranges studied in this work) do not significantly alter the processability (melting) of glasses in the system. That is, viscosity, electrical conductivity, and liquidus temperature values of the glasses studied remain within acceptable limits (for example, viscosity at 1100°C <100 poise, liquidus temperature <1000°C). These parameters, of course, should be tested and confirmed in the full-scale melter now in operation at West Valley Nuclear Services Co., Inc.

Recommendations for future work are to:

1. Examine the influence of FeO on the above properties, especially phase stability during cooling.
2. Examine the influence of cooling rate on crystal growth, especially at the "nose" of the TTT diagram.
3. Expand the data base for the viscosity - composition - temperature computer program to include such compounds as SiO₂, Na₂O, Li₂O, and also for higher loading levels of P₂O₅, Al₂O₃, and MnO₂.
4. Examine the effect of increasing CaO on phase stability.
5. Incorporate transmission electron microscopy in the study of initial stages of crystallization during cooling from the melt and also during isothermal heat treatments.
6. Develop a quantitative TTT diagram for composition chosen to be the final West Valley reference glass.

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