Influence of low concentration V and Co oxide doping on the dissolution behaviors of simplified nuclear waste glasses

Xiaonan Lu¹, James J. Neeway², Joseph V. Ryan², Jincheng Du^{1*}

¹Department of Materials Science and Engineering, University of North Texas,
Denton, TX 76203

²Pacific Northwest National Laboratory, Richland, WA 99354

*Corresponding Author: Jincheng.du@unt.edu

Abstract

Transition metal oxides are commonly present in nuclear waste and they can alter the structure, property and especially dissolution behaviors of the glasses used for waste immobilization. In this paper, we investigated vanadium and cobalt oxide induced structural and properties changes, especially dissolution behaviors, of International Simple Glass (ISG), a simulant nuclear waste glass system. Static chemical durability tests were performed at 90 °C with a pH value of 7 and a surface-area-to-solution-volume of 200 m⁻¹ for 112 days on three glasses: ISG, ISG doped with 0.5 mol% Co₂O₃, and ISG doped with 2.0 mol% V₂O₅. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was used to analyze the dissolved ion concentrations. It was found that doping with vanadium and cobalt oxide, even at the low doping concentration, significantly reduced the extent of the ISG glass dissolution. Differential Scanning Calorimetry (DSC) analysis showed that vanadium oxide doping reduced the glass transition temperature (T_g) while cobalt oxide did not significantly change the T_g of ISG. X-ray diffraction (XRD), Raman spectrometry and scanning electron microscopy (SEM) were used to analyze the glass samples before and after corrosion to understand the phase and microstructure changes. These results show that transition metal oxide can have a profound effect on the physical properties and dissolution behaviors of nuclear waste glasses.

Keywords: boroaluminosilicate glass, nuclear waste glass, chemical durability, characterization, transition metal oxide

1. Introduction

Vitrification is a mature process and space saving technology for nuclear waste disposal. Additionally, the amorphous nature of glass makes it relatively insensitive to the effects of radiation and allows the incorporation of a wide range of elements [1,2]. To ensure the long-term stability of the glass the chemical durability as a function of several variables must be understood.

Numerous factors are known to alter the chemical durability of glass [3-7]. These factors include glass composition [4], leachant composition [8,9], temperature [10-12], glass surface-area-to-solution-volume ratio (S/V) [6,13], pH [4,12,14,15], waste loading [16,17], and the effect of radiation doses [18,19]. Phenomenological analysis findings commonly divided glass alteration into three stages: initial diffusion/hydration, residual rate and rate resumption, based on the leaching rate change as a function of time [20]. Following the first stage, an amorphous, depleted, and hydrated layer, often referred as a gel layer, is formed at the surface of glass [21,22]. The most acceptable mechanisms responsible for the five stages are ion exchange, water molecules attacking bridging oxygen bonds, chemical affinity of initial glass or passivating effect of the alteration layer, reactive diffusion between water or glass elements through the gel layer, and precipitation of secondary phases [23]. Recent findings also support a new mechanism represented by the stoichiometric dissolution of the glass and reprecipitation of an amorphous silica phase on the surface called interfacial dissolution-reprecipitation [24-26]. There is not yet a universally applicable mechanism and the exact one depends on glass compositions and alteration conditions.

Borosilicate glasses have demonstrated the ability to immobilize radioactive nuclides due to their stability, and relatively easy and inexpensive fabrication process [27]. International Simple Glass (ISG) is a simplified model composition for corrosion study of HLW glass. ISG was developed by researchers from six nations (the USA, France, the UK, Japan, Belgium and Germany) in a collaborative effort to study nuclear waste glass dissolution/corrosion mechanisms [12,20]. The idea is that with a standard composition, and, in a collaborative environment, the results from different groups are more

comparable and detailed mechanism of glass dissolution can be elucidated in an expedited way.

To date, several studies have been performed with ISG and here we summarize the findings from a few of those. Inagaki et al. [12] have investigated the initial dissolution rate of ISG under dynamic leaching conditions with a variety of pH (3-10) and temperatures (25-90 °C). Static chemical durability tests on ISG were also studied by Fournier et al. [14] at high pH and temperature to accurately measure the time and rate of resumption of alteration. Gin et al. [15] investigated the corrosion behavior of ISG under alkaline condition, which leads to an extremely high solubility of silicon and rapid dissolution. Reiser et al. [9] have started investigating the alteration of ISG in an iron-rich environment, which is present in the container that will hold the waste glass. Chemical durability of ISG containing rare-earth oxides (10 and 15 mol%) was studied by Mohd Fadzil et al. [17], which revealed a relatively good ability of ISG for immobilizing rare earth oxide waste. Other properties, such as topography, surface chemical composition, as well as thermal and mechanical properties of ISG have recently been studied [17,28-30].

Transition metal (TM) oxides have been found to strongly influence the structural and physical properties including the chemical durability of oxide glasses. For example, it is known that incorporation a high valence cation, such as zirconium or hafnium, even at low concentrations, into oxide glasses can significantly improve the chemical durability, which is explained by its high cation field strength [2,31-36]. Fe^{3+} and Zn^{2+} ions were also found to improve the mechanical and chemical durability of oxide glasses due to their structural role as glass formers [37]. The presence of ZnO in borosilicate glass was found to significantly decrease the initial dissolution rate but increase the residual rate [6]. TiO_2 is less effective in terms of decreasing the initial dissolution rate of soda-lime borosilicate glass as compared to ZrO_2 , but a drop of the rate can be observed when 4 mol% TiO_2 is added into the base glass in comparison with a smaller amount of TiO_2 added [31]. On the contrary, adding MoO_3 (0.5, 1.0, 2.0, and 4.0 mol%) into alkali borosilicate glasses causes phase segregation which leads to a decrease of chemical durability [38].

Although a number of chemical durability studies and the effect of glass composition on representative nuclear waste glasses have been performed, the effect of weakly soluble oxides in glasses, such as TM oxides, on the leaching behavior of glasses and their influence on gel layer formation and properties are still poorly understood. Our understanding of the effects of glass composition and structure on the chemical durability is still incomplete, as each kinetic regime of glass dissolution has a specific composition dependency, for instance, Zn in borosilicate glass has different effects on initial and residual rate [6], and synergistic effects of each glass component in the glass system exist [39]. The purpose of this work is to study the effect of TM oxide addition, especially at low concentration doping, on the thermal properties and dissolution behaviors of ISG-based glasses. More systematic studies of wider doping concentration ranges are being studied and will be reported separately.

ISG was used as the base glass composition due to the availability of the wide range of dissolution data under different conditions as a result of studies from the international community. To avoid the interaction effect, only one type of TM oxide was introduced in each sample. Co_2O_3 and V_2O_5 were chosen in order to study the effects of physical properties and chemical durability upon addition of these dopants. Cobalt and vanadium were chosen to be representative of group V and group VIII transition metals, respectively. In addition, V_2O_5 has been proven to improve sulfur solubility in borosilicate glasses, which is essential for immobilization of sulfate containing HLW [40,41]; therefore, understanding the effects of adding this oxide is beneficial. We have recently studied the influence of TM doping on optical absorption in ISG in order to understand their effect on the performance of laser assisted local electrode atom probe (LEAP) [42].

The rest of the paper is arranged as follows. The experimental details of glass synthesis, characterization such as thermal analysis, diffraction and scanning electron microscopy, and glass dissolution testing procedure and data analysis methods are then introduced. This is followed by results of the effect of Co_2O_3 or V_2O_5 doping on the dissolution, and thermal properties of ISG. Finally the discussion of the current results and conclusion are presented.

2. Experiment details and data analysis methods

2.1. Glass synthesis procedures

The glass samples were prepared by a two-step melting process to ensure homogeneity. Firstly, around of 500 g of ISG glass with composition shown in **Table 1** was melted in a Pt-Rh crucible. The batch of the reagent grade raw transition metal oxide chemicals was mixed in an agate mill and then melted in the platinum crucible at 1275 °C for an hour in an electrical furnace. The melts were poured onto a stainless steel plate to cool to room temperature in air. After cooling, the glass sample was crushed into powders in a tungsten mill. In the second step, 50g ISG powders were mixed with 0.5 mol% Co_2O_3 (ISG+Co) and 2.0 mol% V_2O_5 (ISG+V), respectively, and the mixtures were re-melted at 1350 °C for one hour. The melt was casted into a preheated stainless steel mold. The prepared glass samples were then annealed at T_g (around 550 °C) for 6h and cooled down to room temperature at a rate of 60 °C/h. The ISG+V glass showed light green color and the ISG+Co glass showed blue-purple color. The color of both glass samples was homogeneous suggesting homogeneity of the glasses.

Oxide	Al_2O_3	B_2O_3	CaO	Na_2O	SiO_2	ZrO_2
mol %	3.84%	15.97%	5.73%	12.65%	60.20%	1.62%
wt %	6.10%	17.30%	5.00%	12.20%	56.30%	3.10%

Table 1. Chemical Composition of ISG.

Ingots of standard ISG (provided by MO-SCI Corporation), ISG+V and ISG+Co were crushed and sieved to particle sizes of 63 μm -125 μm . Four coupons (about 5 mm $\times$ 5 mm) of each sample were polished to 0.04 μm . The powder samples and coupons were washed in both deionized (DI) water and then ethanol three times ultrasonically for 3 minutes. The washed powder and coupon samples were dried in an oven at 90 °C overnight before being used in the chemical durability tests.

2.2. Physical property characterization

Differential scanning calorimetry (DSC) was carried out on a NETZSCH STA 499 F3 in an argon environment with a gas flow of 60 mL/min, a heating rate of 5 °C/min,

with a powdered glass sample (particle size between 63 μm to 125 μm) weighing between 23 mg and 25 mg in an Al_2O_3 pan.

Environmental scanning electron microscopy (ESEM) was conducted on an FEI Quanta ESEM with a spot size of 3.0 or 3.5 μm and electron energy of 15 kV to 30 kV to observe surface tomography of altered bulk samples after Au coating. Energy dispersive spectroscopy (EDS) was performed on an EDAX (TSL) EDS / EBSD system configured with the ESEM.

Glass powders before and after chemical durability tests were characterized with high resolution X-ray diffraction (XRD) on a Rigaku Ultima III with a scanning speed of $2^\circ/\text{min}$ and a step of $0.05^\circ/\text{point}$.

Almega XR Raman spectrometer (Thermo Electron) was used for characterization of glass powders before and after chemical durability tests with an excitation wavelength of 532 nm and a spectral resolution of 2 cm^{-1} .

2.3. Chemical durability tests

Static chemical durability tests were performed at $90 \pm 1^\circ\text{C}$ in a compact air forced convection oven (MTI Corporation) for 112 days with a glass surface-area-to-solution-volume (S/V) ratio of 200 m^{-1} . The geometric surface area of glass sample was estimated from an equation provided in McGrail et al. [43].

$$S_{GEO} = \frac{3}{\rho r} \quad (1)$$

where S_{GEO} is the specific surface area in m^2/g , r is the average radius of the particle (m), and ρ is the particle density (g/m^3). In this case, particle density used for calculation is $2.49726\text{ g}/\text{cm}^3$, calculated by the method developed by Fluegel [44]. The average radius of the particle is 47 μm . Therefore, the estimated geometric surface area of the glass powder is $0.02556\text{ m}^2/\text{g}$. In addition, the density of standard ISG was measured using specific gravity of solids method with density bottles (10 mL and 25 mL) at room temperature. Four measurements were carried on standard ISG powders with a particle size between 63 μm to 125 μm , and a mass of about 1 g for the 10 mL density bottle and about 5 g for the 25 mL density bottle. Bubbles in the glass powders and deionized water were removed ultrasonically for at least 30 minutes until there was no visible bubble

movement. It yielded a density of $2.523 \pm 0.043 \text{ g/cm}^3$, when the density of distilled water used for calculation was 0.99704 g/cm^3 .

Buffer solution with a pH value of 7 was prepared using 0.2 mol/L of tris (hydroxymethyl) aminomethane (TRIS) buffer solution in 0.1 mol/L HNO_3 solution according to a study by Rajmohan et al. [4]. There was no stirring during the whole chemical durability tests. A blank buffer solution was added as a reference to show whether elements leached from the PFA standard jar (Savillex Corporation) to confirm that the cleaning process was thorough.

5 mL solution aliquots were obtained at 1 day, 7 days, 14 days, 28 days, 56 days and 112 days (± 0.5 hour). Measurements of pH were performed using room temperature solutions on a bench-top pH/mV meter (Sper Scientific) with an accuracy of ± 0.02 pH. The aliquots were filtered to 10000 Da ($0.45 \mu\text{m}$) with syringe filters, then acidified with 5 mL of 0.5 N HNO_3 to prevent the formation of colloids. Corroded coupon samples were obtained at 7 days, 56 days and 112 days, and cleaned in ethanol and air-dried. At the end of the corrosion test, powder samples were obtained and washed in ethanol, then dried at 90°C overnight.

Solution analysis was carried out by Varian 820 inductively coupled plasma-mass spectrometry (ICP-MS) with an uncertainty of $\sim 3\%$. Solution samples were prepared by diluting the original solution samples by a factor of 100 with 2% (0.16 N) HNO_3 . Mixed standard solutions for calibration curves of ICP-MS were prepared in 2% HNO_3 at 100, 250, 500, 750, 1000 $\mu\text{g/L}$ for silicon, sodium, calcium, aluminum and boron, and 10, 25, 50, 75, 100 $\mu\text{g/L}$ for zirconium, vanadium and cobalt.

Silicon concentration in the solutions could not be determined accurately in this experiment because the R^2 value of silicon standard curve was less than 0.99. This situation might be caused by hydrolyzation of Si in the standard solutions. Additionally, Shabani et al. [45] have investigated the polyatomic species derived from silicon sample solution in the plasma, such as SiO , SiOH , etc., which may be another reason for the failure of Si concentration analysis.

2.4. Dissolution data analysis

ICP-MS results were used to calculate the normalized mass loss (NL, g/m^2) from the following equation,

$$NL_i = \frac{C_i}{X_i \frac{S}{V}} \quad (2)$$

where C_i is the concentration (g/m³) of element i in solution, S/V is the glass surface-area-to-solution-volume ration (m⁻¹) and X_i is the mass fraction of element i in the glass. The decreasing volume of solution due to sampling was taken into account when calculating the NL.

Altered glass percentage, altered glass equivalent thickness and retention factor were also calculated according to the study by Rajmohan et al. [4].

The altered glass percentage ($AG_B\%$) calculation is

$$AG_B\% = \frac{m_{boron}^{leached}}{m_{boron}^0} = \frac{m_{boron}^{leached}}{m_{glass}^0 \cdot \chi_B} = \frac{C_B^t \cdot V^t + \sum_{i=1}^{t-1} C_B^i \cdot V_{sv}^i}{m_{glass}^0 \cdot \chi_B} \quad (3)$$

where C_B^i is the boron concentration (g/m³) at time i in solution, C_B^t is the boron concentration (g/m³) at time t in solution, V^t is the solution volume (m³) remaining in the reactor at time t , V_{sv}^t is the solution volume (m³) sampled at the time t , m_{glass}^0 is the initial mass of glass powder (g) and χ_B is the boron mass fraction in the glass (g/g).

Altered glass equivalent thickness $Eq(i)$ is obtained from the altered glass percentage $AG_i\%$

$$Eq(i) = (1 - (1 - AG_i\%)^{\frac{1}{3}})R_0 \quad (4)$$

where

$$R_0 = \frac{3}{\rho S_p} \quad (5)$$

where ρ is glass density (g/m³). It is assumed that glass grains are perfect spheres and have the same specific surface area, S_p (m²/g).

The retention factor (RF) for element i in the glass alteration products can be calculated using

$$RF_i = 1 - \frac{Eq(i)}{Eq(B)} \quad (6)$$

3. Results

3.1. Effects of Co_2O_3 or V_2O_5 on transition temperature of ISG

DSC curves of standard ISG, ISG+Co, and ISG+V are shown in Fig. 1. The glass transition temperatures (T_g) were determined by intersecting tangents from the DSC curves with visual selection as shown in Fig. 1. Estimated errors of reported T_g are ± 3 $^{\circ}\text{C}$, according to a study by Guerette [29], where visual selection was also used when determining T_g . Moreover, T_g of ISG in the study by Guerette et al. is 575 ± 3 $^{\circ}\text{C}$ measured by differential thermal analysis in N_2 environment with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ [29]. The T_g of ISG+Co is 6 $^{\circ}\text{C}$ higher than the un-doped ISG, while V_2O_5 reduces the T_g of ISG by 19 $^{\circ}\text{C}$.

Fig. 1. DSC curves of ISG (left), ISG+Co (middle), and ISG+V (right) between 400 $^{\circ}\text{C}$ and 800 $^{\circ}\text{C}$ with a heating rate of 5 $^{\circ}\text{C}/\text{min}$.

3.2. Effects of Co_2O_3 or V_2O_5 doping on ISG glass dissolution behaviors

The pH data obtained for the duration of the chemical durability experiments for the blank sample, standard ISG, ISG+V, and ISG+Co are shown in Fig. 2. The pH values of the buffer solutions from standard ISG and ISG+Co were close to the blank sample throughout the entire test, while ISG+V had lower pH values compared to the blank sample beginning at day 28. The difference became larger with extended time and the pH in the ISG+V test was 0.2 pH units lower than the other tests. The reason why V_2O_5 leads to a decrease of pH value might be the reaction of vanadate with either hydroxyl and amino functions of TRIS and forming V(V) complexes [46].

Fig. 2. pH values as a function of time for the blank sample, standard ISG, ISG+V, and ISG+Co. pH values were measured at room temperature.

Comparisons of NLs of Al, B, Ca, Na, Zr, Co, and V in ISG, ISG+V and ISG+Co versus time are shown Fig. 3. B and Na had almost identical leaching behavior, except that B had about 10% higher NLs throughout the entire test. The release of B and Na started to decrease after about 14 days, where NLs of B and Na decreased by about 50% with V or Co oxides doping. Ca had similar NLs among the three glass samples through the test. Al values plateau around 28 days for standard ISG and ISG+Co and 14 days for ISG+V. Standard ISG sample had the highest NL of Al among three samples, while ISG+V had the lowest. NLs of Zr in standard ISG and ISG+Co did not change significantly throughout the entire test, while Zr in ISG+V had about a six times higher NL than ISG and ISG+Co. In terms of dopants in ISG, NL of Co was about eight times higher than V in ISG after 60 days corrosion.

Fig. 3. Comparison of normalized mass losses versus time for B, Na, Ca, Al, Zr, Co, and V in ISG, ISG+V and ISG+Co.

Retention factor of Na, Ca, Al, and Zr in ISG, ISG+V and ISG+Co at 112 days are shown in Table 2. Al and Zr were the elements mostly retained in the gel layer. Even though Si was not detected accurately from the ICP-MS analysis, it is well known that Si should also be retained in the gel layer. The amount of retained Na in the gel layer decreased by about 42% with addition of V_2O_5 or Co_2O_3 in comparison with un-doped

ISG. The amount of Ca retained decreased by ~22% for Co_2O_3 and ~38% for V_2O_5 in comparison with un-doped ISG.

Sample	Retention factor			
	Na	Ca	Al	Zr
ISG	0.172	0.791	0.990	0.999
ISG+V	0.099	0.490	0.985	0.984
ISG+Co	0.099	0.611	0.980	0.997

Table 2. Retention factors of Na, Ca, Al and Zr in ISG, ISG+V and ISG+Co at 112 days.

XRD patterns of standard ISG and 112 days corroded ISG powders are presented in Fig. 4. Due to the large amount of amorphous phase, there was no identification of crystalline phases after 112 days corrosion. XRD patterns of ISG+V and ISG+Co before and after corrosion are the same with un-doped ISG, which are not included in this paper for conciseness. However, in the study by Rajmohan et al. [4], where different conditions were used, XRD patterns of altered borosilicate glass surfaces are able to give some indications for the formation of calcium silicate hydrates after 150 days of alteration, even though clear identification is not possible due to the large amount of amorphous materials in the samples.

Fig. 4. XRD patterns of standard ISG and 112 days corroded ISG powder samples.

Raman spectroscopy was used to identify whether secondary phases were formed on the corroded glass surface. Raman spectra of standard ISG, ISG+Co, and ISG+V powder samples before and after 112 days corrosion are shown in Fig. 5. Peaks at 500 cm^{-1} , 630 cm^{-1} , 1000 cm^{-1} and 1450 cm^{-1} are contributed by Si-O-Si bending band, breathing mode of borosilicate rings, Q^n bands and the vibration band of the BO_3 group, respectively [16,29,47,48]. No secondary phases could be identified after 112 days of corrosion under the experimental conditions used for the three samples. Lower intensities of Raman peaks of ISG+Co samples may be due to the absorption of the 532 nm laser wavelength (532 nm). The UV-Vis spectrum of ISG+Co can be found in another study of ours [42]. An interesting finding is that the peak around 1000 cm^{-1} shifted to lower wavelength as a result of adding V_2O_5 in ISG, which suggested depolymerization according to peak assignments of ISG from a study by Abdelouas et al. [49] This finding is consistent with the decrease of transition temperature induced by adding V_2O_5 in ISG, where lower the connectivity of glass structure would reduce the glass transition temperature. Similar Raman results can be found in a study by Molières et al. [16] where pristine and altered lanthanum-enriched borosilicate glasses were successfully characterized by Raman spectroscopy. Q^n bands shifted to lower wavenumbers with increasing lanthanum content in their study, while Si-O-Si shifted to higher wavenumbers. Raman spectra of the altered glass without lanthanum indicated complete polymerization of the silicate network, and the Q^n bands were better defined for the samples containing lanthanum [16].

Fig. 5. Raman spectra of standard ISG (left), ISG+Co (middle), ISG+V (right) powder samples before and after 112 days' corrosion test.

3.3. Surface analyses

SEM images of standard ISG and ISG corroded for 7 days, 56 days and 112 days are shown in Fig. 6. Standard ISG started showing cracking after 7 days corrosion and this phenomenon became severe after 56 days. Cracks formed on the gel layer may be due to surface tension generated from evaporation of water in the gel layer during the air-drying process. This could be avoided by using the critical drying method to get around the surface tension induced damage during evaporation [50]. Possible precipitates were observed on the surface of the ISG sample corroded for 112 days. However, no secondary phase was detected with XRD and Raman spectroscopy study of the corroded samples. This can be due to the small volume of the secondary phase formed on the surface. SEM images of ISG+V and ISG+Co before and after corrosion are not presented in the paper, since they were almost the same as the images of standard ISG.

Fig. 6. SEM images of standard ISG (a), 7 days (b), 56 days (c) and 112 days (d) corroded ISG.

EDS analysis of cations in un-doped ISG and 112 days corroded ISG was performed, as presented in Table 3. Boron was not detected with the EDS analysis. The results show that the corroded glass surface has a decrease of Na and an increase of Si while Al remains as a similar fraction as compared to pristine ISG. This suggests that the corroded glass is covered by an alteration layer that is rich in silica. Although EDS analysis could not give accurate composition changes of the gel layer due to its large interaction volume, the trend of increasing silicon and decrease of sodium content is evident here, which is also supported by solution analysis. EDS analysis was used to study corroded nuclear waste glass samples by Weaver et al. [30] and a decrease of sodium content of the altered layer as compared to the bulk was observed.

Element (at.%)	Standard ISG	112 days corroded ISG
Na	6.7	1.9
Al	5.0	6.1
Si	76.3	84.8
Ca	12.1	7.2

Table 3. Gross compositional analysis of cations in standard ISG and 112 days corroded ISG with EDS.

4. Discussion

The ICP-MS analysis results of the dissolution studies indicate B and Na have almost identical leaching behaviors. V_2O_5 or Co_2O_3 at the doping level below 2 mol% was found to significantly reduce the dissolution rate as reflected in the large decrease of NL for B and Na. Ca in the three studied glasses showed similar NL values during the chemical durability tests. A decrease in NL of Ca was observed after 56 days, which might be due to the precipitation of secondary phases (such as calcium silicate hydrates). Even though both Al and Zr had relatively low NLs (less than 0.6 g/m^2) as compared to other elements, ISG+V had the lowest NL of Al and the highest NL of Zr. As for the NL of dopants in ISG, NL of V was less than Co even though the doping concentration is higher for V.

The retention factor calculated from the dissolution data indicated that Al and Zr were the elements most retained in the gel, consistent with a study by Rajmohan et al. [4]. Even though Si was not able to be determined, it is well known that Si should also be retained in the gel. Some Ca^{2+} ions are retained in the gel layer and play the role of

charge compensators for Al and Zr in the studied glasses; otherwise, as observed in dissolution of calcium-free glasses, Na would be partially retained in the alteration layer as a charge compensator which would result in different dissolution behavior of B and Na [4]. V₂O₅ or Co₂O₃ doping reduced the amount of Ca retained in the gel layer, with the larger reduction for V₂O₅ doping. This result suggests that some V or Co ions are retained in the amorphous gel layer to compensate the charge of Al in the network instead of Ca, where higher charge state and doping concentration of V ions compared with Co ions might be the reasons that larger reduction of Ca retained in gel layer for V₂O₅ doping. Further systematic study of concentration effect of the two oxides is required.

According to our previous study of UV-spectra of V₂O₅ or Co₂O₃ doped ISG [42], where ISG+V has an absorption cutoff at 400 nm and ISG+Co has an absorption peak at 450-700nm and a cutoff at 300nm, and other studies on the charge state and local environment of V or Co in borosilicate glasses with optical absorption [51,52], X-ray absorption [40,53], NMR [41], tetrahedral V⁵⁺ and octahedral Co²⁺ would be assumed to be the most dominated species in ISG structure. Future investigations are needed on structural roles and local environment of cations in ISG. Under the circumstances, according to field strength of the interstitial cations,

$$\varepsilon = \frac{Z_c}{(r_c + r_o)^2} = \frac{Z_c}{a^2}$$

where Z_c is the valence of the cation, and a is the ion-oxygen bond distance, which equals to the sum of ionic radius of cation r_c and ionic radius of oxygen ion r_o [54]. Tetrahedral V⁵⁺ has a larger field strength due to a higher charge state and a smaller Shannon ionic radius (0.355Å) as compared with octahedral Co²⁺ (0.65Å for low spin and 0.745Å for high spin) [55]. This may be one of the reasons that ISG+V had the highest chemical durability among all three glasses. Due to its high field strength, vanadium and cobalt ions are expected to be located in the modifier and non-bridging oxygen (NBO) rich regions based on the modified random network theory. They will increase the bonding strength of modifier rich region thus increasing the chemical durability as we observed. Molecular dynamics based computer simulations of Eu₂O₃ doped silica and sodium silicate glass showed that Eu³⁺ ions indeed enter the modifier-rich regions in modified glasses and have higher coordination numbers and more

symmetric local environments as compared to in pure silica [56,57]. However, at much higher doping concentrations of TM oxide, their effect on chemical durability might change. For example, it was found by Douglas et al. [58] in vanadium oxide (0.1 to 2.0 mol%) doped soda lime silicate glasses that low doping increases T_g and density of the glass and surface tension of the melt. At doping concentrations higher than 1.5 mol%, vanadium oxide leads to a rapid decrease in these properties [58]. This was explained by the changing structural role of vanadium with concentration. At low concentration, vanadium ions enter the alkali-rich regions and strengthen the glass structure, while at high concentrations, vanadium ions (V^{5+}) become four-fold coordinated, replace Si^{4+} to enter and weaken the glass network [58]. Hence the effect of TM oxide on the dissolution behavior and physical properties can be more complicated due to similar effects of changing structure roles of TM ions in the glasses.

DSC thermal analysis showed that the T_g of ISG+Co is essentially the same as that of ISG within experimental error ($\pm 3^\circ C$). On the other hand, ISG+V had a noticeable decrease of T_g . Siligardi et al. [59] have studied small amount (0.1, 0.5, 1.0 mol%) of vanadium oxide induced changes in CaO-ZrO₂-SiO₂ glasses. It was also found that V₂O₅ doping leads to a decrease of T_g , consistent with our findings. However, it was found in that work that V₂O₅ doping leads to a decrease of chemical durability of the base glass. This might be due to the presence of ZrO₂, which is known to significantly increase the corrosion resistant of oxide glasses [2,31-36].

5. Conclusions

Static chemical durability tests of ISG+Co, ISG+V and standard ISG samples were performed and the dissolution behaviors up to 112 days were studied using ICP-MS. The results show that doping with vanadium and cobalt oxide, even at low doping levels, significantly reduce the extent of dissolution, which was clearly shown by the reduction of the normalized mass losses of Na and B as compared to un-doped ISG. Interestingly, the dissolution product concentration analyses suggested that addition of transition metal oxide especially V₂O₅ in ISG significantly reduce the retention factor of Ca in the amorphous gel layer. The effects of TM oxide doping on thermal properties were also studied using DSC analyses and it was found that vanadium oxide doping reduce the T_g

of ISG while Co_2O_3 doping did not significantly change the T_g of standard ISG. The results suggest that further study of concentration effect of the two oxides, as well as other TM oxides and rare earth oxides, on ISG dissolution behaviors is necessary for a complete understanding of the doping effect. These work is underway and will be presented in future publications.

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