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

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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 the dissolution behavior, 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% Co_2O_3, and ISG doped with 2.0 mol% V_2O_5. 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.

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 waste 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 divide 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 to 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

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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 of 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 that 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 shown 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 is 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, 50 g 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 cast into a preheated stainless steel mold. The prepared glass samples were then annealed at T_g (around 550 °C) for 6 h and cooled down to room temperature at a rate of 60 °C/h. The ISG + V glass showed a light green color and the ISG + Co glass showed a blue-purple color. The color of both glass samples was homogeneous suggesting homogeneity of the glasses.

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 × 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 min. 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°/min and a step of 0.05°/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 ± 1 °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].

$$S_{GEO} = \frac{3}{\rho r} \tag{1}$$

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 2.497 g/cm^3, calculated by the method

Table 1
Chemical composition of ISG.

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%