MoO₃ Solubility and Chemical Durability of V₂O₅-Bearing Borosilicate Glass

Minako Nagata and Toru Sugawara *

Abstract: In the vitrification of high-level radioactive liquid waste (HLW), the separation of sodium-molybdate melts is a problem because it reduces the chemical durability of the vitrified waste. A glass with both high MoO₃ solubility and chemical durability is required for the safe disposal of radioactive waste. In this study, we investigate the effects of vanadium oxide on the phase separation of the molybdenum-rich phase and the water resistance of the resulting glass by phase equilibrium experiments and chemical durability test. Phase equilibrium experiments were performed on SiO₂-B₂O₃-Al₂O₃-ZnO-CaO-Na₂O-Li₂O-MoO₃ system glasses and on glasses with V₂O₅ added. The results showed that MoO₃ solubility increased when V₂O₅ was added. The increase in MoO₃ solubility in borosilicate melts may be associated with the viscosity-lowering effect of V₂O₅. Chemical durability tests were performed on borosilicate glass compositions obtained from phase equilibrium experiments. The normalized leaching rates of V₂O₅-bearing glasses were higher than those of other glasses. This is due to the higher network modifier/network former ratio of the glass tested. The normalized elemental mass loss of glass containing waste components increases with increasing leaching duration. This suggests that the waste component prevents the formation of a gel layer at the reaction front.

Keywords: glass; high-level radioactive waste; phase separation

1. Introduction

High-level radioactive liquid waste (HLW) generated in the spent fuel reprocessing process melts with glass and is geologically disposed of as vitrified waste [1–8]. Glass used for vitrification requires high chemical durability. Many countries, including Japan, plan to use borosilicate glass for HLW vitrification [9–13]. Borosilicate glass is considered durable, easy to manufacture, and capable of homogeneously dissolving various elements. In the vitrification process of HLW, it is necessary to pay attention to the behavior of molybdenum, which is one of the fission products. Molybdenum has low solubility in silicate melts and separates into borosilicate melts and sodium-molybdate melts by liquid-liquid immiscibility [14] during the melting stage. The molybdenum-rich separated phase, called as the yellow phase (YP), is highly soluble in water and can dissolve various fission products [15]. Therefore, the separation of YP significantly reduces the chemical durability of the vitrified waste [16,17]. The crystallization of the molybdenum phase has been investigated for glasses with various compositions [18–29]. It has been indicated that the solubility of MoO₃ in borosilicate glasses increases with increasing B₂O₃/SiO₂ ratio [19,25,28,29] and decreasing Al₂O₃ content [25,28,29].

In order to improve the solubility of molybdenum in waste glass, the effect of an additive component has also been examined. One of the candidates is vanadium-bearing glass. Manara et al. [30] reported that V₂O₅ added borosilicate glass exhibits a high immo-
bilizing capacity for sulfur containing HLW. Lian et al. [26] indicated that the crystallization tendency of powellite (CaMoO₄) was suppressed in V₂O₅ added borosilicate glasses, and the molybdenum solubility was improved. Moreover, chemical durability test (PCT) results showed that the normalized leaching rate of V₂O₅-bearing glass remained at a much lower level than that of standard borosilicate glass. Sugawara et al. [29] indicated that the addition of V₂O₅ accelerates the crystallization of powellite when the glass is slowly cooled (1 °C/min). This is the opposite result mentioned by Lian et al. [26], suggesting that cooling rate affects the crystallization tendency of powellite.

Although the crystallization of powellite has been investigated in detail, the effect of vanadium on the phase separation of sodium-molybdate, the main component of YP, has not yet been reported. In this study, we investigated the liquid-liquid immiscibility of V₂O₅-bearing MoO₃-rich borosilicate melt by phase equilibrium experiments. We also report the water resistance of the resulting glass through a chemical durability test.

2. Experimental

2.1. Strategy

First, we describe the flow of our experiments using the schematic phase diagram shown in Figure 1. The initial composition of experimental material is C in Figure 1, which is a composition with X mol% MoO₃ added to composition A. When the C is kept at temperature T₁ and equilibrated, it separates into a silicate melt (D) and a molybdate melt (E). The composition F is the normalized composition of D without MoO₃. Then, the MoO₃ content of D is equal to the MoO₃ solubility of F (Y mol%) under equilibrium conditions.

In previous studies [19–24,26,27,29], solubility and crystallization of molybdenum phases have been examined by using glasses with a relatively smaller amount of MoO₃ (<10 wt% or 5 mol%, for example, composition B in Figure 1). In this case, because MoO₃ content is less than equilibrium solubility at temperature (T₁), phase separation and/or crystallization may occur during cooling, even if it is a single liquid at T₁. The opposite effect of vanadium oxide on the powellite crystallization described above may have been caused by the different cooling rate, quench in [26] and slow cooling in [29].

In contrast, phase equilibrium experiments for the samples with an excess amount of MoO₃ provide equilibrium solubility. Based on those experiments, we have determined the phase separated compositions D and E in the borosilicate systems and used them for the thermodynamic analysis of liquid-liquid immiscibility [25,28]. In this study, we determined equilibrium MoO₃ solubility by phase equilibrium experiments at 1200 °C or 1000 °C for a V₂O₅-bearing borosilicate system.

![Figure 1. Schematic phase diagram showing immiscibility between silicate liquid and molybdate liquid in (a) the pseudo-ternary system of SiO₂-MoO₃-ΣRO (other oxides) estimated from the phase relationship of the SiO₂-MoO₃-NaO system [31] and (b) the pseudo-binary system between D' and](image-url)
E' in (a). The black solid curve represents the phase boundary between a single liquid and two liquids at temperature T₁, and the gray curve is at temperature T₂ (T₁ > T₂). The initial composition of the phase equilibrium experiments in this study is composition C, which is composition A with X mol% MoO₃ added. Since the C is in the two-phase region, it separates into a silicate melt of composition D and a molybdate melt of composition E when kept at T₁. The MoO₃ content in composition D (Y mol%) is equal to the saturation solubility of MoO₃ for composition F.

2.2. Phase Equilibrium Experiments

Chemical composition of starting materials is shown in Table 1.

The 19A2 composition is borosilicate glass, which is expected to be used in Japan for HLW vitrification [29,32]. The difference between the 19A2 and glass compositions of Lian et al. [26], who investigated the effect of vanadium, is that our glass has a higher Na₂O/CaO ratio and contains ZnO and LiO. The 21E has a composition of 19A2 with V₂O₅ added. The 21E2 has a composition with an increased B₂O₃/SiO₂ ratio compared to the 21E in order to improve the MoO₃ solubility.

Reagent grades SiO₂, B₂O₃, Al₂O₃, ZnO, CaCO₃, Na₂CO₃, Li₂CO₃, V₂O₅, and MoO₃ were weighed and mixed in an agate mortar. The mixed sample was placed in a platinum crucible, covered with an alumina lid, and held in a heating furnace at 1200 °C or 1000 °C for 24 h. Then it was quenched by cooling the bottom of the crucible with water.

After the experiment, the sample separated into upper glass and lower precipitate. A few pieces of glass and precipitate were randomly selected, mounted in epoxy, and polished under oil. Backscattered electron images (BEI) of glass were observed using electron probe microanalysis (EPMA).

The Li₂O content of experimental samples was analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), B₂O₃ by EPMA, and other elements by X-ray Fluorescence analysis (XRF). For ICP-AES analysis, the sample was crushed, and acid decomposition was performed. The XRF analysis was carried out by the glass bead method.

The amounts (mass %) of phase separated glass, p and precipitate, q were determined by mass-balance calculation. Let x and y be the analytical values of oxide components (mass %) for glass and precipitate, respectively, and X be the initial composition. Then, the p, q and the amount of B₂O₃-loss by volatilization during the experiment, r were obtained by minimizing the residual, σ expressed by the following equation:

\[
\sigma = \sqrt{\frac{1}{n} \left( \sum \frac{p}{100} x_i + \frac{q}{100} y_i - X_i \right)^2 + \left( \frac{p}{100} X_{B_2O_3} + \frac{q}{100} r - X_{B_2O_3} \right)^2}
\]

where i represents oxides other than B₂O₃.

Our preliminary experiments confirm that most of the B₂O₃ loss occurs within 6 h, after which the composition of the sample remains constant.

Table 1. Chemical composition of samples for phase equilibrium experiments (mol%).

<table>
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<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>B₂O₃</th>
<th>Al₂O₃</th>
<th>ZnO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>Li₂O</th>
<th>V₂O₅</th>
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<td>16.0</td>
<td>6.2</td>
<td>0.0</td>
<td>13.0</td>
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<tr>
<td>21E</td>
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<td>14.8</td>
<td>2.3</td>
<td>1.7</td>
<td>5.3</td>
<td>16.0</td>
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<td>1.7</td>
<td>5.3</td>
<td>16.0</td>
<td>6.2</td>
<td>2.4</td>
<td>13.0</td>
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2.3. Chemical Durability Test

A chemical durability test was conducted to investigate the water resistance of the borosilicate glass after phase separation (D in Figure 1). In order to prevent the difference in leaching rate due to the difference in MoO₃ content, Glass compositions were normalized to 100% without MoO₃ (F in Figure 1), and then 2mol% MoO₃, which is lower than the solubility limit, was added for all glasses. The glass composition is shown in Table 2.
For comparison, we also tested simulated HLW glass containing waste components (Bead composition).

The chemical durability test was conducted in accordance with MCC-3. The glass samples were crushed and sieved to adjust the particle size to 40–75 μm, ultrasonically cleaned in acetone, and dried. For the leaching solution, 1 L of ultrapure water was adjusted to pH 9 (room temperature) using KOH aqueous solution. A Teflon container was placed on a magnetic stirrer with a hot plate, and a thermocouple was attached to the container to measure the experimental temperature. The experiment was conducted at 90 °C. Once the temperature of the leaching solution in the Teflon container stabilized at 90 °C, 0.235 g of glass powder was added to the leaching solution. The solution was stirred during the test, but the water was not replaced. The leachates were collected after 2, 4, 6, 8, 24, 30, and 48 h, and the concentrations of Si and B were investigated using ICP-AES. The normalized leaching rate was obtained from the concentration of the leachate using the following formula,

\[ LR_i = \frac{C_i}{f_i \cdot (SA/V) \cdot \Delta t} \]

where LR is the normalized leaching rate (g/m²d), Ci is the concentration of element i in the leachate (g/L), fi is the weight fraction of element i in glass, V is the leachate volume (L), SA is the surface area of the powder sample (m²), and Δt is the experiment time (days). The SA was determined using a surface area analyzer in BET nitrogen adsorption. The SA was approximately 0.5 m²/g and the SA/V ratio was approximately 118 m⁻¹.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>B₂O₃</th>
<th>Al₂O₃</th>
<th>ZnO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>Li₂O</th>
<th>V₂O₅</th>
<th>MoO₃</th>
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<td>11.3</td>
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<td>2.3</td>
<td>5.1</td>
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<td>9.0</td>
<td>2.1</td>
<td>2.0</td>
<td>70.0</td>
<td>30.0</td>
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</tr>
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<td>2.3</td>
<td>3.8</td>
<td>10.6</td>
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<td>0.0</td>
<td>2.0</td>
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<td>Waste components in Bead</td>
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<td>MnO₂</td>
<td>Fe₂O₃</td>
<td>CoO</td>
<td>NiO</td>
<td>ZrO₂</td>
<td>BaO</td>
<td>La₂O₃</td>
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<td>0.25</td>
<td>0.62</td>
<td>0.35</td>
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<td>0.30</td>
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3. Results and Discussion

3.1. Phase Separation of Borosilicate Melt and Molybdate Melt

After the experiment, the sample separated into silicate glass in the upper part and a molybdenum-rich precipitate in the lower part (Figure 2). It is considered that the glass in the upper part corresponds to the HLW glass, and the precipitates can be regarded as simulated YP. As for the appearance of the glass, 19A2 was white, and 21E and 21E2 were slightly yellowish. The precipitate of 19A2 was ivory and more brittle than glass, and those of 21E and 21E2 were ocher and slightly harder than that of 19A2.

Figure 3 shows backscattered electron images of the glass and precipitate. Spherical particles and holes with a diameter of about 1–3 μm were observed in the glass. They were higher at 1200 °C than at 1000 °C and more pronounced at 21E and 21E2 than at 19A2. Similar textures have been previously reported in MoO₃-bearing sodium-rich silicate glasses [29,33].

EPMA analysis indicated the spherical particles were Powellite (CaMoO₄). The white color of the glass (Figure 2) is derived from those powellite particles. These powellites were not originally precipitated at experimental temperatures and are considered to have been formed by nucleation and crystal growth during cooling.
It is likely that the sodium-molybate phase (Na₂MoO₄, Na₂Mo₂O₇) was also crystallized from molybdate melt formed by secondary phase separation during cooling (H in Figure 1). However, it is speculated that it was lost by polishing and holes were left since Na₂MoO₄ is water soluble (solubility of 653 g/L) [34]. Sugawara et al. [29] reported that the frequency and size of holes on the sample surface are related to the intensity of Na₂MoO₄·2H₂O in bulk glasses measured by XRD.

The fact that there were fewer powellite at 1000 °C than at 1200 °C was due to a decrease in MoO₃ solubility at lower temperatures. Similarly, powellite was more pronounced in 21E2 than in 19A2 at constant temperature (Figure 3), indicating that the addition of V₂O₅ increased MoO₃ solubility.

![Figure 2](image-url)

Figure 2. Appearance of glass and precipitate was observed for 19A2 and 21E compositions after phase equilibrium experiments at 1200 °C.

The precipitates consisted of spherical silicate glass with a diameter of 5–15 μm (black spherical phase in Figure 3) and a molybdate matrix. It is considered that they were molybdate melts at experimental temperatures. The proportion of spherical silicate phase was greater at 1200 °C than at 1000 °C.
Table 3 summarizes the chemical composition of silicate glass and molybdenum-rich precipitates. B₂O₃ and Al₂O₃ were partitioned into silicate phases, while Na₂O, Li₂O, and V₂O₅ were enriched in molybdate phases. The MoO₃ solubility was 4.3 mol% for 19A2 at 1200 °C, increased to 5.6 mol% for 21E and 8.6 mol% for 21E2, and decreased with decreasing temperature. The fact that there were fewer powellite crystals at 1000 °C than at 1200 °C was consistent with a decrease in MoO₃ solubility at lower temperatures. Similarly,
powellite and sherical holes were more pronounced in 21E2 than in 19A2 at the same temperature (Figure 3). This is also in agreement with the increase in MoO$_3$ solubility.

Table 4 shows the results of the mass balance calculation. The volatilization loss of B$_2$O$_3$ during the experiment was 5–8 mass%. The proportion of the phase separated molybdate phase was in the range of 22–33 mass% and the smallest in the 21E2 at 1200 °C.

The solubility of MoO$_3$ in the borosilicate melt was improved by the addition of V$_2$O$_5$ (Table 3). This can be discussed from the viewpoint of melt viscosity and structure.

In general, it is known that the MoO$_3$ solubility in silicate melts increases as the degree of polymerization of the melt decreases. For example, MoO$_3$ solubility increases with increasing Na$_2$O/SiO$_2$ ratio in the SiO$_2$-Na$_2$O-MoO$_3$ system [31] and B$_2$O$_3$/SiO$_2$ ratio in sodium-borosilicate glass [19,25,28,29] and decreasing Al$_2$O$_3$ content in alumino-borosilicate glass [25,28,29]. The degree of polymerization of the silicate melt is related to the magnitude of the viscosity. Therefore, the compositional dependence of MoO$_3$ solubility can be roughly discussed by using melt viscosity [28,29].

The addition of a viscosity-reducing component to silicate melt leads to depolymerization of the borosilicate network and facilitates the incorporation of large-sized MoO$_3^-$ ions into the melt structure. Ferkl et al. [35] discussed the compositional dependence of the viscosity of low-level waste glass melts based on the analyses of the augmented Adam-Gibbs model. According to the report, V$_2$O$_5$ is the component that decreases the viscosity. This suggests that vanadium is the component that suppresses phase separation and increases molybdenum solubility.

Lian et al. [26] investigated the crystallization behavior of the molybdenum phase in glasses of SiO$_2$-B$_2$O$_3$-Al$_2$O$_3$-Na$_2$O-CaO-V$_2$O$_5$-MoO$_3$ systems quenched at 1300 °C. They reported that when the glass composition is constant, an increase in V$_2$O$_5$ suppresses powellite crystallization. The glass transition temperatures (Tg) of the glasses by Lian et al. decreased with increasing V$_2$O$_5$ content. Since Tg is approximately equal to the temperature at which the viscosity of the supercooled melt reaches 10$^3$ Pa·s, the decrease in Tg represents a decrease in isothermal viscosity. In other words, the conclusion of Lian et al. [26], showing the suppression of powellite by vanadium, can also be explained in terms of melt viscosity.

Spectroscopic studies on borosilicate glasses containing vanadium and molybdenum [36] indicate that MoO$_3^-$ ions coordinate preferentially with alkali ions such as Na$^+$. However, when vanadium is added, the VO$_2$ unit associates with alkali ions, which prevents the formation of sodium molybdate and suppresses YP generation. These are consistent with our experimental results, which showed that V$_2$O$_5$-bearing glasses increase the solubility of MoO$_3$.

Table 3. Chemical composition (mol%) of glass and precipitate obtained from phase equilibrium experiments. The glass composition by Lian et al. [26] is also indicated for comparison.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp./°C</th>
<th>SiO$_2$</th>
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<th>Al$_2$O$_3$</th>
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Table 4. Results of the mass balance calculation (mass %).

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</table>

3.3. Chemical Durability Test

Figure 4 shows the normalized leaching rates of Si and B against water in each glass. The normalized leaching rate decreased sharply until 24 h later, and then the rate of decrease slowed down. The leaching rate of V₂O₅ added glasses (21E, 21E2) was higher than that of 19A2. Bead glass had the slowest leaching rate at the beginning, but it reversed after 24 h and was the fastest after 48 h.

Figure 4. Normalized leaching rate of (a) Si and (b) B from glass to water as a function of time.

The leaching rate of V₂O₅-bearing glass (21E, 21E2) was higher than that of 19A2, resulting in lower chemical durability (Figure 4). The water resistance of silicate glass is considered to be dependent on the bond strengths of the oxide components. The bond strengths are as follows: SiO₂: 444, BO₃/2: 372, VO₅/2: 377–469, AlO₃/2: 331–423, ZnO: 301, CaO: 134, NaO: 84 and LiO: 151 (kJ/mol) [37]. The network former and intermediate components (SiO₂, BO₃/2, VO₅/2, AlO₃/2, ZnO) show generally higher bond strengths, and the chemical durability increases with increasing proportions of these oxides. Therefore, the V₂O₅ may have improved the chemical durability, as reported by Lian et al. [26].

In this study, however, the V₂O₅-bearing glass showed a higher normalized leaching rate. This can be attributed to differences in the ratios of components other than vanadium (Figure 4). The MCC-3 test was performed on the glass composition obtained after phase separation (F in Figure 1). The V₂O₅-bearing glasses, 21E and 21E2, had a higher network modifier (NM)/network former (NF) ratio than that of vanadium-free glass (19A2). For this reason, it is considered that the 21E and 21E2 glasses decreased their chemical durability despite the addition of vanadium oxide.

Bead glass, which contains the simulated waste components, initially had the slowest leaching rate, but this was reversed after 24 h, and the test results showed the fastest leaching rate after 48 h (Figure 4). Figure 5 shows the normalized elemental mass loss (NL). The NL of the simulated bead glass varied linearly with time, unlike the glass without the waste component (19A2, 21E, 21E2). This result may be related to the layer formed on the contact surface by the reaction of glass and water. The reaction between glass and water
initially results in the dissolution of glass. Then, the dissolution rate gradually decreases and approaches a constant rate. The slow dissolution of glasses over long periods of time is generally attributed to the saturation of silica in the solution. As the glass reacts with water, a gel layer is formed on the surface of the glass due to the repolymerization of dissolved silica. The dissolution of glass when the solution is close to saturation is thought to be prevented by the formation of a gel layer [38–43].

Cailleteau et al. [43] carried out chemical durability tests for SiO$_2$-ZrO$_2$-B$_2$O$_3$-Na$_2$O-CaO glasses to investigate the effect of changes in the gel structure on the leaching rate. They reported that the densification of the gel formed on the glass surface reduced the rate of alteration. It was also reported that an increase in the percentage of the insoluble element ZrO$_2$ in the glass suppressed the densification of the gel and increased the degree of corrosion of the glass after the experiment. In the Bead composition of this study, it is possible that the presence of the waste component prevented the formation of a gel layer at the reaction front that could inhibit glass corrosion, and that leaching continued.

4. Conclusions

In this study, phase equilibrium experiments and chemical durability tests were performed on the glasses in the system SiO$_2$-B$_2$O$_3$-Al$_2$O$_3$-ZnO-CaO-Na$_2$O-Li$_2$O-V$_2$O$_5$-MoO$_3$ to investigate the applicability of vanadium added glass to radioactive waste treatment. Phase equilibrium experiments were performed at 1200 °C and 1000 °C for compositions with an excess amount of MoO$_3$ (13 mol%) to separate the molybdate melts. The addition of V$_2$O$_5$ suppressed the phase separation of the molybdenum phase and increased MoO$_3$ solubility in the borosilicate melt. This may be related to the fact that V$_2$O$_5$ causes the depolymerization of silicate melt, facilitating the incorporation of MoO$_4^{2-}$ ions into the structure. Vanadium-bearing glass is thought to suppress the occurrence of the yellow phase in the vitrification of high-level waste.

The chemical durability tests were performed for the borosilicate glass composition obtained from the phase equilibrium experiments. No improvement in water resistance was observed due to the high network modifier/network former ratio of vanadium-bearing glass. The normalized elemental mass loss of simulated HLW glass containing waste components (Bead composition) increased linearly with time. This suggests that the waste component prevents the formation of a gel layer by reaction with water. A more detailed comparative study of the effect of vanadium addition on the chemical durability of glass is needed, considering not only the major components but also the effect of waste components.
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