Leaching Rate of the Borosilicate Glass Containing Molybdenum Oxide – 15546

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ABSTRACT
To clarify the influence of Mo content in borosilicate glass on its leachability, the leaching test based on PCT-A and NMR measurement of ^{29}Si and ^{11}B were carried out for a several glass specimens in which ratios of MoO_3 to a host borosilicate glass of 65 wt% SiO_2 - 20 B_2O_3 - 15 Na_2O ranged from 0 to 12 wt%. The leaching amounts of the all elements increased with increasing the content of MoO_3 greater than the solubility in the glass, 2.0 wt%. Forming water-soluble molybdate caused not only increasing the leaching amounts of Na and Mo but also those of the glass forming elements, Si and B. NMR results show that effect of Mo on the borosilicate glass structure was to extract Na in the main network of SiO_2 and B_2O_3 in the glass.

INTRODUCTION
High-level radioactive wastes (HLW) are generated from reprocessing of the used nuclear fuels. To isolate from human living environment, HLW are vitrified in borosilicate glass to dispose in deep geological repository in Japan. Molybdenum contained in HLW is one of the concerned elements because of its low solubility in the glass [1]. Although radiotoxicity of Mo is not so significant, Mo would form a water-soluble and segregated phase with significant radioactive elements as counter cations [2]. An example of the phase is Cs_2MoO_4 which should be confined for a long time of period in the borosilicate glass [3]. To prevent substantial leaching of the radioactive nuclides from the vitrified wastes, it is important to clearly the leaching behavior of the glasses containing Mo. The leaching rates of glasses containing Mo were reported by many researchers [4-6]. In those studies, the compositions of the glasses were complex as they were set to be similar to those for HLW in practical use, *i.e.*, there is no generality of the effect of containing Mo on the glass leachability. To clarify effect of Mo containing in the glass, it is necessary to investigate that of Mo containing in the pure glass consisted of SiO_2, B_2O_3 and Na_2O.

The present study aimed to clarify the influence of Mo content in borosilicate glass on its leachability. Leachability of glass specimens in which ratios of MoO_3 to a host glass of 65 wt% SiO_2 - 20 B_2O_3 - 15 Na_2O, were different were clarified by the leaching test, PCT-A [7]. The composition of the host glass was referred to ordinary that of the glass used in the vitrification of HLW in Japan [8]. Additionally, the glass network structure was clarified by MAS NMR measurement of ^{29}Si and ^{11}B.

METHODS
Compositions of the seven glass specimens employed in this study are listed in TABLE 1. All specimens were prepared by mixing the reagent powders of SiO_2, B_2O_3, Na_2CO_3 and MoO_3 and melted in platinum crucibles in air atmosphere and then quenched at room temperature. Each oxide was of reagent grade and purchased from Wako Pure Chemical Ind., Ltd., Japan. All prepared specimens were visually observed and analyzed by XRD (Maniflex, Rigaku Co., Japan).

TABLE 1. Glass specimens prepared in this study.

Contents, wt%	Specimens						
	A	B	C	D	E	F	G
SiO_2	65	64	64	64	63	62	57
B_2O_3	20	20	20	20	19	19	18
Na_2O	15	15	15	14	14	14	13
MoO_3	0	1.2	2.0	2.1	3.4	5.6	12

The procedure of the leaching test referred to PCT-A [7] was briefly described as follows. The specimens were crushed and sieved to 74 – 149 µm and washed by pure water and ethanol (purity 99.5%, Wako Pure Chemical Ind., Ltd., Japan). A 5 g of the specimen and a 50 ml of pure water were put in a PFA vessel and placed in a thermostatic chamber (SDN27P, Sansyo, Co., Ltd., Japan) kept at 90°C. After 7 days, the leachate was filtered by a filter of which mean pore size was 0.45 µm (Advantec, Ltd., Japan). Concentrations of Si, B, Na and Mo in the leachate were measured by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (ICPS-7000, Shimadzu Co., Ltd., Japan). Additionally, mass of the specimen after the leaching test was measured by an electronic balance (GR-300, A&D Co., Ltd., Japan). The leaching rate, L, was calculated by the following equation using the mass change.

$$L = \frac{m_i - m_f}{St}$$ (Eq. 1)

Where m_i is mass of the initial glass, m_f is mass of the glass after leaching, S is surface area of the particles of the crushed glass and t is a period of the leaching test, 7 days. Surface area was calculated from density of the glass specimens measured by pycnometer (Miyahara Measuring Instruments Co., Ltd., Japan). Based on the appendix of reference of PCT-A test, the glass particles were assumed spheres with a diameter of 112.0 µm [7].

NMR spectrum of [11]B and [29]Si were measured by ECA-700 (16.43 T) (JEOL, Ltd., Japan) at a frequency of 700 MHz. Those of [11]B were referenced to boron phosphate solid taken as 3.3 ppm. Those of [29]Si were referenced to tetramethylsilane.

RESULTS AND DISCCUSION
TABLE 2 shows the results of visual observation and XRD analysis of the specimens. The specimens containing MoO_3 not greater than 2.0 wt% were transparent, while the others were opaque. The presence of a white precipitate and phase segregation were observed in Specimen G. As a result of XRD for the specimens, the white precipitate was identified as Na_2MoO_4 crystal. It was considered that the opacity of Specimens D, E and F were due to formation of the Na_2MoO_4 phase. We determined that the solubility of MoO_3 in borosilicate glass used in this study was 2.0 wt%. The part of opaque glass of Specimen G contained MoO_3 at 7.6 wt%.

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TABLE 2. Appearance and XRD pattern of the glass specimens.

	Specimens						
	A	B	C	D	E	F	G
Appearance	transparent			opaque			white precipitate
XRD pattern	no peak						Na_2MoO_4 crystal

The concentration of each element of the leachate was obtained by leaching test for Specimens A, B, C and E shown in Fig. 1. Leaching Mo was confirmed in the leachate from Specimens B and C which contained Mo. On the other hand, in Specimen E, the leaching amounts of all elements increased beyond the error bars compared with Specimens A, B and C. Forming water-soluble molybdate caused not only increasing the leaching amounts of Na and Mo but also the other constituent, Si and B, in the glass.
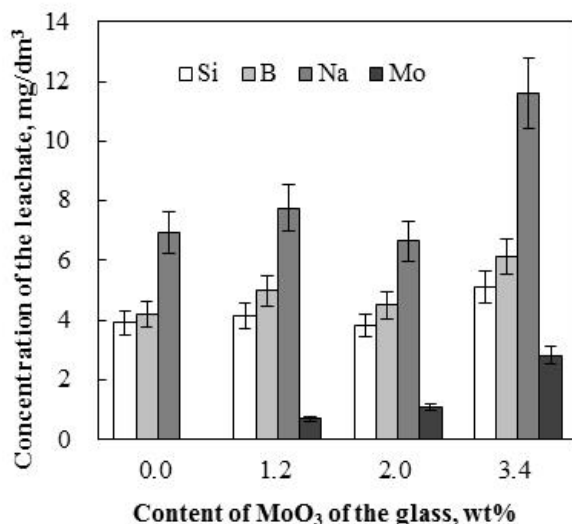

Fig. 1. Content of the elements of the leachate.

TABLE 3 lists the overall leaching rates of the specimens calculated by Eq. 1. The rates of the glasses containing MoO_3 not greater than 2.0 wt%, Specimens A, B and C, were nearly constant, approximately 0.2 g m^{-2}day^{-1}. On the other hand, that of the glass containing MoO_3 at 3.4 wt%, Specimen E, obviously increased.

TABLE 3. Leaching rate of the glass specimens.

Specimens	A	B	C	E
Leaching rate, g m^{-2}day^{-1}	0.19±0.02	0.21±0.02	0.21±0.02	0.33±0.03

Fig. 2 shows the results of NMR measurement of [11]B of all the specimens shown in TABLE 1. In the NMR spectra of [11]B, narrow peaks around 3 ppm and broader peaks around 17 ppm are derived from

boron units of tetrahedrally coordination and three coordination, namely B4 and B3, shown in Fig. 3, respectively. Fig. 4 shows NMR spectra of ^{29}Si. Those have one peak derived from tetrahedrally coordination silicon, Qn, where n is the number of bridging oxygen. The peak includes small peaks whose center is around −80 ppm and large peak around −92 ppm. Those are derived from Q3 and Q4 shown in Fig. 5, respectively.
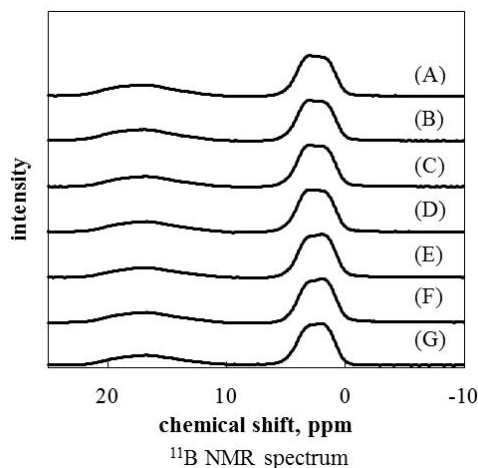

Fig. 2. NMR spectrum of ^{11}B. The content of MoO_3 in the specimens was (A) 7.8, (B) 5.6, (C) 3.4, (D) 2.1, (E) 2.0, (F) 1.2 and (G) 0 wt%.
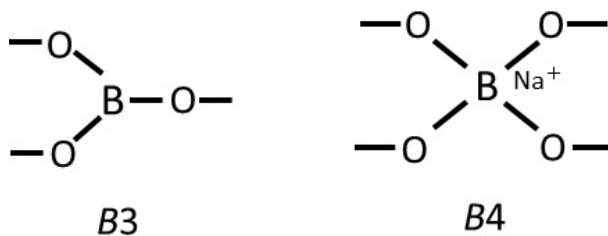

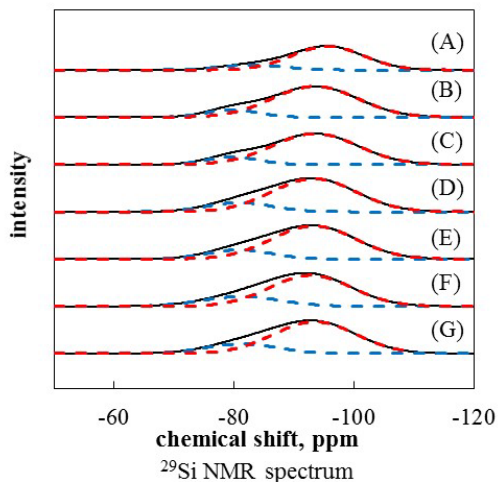Fig. 3. Structural units of boron observed in the glasses.

Fig. 4. NMR spectrum of ^{29}Si. The content of MoO_3 in the specimens was (A) 7.8, (B) 5.6, (C) 3.4, (D) 2.1, (E) 2.0, (F) 1.2 and (G) 0 wt%.
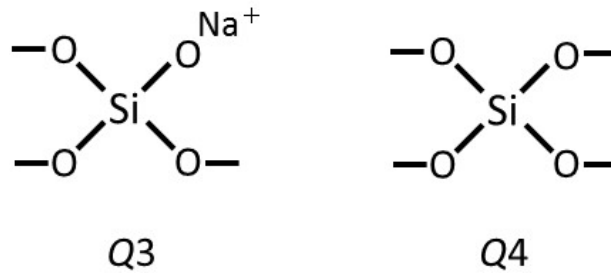
Fig. 5. Structural units of silicon observed in the glasses

Fig. 6 shows that the change of the structural unit of the specimen which is calculated from NMR spectrum plotted against the content of MoO_3 in the glass. Value of N_{B4} and N_{Q4} defined respectively using the following equations.

$$N_{B4} = \frac{n_{B4}}{n_{B3} + n_{B4}}$$ (Eq. 2)

$$N_{Q4} = \frac{n_{Q4}}{n_{Q3} + n_{Q4}}$$ (Eq. 3)

Where n_i is the number of structural unit i. With increasing the content of MoO_3 from 0 wt% to 2.0 wt%, N_{B4} was constant, while N_{Q4} increased. The added Mo bonded to Na forming the non-bridging oxygen in $Q3$ of the Si unit, and incorporated into the glass structure. On the other hand, N_{B4} decreased when the content of MoO_3 was greater than 2.1 wt%. N_{Q4} was constant in those glasses, *i.e.*, the added Mo bonded to Na forming $B4$ of the B unit, on the contrary.
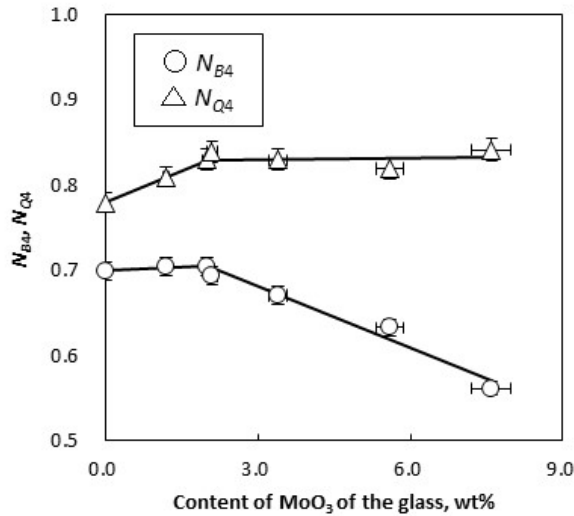

Fig. 6. Variation of N_{Q4} and N_{B4} with concentration of MoO_3 of the glass.

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The change of structural unit of B was plotted against Na content in the glass as shown in Fig. 7. As for borosilicate glass, a model of the relationship between structure and composition were proposed by Dell [9]. In the model, the change of structural units of B can be explained by the mole ratio of SiO_2 to B_2O_3, K, and that of Na_2O to B_2O_3, R. Values of K and R of the base glass were 3.6 and 0.8, respectively. Fig. 7 (a) shows that the change of structural units of B plotted against R in the specimens. The plots were not on the line predicted by model [9]. We presumed that all Mo in the glass formed Na_2MoO_4 and defined R' using following equation.

$$R' = \frac{x_{Na_2O} - x_{MoO_3}}{x_{B_2O_3}}$$
(Eq. 4)

Where x_i is mole fraction of i. Dependence of the structure on composition of the specimens arranged by R' is shown in Fig. 7(b). The N_{B4} re-plotted against R' were on the line. Effect of Mo on the borosilicate glass structure was to extract Na in the main network of SiO_2 and B_2O_3 in the glass.
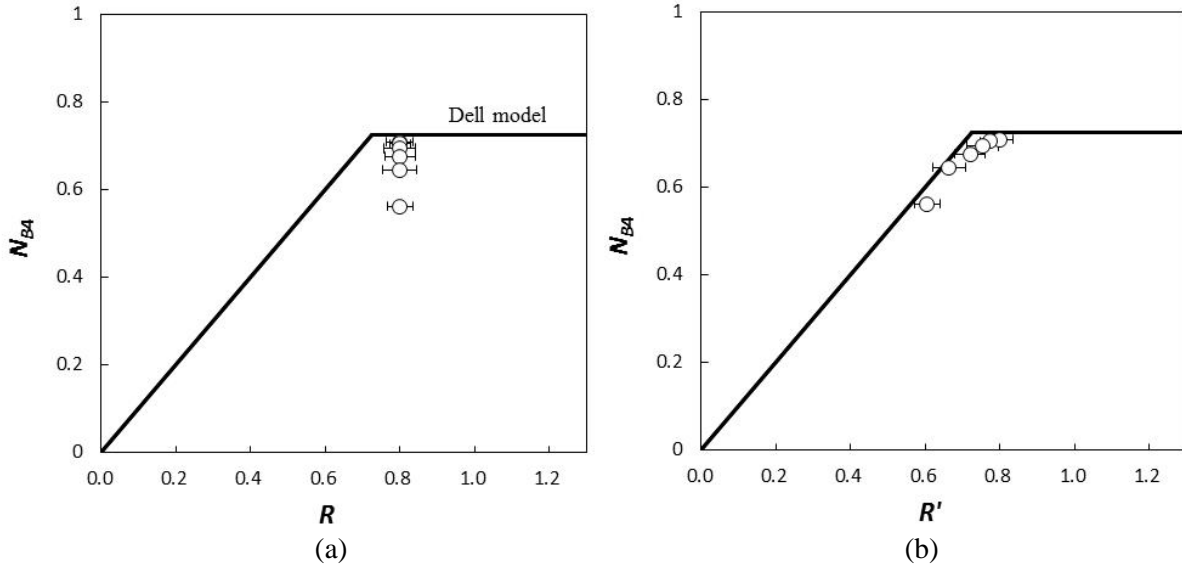

(a)   (b)

Fig. 7. The relationship between structure and composition of the glass.

CONCLUSIONS

The solubility of MoO_3 in the borosilicate glass composed of 65 wt% SiO_2 – 20 B_2O_3 – 15 Na_2O was 2.0 wt%. The leaching rates of the glasses containing MoO_3 not greater than the solubility were constant. The leaching amounts of the all elements increased with increasing the content of MoO_3 greater than the solubility in the glass. A water-soluble molybdate, Na_2MoO_4, formed and caused not only increase of the leaching amounts of Na and Mo but also the other constituents, Si and B.

From the results of NMR measurements, in the glass used in this study, with increasing the content of MoO_3 from 0 wt% to 2.0 wt%, the added Mo bonded to Na forming non-bridging oxygen in Q3 of the Si unit, and incorporated into the glass structure. On the other hand, when the content of MoO_3 in the glass was greater than 2.1 wt%, the added Mo bonded to Na forming B4 of the B units. The change of the structure unit of B affected by Na content can be described by the Dell's model which is well-known as a model representing the structure in borosilicate glass with correcting the contribution of Na on the glass structure by Mo content.

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