15546 Leaching Rate of the Borosilicate Glass Containing Molybdenum Oxide

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Introduction

High-level radioactive wastes (HLW) are vitrified in borosilicate glass to dispose in deep geological repository in Japan. Molybdenum contained in HLW would form a water-soluble and segregated phase with significant radioactive[1][2]. An example of the phase is Cs_2MoO_4 [3].

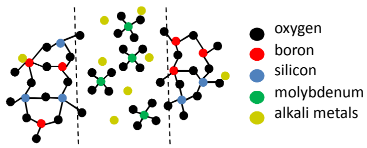

Fig. 1. Schematic representation of borosilicate glass which has separated Mo phase

A model of the relationship between structure and composition were proposed by Dell [4]. In the model, the change of structural units of B can be explained by the mole ratio of Na_2O to B_2O_3, *R*.

$$R = \frac{x_{Na_2O}}{x_{B_2O_3}} \qquad N_{B4} = \frac{\text{the number of B4}}{\text{the number of all boron}}$$

x_i : mole fraction of i

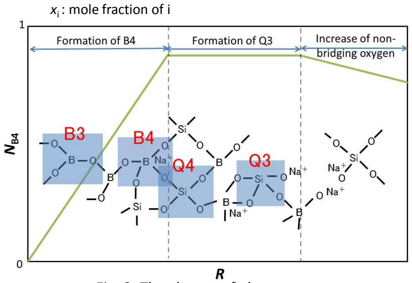

Fig. 2. The change of glass structure explained by Dell's model [4]

Objectives

To prevent substantial leaching of the radioactive nuclides from the vitrified wastes, it is important to clarify the effect of the contained Mo on glasses. The present study aimed to clarify the influence of Mo content in borosilicate glass on its leachability and its structure.

Methods

Preparation of the specimens

All specimens were prepared for the reagent powders of SiO_2, B_2O_3, Na_2CO_3 and MoO_3

Table 1. Glass preparation condition

Crucible	platinum
Temperature, ˚C	1200
Time, h	3
Atmosphere	in air

Table 2. 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

MAS NMR

NMR spectra of ^{11}B and ^{29}Si were measured by ECA-700 (16.43 T) (JEOL, Ltd., Japan) at a frequency of 700 MHz.

Leaching test

The leaching test was based on PCT-A[5]

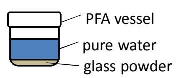

Fig. 3. Leaching test

Table 3. Experimental condition

Specimen mass, g	5.0
Glass particle diameter, µm	74 - 149
Volume of pure water, cm³	50.0
Temperature, ˚C	90
Holding time, d	7

Leaching rate

$$L = \frac{m_i - m_f}{St}, \text{ g m}^{-2}\text{ d}^{-1}$$

m_i : mass of the initial glass, g
m_f : mass of the glass after leaching, g
S : surface area of the glass particles, m²
t : holding time, d

The concentrations of Si, B, Na and Mo in the filtered leachate were measured by an inductively coupled plasma atomic emission spectrometer (ICP-AES) (ICPS-7000, Shimadzu Co., Ltd., Japan).

Reference

[1] H. Tanaka *et al.*, *Journal of the Ceramic Society of Japan*, **93**, 40-47 (1985).
[2] D. Caurant *et al.*, *Journal of Nuclear Materials*, **90**, 774-783 (2007).
[3] D. Caurant *et al.*, *Journal of Nuclear Materials*, **396**, 94-101 (2010).
[4] W. J. Dell *et al.*, *Journal of Non-Crystalline Solid*, **58**, 1-16 (1983).
[5] C. M. Jantzen *et al.*, ASTM C 1285-94 (1997).

Results and Discussion

Glass specimens

Table 4. Appearance and XRD pattern of the specimens

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

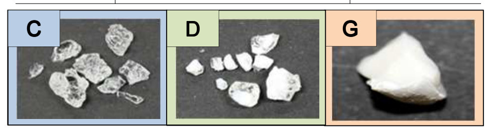

Fig. 4. Appearances of Specimens C, D and G

The solubility of MoO_3 in borosilicate glass used in this study was 2.0 wt%. The part of opaque glass of Specimen G containing MoO_3 at 7.6 wt%.

Leaching rate of the specimens

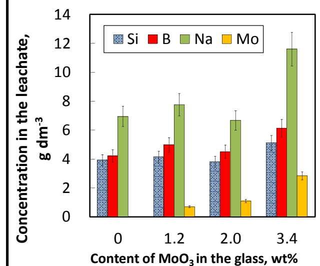

Fig. 5. Elemental concentration in the leachate

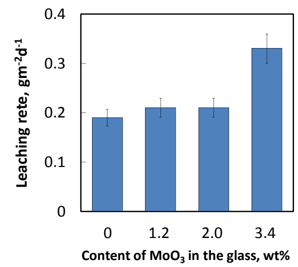

Fig. 6. Leaching rate of the glasses

In Specimen E, the leaching amounts of all elements increased 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 constituents, Si and B, in the glass.

Glass structure

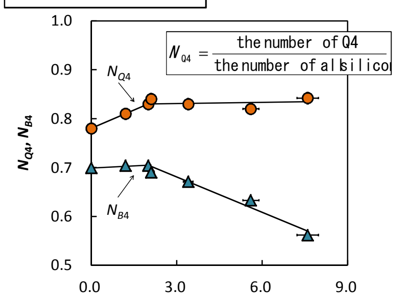

Fig. 7. Variations of N_{Q4} and N_{B4} with content of MoO_3 in the glass

With increasing the content of MoO_3 to the solubility, 2.0 wt%, the added Mo bonded to Na forming the non-bridging oxygen in Q3. When the content of MoO_3 was greater than the solubility, the added Mo bonded to Na forming B4.

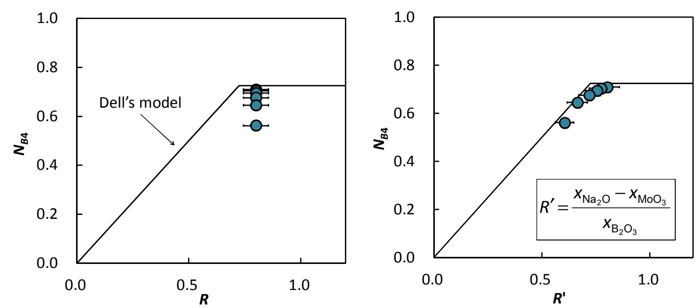

Fig. 8. The relationship between structure and composition of the glass

We defined R' as some Na in the glass were consumed by the formation of Na_2MoO_4 with added Mo. The N_{B4} re-plotted against R' were on the Dell's model. 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.

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. A water-soluble molybdate, Na_2MoO_4, caused not only increase of the leaching amounts of Na and Mo but also the other constituents, Si and B.
- In the glass used in this study, with increasing the content of MoO_3 from 0 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 with modifying the contribution of Na on the glass structure by Mo content.