



Release of boron and cesium or uranium from simulated borosilicate waste glasses through a compacted Ca-bentonite layer

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Abstract

The long-term release behavior of some elements from simulated borosilicate waste glasses (S-, K- and A-glass) in contact with a domestic compacted Ca-bentonite block and synthetic granitic groundwater at 80°C under argon atmosphere has been studied by dynamic leach tests since 1997 at KAERI. S- and K-glass differ mainly in their aluminum content, and A-glass contains 19.35 wt% UO₂ instead of fission product elements. Up to the present, the mass loss is almost the same as the normalized boron loss. This means that boron is an indicator on the dissolution of borosilicate waste glass. The leach rates of boron from K- and S-glasses after 861 days were approximately 3.1×10^{-2} and 3.0×10^{-2} g/m² day, respectively. However, the release rates of cesium through the bentonite block from K- and S-glasses were about 1/10th of the release rate of boron, which were almost the same around 2.5×10^{-3} g/m² day. This may be due to their adsorption on the bentonite. The leach rate of boron from the A-glass was about 5.4×10^{-2} , but the leach rate of uranium from the A-glass specimen was quite low, below 4×10^{-7} g/m² day. The low concentration of uranium in the leachates suggests that it hardly moves in a compacted bentonite block. By the EPMA, a yellowish uranium compound was deposited on the surface of the bentonite in contact with the A-glass specimen. The species of this phase should be identified to understand the release mechanism of uranium. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

A generic disposal concept for high-level radioactive waste (HLW) is being developed under the assumptions that an underground repository would be located in a type of crystalline rock in Korea and an appropriate multi-barrier system (such as engineered and natural barriers) would be provided for the isolation of the HLW from the biosphere. For assessing the long-term performance of waste isolation, the effects of various reactions and interactions occurring in the engineered barrier system, such as corrosion of waste form, canister and overpack, alteration of buffer materials, and chemical interactions of the constituents released from waste

products with them [1], should be fully understood. In 1997 KAERI began to study the leach behavior of some elements from simulated borosilicate waste glasses in contact with a compacted bentonite block under synthetic granitic groundwater in order to understand the long-term release behavior of radionuclides from vitrified waste products under repository condition.

This paper briefly describes the results on the leaching behavior of simulated borosilicate waste glasses with domestic Ca-bentonite buffer for exposure of about 2.4 years in synthetic granitic groundwater at 80°C.

2. Experimental

Three kinds of simulated borosilicate waste glasses were fabricated with oxides, carbonate and/or fly ash at around 1200°C as shown in Table 1, and then annealed at 500°C for 1 h [1]. 18 mmØ × 2.5 mm disc-type

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Table 1
Chemical compositions of simulated waste glasses

Oxide	Glass		
	S (wt%)	K (wt%)	A (wt%)
SiO ₂	45.28	44.90	38.99
B ₂ O ₃	13.97	13.95	12.10
Na ₂ O	9.81	10.43	16.26
Al ₂ O ₃	4.91	12.70	9.22
CaO	4.04	0.70	0.51
MgO	–	0.35	0.25
Li ₂ O	1.98	–	–
ZnO	2.50	–	–
Fe ₂ O ₃	2.91	2.98	2.17
P ₂ O ₅	0.28	–	–
NiO	0.74	0.33	–
Cr ₂ O ₃	0.51	–	–
TiO ₂	–	0.52	0.37
K ₂ O	–	1.07	0.78
TeO ₂	0.23	0.23	–
Cs ₂ O	1.42	1.42	–
SrO	0.33	0.33	–
Pr ₂ O ₃	0.44	0.44	–
ZrO ₂	2.65	1.65	–
MoO ₃	1.70	1.70	–
MnO ₂	0.72	0.72	–
CdO	0.33	0.33	–
CoO	0.12	0.12	–
BaO	0.60	0.60	–
CeO ₂	0.93	0.93	–
SnO ₂	0.02	0.02	–
La ₂ O ₃	0.90	0.90	–
Nd ₂ O ₃	1.59	1.59	–
Sb ₂ O ₃	0.01	0.01	–
Y ₂ O ₃	0.20	0.20	–
Ag ₂ O	0.03	0.03	–
UO ₂	0.52	0.52	19.35
ThO ₂	0.33	0.33	–
Total	100.00	100.00	100.00

specimens and crushed samples (1–2 mm) were used to observe the surface alteration phenomena and to evaluate the leach behavior of some elements from the glasses under compacted Ca-bentonite with a density of 1.4 Mg/m³. Each leach cell was containing a glass sample sandwiched between the bentonite blocks, of which the weight is 16 g, and Ar-purged synthetic granitic groundwater (pH = 7.8) was used as a leachant. After the leachant flew through leach cells in an oven at 80°C, it was collected in Teflon® bottles. The overall flow scheme for the leach tests is shown in Fig. 1. Teflon® discs with the same dimensions were used in place of glass discs for the blank test.

Each leachate was analyzed by inductively coupled plasma – atomic emission spectrometry (ICP–AES, Jobin-Yvon JY-50P), ICP – mass spectrometry (ICP–MS, VG Elemental PQ-3), atomic absorption spectroscopy (AAS, Perkin Elmer 5100PC), ion chromatography (IC,

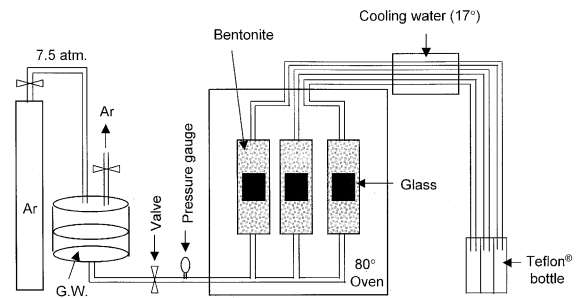


Fig. 1. Schematic diagram of dynamic leach test.

Waters ILC-1) and total organic carbon analyzer (TOC, Astro 2001-2). The surfaces of each disc-type specimen and the bentonite before and after its leaching were observed by electron probe micro analyzer (EPMA, Jeol, JXA 8600), X-ray diffractometer (XRD, Simens D5000), X-ray photoelectron spectrometer (XPS, Fisons 220i) and an optical microscope.

3. Results and discussion

3.1. Analysis of leachates

As shown in Fig. 2, the pH of the leachates gradually increased from 4.8 to about 8.0 for the leaching up to 836 days. The initial pH was mainly due to the dissolution of sulfate from bentonite. The higher values of pH in leachates than that in blank solution with similar flow

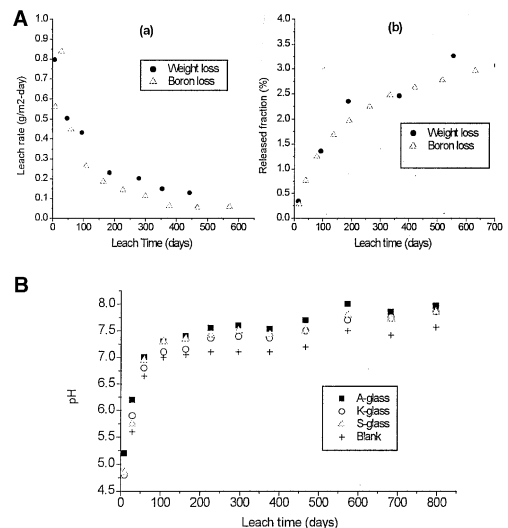


Fig. 2. Variation of pH of leachates as a function of leach time. (A) Comparison of weight and boron released from K-glass disc: (a) leach rates; (b) accumulated fractions. (B) Variation of pH of leachates as a function of leach time.

rate suggest that released components from glass also contribute to the increase of pH.

The weight loss of and the boron released from the disc specimens of the K-glass were measured, and their leach rates and the cumulative release fraction are illustrated in Fig. 3. As shown in this figure, the mass loss is almost the same as the normalized boron loss. This means that boron is an indicator on the dissolution of a borosilicate waste glass [2].

The concentration of silicon in the leachates with the crushed glass samples was in the range of 30–60 mg/l, which was comparable with that from bentonite without the glass sample and independent upon their leaching time. However, the release rates of boron from the crushed glass samples rapidly decreased with an increase of leaching time up to around 200 days, and then sluggishly decreased (see Fig. 4). The release fraction of boron from the A-glass is higher than those from the K- and S-glasses. This may be due to the difference of their components (see Table 1) and the high flow rate with regard to the glass surface area, which was 533 ml/m² day, compared with the flow rate of around 392 and 306 ml/m² day for K- and S-glasses, respectively. The leach rates of boron from the A-, K- and S-glasses after 861 days were approximately 5.4×10^{-2} , 3.1×10^{-2} and 3.0×10^{-2} g/m² day, respectively, and the leach rates of molybdenum from these specimens were almost the same as the values of their boron leach rates.

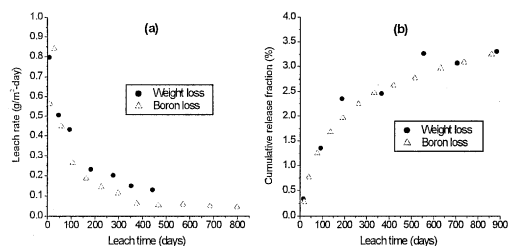


Fig. 3. Comparison of the mass loss and the normalized boron loss of K-glass disc: (a) leach rates; (b) cumulative release fractions.

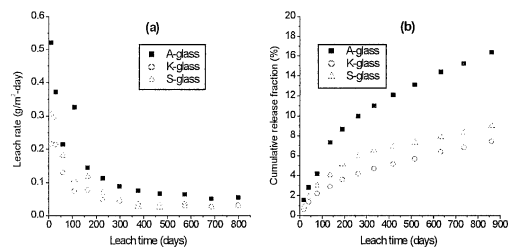


Fig. 4. Comparison of the normalized boron loss of crushed A-, K- and S-glass: (a) leach rates; (b) cumulative release fractions.

By the analysis using ICP-MS, the concentrations of U, Nd, La and Zr in the leachates were below 1 mg/m³, and the leach rate of uranium from the A-glass specimen is quite low, below 4×10^{-7} g/m² day. Though a large amount of uranium was found on the surface of the bentonite in contact with the A-glass, the low concentrations in the leachates suggest that uranium hardly move into the compacted bentonite layer due to the filtration of the uranium species formed. On the other hand, the leach rates of Cs from the K- and S-glasses were almost the same, around 2.5×10^{-3} g/m² day, which was about 1/10th of the release rate of boron. This may be due to adsorption on the bentonite.

3.2. Analysis of the disc-type specimens

The XPS spectra of the specimens before and after their leaching up to about 2.4 years are shown in Fig. 5. As shown in this figure, the leach resistant elements such as U, Fe and Zr on the surface of the specimens are enriched, while the soluble element such as Na is depleted due to the dissolution of these elements from the specimens into the groundwater.

The SEM pictures of the samples before and after their leaching up to about 2.4 years are shown in Fig. 6. By these pictures, all three kinds of glasses before leaching have the same appearance. After leaching, caves of a honeycomb shape were formed in the surfaces of the specimens and the break-out of scales on the surface layers of the A- and S-glasses was discovered. However, the break-out phenomenon on the surface of the K-glass did not appear until a 29-month leaching period. This suggests that the leaching mechanism of the K-glass could be different from the other glasses.

By the EPMA analysis, the contents of Na and Ca on the S-glass specimen surfaces were sharply decreased, while the contents of Mo, Fe, Zr and U increased. In the K-glass specimens the contents of Na and K sharply decreased after leaching, while the contents of Mo, Fe, Zr, U and Ti were increased. In the A-glass specimens the contents of Na sharply decreased after leaching, while the contents of Mo, Fe, U and Ti increased.

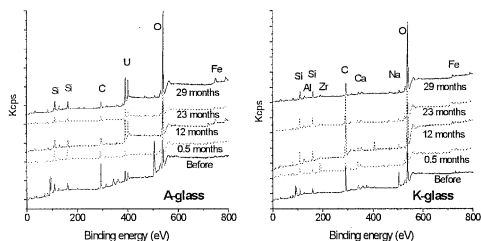


Fig. 5. XPS spectra of the specimens before and after leaching.

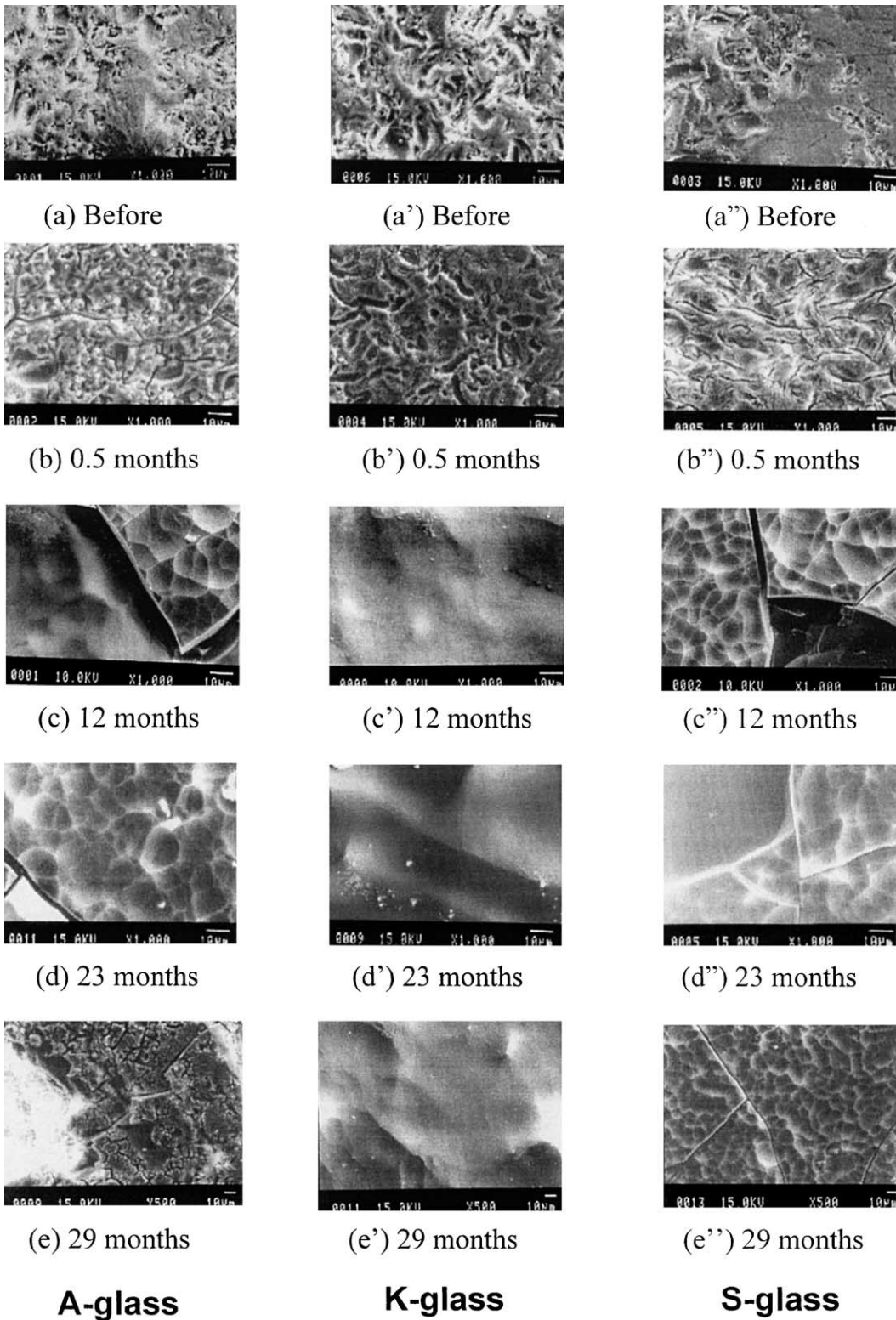


Fig. 6. SEM images of the specimens before and after leaching.

3.3. Analysis of bentonite

EPMA results indicated that there were no differences, except the depletion of sulfur, between the bentonite samples before and after the flowing of synthetic groundwater through the bentonite layers with the glass specimens up to about 2.4 years. However, a yellowish uranium compound was deposited on the surface of the bentonite in contact with the A-glass specimen. This phase could not be identified so far.

4. Conclusion

Boron can be used as an indicator on the dissolution of borosilicate glass in the tested bentonite. The leach rate of boron was related to the glass composition and to the ratio of the glass surface area to the volume of leachate passed through the specimens.

Uranium was retarded by compacted bentonite. However, the species of yellowish uranium deposited on the bentonite should be identified to clearly understand the release mechanism of uranium from vitrified waste with high uranium content.

There was no difference in the composition of the bentonite except for the depletion of sulfur, and in the properties of the bentonite before and after leaching up to about 2.4 years.

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References

- [1] S.S. Kim, G.H. Lee, J.G. Lee, K.Y. Jee, K.S. Chun, *Anal. Sci.* 13 (1997) 361.
- [2] S.S. Kim, J.G. Lee, I.K. Choi, G.H. Lee, K.S. Chun, *Radiochim. Acta* 79 (1997) 199.