

Characterization of simulated Al₂O₃-containing nuclear waste glass

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Glass and glass-ceramics are an attractive waste form for the permanent disposal of high-level radioactive waste. Although typical waste sludge from the processing of spent reactor fuel contains more than 30 elements of wildly different ionic sizes and properties, these elements are chemically soluble in many glass-forming compositions with reasonable chemical durability. The chemical corrosion of the waste by water is important since this corrosion could ultimately release biologically toxic radionuclides to the biosphere.

The corrosion of glass by water has been studied for many years but the corrosion mechanisms are still not fully understood. Many glass compositions exhibit selective ion removal of one or more of the constituent oxides. The alkali metal ions (Na⁺, K⁺, or Cs⁺) are particularly susceptible to selective leaching [1]. Many studies have shown that alkali leaching has two mechanisms. One is the diffusion-controlled mechanism whereby alkali ions diffuse to the glass surface and ion exchange with H₃O⁺ from the surrounding solution, and the other is the dissolution of the glass network by hydroxyl ion attack of the Si–O bond [2–6].

The alkali ion release mechanism is subjected to the diffusion-controlled mechanism and at longer corrosion times becomes controlled by the glass network dissolution mechanism. The time when this transition occurs depends on the glass composition. In order to increase the chemical durability of the nuclear waste glass, a favorable microstructure is tailored by controlled crystallization of the simulated nuclear waste glass, which was obtained by quenching the glass.

In this study, the possibility of using the glass and glass-ceramics of Al₂O₃-containing sodium borosilicate as nuclear waste materials was examined and some infrared measurements were carried out to investigate the Na leaching mechanism as well as the influence of the controlled surface crystallization on effectively increasing the chemical durability.

Table I shows the glass compositions in this study. The complex composition of the simulated nuclear waste glass PNL-7668 [7] was simplified to a composition of the sodium-borosilicate glass (S-1). To investigate the effect of the amount of Al₂O₃ in glass A-1 and A-2 were prepared. In D-1 glass, CaO, TiO₂, and MgO

were contained for crystallization. Glasses were made by melting in Pt crucible in air at 1500 °C for 3 hr. The melt was poured into a steel mold to make block specimens (approximately 10 × 10 × 15 mm) and annealed at 500 °C.

The complicated bonding characteristics of glass prior to and after leaching were examined by means of infrared reflection absorption spectroscopy (IRRAS). For infrared measurements, a model Mattson 5000

TABLE I Glass compositions of the simulated waste glass

	SiO ₂	Na ₂ O	B ₂ O ₃	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	TiO ₂
S-1	63.64	16.2	11.0	9.16				
A-1	56.64	16.2	11.0	9.16	7.0			
A-2	50.64	16.2	11.0	9.16	13.0			
D-1	40	10	10	5	15	10	7	3

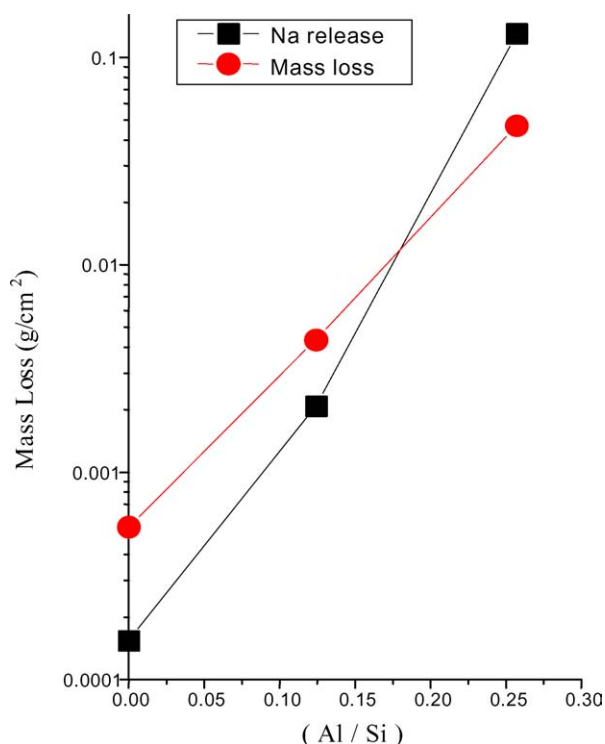


Figure 1 Effect of Al₂O₃ on Na release and mass loss in HCl (pH = 1.5) solution after 14 days.

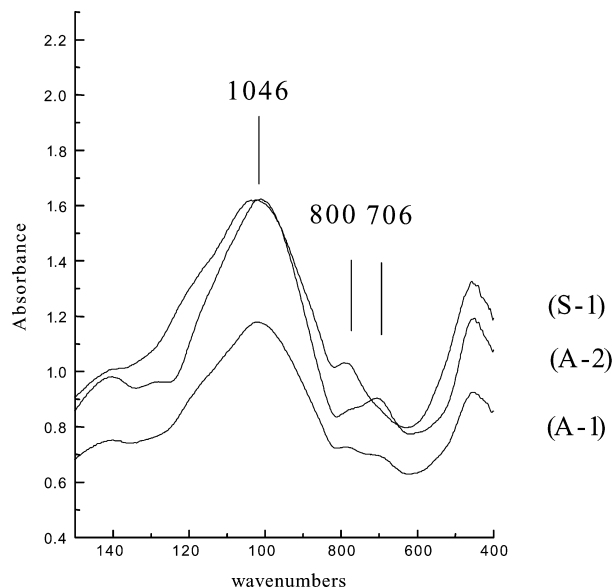


Figure 2 IRRAS spectra of Al_2O_3 before leaching tests.

FT-IR spectrometer with high sensitivity was used in all measurements.

For crystallization, D-1 glass was nucleated at 650°C for 5 hr and crystallized at 900°C for 10 hr. The crystalline phases were identified with X-ray ($\text{Cu K}\alpha$) powder diffraction (Model: Rigaku RINT 2000, Japan) method and their microstructure was observed with scanning electron microscopy (SEM, Model: Jeol JSM-5400, Japan). The crystalline and glassy regions were identified by selected area diffraction and further confirmed by dark- and bright-field image. Energy dispersive spectroscopy (EDS) was also used to determine the relative elemental composition of various phases.

The leach tests were performed according to the Materials Characterization Center, MCC-1, Static Leach Test Procedure [8]. The D-1 glass and glass-ceramic were suspended in pH 1.5 (HCl) by a Teflon thread attached to the lid of a sealed Teflon container and leached at $90 \pm 4^\circ\text{C}$. The concentrations of Na in the leached solution were determined by inductively coupled argon plasma (ICP).

Na release in HCl solution (pH = 1.5) was monitored for 14 days and shown in Fig. 1. By increasing the content of Al_2O_3 in glass, Na release is rapidly increased. Transmission spectra of the glass was measured using the infrared microscope combined with FT-IR in the wavelength region 4000 cm^{-1} at 400°C to monitor the increase of Na release. The position, shape, and intensity of the Si—O stretching vibration will be dependent on the quantity of the alkali ion added [9, 10].

A comparison of infrared spectra in Fig. 2 shows the effect of Al_2O_3 in untreated glasses. By increasing the content of Al_2O_3 in glass, the intensity of the tetrahedral Al—O stretching band assigned to around 700 cm^{-1} is increased. This result explains that Al_2O_3 , as a network former, takes part in the glass network. Fig. 3 shows a comparison of infrared reflection spectra for S-1 and A-2 glasses which were exposed to the same corrosion conditions. Ernsberger [11] showed that molecular water in glass is absorbed at around 1630 cm^{-1} for the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ glass. This band is observed in an A-2 glass when it is leached in HCl (pH = 1.5) solution. For an S-1 glass, this band is not observed. From this result, it could be expected that the mechanism of an A-2 glass corrosion may include water diffusion, whereas for an S-1 glass the

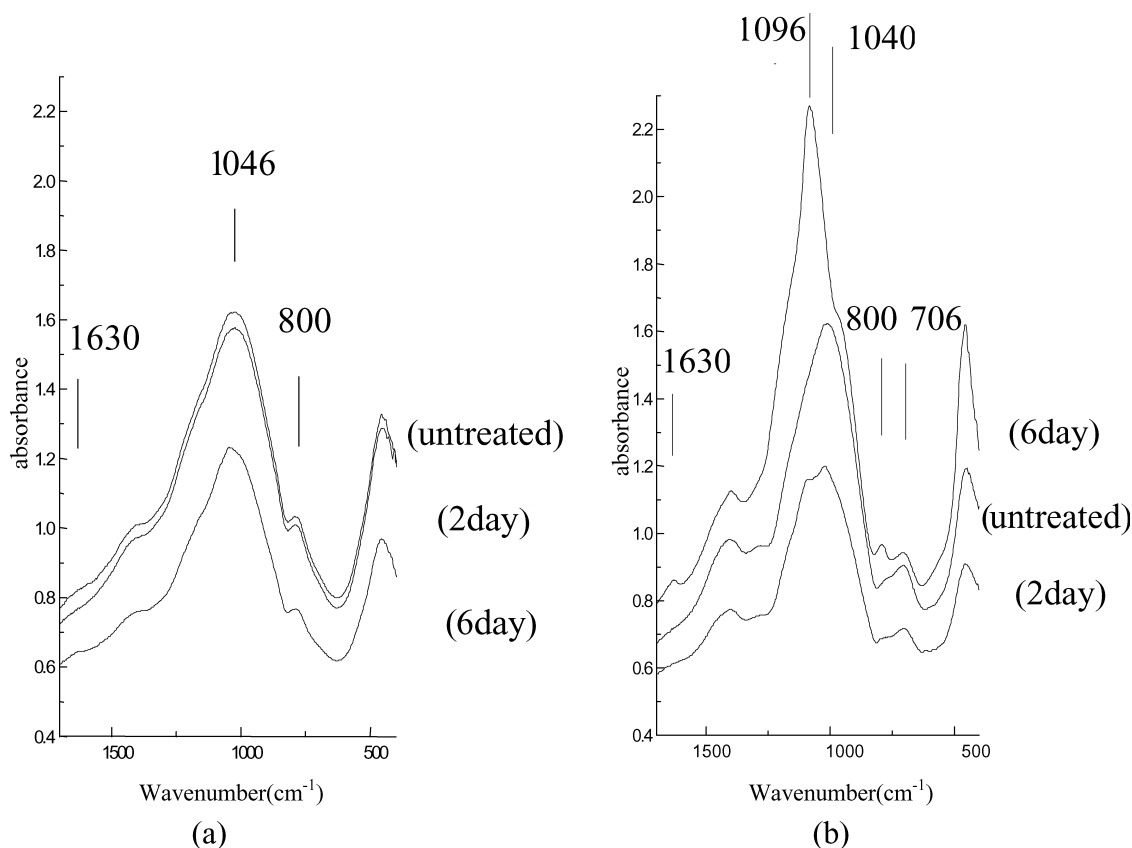


Figure 3 IRRAS spectra of leached glass S-1 (a) and A-1 (b) in HCl (pH = 1.5) solution.

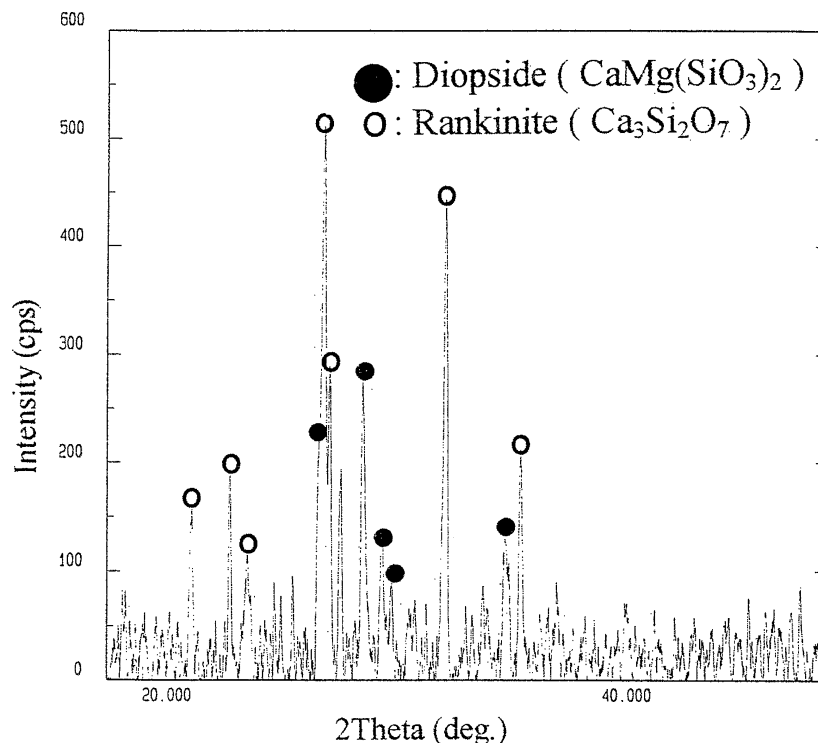


Figure 4 XRD spectrum of surface crystallized D-1 glass-ceramics.

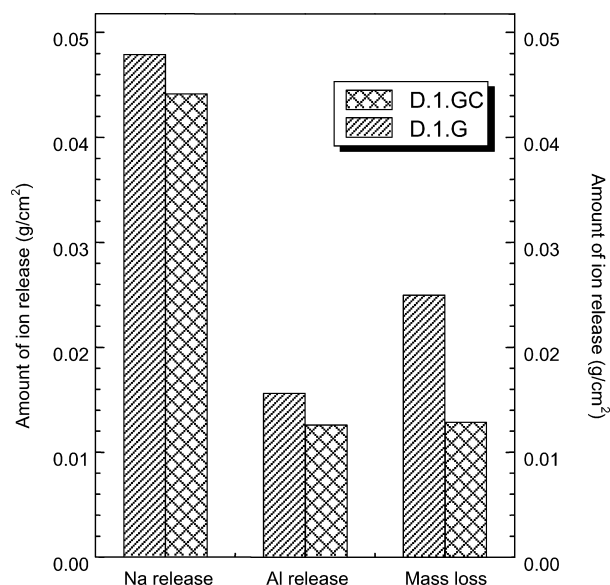


Figure 5 Amount of ionic release and mass loss of devitrified (D.1.G) and as-annealed (D.1.GC) glasses.

mechanism may only be an ion exchange between H^+ and M^+ in the ratio of 1:1 or 1:2 for M^+ and M^{++} , respectively. In an A-2 glass, tetrahedral Al-O band intensity decreases whereas the Si-O non-bridging band in alkali meta-silicate glass (around 800 cm^{-1}) increases and also a Si-O-H group [12], which absorbs at around 1100 cm^{-1} like a Si-O-Si linkage, rapidly increases. This may be due to the dissolution of tetrahedral Al-O glass network in HCl solution.

In order to inhibit the Na release from the Al_2O_3 -containing glass, controlled surface crystallization was performed. An XRD analysis in Fig. 4 shows

that the glass has been crystallized into Diopside ($CaMg(SiO_3)_2$) and Rankinite ($Ca_3Si_2O_7$) near the surface. Fig. 5 shows the result of leaching tests of devitrified glasses and as-annealed glasses. Devitrified glasses showed a greater chemical resistance to acid attack than as-annealed glasses. SEM micrograph of glass-ceramic (Fig. 6a) shows a microstructure consisting of two different types of phases, that is, crystalline phase existing on the surface and glassy phase existing in the inner part of glasses. An EDS analysis of annealed glass and a devitrified sample are shown in Fig. 6b. The crystalline regions of the devitrified microstructure contain a smaller amount of Al as compared to the glassy regions. During extraction, most of the surface exposed to the acidic extraction fluid is an Al-deficient crystalline matrix. This microstructure can protect the glass network of Al_2O_3 -containing glass matrix from the dissolution of the glass matrix in an acidic solution.

As the content of Al_2O_3 increases in the model nuclear waste glass matrix, Na release is rapidly increased. In our previous study [13], we mentioned about the possibility of Na release in HCl solution for the same composition glass. In the present study, FT-IR analysis clearly shows that Al_2O_3 takes part in the glass network, and the leaching mechanism in the Al_2O_3 -containing glass is the dissolution of the glass network in solution.

By means of controlled surface crystallization, a favorable microstructure was developed where a high-Al glassy phase was shielded by an Al-free crystalline phase which could isolate a high-Al glassy phase from the extraction fluid. This microstructure can be obtained by controlled surface crystallization and results in a reduced Na release rate.

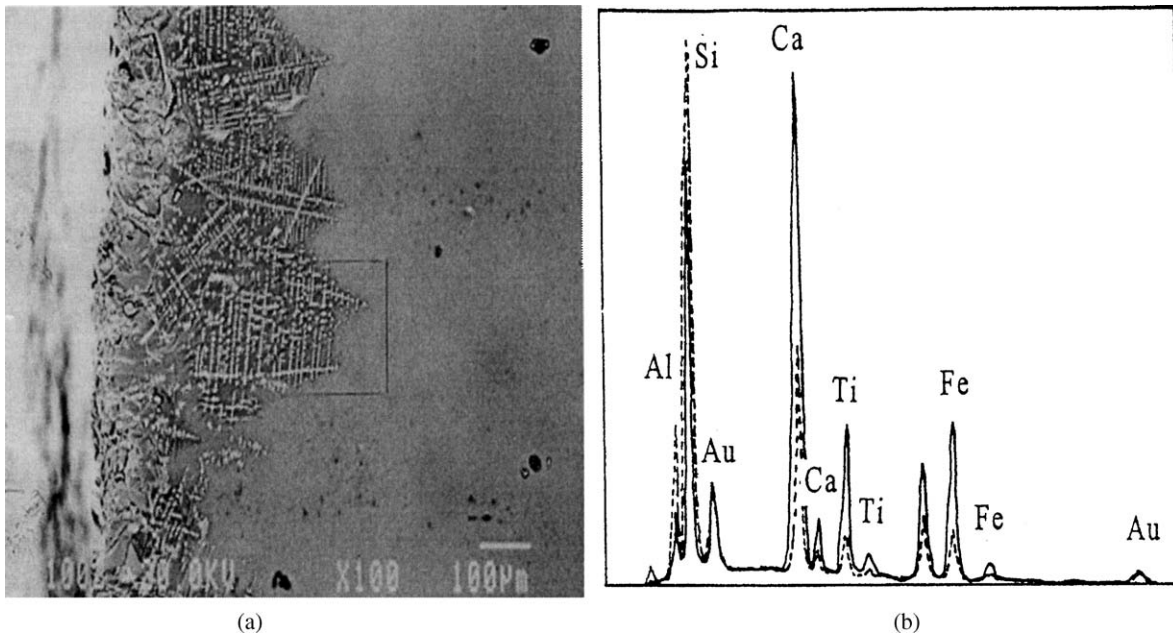


Figure 6 SEM analysis of surface crystalline phase of D-1 glass-ceramic (a) and EDS of crystalline phase (solid line) and amorphous phase (dashed line) (b) in the devitrified glass microstructure.

Acknowledgments

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