Dissolution and hydrothermal reaction behaviors of CaO–Al$_2$O$_3$–SiO$_2$ glasses in highly alkaline aqueous solutions

Yuichi HAMAZAKI$^1$ and Hiromichi TAKEBE$^{1,}$*

$^1$Graduate School of Science and Engineering, Ehime University, Matsuyama 790–8577, Japan

The dissolution behavior of calcium aluminosilicate (CAS) glasses with various CaO and Al$_2$O$_3$ concentrations was investigated at 180 °C in NaOH aqueous solutions with an initial pH of 13.2–14.0. A CaO–Na$_2$O–Al$_2$O$_3$–SiO$_2$–H$_2$O (C–N–A–S–H) layer was formed on the immersed glass surface due to the dissolution and penetration of the glass and solution constituents. An excellent alkali durability was achieved by the minimization of Al$_2$O$_3$ addition and a [CaO]/[SiO$_2$] molar ratio of 1.10–1.20 for the glass composition design. The results of the infrared spectroscopy indicated that the C–N–A–S–H layer contained H$_2$O and CO$_3^{2-}$ species from the ambient atmosphere and consisted of the network structure of SiO$_2$–AlO$_4$ tetrahedra. The hydrothermal reactions between the CAS glasses and NaOH solution promoted the formation of the C–N–A–S–H layer and precipitation of Ca(OH)$_2$ with an immersion time. Stable Al-substituted tobermorite and hillebrandite phases were finally formed on the immersed glass surfaces due to the hydrothermal reactions.

Key-words: Aluminosilicate glass, Chemical durability, Microstructure, Infrared spectroscopy, Hydrothermal reaction

1. Introduction

Recently, aluminosilicate (AS) glasses and their related byproducts (e.g., slag and fly ash) with controlling reactivity under highly alkaline environments have attracted considerable attention as attractive alkali-activated binders and geopolymers for low CO$_2$ materials that can be used as alternatives to Portland cements.$^1$–$^3$ However, the chemical durability in highly alkaline solutions at pH ≥ 12 for glass fiber reinforced cements degrades due to the addition of Al$_2$O$_3$ in AS glasses.$^4$ Moreover, AS glasses exhibit excellent thermal and mechanical properties, including a high glass transition temperature, low coefficient of thermal expansion,$^5$ and high Young modulus and hardness,$^6$ depending on the Al$_2$O$_3$ concentration. In view of these inconsistent properties related to the addition of Al$_2$O$_3$, it is important to have sufficient understanding of the composition dependence of the dissolution and reaction behaviors in high alkaline environments of basic CaO–Al$_2$O$_3$–SiO$_2$ (CAS) glasses.

This understanding of CAS glasses in alkali solutions is important for designing the composition of ubiquitous CAS glasses without the need of including special components, such as ZrO$_2$ and Y$_2$O$_3$,$^7$–$^9$ to control the alkali durability of alkali-activated materials for a sustainable society. In this study, the dissolution and hydrothermal reaction behaviors of ternary CAS glasses with various Al$_2$O$_3$ concentrations are examined in terms of the crystalline phase and microstructure.

2. Experimental procedure

Glass compositions of (55 – x)CaO–xAl$_2$O$_3$–45SiO$_2$, where x = 3, 5, 15, 25 in mol %, were selected for a series of constant SiO$_2$ samples with various Al$_2$O$_3$ concentrations. Herein, the glass composition is characterized and described in terms of the molar ratio of [CaO]/[SiO$_2$] (Ca/Si molar ratio) and Al$_2$O$_3$ concentration.

CaCO$_3$ (99.99 % cationic purity), α-Al$_2$O$_3$ (99.99 % cationic purity), and SiO$_2$ (99.9 % cationic purity) powders were utilized as the raw materials. A 40-g sample of the mixed batch was melted at 1,600 °C for 2 h in air using a platinum crucible. The glass melt was poured onto a preheated stainless mold and then annealed at the glass transition temperature $T_g$ plus 50 °C for 1 h and then slowly cooled to room temperature for 8 h.

The dissolution behavior of the glass samples in the alkali solution was evaluated using the MCC-2 static high-temperature leaching test method.$^{10}$ As presented in Fig. 1, the CAS glass plate with a dimension of 9 × 9 × 2 mm with six polished surfaces was suspended by a fluorooethylene resin thread in an approximately 1.3-mol/L NaOH aqueous solution at a pH of 13.2–14.0 with 50 mL in volume in a PTFE sealed vessel (TAF-SR-50, Taiatsu Techno Co., Tokyo, Japan). The vessel, including the suspended glass plate, was held at 180 °C in an oven with
a high-precision temperature control (DF411, Yamato, Japan). After the immersion tests, the glass samples were removed from the NaOH aqueous solution and then rinsed with ultrapure water (18.2 MΩ·cm) at 60 °C to remove the absorbed liquid on the surface. Subsequently, the glass sample was dried at 70 °C for 7 h in air.

The microstructure and cationic element distribution of the surface and cross section of the glass samples were observed via scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM-EDS) analysis for the initial corrosion stage of the samples immersed for 1–6 h and for the crystalline layers formed on the glass sample surfaces of the samples immersed for 72 h. The crystalline phases formed on the surface of the immersed bulk glass samples were detected via X-ray diffraction (XRD) analysis (X’Pert Powder Diffractometer, PANalytical, Netherlands), with the diffractometer operating at 45 kV and 40 mA using Cu–Kα radiation between 10 and 90° 2θ. The grazing incidence method (2θ-ω) was employed for the XRD measurements with an incident angle ω of <10°. Infrared spectroscopy (IR Prestige-21, SHIMADZU, Kyoto, Japan) was used to evaluate the AS network structure and other molecular species. The CAS glass powder ground from the as-prepared glasses and the powdered samples with a mass of 450 mg were homogeneously mixed for the IR measurements. The slope of the thickness variation was large in the initial Ca/Si atomic ratios and thickness via microstructure observation.

Table 1 presents the results of the composition analysis of the selected points in the altered layers demonstrated in Fig. 2. The altered layer was composed of reduced Al concentrations compared with the as-prepared glasses and of a small amount of Na in addition to Ca and Si as cationic constituents. The results of the SEM-EDS analysis revealed that the altered layer was a calcium–sodium–alumino–silicate hydrate (CaO–Na2O–Al2O3–SiO2–H2O; hereinafter referred to as C–N–A–S–H) gel, which consisted of calcium silicate hydrate (CaO–SiO2–H2O)11 and contained small amounts (<10 mol%) of Na2O and Al2O3. In the CAS glass samples with small Ca/Si atomic ratios and large Al2O3 concentrations, thick C–N–A–S–H layers were formed.

Figure 3 presents the variation in the thickness of the C–N–A–S–H layer according to the immersion time for four types of CAS glasses. For all the CAS glasses, the thickness increased linearly according to the immersion time. The slope of the thickness variation was large in the

| Initial [CaO]/[SiO2] | Altered layer (cationic ratio) | Ca | Na | Al | Si | Ca/Si |
|----------------------|-------------------------------|----|----|----|----|--------|
| 0.67                 |                               | 48.5 ± 1.1 | 3.8 ± 0.4 | 4.2 ± 1.3 | 43.5 ± 0.9 | 1.11   |
| 0.89                 |                               | 47.6 ± 0.9 | 5.9 ± 1.0 | 3.4 ± 0.2 | 43.1 ± 0.3 | 1.10   |
| 1.11                 |                               | 50.2 ± 0.6 | 4.2 ± 0.3 | 2.8 ± 0.3 | 42.7 ± 0.6 | 1.18   |
| 1.16                 |                               | 49.3 ± 2.6 | 4.4 ± 2.4 | 2.7 ± 0.6 | 43.6 ± 0.9 | 1.13   |

3. Results

Figure 2 presents the SEM micrographs of the cross section of the CAS glass samples after immersion for 3 h. The surface layer with a composition altered from that of the as-prepared glasses (hereinafter referred to as “altered layer”) was formed on all glass sample surfaces. The altered layer was characterized in terms of composition and thickness via microstructure observation.

Figure 2 presents the SEM micrographs of the cross section of the CAS glasses immersed in an approximately 1.3-mol/L NaOH solution at 180 °C for 3 h. The cationic ratios of the altered layers were analyzed via SEM-EDS (Table 1). Initial Ca/Si: (a) 0.67, (b) 0.89, (c) 1.11, and (d) 1.16.
CAS glasses with compositions of small [CaO]/[SiO₂] (Ca/Si) molar ratios and high Al₂O₃ concentrations. Figure 4 presents the variation in the Ca/Si molar ratio of the altered layer according to the immersion time. The plots at an immersion time of zero denote the initial Ca/Si molar ratios for each CAS glass. After immersion of ≥2 h, the Ca/Si molar ratio of the altered layer leached in the range of 1.00 to 1.20 in all CAS glasses. The results indicated that the CAS glass with a similar composition to the altered (C–N–A–S–H) layer with a Ca/Si molar ratio of 1.00–1.20 exhibited excellent alkali durability in the NaOH aqueous solution for 3 and 6 h. Table 2 presents the results of the composition analysis at the 1–7 positions in the SEM micrographs in Figs. 6(a), 6(c), 6(e), and 6(g) for a 3-h immersion. The results are the averaged values of three analyses and are expressed as cationic ratios of the elements Ca, Na, Al, and Si. The Al element concentration decreased in all surfaces of the immersed CAS glasses compared with that in the as-prepared glasses. This result indicates that all the immersed glasses formed the C–N–A–S–H layer on their surface. At a Ca/Si molar ratio of ≥0.89, platelike precipitates were observed, with their sizes increasing with the increase in immersion time. These crystalline precipitates were identified as Ca(OH)₂ from the SEM-EDS composition analysis (positions 2, 4, and 6 in Table 2) and the XRD patterns presented in Fig. 5. At Ca/Si molar ratios of 1.11 and 1.16, needlelike precipitates were observed around the Ca(OH)₂ plates [Figs. 6(f)–6(h)].

Figure 7 presents the XRD patterns of the surfaces of the CAS glasses immersed for 72 h. Some unknown diffraction peaks exist for further studies. A tobermorite (TB) [Ca₆(Si₆O₁₈)·4H₂O] phase was confirmed at Ca/Si molar ratios of 0.67 and 0.89, both a TB phase and a hillebrandite (HB) [Ca₂(SiO₃)(OH)₂] phase were confirmed at Ca/Si = 1.11, and a HB phase was confirmed at Ca/Si = 1.16.

Figures 8(a) and 8(b) presents two representative SEM micrographs of the surfaces of the CAS glasses immersed for 72 h. Here, Al₂O₃-containing TB (Al-substituted TB) plates at Ca/Si = 0.67 [Fig. 8(a)] and needlelike HB precipitates at Ca/Si = 1.16 [Fig. 8(b)] were formed. SEM-EDS point analysis was employed to determine the Ca/Si molar ratios of the TB and HB precipitates. The average Ca/Si molar ratios at three specific points were 0.80 and 2.00 for the TB and HB precipitates, respectively (Table 3).

Figure 9 presents the IR spectra of representative as-prepared CAS glass samples and the altered layer samples for the 3-h immersion. The CAS glasses exhibited absorption bands owing to the chemical shift of the Si–O ν₃ vibration with the peaks at 900–960 cm⁻¹. Generally, these
absorption bands are assigned to the \([\text{Si}_n\text{Al}_m\text{O}_{3n+2}]^{\text{2+}}\) ring and \((\text{Si}_2\text{O}_7)^{\text{6−}}\) chain structures\(^5\) in CAS glasses. The \(\text{CaN}_{\text{A-S-H}}\) layer mainly consists of \(\text{SiO}_4\)–\(\text{AlO}_4\) tetrahedra at a peak of 960 cm\(^{-1}\) and contains \(\text{H}_2\text{O}\) at the absorption band of 1,640 cm\(^{-1}\)\(^1\(^2\) and \(\text{CO}_3^{2−}\) species at 1,460 and 860 cm\(^{-1}\).\(^1\(^2\) The \(\text{CO}_3^{2−}\) species contained was probably due to the dissolution of \(\text{CO}_2\) gas in the ambient air atmosphere.

### 4. Discussion

As presented in Fig. 2, the \(\text{C-N-A-S-H}\) layers\(^4\(^,\)\(^1\(^3\)\) were formed on all the CAS glass surfaces immersed in the highly alkaline NaOH aqueous solution. The thicknesses

#### Table 2. Composition analysis of the surface layer of the CAS glasses immersed in an approximately 1.3-mol/L NaOH solution at 180 °C for 3 h. The surface layers are presented in Figs. 6(a), 6(c), 6(e), and 6(g)

| Position | Element (cationic ratio) | Classification |
|----------|-------------------------|-----------------|
| 1        | Ca 40.3 ± 3.0, Na 5.2 ± 0.7, Al 3.9 ± 0.2, Si 50.6 ± 2.3 | Surface layer   |
| 2        | Ca 97.5 ± 1.4, Na 1.6 ± 0.4, Al 2.6 ± 1.3 | Ca(OH)_2        |
| 3        | Ca 42.9 ± 2.2, Na 13.8 ± 0.8, Al 23.1 ± 1.9, Si 41.0 ± 3.4 | Surface layer   |
| 4        | Ca 100.0 ± 0.0, Na 0.0, Al 0.0 | Ca(OH)_2        |
| 5        | Ca 43.8 ± 0.1, Na 16.9 ± 1.5, Al 21.8 ± 0.9, Si 37.5 ± 0.7 | Surface layer   |
| 6        | Ca 100.0 ± 0.0, Na 0.0, Al 0.0 | Ca(OH)_2        |
| 7        | Ca 65.7 ± 6.9, Na 6.3 ± 0.9, Al 28.0 ± 6.9 | Precipitate (needlelike) |

---

**Fig. 6.** SEM micrographs of the altered layer of the CAS glasses immersed in the approximately 1.3-mol/L NaOH solution at 180 °C for 3 and 6 h. (a) Ca/Si = 0.67, 3 h; (b) Ca/Si = 0.67, 6 h; (c) Ca/Si = 0.89, 3 h; (d) Ca/Si = 0.89, 6 h; (e) Ca/Si = 1.11, 3 h; (f) Ca/Si = 1.11, 6 h; (g) Ca/Si = 1.16, 3 h; and (h) Ca/Si = 1.16, 6 h. The points numbered 1–7 were analyzed via SEM-EDS (Table 2).

**Fig. 7.** XRD patterns of the surface layer in the CAS glasses immersed in the approximately 1.3-mol/L NaOH solution (pH = 13.2–14.0) at 180 °C for 72 h.
Ca/Si ratio of 1.00–1.20, independent of the initial glass compositions (Table 1 and Fig. 4). The CAS glass with an altered layer of similar initial composition exhibited a small variation in the thickness of the C–N–A–S–H layer after the immersion tests. That is, the formation of the altered layer accompanying the glass and solution constituents determined the alkali durability.

As presented in Figs. 5 and 6, the XRD and SEM results revealed that Ca(OH)$_2$ platelets were formed on the surfaces of the C–N–A–S–H layers in all the CAS glasses. The formation of the Ca(OH)$_2$ precipitates on the sample surfaces was considered to be caused by the Ca ions originating from a specific glass constituent. At a Ca/Si molar ratio of $\geq 1.11$, needlelike precipitates were formed around the Ca(OH)$_2$ platelets. Figures 7 and 8(b) demonstrate the formation of the HB needles at a Ca/Si molar ratio of $\geq 1.11$.

Calcium silicate hydrates, such as TB and HB, can be easily formed via hydrothermal reactions using Ca(OH)$_2$ and non-crystalline SiO$_2$ as the raw materials. Mitsuda$^{11)}$ proposed that the type of hydrothermally synthesized phase depended on the reaction temperature, Ca/Si ratio, and microscopic morphology of the raw materials. In this study, the immersion temperature was 180 °C, and the Ca/Si ratio of the initial glass composition was in the range of 0.67–1.16. Elsewhere, Nobugai$^{17)}$ synthesized TB precipitates via a hydrothermal reaction between crystalline calcium silicate hydrate (C–S–H, Ca/Si = 1.5) and quartz at 180 °C with a total Ca/Si ratio of 0.8. In the hydrothermal formation of TB, low C–S–H was formed at the initial stage of the reaction before the formation of crystalline TB due to the ordering of the C–S–H gel along the (001) direction.$^{16)}$ The addition of Al$_2$O$_3$ in small amounts (a few percent) is known to promote the phase change from non-crystalline C–A–S–H to Al-substituted TB.$^{12),18)}$

As presented in Fig. 4, the Ca/Si ratio of the altered layer converged at 1.00–1.20 following the immersion of the CAS glasses in the alkali aqueous solution at 180 °C for $\geq 2$ h. The Ca/Si ratio of this altered layer was close to the value of the TB crystals, which remained stable under various immersion conditions.$^{14)}$

The results of IR spectroscopy, as presented in Figs. 9(a) and 9(b), revealed that the complex-network structure$^5)$ of SiO$_2$–AlO$_4$ tetrahedra was partially similar to the chain and ring structures of Al-substituted TB.$^{12),14),18)}$ These network similarities contributed to the promotion of the phase transition from the low-crystalline C–N–A–S–H layer to the Al-substituted TB. No formation of xonotlite [Ca$_{6}$(Si$_{6}$O$_{17}$)(OH)$_{2}$]$^{11),16),17)}$ was observed in this study. The introduction of a small percentage of Al$_2$O$_3$ greatly inhibited the formation of xonotlite, as Kalousek pointed out.$^{19)}$ and maybe stabilized the Al-substituted TB due to the combination of AlO$_4$ tetrahedra and H$^+$ species for local charge neutrality.

Figure 10 presents the dissolution and reaction behaviors of CAS glasses in schematic terms. In all the CAS glasses, the C–N–A–S–H layer was formed by the dissolu-
ion and penetration of the glass and solution constituents. The metastable C–N–A–S–H layer exhibited a Ca/Si value of 1.00–1.20. The Ca/Si value is close to one [0.80 in Fig. 8(a) and Table 3], which was exhibited by the stable TB crystals under hydrothermal conditions. After the altered layer was formed, at a Ca/Si ratio of ≥0.89, the Ca ions dissolved in the alkaline aqueous solution were saturated and precipitated as Ca(OH)₂ plates (Fig. 5).

With the increase in immersion time, the continuous dissolution and penetration of the glass and solution constituents contributed to the enhancement of the thickness of the altered layer (Fig. 3) and promoted the growth of the stable crystalline phases via hydrothermal reactions. The C–N–A–S–H-based precipitates were formed via the following two patterns, depending on the initial Ca/Si ratio of the glass samples. In Type I, the precursor C–N–A–S–H layer itself crystallized to the stable TB with a Ca/Si ratio similar to that of the altered layer [the analyzed example of Fig. 8(a); Ca/Si = 0.80 (Table 3)]. In Type II, the Ca(OH)₂ plates precipitated on the altered layer during the initial stage of immersion were dissolved in the solution before the HB precipitates with richer Ca content than the Ca/Si of the altered layer were formed [the analyzed sample of Fig. 8(b); Ca/Si = 2.00 (Table 3)].

5. Conclusions

CAS glasses in a series of (55 – x)CaO–xAl₂O₃–45SiO₂, where x = 3, 5, 15, and 25 in mol%, were immersed in an approximately 1.3-mol/L NaOH aqueous solution with a pH range of 13.2–14.0 at 180°C. The C–N–A–S–H layers were formed on all the CAS glass surfaces after immersion in the highly alkaline solution due to the dissolution and penetration of the glass and solution constituents. The increasing rate of the altered layer thickness determined the alkali durability of the CAS glasses.

By minimizing the Al₂O₃ concentration and forming a similar Ca/Si molar ratio of the C–N–A–S–H layer for the composition design of CAS glasses, an excellent alkali durability was achieved. The IR spectroscopy analysis revealed that the C–N–A–S–H layer consisted of the complex-network structure of SiO₄–AlO₄ tetrahedra and contained H₂O and CO₃²⁻ species. The network structure of the altered layer was partially similar to the chain and ring structures of the SiO₄–AlO₄ of the Al-substituted TB. The similarity in the local structure may have promoted the transformation from the C–N–A–S–H layer to the Al-substituted TB. Under the highly alkaline solution conditions at 180°C, hydrothermal reactions occurred on the surfaces of the CAS glasses. The hydrothermal reactions between the C–N–A–S–H layer, various ions existing in the solution, and CaCO₃ and Ca(OH)₂ precipitates contributed to the formation of the Al-substituted TB and HB.

References

1) S. A. Bernal and J. L. Provis, *J. Am. Ceram. Soc.*, 97, 997–1008 (2014).
2) T. Luukkonen, Z. Abdollahnejad, J. Ylimieri, P. Kinnunen and M. Illikainen, *Cement Concrete Res.*, 103, 21–34 (2018).
3) N. T. Abbel-Ghani, H. A. Elsayed and S. AbdelMoied, *HBRC Journal*, 14, 159–164 (2018).
4) H. Ohta, *New Glass*, 11, 69–74 (1989) [in Japanese].
5) S. Takahashi, D. R. Neuville and H. Takebe, *J. Non-Cryst. Solids*, 411, 5–12 (2015).
6) S. Inaba, S. Todaka, Y. Ohta and K. Morinaga, *Jpn. Inst. Met.*, 64, 177–183 (2000) [in Japanese].
7) N. Koshizaki, *Yogyo-Kyokai-Shi*, 95, 404–411 (1987) [in Japanese].
8) V. T. Yilaz, E. E. Lachowski and F. P. Glasser, *J. Am. Ceram. Soc.*, 74, 3054–3060 (1991).
9) T. Uwabe, M. Tanaka, H. Kugai, N. Shimizu and S. Suzuki, *Report of Tokyo Metropolitan Industrial Technology Center*, 26, 77–80 (1997) [in Japanese].
10) H. Takebe, N. Kitamura, I. Amamoto, H. Kobayashi, T. Tszuki and N. Mitamura, *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B*, 57, 213–217 (2016).
11) T. Mitsuda, *J. Mineralogy, Petrology and Economic Geology*, 3, 317–329 (1982) [in Japanese].
12) K. Sankar, P. Stykoski and W. M. Kriven, *J. Am. Ceram. Soc.*, 102, 3175–3190 (2019).
13) K. Nakamoto, “Infrared and Raman Spectra of Inorganic and Coordination Compounds”, 4th ed., John Wiley & Sons, Toronto (1986) pp. 101–188.
14) R. J. Myers, S. A. Bernal, R. S. Nicolas and J. L. Provis, *Langmuir*, 29, 5294–5306 (2013).
15) K. Sankar, A. Sutrisno and W. M. Kriven, *J. Am. Ceram. Soc.*, 102, 3204–3227 (2019).
16) K. Takemoto, *Yogyo-Kyokai-Shi*, 73, C91–C97 (1965) [in Japanese].
17) K. Nobugai, M. Tokonami, K. Takahashi and T. Mitsuda, *J. of the Mineralogical Soc. Jpn.*, 14, 172–180 (1980) [in Japanese].
18) G. L. Kalousek, *J. Am. Ceram. Soc.*, 40, 74–80 (1957).