

Aqueous alteration of Japanese simulated waste glass P0798: Effects of alteration-phase formation on alteration rate and cesium retention

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Abstract

Aqueous alteration tests were performed with a Japanese simulated waste glass P0798 in alkaline solutions as a function of pH or species/concentration of alkaline metals in the solution in order to evaluate the alteration conditions determining whether smectite (2:1 clay mineral) or analcime (zeolite) forms as the major alteration-phase. XRD analysis of the alteration-phases showed that smectite forms at any pH between 9.5 and 12, and analcime forms at pH above 11, though the formation also depends on species and concentrations of alkaline metals in the solution. These results cannot agree with the thermodynamically predicted phase stability, e.g., smectite is more stable than the thermodynamic prediction shows. On the basis of the results of alteration conditions, the alteration tests were performed under smectite forming conditions, where only smectite forms or no crystalline phases form, in order to evaluate the alteration rate and the mechanism of cesium release/retention. The results showed that the glass alteration proceeds slowly in proportion to square root of time under smectite forming conditions, which indicates that the alteration rate can be controlled by a diffusion process. It was suggested that the alteration rate under smectite forming conditions is independent of the pH, alkaline metal species/concentration in the solution and whether smectite actually forms or not. The results also indicated that most of cesium dissolved from the glass can be retained in the alteration-phases by reversible sorption onto smectite or irreversible incorporation into analcime, pollucite or solid solutions of them.

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1. Introduction

A large number of studies on aqueous corrosion of high-level radioactive waste glass have shown that the glass reacts with water to form more stable solid phases following an initial dissolution stage of silica network hydrolysis. This process of transformation from the original glass to another solid

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phases can be defined as ‘glass alteration’, and the alteration products usually forming at the glass surface are called ‘secondary phases’ or ‘alteration-phases’. Since the chemical composition of the waste glass is similar to that of aluminosilicate minerals observed in natural environments for the major elements, the major alteration-phases are expected to be aluminosilicate phases. Many types of the alteration-phases can form depending on the alteration conditions. Recent studies have indicated that smectite (2:1 clay mineral) and analcime (zeolite) can be identified to form as the major alteration-phases under neutral to slightly basic solution conditions, and the alteration-phase formation can affect largely the glass alteration rate, e.g., formation of analcime can accelerate the glass alteration by consuming silica or alumina from solution [1–5]. Since the glass alteration usually leads to the release of radionuclides from the glass, the glass alteration rate can be assumed to equal to the long-term release rate for soluble radionuclides such as cesium. On the other hand, the alteration-phases such as smectite and analcime can retain some radionuclides including cesium by sorption or incorporation [4]. Therefore, the alteration-phase formation are expected to be a dominant process controlling the radionuclide release rate. Further, the release and retention of cesium can be one of key phenomena affecting the performance of the geological disposal since cesium-135 is one of the most critical radionuclides controlling the exposure dose rate for the biosphere in the safety assessment [6].

Thermodynamic calculations have been applied to prediction of the potential alteration-phases forming during the long-term disposal periods. The calculations indicated that amorphous silica, chalcedony, analcime, smectite, kaolinite, gibbsite, or other phases can form depending on the glass composition, alteration conditions and reaction progress [1,2,7–9]. On the other hand, the alteration-phases actually forming in the alteration tests have been analyzed using some analytical techniques [3–5,10–13]. The analysis pointed out, unfortunately, that current thermodynamic calculations rarely predict the actually forming phases. Disagreement between the thermodynamically predicted phases and the actually forming phases is partly caused by uncertainty in the thermodynamic data, because the actually forming phases are non-ideal phases with impurity and crystallographic defects. A poor understanding of its kinetics is also supposed to cause the disagreement. Therefore, a sound

understanding of the actual alteration-phase formation, including both thermodynamic and kinetic analysis, is essential for a valid evaluation of the long-term glass performance.

The purpose of this study is to estimate the aqueous alteration rate of a Japanese simulated waste glass P0798 under smectite forming conditions following an empirical evaluation of the alteration conditions determining whether smectite or analcime forms as the major alteration-phase. It is also the purpose to understand mechanism of the associated cesium release and retention under these conditions. Static aqueous alteration tests were performed with P0798 glass in some alkaline solutions as a function of pH, species/concentration of alkaline metals in the solution, temperature and time. In addition to measurement of solution concentrations of major elements dissolved from the glass, crystalline alteration-phases forming in the altered glass were analyzed by use of an X-ray powder diffractometer (XRD) and an electron microscopy (TEM/EDS). On the basis of the experimental results with thermodynamic analysis, the glass alteration rate and mechanism of the associated cesium release/retention are discussed in relation to the alteration-phase formation.

2. Experimental

2.1. Glass specimen

The test glass was a Japanese simulated waste glass P0798 with a chemical composition close to the French R7T7 glass or SON68 glass, as shown in Table 1 [14]. The glass was milled and sieved to obtain the glass powder with grain sizes under 38 μm . The glass powder was ultrasonically cleaned in ethanol, and was used as a glass specimen. The specific surface area was measured to be 0.49 m^2/g by the BET method using Kr gas. It was also measured by the stereological analysis based on SEM observation [15] to be 0.15 m^2/g . The difference between them suggested that a certain amount of fine glass particles remains on the glass grain.

2.2. Alteration test procedure

The glass specimen and the alkaline solution were placed in a reaction vessel composed of Teflon (PTFE) inner vessel and stainless steel outer vessel as shown in Fig. 1, and static alteration tests were performed at elevated temperatures. Two types of

Table 1
Chemical composition of P0798 simulated waste glass [13]

SiO ₂	46.60	Rb ₂ O	0.11	SeO ₂	0.02
B ₂ O ₃	14.20	Cs ₂ O	0.75	TeO ₂	0.19
Al ₂ O ₃	5.00	SrO	0.30	Y ₂ O ₃	0.18
Li ₂ O	3.00	BaO	0.49	La ₂ O ₃	0.42
CaO	3.00	ZrO ₂	1.46	CeO ₂	3.34
ZnO	3.00	MoO ₃	1.45	Pr ₆ O ₁₁	0.42
		MnO ₂	0.37	Nd ₂ O ₃	1.38
Na ₂ O	10.00	RuO ₂	0.74	Sm ₂ O ₃	0.29
P ₂ O ₅	0.29	Rh ₂ O ₃	0.14	Eu ₂ O ₃	0.05
		PdO	0.35	Gd ₂ O ₃	0.02
Fe ₂ O ₃	2.04	Ag ₂ O	0.02		
NiO	0.23	CdO	0.02	Total	100
Cr ₂ O ₃	0.10	SnO ₂	0.02		

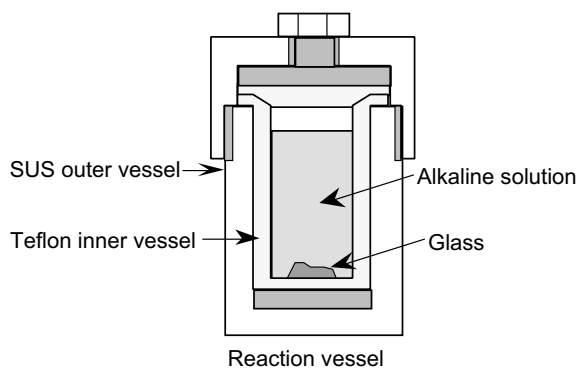


Fig. 1. Schematics of alteration test apparatus.

the alteration tests were performed, i.e., Test 1 designed to evaluate the alteration conditions determining whether analcime or smectite forms as the major alteration-phase, and Test 2 designed to evaluate the alteration rate under smectite forming conditions and the associated cesium release/retention mechanism. Test 1 was performed with NaOH solutions as a function of NaOH concentration (0.03, 0.1 M), temperature (90, 120, 150 °C) and time (up to 200 days). The ratio of glass specimen mass (0.5 g) to solution volume (20 ml) was 25 g/l (S/V ratio equals 12000 m^{-1} if the specific surface area is $0.49\text{ m}^2/\text{g}$), and the pressure was the equilibrium water vapor pressure at each corresponding temperature. Analogous alteration tests with deionized water and with 0.1 M KOH solution were performed for comparison. Test 2 was performed in 0.001 M NaOH solutions, in which Na⁺ concentration was adjusted by addition of NaCl solution, at 120 °C as a function of Na⁺ concentration (0.003, 0.01, 0.03, 0.1, 0.3 M) and time (up to 150 days). The ratio of

Table 2
Summary of alteration test conditions

	Test 1	Test 2
Test type	Static	Static
Glass	P0798 glass grain size: under 38 μm weight: 0.5 g	P0798 glass grain size: under 38 μm weight: 0.3 g
Solution	<ul style="list-style-type: none"> • 0.1 M NaOH • 0.03 M NaOH • deionized water (DIW) • 0.1 M KOH volume: 20 ml	0.001 M NaOH + NaCl [Na ⁺] = 0.003 M, 0.01 M, 0.03 M, 0.1 M, 0.3 M volume: 20 ml
S/V ratio	12000 m^{-1}	7400 m^{-1}
Temperature	90 °C, 120 °C, 150 °C (120 °C for 0.1 M KOH)	120 °C
Duration	Up to 200 days (up to 90 days for 0.1 M KOH)	Up to 150 days

glass specimen mass (0.3 g) to solution volume (20 ml) was 15 g/l (S/V ratio equals 7400 m^{-1}), and the value of initial solution pH was 10.8. The test conditions are summarized in Table 2.

At the end of both tests, the reaction vessel was cooled to room temperature, and the solution pH was measured immediately. The solution was passed through a filter of NMWL 10000 with pore size of approx. 1.8 nm for solution analysis. Solution concentrations of Si, B, Na, Al, Li and Cs in the filtrates were measured using an inductively coupled plasma mass spectrometer (ICP-MS, Yokogawa PMS-2000) or an atomic absorption spectrophotometer (Shimadzu AA-6700). The altered glass separated from the solution was dried at 50 °C for 1 day, and the glass with dry weight of 0.1 g was dispersed in deionized water of 1.2 ml ultrasonically. After mounting the dispersed glass on a low reflection glass slide, it was dried again at 50 °C for 1 day for XRD analysis. Crystalline alteration-phases formed in the altered glass were analyzed with XRD (Shimadzu XD-D1) using CuK_α radiation at a scanning rate of 1°/min. For some altered glasses, the alteration-phases were analyzed with TEM/EDS (JEOL JEM4010 with Oxford Instruments EDS system) after embedding in epoxy resin and thin-slicing by ultramicrotomy.

3. Results and discussion

3.1. Conditions for alteration-phase formation

Fig. 2 shows XRD patterns of the altered glasses from Test 1 at 150 °C for 200 days as a function of

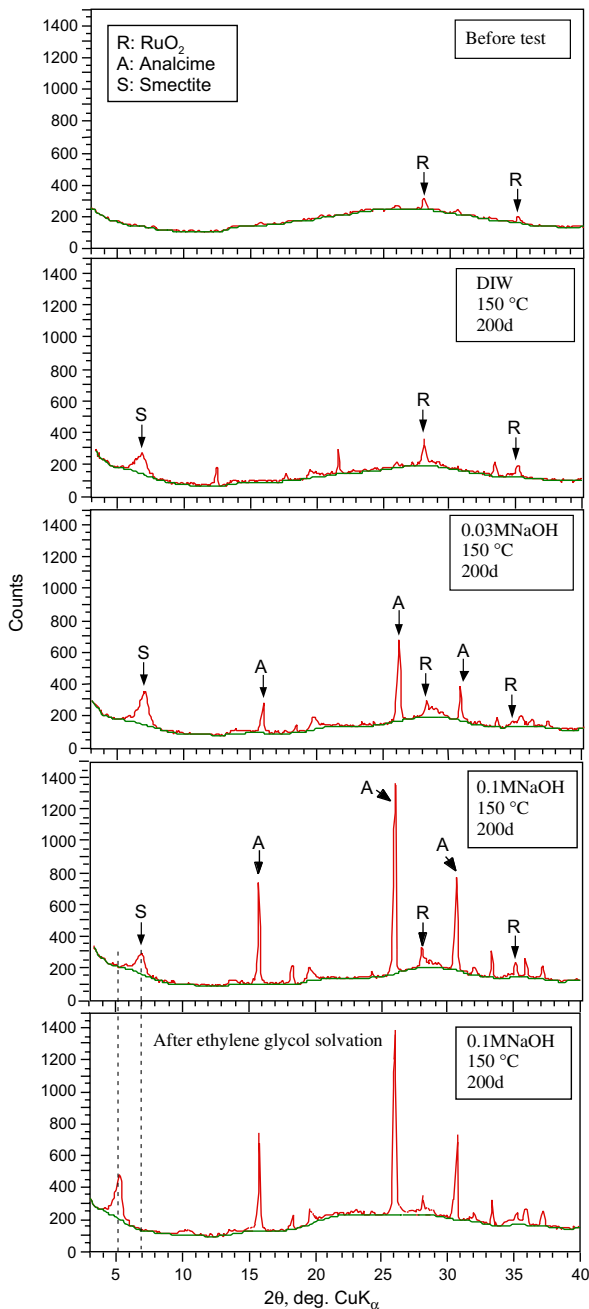


Fig. 2. XRD patterns of the altered glasses from Test 1 at 150 °C for 200 days as a function of NaOH concentration in solution.

NaOH concentration in solution. A broad peak marked by ‘S’ at around $2\theta = 7^\circ$ ($d = 1.25$ – 1.30 nm) indicates smectite to form, since the peak was shifted to $2\theta = 5.2^\circ$ ($d = 1.70$ nm) after ethylene glycol solvation. Taking the glass composition into account, the smectite can be estimated to be Na-beidellite ($\text{Na}_{0.33}\text{Al}_2\text{Si}_{3.67}\text{Al}_{0.33}\text{O}_{10}(\text{OH})_2$). Strong peaks

marked with ‘A’ at $2\theta = 15.8^\circ$, 26.0° and 30.6° indicate analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) to form. Small peaks marked by ‘R’ at $2\theta = 28.0^\circ$ and 35.1° indicate small amount of crystalline RuO_2 phase existing in the glass before and after the tests. Summarizing the phases to form as a function of NaOH concentration, only smectite was identified to form as the major alteration-phase in the tests with deionized water, while both analcime and smectite were identified to form in the tests with 0.03 M NaOH solution and with 0.1 M NaOH solution. The amount of analcime increased with NaOH concentration, while that of smectite was independent of NaOH concentration.

Fig. 3 shows XRD patterns of the altered glasses from Test 1 with 0.03 M NaOH solution at 150 °C as a function of alteration period. The amount of analcime increased rapidly within 10 days, and then it was almost constant until 200 days, which indicates that analcime formation proceeded rapidly and completed within 10 days. On the contrary, smectite formation proceeded slowly. Fig. 4 shows XRD patterns of the altered glasses from Test 1 with 0.03 M NaOH solution for 200 days as a function of temperature. The amount of analcime increased with temperature, on the contrary, that of smectite decreased with temperature. Fig. 5 shows XRD patterns of the altered glasses from Test 1 with 0.1 M KOH solution at 120 °C as a function of time. It is noted that no crystalline phases were identified to form within 90 days in the tests with 0.1 M KOH solution.

Fig. 6 shows the results of TEM observation for a cross section of the altered glass from Test 1 with 0.1 M NaOH solution at 150 °C for 30 days. Two types of the phases can be observed, a fibrous phase covering outer surface of the altered glass and a dark particle phase with 1 μm size on the fibrous phase. Fig. 7 shows a higher magnification view of the fibrous phase (Area 1 in Fig. 6). Since the fibrous phase has the layer lattice structure with basal spacing of approx. 1.3 nm, it can be identified as smectite. The EDS analysis for Area 1 (smectite phase) shown in Fig. 8 indicates that the smectite phase contains a certain amount of iron, which suggests substitution of Fe^{3+} for Al^{3+} in the octahedral layer. While the dark particle phase can be identified as analcime from the EDS analysis for Area 2 shown in Fig. 8. It is noted that the analcime phase contains small amount of cesium. The cesium release/retention is discussed in the later section.

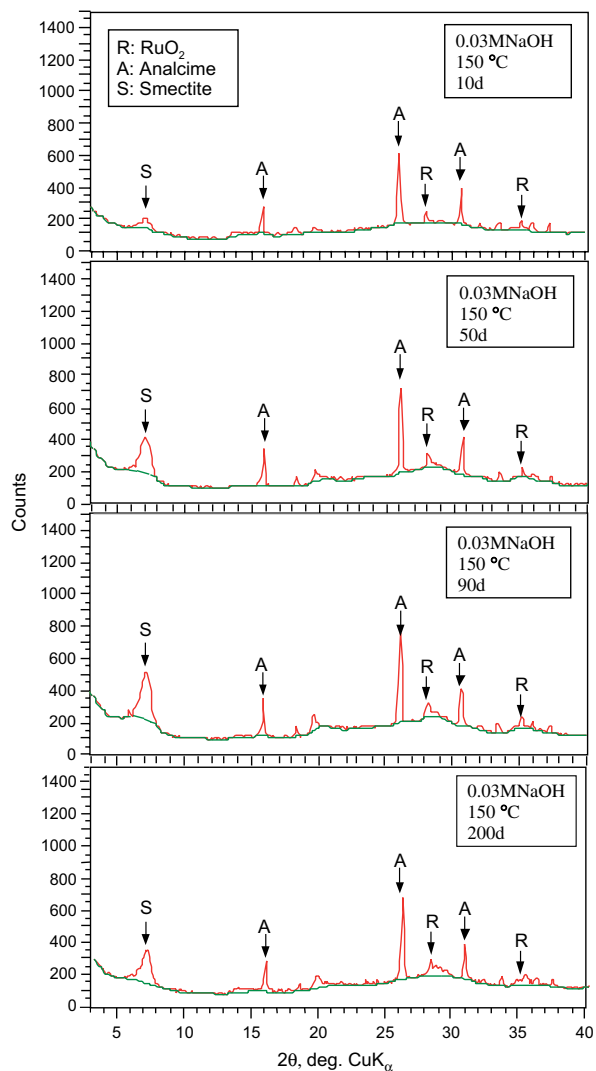


Fig. 3. XRD patterns of the altered glasses from Test 1 with 0.03 M NaOH solution at 150 °C as a function of alteration period.

The evolution of the solution pH in Test 1 is shown in Fig. 9. For each test condition the pH approached a steady state value. For the tests with deionized water, the pH increased to reach the value of 9.5–10 within 30 days at any temperature. For the tests with 0.03 M NaOH solution and with 0.1 M NaOH solution, the pH decreased to approach the value of 10.5–11 and the value around 12, respectively. A similar evolution of the solution pH has been observed in some previous studies where analyses by use of thermodynamic calculations have suggested that a balance between alkali metal dissolution from the glass and dissociation of dissolved

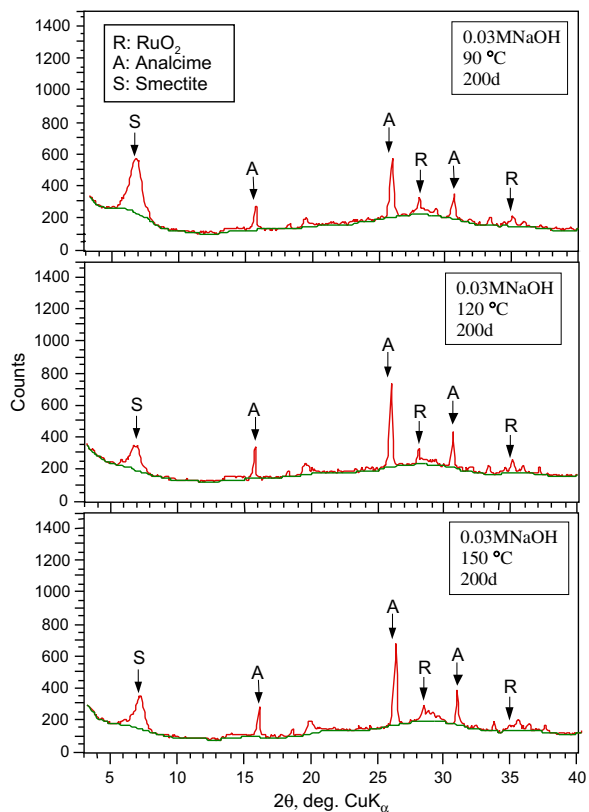


Fig. 4. XRD patterns of the altered glasses from Test 1 with 0.03 M NaOH solution for 200 days as a function of temperature.

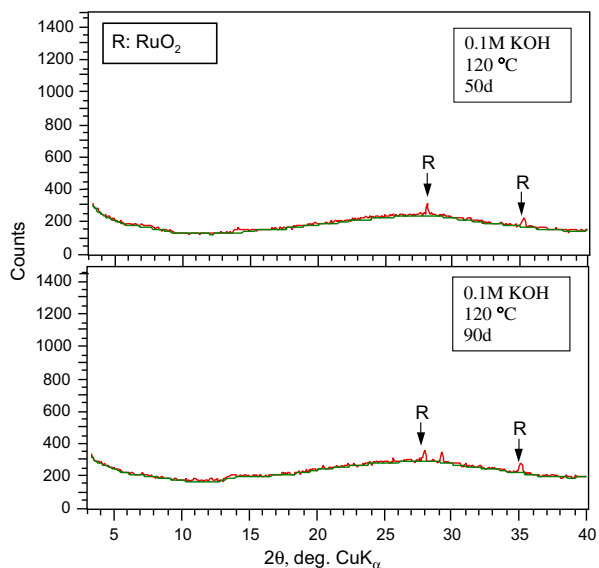


Fig. 5. XRD patterns of the altered glasses from Test 1 with 0.1 M KOH solution at 120 °C as a function of time.

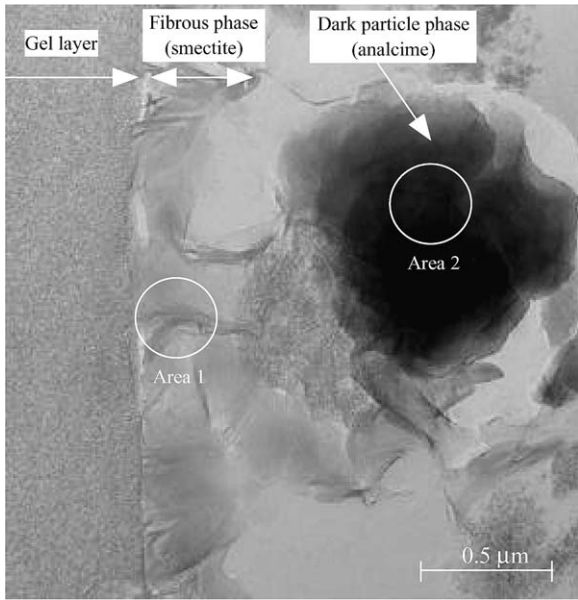


Fig. 6. TEM observation for cross section of the altered glass from Test 1 with 0.1 M NaOH solution at 150 °C for 30 days. Area 1 of smectite phase for higher magnification view and for EDS analysis, Area 2 of analcime phase for EDS analysis.



Fig. 7. Higher magnification view of the fibrous phase (Area 1 in Fig. 6) in the altered glass from Test 1 with 0.1 M NaOH solution at 150 °C for 30 days.

silica can result in a steady state of the pH [7–9,14]. For the present tests, therefore, it is suggested that each steady state of the pH can be attained from a balance between the alkali metal dissolution and the silica dissociation. Although temperature-dependence of the steady state value was small,

the rate at which the pH approaches the steady state value increased with temperature, e.g., the pH reached each steady state value within 10 days at 150 °C. In comparison with the development of smectite shown in Fig. 3, the pH evolved quickly, which also suggests that the pH evolution can be controlled by the balance between alkali metal dissolution and silica dissociation rather than by smectite formation. For the tests with 0.1 M KOH

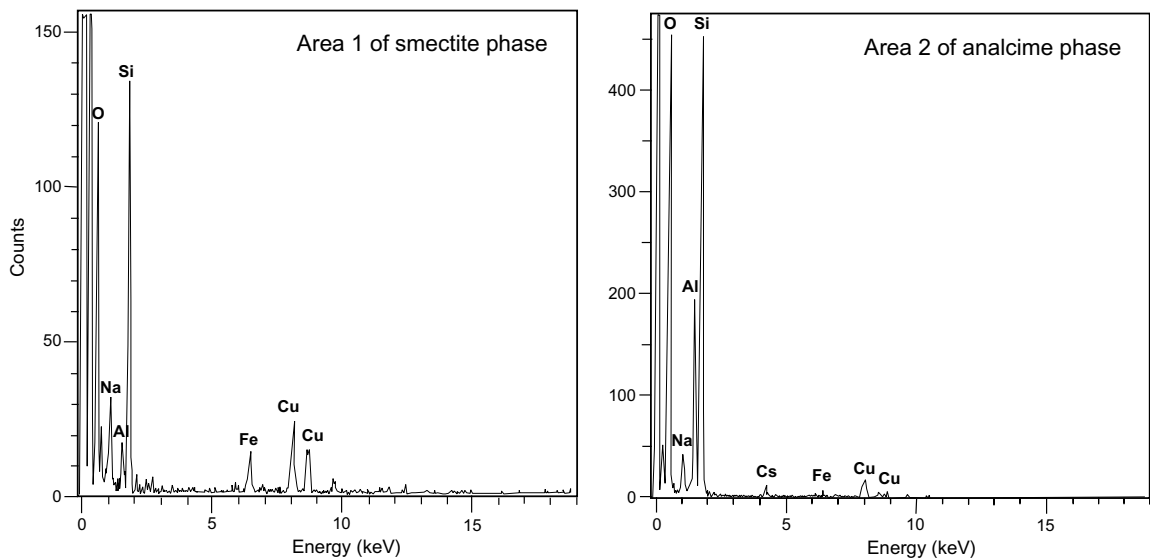


Fig. 8. EDS analysis of smectite phase (Area 1 in Fig. 6) and analcime phase (Area 2) in the altered glass from Test 1 with 0.1 M NaOH solution at 150 °C for 30 days. Peaks for Cu are originating from grids of meshes in TEM.

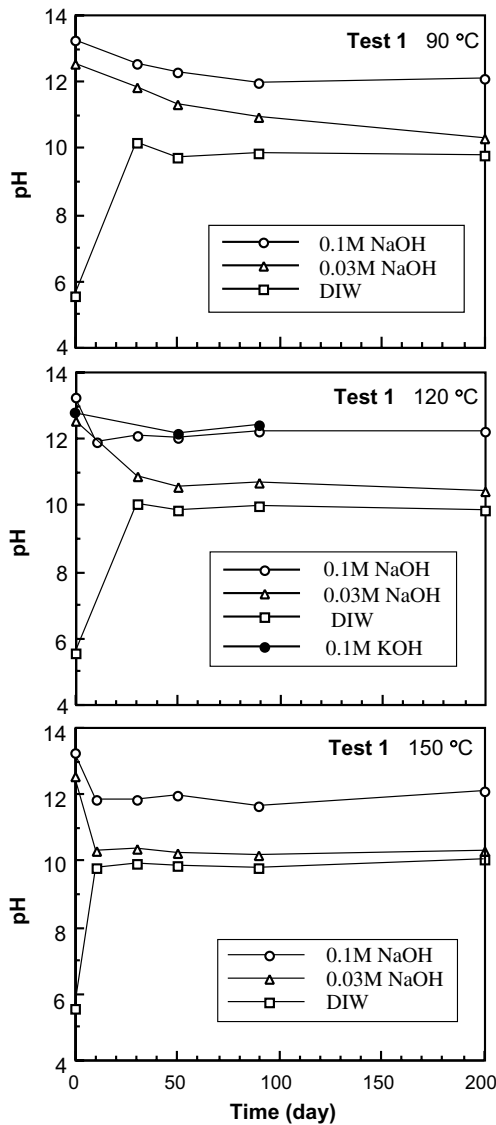


Fig. 9. Evolution of solution pH in Test 1.

solution, the pH approached the value around 12 in a similar manner as that in the tests with 0.1 M NaOH solution.

From the experimental results described above, conditions of the alteration-phase formation can be summarized as a function of pH as follows. Since smectite was identified to form under any test condition, it is concluded that smectite can form at any pH between 9.5 and 12. On the other hand, analcime was identified to form only in the tests with 0.03 M NaOH solution and 0.1 M NaOH solution, which indicates that analcime can form at pH above 11. In the tests with 0.1 M KOH solution no crystal-

line phases were identified to form though pH reached around 12, which indicates that not only pH but also species and concentration of alkaline metals in the solution can greatly affect the alteration-phase formation and the formation rate. Regarding the solution concentration of sodium, there was no remarkable difference between the tests with 0.1 M KOH solution and that with deionized water, since a certain amount of sodium was dissolved from the glass for both tests. However, smectite was identified to form only in the tests with deionized water. Therefore, it is suggested that not only the sodium concentration but also the ratio of $[Na^+]/[K^+]$ can affect the alteration-phase formation.

Gin and Mestre [3] and Ribet and Gin [5] have identified formation of two types of alteration-phases during aqueous alteration of R7T7 glass at 90 °C at pH between 7 and 11.5, i.e., phyllosilicate phase forming at pH between 7 and 11.5 and zeolite phase (analcime or merlinoite) forming at pH above 11. Since the phyllosilicate phase can be estimated to be smectite, the present results are identical with their results. Taking these results in consideration, it is concluded that smectite can form at any pH between 7 and 12 while analcime can form at pH above 11, though their formation depends on species and concentrations of alkaline metals in the solution.

3.2. Alteration rate

The evolution of solution concentrations of boron and silicon in Test 1 is shown in Fig. 10, as the normalized concentration, NC_i , calculated by the following equation:

$$NC_i = C_i/f_i, \quad (1)$$

where C_i and f_i represent the solution concentration of element i , and the fraction of element i in the original glass, respectively. If the whole amount of element i in the original glass dissolves into the solution, the value of NC_i equals 25000 g/m³ in Test 1 condition. The concentrations for boron increased with time, on the contrary, the concentrations for silicon were almost constant after 10 days at the values smaller than that for boron in any conditions. The concentrations for aluminum were also constant after 10 days at the values much smaller than that for boron and silicon, i.e., the values of NC_i were less than 200 g/m³ in any conditions. Since dissolution of boron can be an alteration indicator, the

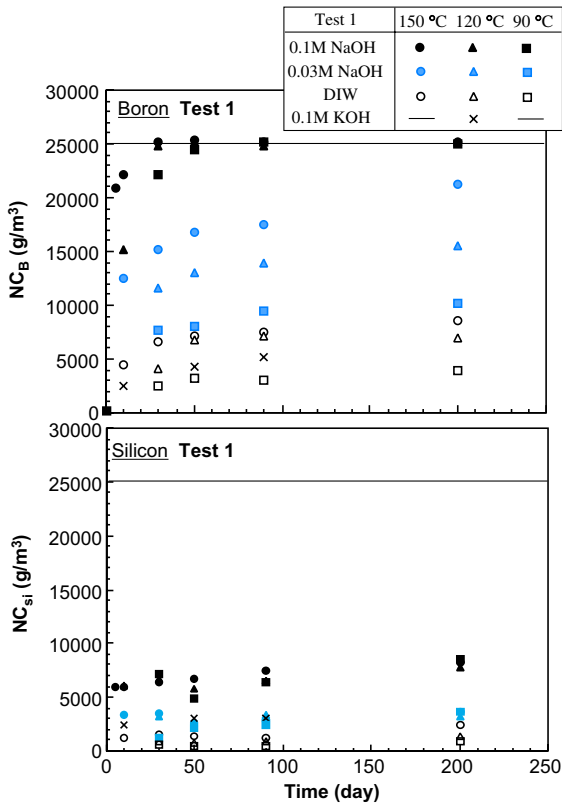


Fig. 10. Normalized concentrations for boron, NC_B in Test 1.

results in Fig. 10 indicate that the glass alteration rate increases with NaOH concentration. In the tests with 0.1 M NaOH solution, the alteration rate was much higher than that in the tests with other solutions, and the values of NC_i for boron reached 25000 g/m^3 within 50 days at any temperature. Two types of potential mechanism can be supposed for interpreting the extremely high alteration rate in the tests with 0.1 M NaOH solution. One is the effects of high pH which can increase silica solubility dramatically at pH above 10, and the other is the effects of analcime formation which can accelerate the glass alteration by consuming silica or alumina from solution. The comparison with the results of the tests with 0.1 M KOH solution, which showed the low alteration rate even at pH around 12, indicates that analcime formation can mainly contribute to the extremely high alteration rate.

On the basis of the results of Test 1, the conditions of Test 2 were chosen to be 0.001 M NaOH solution (initial pH of 10.8) at $120 \text{ }^\circ\text{C}$ as smectite forming conditions. In order to evaluate mechanism of cesium release/retention, the tests were performed in the solutions with some different sodium

concentrations (0.003–0.3 M) adjusted by addition of NaCl. Fig. 11 shows the evolution of the solution pH in Test 2. For the solutions with any sodium concentration, the pH values were almost constant in the range from 9.5 to 10 for up to 150 days except for the initial few days. The initial small decrease in pH can be caused by dissociation of silica dissolved from the glass rather than by smectite formation as discussed in the previous section. Fig. 12 shows the evolution of sodium concentrations in the solutions. The sodium concentration for each solution was almost constant for up to 150 days except for the solution with $[\text{Na}^+] = 0.003 \text{ M}$ where dissolution of sodium from the glass caused an increase in the concentration. Fig. 13 shows XRD patterns of the altered glasses from Test 2 for 80 days as a function

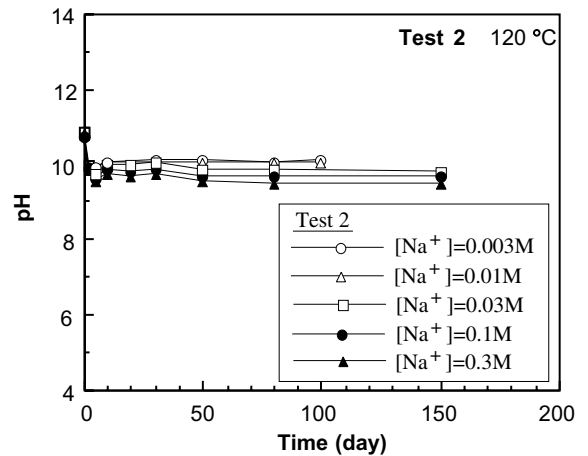


Fig. 11. Evolution of solution pH in Test 2.

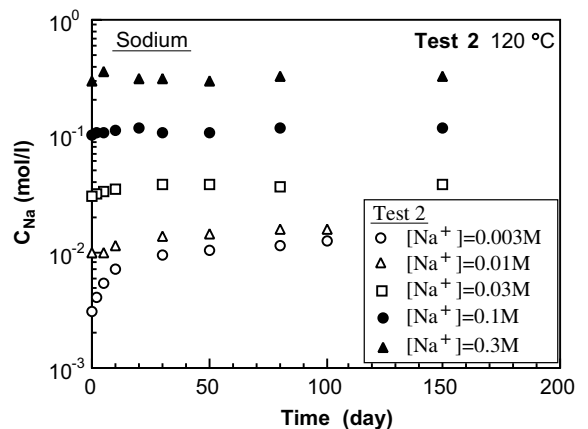


Fig. 12. Evolution of solution concentrations of sodium in Test 2.

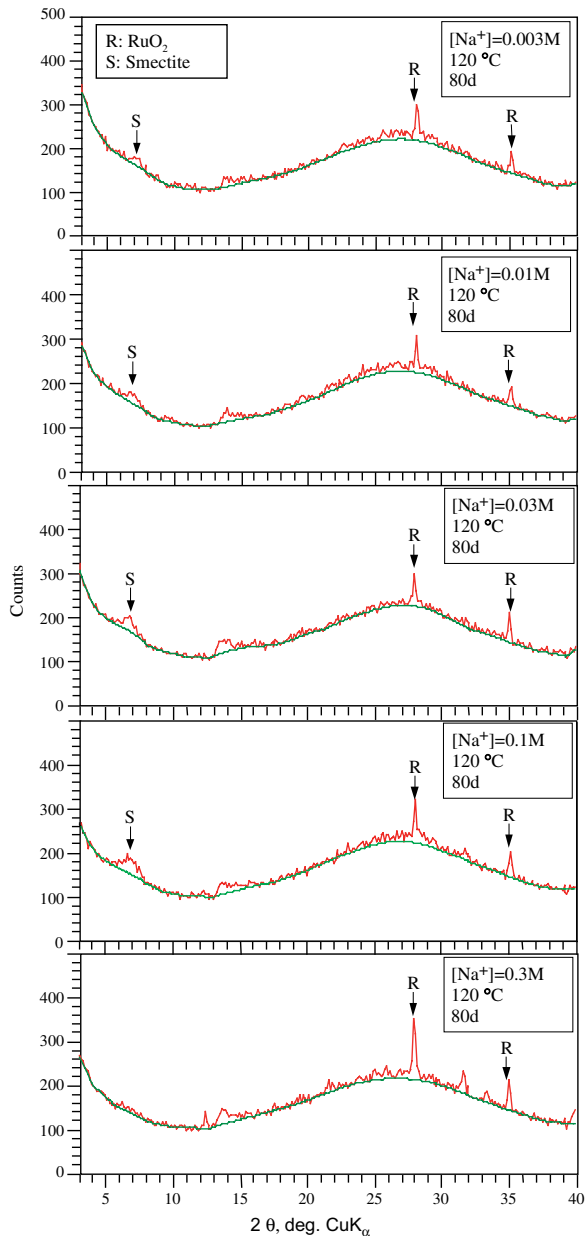


Fig. 13. XRD patterns of the altered glasses from Test 2 for 80 days as a function of sodium concentration.

of the sodium concentration. As expected, only smectite was identified to form as the major alteration-phase in any solution except for the solution with $[\text{Na}^+] = 0.3 \text{ M}$. The results also indicate that the amount of smectite increases with the sodium concentration up to 0.1 M, however, smectite formation was not identified in the solution with $[\text{Na}^+] = 0.3 \text{ M}$. Since the sodium concentration was adjusted by addition of NaCl, it is supposed

that the high concentration of Cl^- may prevent smectite formation.

Fig. 14 shows the evolution of the normalized concentrations for boron, silicon and aluminum in Test 2 performed under smectite forming conditions. If whole amount of element i in the original glass dissolves into the solution, the value of NC_i equals 15000 g/m^3 in Test 2 condition. The concentrations for boron increased with time, on the contrary, the concentrations for silicon were almost constant after 10 days at the values one order of magnitude smaller than that for boron. The concentrations for aluminum were also constant after 10 days at the values much smaller than that for boron and silicon. The results indicate that the glass alteration rate estimated from boron dissolution is independent of the sodium concentration, though the rate of smectite formation varied with the sodium concentration as shown in Fig. 13. Therefore, it is suggested that the glass alteration rate under smectite forming conditions is independent of whether smectite actually forms or not.

For evaluation of the glass alteration rate in relation to the alteration-phase formation, the concentrations for boron in Test 2 were compared with those in Test 1 by converting to the normalized mass loss, NL_i , calculated by the following equation:

$$\text{NL}_i = (C_i/f_i)(V/S) = \text{NC}_i(V/S), \quad (2)$$

where S and V represent the initial glass surface and the solution volume, respectively. The normalized mass loss for boron in Test 1 and Test 2 is shown in Fig. 15 plotted as a function of square root of time. It can be seen that the glass alteration rate can be divided into two groups depending on the major alteration-phases. One is the low rate under smectite forming conditions where only smectite was identified to form or no crystalline phases to form, and the other is the high rate under analcime and smectite forming conditions where both analcime and smectite were identified to form. Under smectite forming conditions the glass alteration proceeded slowly in proportion to square root of time, which indicates that the glass alteration proceeds controlled by a diffusion process. It is noted that any data under smectite forming conditions including the tests with 0.1 M KOH solution is almost plotted on a single straight line, which suggests that the diffusion-controlled process under smectite forming conditions is independent of the pH, alkaline metal

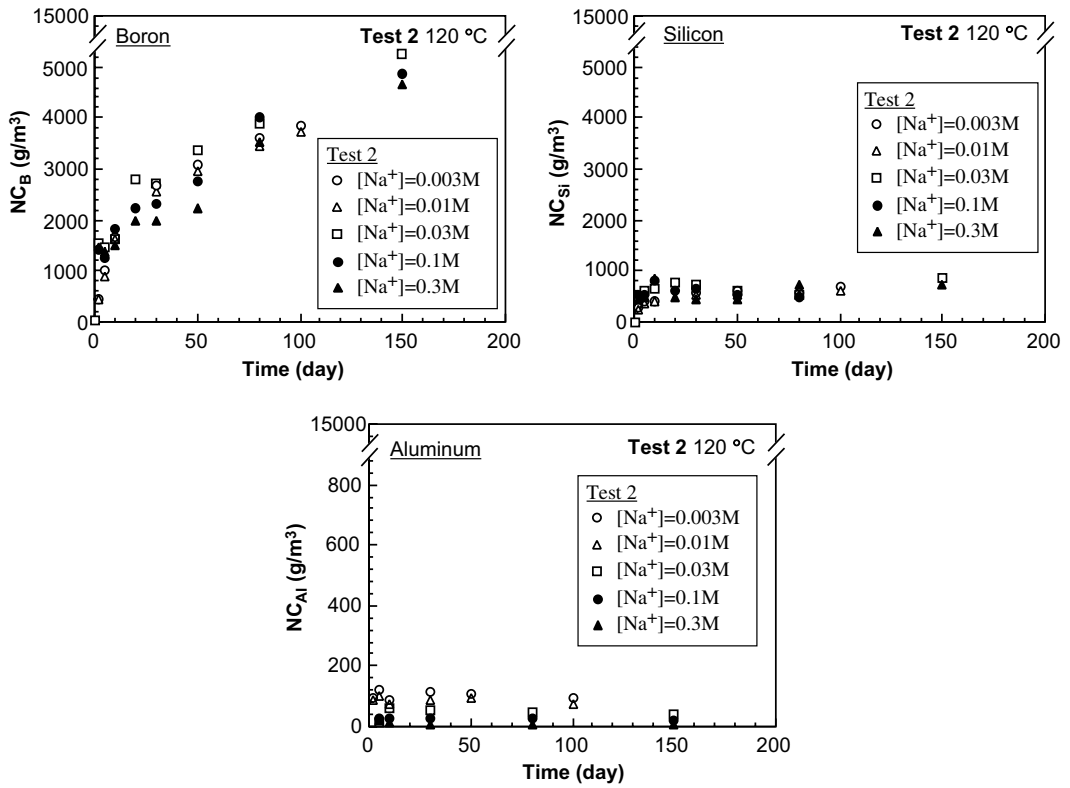


Fig. 14. Normalized concentrations for boron and silicon, NC_i , in Test 2.

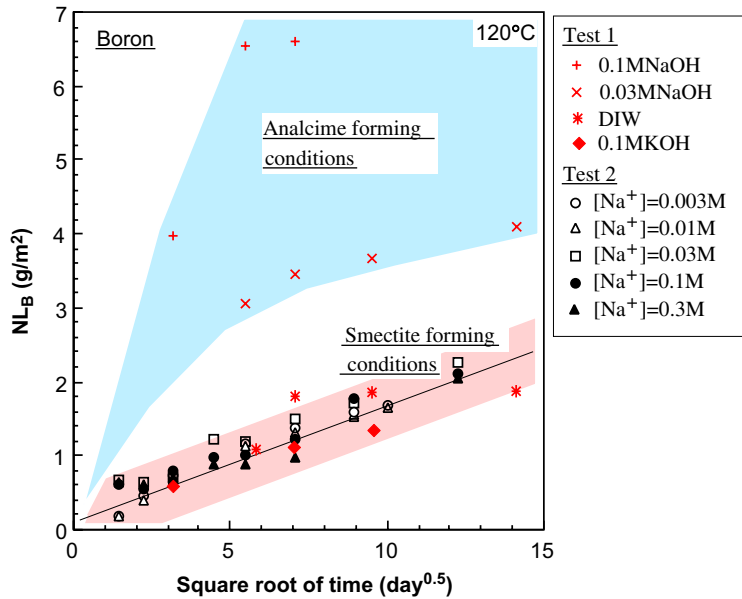


Fig. 15. Normalized mass loss for boron, NL_B , in Test 1 and Test 2 as a function of square root of time.

species/concentrations in the solution and whether smectite actually forms or not.

The process controlling the long-term alteration rate of the waste glass is much more subjected to

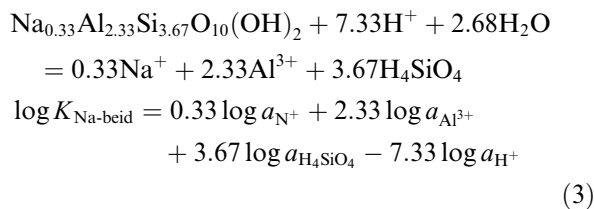
controversy, and further research works are in progress worldwide [3,5,16–18]. One of the facts which make the process complicated is that the process changes sensitively depending on the alteration conditions such as the glass composition, solution chemistry, temperature, time and etc. The present results suggest that the alteration-phase formation is one of the major factors determining the rate controlling process. Since the waste glass disposal conditions for Japan and some countries are assumed to be smectite forming conditions (pH below 11), further studies are required to be focused on evaluation of the alteration and its kinetics under smectite forming conditions.

3.3. Stability of alteration-phases in comparison with thermodynamic calculation

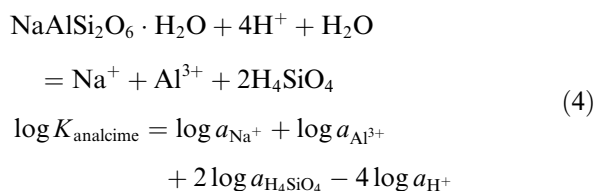
Stability relationships between smectite and analcime can be determined by use of thermodynamic calculations. Although computer codes such as PHREEQC [19] are available for the calculation, simple calculations are also suitable for the present case as follows.

The mineral-solution equilibrium for both phases can be represented by the following equations:

Smectite (Na-beidellite):

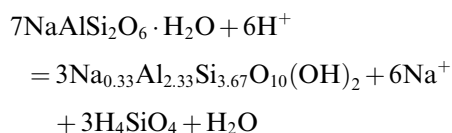


Analcime:



Equilibrium between two phases can be represented by the following equation:

Analcime–Na-beidellite:



$$\begin{aligned} \log K_{\text{analcime-Na-beid}} & = 7 \log K_{\text{analcime}} - 3 \log K_{\text{Na-beid}} \\ & = 6 \log a_{\text{Na}^+} + 3 \log a_{\text{H}_4\text{SiO}_4} - 6 \log a_{\text{H}^+} \end{aligned} \quad (5)$$

From Eq. (5), the boundary between analcime and Na-beidellite can be determined as a function of activities of Na^+ , H_4SiO_4 , and H^+ . It is convenient to display the boundary on a two-dimensional graph with $\log(a_{\text{Na}^+}/a_{\text{H}^+})$ and $\log a_{\text{H}_4\text{SiO}_4}$ axes. Fig. 16 shows the boundary at 120 °C calculated with use of published thermodynamic data [20] listed in Table 3 as a solid line as well as silica solubilities.

The conditions for actually forming phases determined by the present alteration tests can be plotted over the calculated phase stability relationships in Fig. 16 for comparison. The conditions for both Test 1 (at 120 °C for 90 days and 200 days) and Test 2 (at 120 °C for 80 days and 150 days) are plotted in Fig. 16 as symbols in consideration of the alteration-phases identified to form. In Fig. 16 the smectite forming conditions represent the conditions where only smectite was identified to form or no crystalline phases, and analcime forming conditions represent the conditions where both analcime and smectite were identified to form as described in the previous section. In evaluation of the conditions, the value of activity of H_4SiO_4 was estimated from the measured concentrations of dissolved silica in consideration of dissociated silica species listed in Table 3. The value of activity of Na^+ was estimated from the measured concentration of dissolved Na by use of the activity coefficient calculated by Debye–Hückel equation on the assumption that the dissolved species is only Na^+ . The comparison indicates that the actually forming phases cannot agree with the calculated one, e.g., smectite actually forms in the conditions where analcime is calculated to be stable. Although the present estimation of the activities from the measured concentrations may contain a certain errors, smectite can be evaluated to be much more stable than the thermodynamic calculation. The disagreement between the actually forming phases and the calculated phases is partly caused by uncertainties in the thermodynamic data, because the actually forming phases are non-ideal phases with impurities and crystallographic defects. It may be impossible to evaluate completely the effects of impurity and crystallographic defects on the thermodynamic data for these phases because

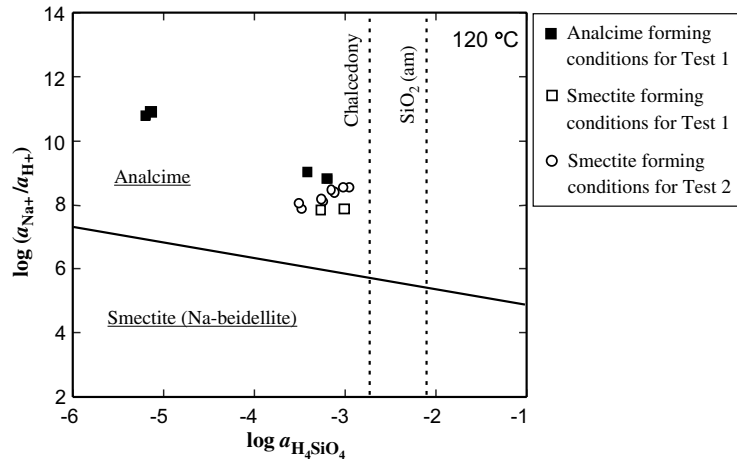


Fig. 16. Stability relationships between smectite and analcime at 120 °C, comparison between thermodynamic calculations and experimental results.

Table 3
Thermodynamic data used for calculation of phase stability relationship [20]

Reaction	log K (25 °C)	log K (120 °C) ^a
<i>Smectite (Na-beidellite)</i> : $\text{Na}_{0.33}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2 + 2.68\text{H}_2\text{O} + 7.32\text{H}^+$ $= 0.33\text{Na}^+ + 2.33\text{Al}^{3+} + 3.67\text{H}_4\text{SiO}_4$	5.647	2.717
<i>Analcime</i> : $\text{NaAlSi}_2\text{O}_6 + 4\text{H}^+ + \text{H}_2\text{O} = \text{Na}^+ + \text{Al}^{3+} + 2\text{H}_4\text{SiO}_4$	6.948	-2.304
<i>Analcime-Smectite</i> : $7\text{NaAlSi}_2\text{O}_6 + 6\text{H}^+ = 3\text{Na}_{0.33}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$ $+ 6\text{Na}^+ + 3\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	31.70	25.93
<i>Amorphous silica</i> : $\text{SiO}_2(\text{am}) + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$	-2.71	-2.102
<i>Chalcedony</i> : $\text{SiO}_2(\text{Chalcedony}) + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$	-3.728	-2.727
$\text{H}_4\text{SiO}_4 = \text{H}^+ + \text{H}_3\text{SiO}_4^-$	-9.83	-8.863
$\text{H}_3\text{SiO}_4^- = \text{H}^+ + \text{H}_2\text{SiO}_4^{2-}$	-13.17	-11.14

^a Determined by use of an empirical polynomial in Ref. [20].

of their variety. Therefore, much more empirical studies in combination with both thermodynamic and kinetic analysis are required for evaluation of the alteration-phase formation under actual disposal conditions.

3.4. Release and retention of cesium

Fig. 17 shows the evolution of the normalized concentrations for cesium in Test 1 at 120 °C. Although cesium is a soluble element such as boron, the concentrations for cesium were more than one order of magnitude lower than that for boron described in Fig. 10 for any tests with NaOH solutions. The results indicate that most of cesium dissolved from the glass is retained in the glass surface layer. For the tests with 0.1 M KOH solution where no crystalline phase formation was identified, the concentrations for cesium were higher

than that for the tests with NaOH solutions where formation of smectite and analcime was identified. The comparison between them suggests potential mechanisms for the cesium retention as follows: (1) sorption onto the alteration-phase (smectite) by ion-exchange, and (2) incorporation into the alteration-phase (analcime). Fig. 18 shows the normalized concentrations for cesium in Test 2 as a function of the solution concentration of sodium, where only smectite was identified to form or no crystalline phases to form. The results showed that the concentrations for cesium increased with the sodium concentration, which suggests that major mechanism of the cesium retention under smectite forming conditions is sorption onto smectite by ion-exchange.

In order to confirm the cesium retention mechanism, cesium desorption tests were performed for two altered glasses, the glass altered under smectite

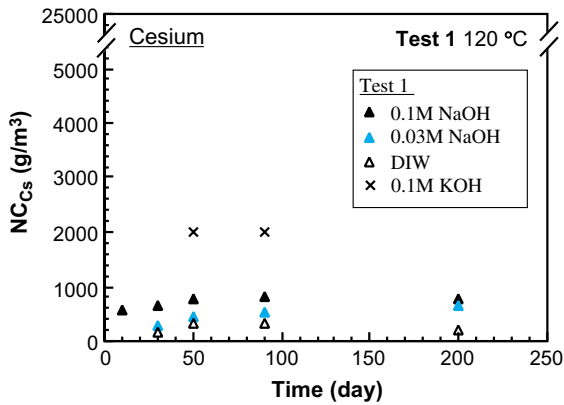


Fig. 17. Normalized concentrations for cesium in Test 1 at 120 °C.

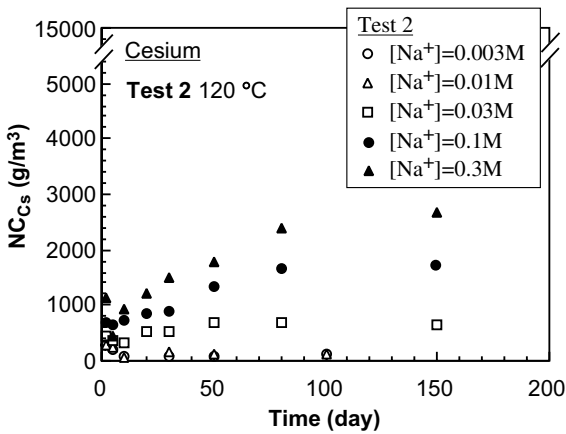


Fig. 18. Normalized concentrations for cesium in Test 2 at 120 °C as a function of the solution concentration of sodium.

forming conditions (Test 1 with deionized water at 120 °C for 90 days) and that altered under analcime forming conditions (Test1 with 0.1 M NaOH solution at 120 °C for 90 days). For both alteration conditions, the normalized concentrations for cesium were less than a 20th of that for boron. If cesium is sorbed onto smectite by ion-exchange, the sorbed cesium can be desorbed by NaCl solution. Conditions of the desorption tests are summarized in Table 4. Fig. 19 shows the cumulative desorption ratio, $R_{\text{desorp-Cs}}$, calculated by the following equation:

$$R_{\text{desorp-Cs}} = \text{NC}_{\text{Cs}}(\text{desorp}) / \text{NC}_{\text{B}}, \quad (6)$$

where NC_{B} is the normalized concentration for boron and $\text{NC}_{\text{Cs}}(\text{desorp})$ represents the normalized concentration for cesium calculated from the cumulative amount of desorbed cesium. If the value of $R_{\text{desorp-Cs}}$ equals 1, the whole amount of cesium dissolved from the glass congruently with boron would

Glass	<ul style="list-style-type: none"> Altered under smectite forming condition (Test 1 with DIW at 120 °C for 90 days) Altered under analcime forming condition (Test 1 with 0.1 M NaOH at 120 °C for 90 days)
Solution	0.3 M NaCl
Glass/solution ratio	0.1 g/20 ml
Temperature	90 °C
Time	1 day
Number of desorption	Up to four times (At each time solution was replaced by fresh one.)

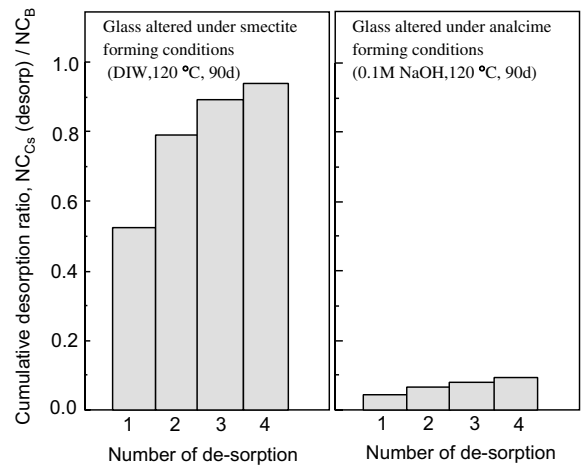


Fig. 19. Cumulative cesium desorption ratio by 0.3 M NaCl solution for altered glasses.

be sorbed by ion-exchange. For the glass altered under smectite forming conditions, the value of $R_{\text{desorp-Cs}}$ was more than 0.9 at four times of desorption, which indicates that sorption onto smectite by ion-exchange is the major mechanism for cesium retention under smectite forming conditions. For the glass altered under analcime forming conditions, however, the value of $R_{\text{desorp-Cs}}$ was less than 0.1, which suggests that the sorption by ion-exchange is the minor mechanism for cesium retention under analcime forming conditions. The EDS analysis for alteration-phases shown in Fig. 8 indicates that analcime contains a small amount of cesium. Analcime can form a series of solid solutions with pollucite with the formula of $\text{Cs}_x\text{Na}_{1-x}\text{AlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ by substitution of Na^+ by Cs^+ [21]. Therefore, incorporation into the solid solutions between analcime and pollucite is suggested to be the major mechanism for

cesium retention under analcime forming conditions. For further understanding, much more quantitative evaluation is required for the cesium retention under disposal conditions for long-term.

4. Conclusion

In the present study, aqueous alteration tests were performed for a Japanese simulated waste glass P0798 under various solution conditions, and an empirical evaluation was done for the alteration conditions determining whether smectite or analcime forms as the major alteration-phase. The results indicated that smectite forms at any pH between 9.5 and 12, while analcime forms at pH above 11, though the formation depends on species and concentrations of alkaline metals in the solution. These empirical results do not agree with a simple thermodynamic analysis for phase stability calculated by use of published thermodynamic data, e.g., smectite is more stable than the thermodynamic calculations. Under smectite forming conditions the glass alteration proceeded slowly in proportion to square root of time, which indicates that the glass alteration rate can be controlled by a diffusion process. It was suggested that the glass alteration rate under smectite forming conditions is almost independent of the pH, alkaline metal species/concentrations in the solution and whether smectite actually forms or not. On the other hand, the glass alteration rate under analcime forming conditions was much higher.

The present results also indicated that most of cesium dissolved from the glass can be retained in the alteration-phases by sorption or incorporation. Under smectite forming conditions reversible sorption onto smectite by ion-exchange can be the major retention mechanism. Under analcime forming conditions irreversible incorporation into analcime, pollucite or solid solutions of them can be the major retention mechanism.

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