

Initial Dissolution Rate of the International Simple Glass as a Function of pH and Temperature Measured Using Microchannel Flow-Through Test Method

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International simple glass (ISG) is a six-component alumino-borosilicate glass developed as a reference benchmark glass for six nations collaborating study on high-level nuclear waste glass dissolution/corrosion mechanism. In this study, aqueous dissolution tests were performed for the ISG using microchannel flow-through (MCFT) method to evaluate the initial dissolution rate of glass matrix, r_0 , precisely and systematically as a function of solution pH and temperature. The test results indicated that the r_0 shows a “V-shaped” pH dependence with a bottom at around pH4 at each temperature. Compared with Japanese reference glass of P0798, for which the r_0 showed a “U-shaped” pH dependence with a bottom at around pH6 in our previous study, the ISG shows the higher dissolution rate at basic pH, and lower dissolution rate at neutral to acidic pH. The results also indicated that the r_0 increases with temperature according to an Arrhenius law, and the apparent activation energy evaluated from Arrhenius relation is 62–77 [kJ/mol] at any pH from 3 to 10, which suggests the initial dissolution of ISG proceeds controlled by a surface-reaction mechanism in this pH range.

Introduction

High-level nuclear waste (HLW) generated from reprocessing of spent nuclear fuel is or will be immobilized into borosilicate glass matrix to be disposed of in deep geological formations in several nations including Belgium, France, Germany, the United Kingdom, the USA and Japan. Because aqueous dissolution or corrosion by contact with groundwater is the most probable process by which radionuclides are released from the

glass during the disposal period of more than 10,000 years, the mechanism and kinetics of glass dissolution are required to be evaluated sufficiently for the safety assessment. For the last several decades, therefore, a large number of studies have been performed to advance understandings of the glass dissolution processes. However, there remain some uncertainties in the mechanism and kinetics controlling the long-term glass dissolution under the actual or potential repository conditions. The evaluation of dissolution kinetics is also required for parameterization of a mechanistic model used to determine the rate of glass dissolution or radionuclide release as a function of key environmental

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variables such as the solution composition, pH, solution flow rate, temperature, reaction progress, and time.

To evaluate the glass dissolution kinetics, we need precise and consistent data on the glass dissolution rate measured systematically under various well-constrained conditions. Although a large number of dissolution tests have been performed on the waste glasses throughout the world, there have been only a few data with preciseness and consistency available for the kinetic evaluation, unfortunately. With respect to pH dependence of the glass dissolution rate, for example, we have only a few data available for the kinetic evaluation, because the test conditions such as the solution composition, pH, and the glass surface area, which affect the dissolution rate sensitively, can change easily during the test period against the expectations as a consequence of the nature of current standard test methods such as MCC-1 and PCT tests.^{1,2} For further evaluation of the dissolution kinetics, therefore, we should obtain the precise and consistent data on glass dissolution rate measured systematically under well-constrained test conditions along with improving and developing the test methods.

Several test methods have been developed and applied to measurement of the glass dissolution rate for the last few decades,^{1–3} and they can be categorized into two types, that is, “static method” and “flow-through method.” Although both types have been applied to the measurement, the flow-through method is adequate for evaluation of the dissolution kinetics, for example, measurement of the dissolution rate as a function of the key environmental variables, because the flow-through method can provide any controlled constant solution condition easily over the test duration. Single pass flow-through (SPFT) method is one of major flow-through test methods of great use, and it has been applied to measurement of the glass dissolution rate as a function of environmental variables.^{3–5} In the SPFT method, the powdered glass specimen packed in a reaction cell is usually used to provide a high S/V (glass surface area to solution volume) ratio leading to a quick increase in solution concentrations of dissolved glass constituent elements for precise solution analysis. The use of powdered glass specimen, on the other hand, causes difficulties in accurate determination of the glass surface area, because the surface area actually reacting with solution sometimes differs from that measured by use of BET method for finely powdered glass specimen.⁶ In addition, the progress of glass dissolution

during the test period may cause a certain change in the glass surface area for powdered glass specimen. Because the glass dissolution rate is generally represented with a unit of $[g/m^2/d]$, an error in determination of the surface area causes a major error in determination of the glass dissolution rate. The use of powdered glass specimen also causes difficulties in direct and quantitative analyses of the reacted glass surface with regard to total mass balance, although the quantitative comparison between the solution analysis data and the surface analysis data is required to confirm consistency of the test results. Microchannel flow-through (MCFT) method is a newly developed flow-through test method to provide precise and consistent data of the glass dissolution rate for the kinetic evaluation.^{7–9} In the MCFT method, a coupon shaped glass is used as a specimen, which allows accurate determination of the glass surface area actually reacting with solution. In spite of using the coupon shaped glass specimen, the use of microchannel reactor can provide a relatively high S/V ratio to allow precise solution analysis, by which the glass dissolution rate can be determined precisely. In addition, the use of coupon shaped glass specimen enables direct and totally quantitative analyses of the reacted surface for confirming consistency of the test results.

In this study, therefore, aqueous dissolution tests were performed using the MCFT method for International simple glass (ISG) to evaluate the initial dissolution rate of glass matrix or forward dissolution rate, r_0 , precisely and systematically as a function of solution pH (3–10) and temperature (25–90°C). The ISG is a six-component aluminoborosilicate glass developed as a reference benchmark glass for six nations collaborating study on the waste glass corrosion mechanism.¹⁰ The kinetics controlling the r_0 is expected to differ from that controlling the long-term glass dissolution rate or the residual rate, r_{residual} , which is of great interest for evaluation of the long-term glass performance. However, the r_0 is one of fundamental and intrinsic parameters needed for understanding of the overall glass dissolution mechanism, and the kinetics controlling the r_0 is expected to have certain direct or indirect relations with that controlling the r_{residual} . In addition, the comparison of the r_0 between several reference glasses such as French SON 68 and Japanese P0798, for which the r_0 has been evaluated systematically, may provide new insights for understanding of the glass corrosion mechanism.

Experimental

Glass Specimen

The International simple glass (ISG) was used as a specimen. The ISG is a six-component alumino-boro-silicate glass developed as a reference benchmark glass for international collaborating study on the waste glass corrosion mechanism.¹⁰ To provide homogeneity between samples, a 50 kg batch of the ISG was produced in May 2012 by MoSCI Corporation (Rolla, MO), and glass ingots of 500 g each were distributed for study by the international team. The chemical composition of the ISG is shown in Table I, of which the main components are common to most alumino-boro-silicate nuclear glasses, and the ratios between components are the same as those of SON68 glass (the inactive reference glass of the French R7T7 glass produced by Areva at La Hague). The ingot glass was cut into a coupon shaped one (30 mm × 10 mm × 4 mm size) using diamond saw, and the surface was conditioned by polishing with finally 1 μm diamond paste using alcohol lubricant to prevent selective dissolution of soluble elements such as B and Na during polishing.

Microchannel Flow-Through Test Method

Figure 1 shows schematics of the microchannel flow-through (MCFT) test apparatus. The test apparatus has been originally developed by Okuyama *et al.*^{11,12} to measure both diffusion and sorption coefficients of rock medium, and it has been modified to suit measurement of the glass dissolution/corrosion rate by Inagaki *et al.*^{7–9} The test apparatus consists of three parts: an injection syringe pump, a microchannel reactor unit, and an automatic sampler, being connected with each other with PTFE (Teflon®; DuPont,

Wilmington, DE) tubing. The microchannel reactor unit with PTFE tubing is placed in an oven to maintain the reaction temperature, and the automatic sampler is placed in a glove box to prevent evaporation loss of sampling solution. In the microchannel reactor unit, a face of coupon shaped glass specimen is in contact with a microchannel (20 mm length, 2 mm width, 0.16 mm depth) constructed on a PTFE plate with a spacer sheet, and a solution is injected into the inlet of microchannel at a constant rate with a syringe pump. The injected solution flows through the microchannel reacting with the glass to the outlet, and the outlet solution is retrieved at certain intervals with an automatic sampler to be analyzed for determination of dissolution rate of each glass constituent element at each sampling. Consequently, the glass dissolution/corrosion rate is determined as a function of reaction time by accumulating the rate determined at each sampling. After the test, the glass specimen is removed from the microchannel reactor to be subjected to various kinds of surface analyses, if necessary. Therefore, the glass dissolution/corrosion rate determined from the solution analysis data can be confirmed in an aspect of consistency with the glass surface analysis data such as the glass dissolution depth profile from the initial surface and elemental distribution profile on/in the surface layer.

Test Procedure and Conditions

Aqueous dissolution tests using the MCFT method were performed for the ISG as a function of solution pH (pH 3–10) and temperature (25–90°C) for test duration of up to 5 days with each sampling period of 2–8 h. The inlet solution was 10^{−3} M KCl solution in equilibrium with the atmosphere at 25°C, and the pH was adjusted to be 3, 4, 5.6, 8, and 10 at each test

Table I. Chemical Composition of ISG and P0798 Glass in wt% and Cation mol%

ISG	SiO ₂	B ₂ O ₃	Na ₂ O	Al ₂ O ₃	CaO	ZrO ₂			
wt%	56.2	17.3	12.2	6.1	5.0	3.3			
cation mol%	45.4	24.1	19.1	5.8	4.3	1.3			
P0798	SiO ₂	B ₂ O ₃	Na ₂ O	Al ₂ O ₃	CaO	ZrO ₂	Li ₂ O	Cs ₂ O	Others
wt%	46.6	14.2	10.0	5.0	3.0	1.5	3.0	0.75	19.7
cation mol%	38.5	20.3	16.0	4.9	2.7	0.6	10.0	0.3	6.7

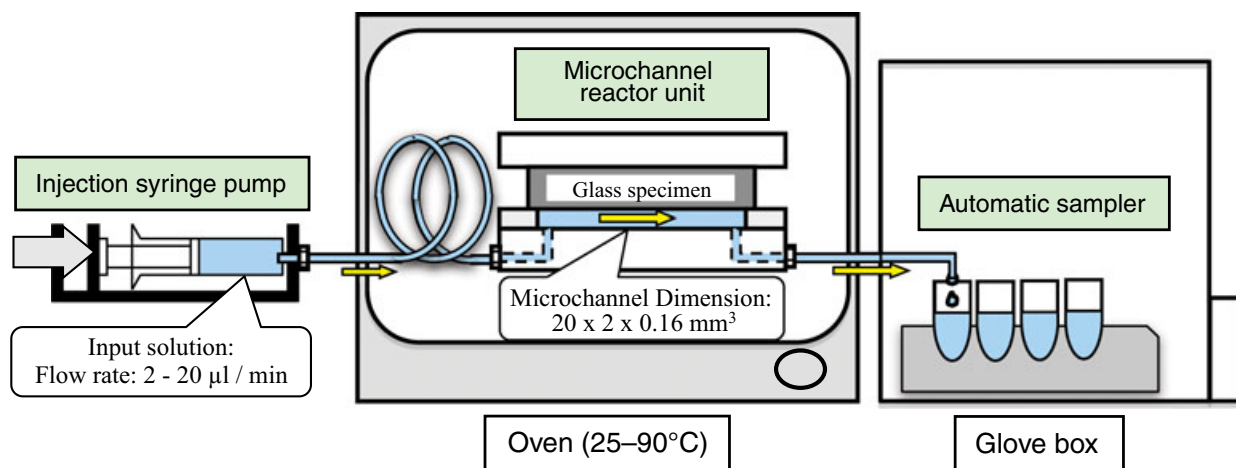


Fig. 1. Schematics of the microchannel flow-through (MCFT) test apparatus.

temperature, respectively, by addition of ultra-pure grade HCl or KOH solutions. Because the solution pH changes with temperature, the pH at each elevated temperature was estimated by use of a geochemical calculation code PHREEQE-C¹³ on the assumption that total amount of dissolved CO₂ (ΣCO_2) in the initial 10^{−3} M KCl solution in equilibrium with the atmosphere at 25°C is conserved at each elevated temperature. After adjustment of pH, the solution was moved immediately into an airtight syringe attached in the injection pump to prevent excess CO₂ dissolution from the atmosphere or CO₂ release from the solution. The solution flow rate was set up to be 2, 5, or 20 [µL/min] depending on the test conditions according to our previous studies^{7–9} where the adequate solution flow rate was evaluated as a function of the glass dissolution rate. In principle, the glass dissolution rate measured using the MCFT method is independent of the solution flow rate if the concentrations of dissolved glass constituent elements in contacting solution are low enough. In practical, however, the solution flow rate affects accuracy and preciseness of the test data of glass dissolution rate, directly or indirectly. In the present tests, therefore, the solution flow rate of 5 [µL/min] was applied for all test cases except for the following few cases. For the case of higher glass dissolution rate at high temperature of 90°C and acidic or basic pH, the higher solution flow rate of 20 [µL/min] was applied to prevent a certain change in solution pH along the solution flow in microchannel as a result of glass dissolution. For the case of lower glass dissolution

rate at low temperature of 25°C and neutral pH, on the other hand, the lower solution flow rate of 2 [µL/min] was applied to provide an output solution with measureable concentrations of dissolved glass constituent elements. The apparent S/V ratio was evaluated to be 6400/m based on the dimension of microchannel (20 mm length, 2 mm width, 0.16 mm depth) shown in Fig. 1 on the assumption that the inner volume of PTFE tube can be ignored. The Reynolds number was calculated for the solution flow in microchannel under the present test conditions (solution flow rate of 5–20 [µL/min]) to be less than 0.5, which indicates that the regime of solution flow was completely laminar flow.

The concentrations of Si, B, Na, and Al in the output solution were measured at each sampling by use of ICP-MS (model 7500c; Agilent Technologies, Inc., Santa Clara, CA) after dilution with ultra-pure grade HNO₃ solution. Table II summarizes the parameters and conditions examined in the present tests.

Determination of Dissolution Rate

The dissolution rate of element *i* from glass was determined at each sampling as normalized dissolution rate, NR_i , using the following equation,

$$NR_i[\text{g}/\text{m}^2/\text{d}] = \frac{C_i}{\Delta t} \frac{1}{f_i} \frac{V}{S} \quad (1)$$

NR_i : normalized dissolution rate of element *i* at each sampling; C_i : concentration of element *i* in output

Table II. Summary of Dissolution Test Conditions and Parameters

Test method	Microchannel flow-through method
Glass	Dimension of microchannel: 20 mm × 2 mm × 0.16 mm International simple glass (ISG) Size: 30 mm × 10 mm × 4 mm Surface condition: polished with 1 μm D.P.
Solution	10 ⁻³ M KCl solution pH 3–10 (adjusted by addition of HCl or KOH)
Temperature	25, 50, 70, 90°C
Solution flow rate	5 [μL/min] Optional case: 20 [μL/min] for the test at 90°C and pH3, pH10 2 [μL/min] for the tests at 25°C and pH4, pH5.6
S/V ratio	Apparently 6400 [m ⁻¹]
Reaction time	Up to 5 [day]
Solution analysis	Concentrations of Si, B, Na, Al in output solution measured using ICP-MS

solution at each sampling; Δt : each sampling period; f_i : mass fraction of element i in original glass; V : output solution volume at each sampling; S : geometric glass surface area in contact with solution.

Consequently, the dissolution rate of element i was determined as a function of reaction time by accumulating the rate determined at each sampling continuously.

Results and Discussion

pH Dependence of Glass Dissolution Rate

Figure 2 shows the test results on the normalized dissolution rate of Si, NR_{Si} , at 70°C as a function of reaction time for each pH. Because Si is the major glass matrix constituent as shown in Table I, the dissolution rate of Si can be assumed to indicate the dissolution rate of glass matrix. In the initial test period of up to 2 days, the dissolution rate decreased or increased slightly with time at any pH and then approached to each constant value. According to our previous study,^{7–9} the relatively higher or lower dissolution rate in the initial test period is suggested to be caused by mainly the larger surface area of initial glass specimen originated from the surface roughness at polishing or by the initial instability of solution flow in microchannel. The surface roughness becomes smoothed and the instability of solution flow goes down as the glass dissolution progresses to provide a constant dissolution rate at the test

period of beyond 2 days. The present test results indicated that the dissolution rate shows the largest

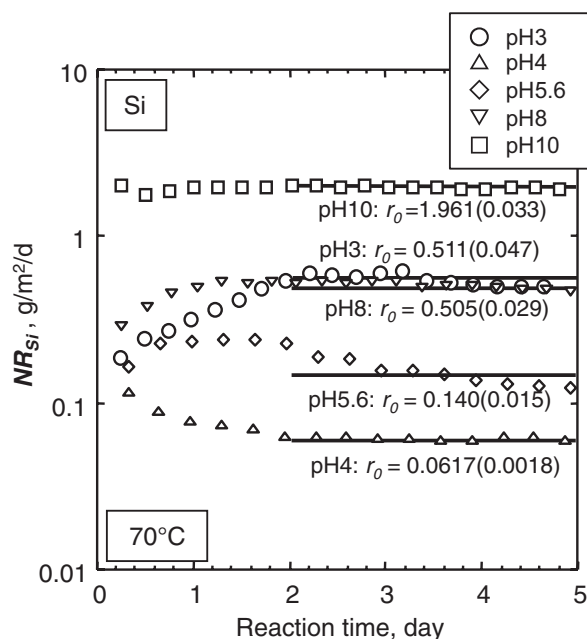


Fig. 2. Normalized dissolution rate of Si, NR_{Si} , as a function of reaction time and pH at 70°C. The value of initial dissolution rate, r_0 , was evaluated for each pH on the assumption that any data of NR_{Si} obtained at the test period of beyond 2 days indicate the r_0 with uncorrelated random errors. Numbers in parentheses represent the estimated standard deviation, 1σ .

Table III. Initial Dissolution Rate, r_0 [g/m²/d], of ISG in 10⁻³ M KCl Solution as a Function of pH and Temperature Measured Using MCFT Test Method

r_0 [g/m ² /d]	$T = 25^\circ\text{C}$	$T = 50^\circ\text{C}$	$T = 70^\circ\text{C}$	$T = 90^\circ\text{C}$
pH3	0.0098 (0.0008)	0.0419 (0.0045)	0.511 (0.047)	0.978 (0.061)
pH4	0.0024 (0.0004)	0.0131 (0.0024)	0.0617 (0.0018)	0.207 (0.031)
pH5.6	0.0092 (0.0013)	0.0268 (0.0020)	0.140 (0.015)	0.877 (0.051)
pH8	0.0208 (0.0026)	0.0405 (0.0029)	0.505 (0.029)	1.34 (0.10)
pH10	0.0285 (0.0017)	0.378 (0.030)	1.96 (0.033)	7.65 (0.17)

Numbers in Parentheses Represent the Estimated Standard Deviation, 1σ .

value at pH10 and the smallest value at pH4 in the examined pH range from 3 to 10.

With respect to the chemical affinity of solution, the concentrations of Si in the output solutions were measured to be around 1.4×10^{-5} M (0.4 ppm) at pH10, and much less than 1.4×10^{-5} M at lower pH for the tests at 70°C. Because these values of Si concentration are much smaller than that of solubility of SiO₂(am) (around 3.0×10^{-2} M at pH 10 and 70°C),¹³ any solution condition examined in the present tests can be evaluated to be far from the saturation. According to a simple chemical affinity model proposed for dissolution of borosilicate waste glasses, the dissolution rate is given by the following equation based on a first-order dissolution rate law,¹⁴

$$R = r_0(1 - a_{Si}/a_{sat}) + r_{residual}. \quad (2)$$

R : dissolution rate of glass matrix; r_0 : initial dissolution rate of glass matrix or forward dissolution rate, which changes depending on pH and temperature; a_{Si} : total activity of dissolved silica in solution or solution concentration of Si; a_{sat} : corresponding activity at saturation or saturated concentration; $r_{residual}$: residual dissolution rate at saturation, which is usually much smaller than r_0 .

In this model, the initial dissolution rate of glass matrix, r_0 , is an intrinsic parameter representing the dissolution rate in Si-free solution, and the dissolution rate decreases with the increase in a_{Si} . Assuming that the chemical affinity model is applicable to the present test results, the dissolution rate of Si measured in the present tests, NR_{Si} , can be assumed to indicate the r_0 at any pH, because the measured value of a_{Si} is much smaller than that of a_{sat} at any pH and the $r_{residual}$ is much smaller than the r_0 .

For evaluating values of the r_0 with the experimental uncertainty, the error was estimated for the NR_{Si} and

r_0 . The NR_{Si} was determined using (Eq. (1)), and the major error source was estimated to be the Si concentration in output solution, C_{Si} , measured using ICP-MS, while the error from other sources can be assumed to be small enough to be neglected. Although the measurement error of C_{Si} varied depending on the test conditions, the value of relative standard deviation (RSD) was <3% under any test condition, which suggests that the RSD can be estimated to be <3% for each data of NR_{Si} . Regarding the error of r_0 , some error sources other than the NR_{Si} should be considered such as deviation or fluctuation of solution pH, solution flow rate and reaction temperature in the micro-channel during the test period. However, it is difficult to estimate each of these errors directly. In the present estimation, therefore, the error of r_0 was estimated on the assumption that any data of NR_{Si} obtained at the test period of beyond 2 days indicate the r_0 with uncorrelated random errors. The evaluated value of r_0 at 70°C is shown in Fig. 2 with the estimated standard deviation, 1σ , for each pH. Under any test condition, the RSD of r_0 was estimated to be approximately 10% or less. Figure 3 shows the r_0 at 70°C as a function of pH, where the error bars representing the estimated standard deviation, $\pm 1\sigma$, are very short and located within symbols for any data. It can be seen that the r_0 shows a good “V-shaped” pH dependence with a minimum at around pH4.

The test results on the normalized dissolution rates of B, Na, and Al at 70°C as well as Si are shown in Fig. 4 as a function of reaction time for each pH. It can be observed that the dissolution rates of B and Na, which are defined as “soluble elements” here, show almost the same value each other at any pH. At pH4 and pH5.6, the dissolution rate of soluble elements was much higher than that of Si, and it decreased continuously with reaction time. The same tendency of selec-

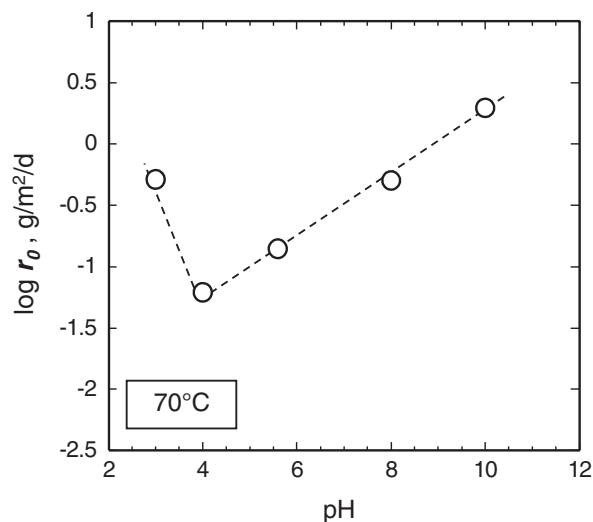


Fig. 3. Initial dissolution rate, r_0 , at 70°C as a function of pH. Error bars representing the estimated standard deviation, $\pm 1\sigma$, are located within symbols.

tive dissolution of soluble elements at neutral to acidic pH has been observed in our previous studies for Japanese reference glass of P0798.^{7,9} Because the solution flow rate from 2 to 20 [$\mu\text{L}/\text{min}$] has been verified to have no remarkable influence on the dissolution rate of both B and Si, we have suggested that the dissolution of soluble elements proceeds controlled by a diffusion process with ion-exchange between soluble elements and water or hydronium ion. Therefore, the present results on ISG also suggest the diffusion-controlled dissolution of soluble elements at neutral to acidic pH. At pH10, on the other hand, the dissolution rate of soluble elements was almost same as that of Si, and it showed an almost constant value over the test duration, which suggests that the increase in pH accelerates the silica glass matrix dissolution and/or depresses the diffusion-controlled dissolution of soluble elements to result in the congruent dissolution, while the dissolution of Al was almost congruent with Si at any pH. At acidic and neutral pH, however, the dissolution rate of Al was slightly lower than that of Si, which suggests that a small amount of Al may remain at the surface to precipitate.

Temperature Dependence of Glass Dissolution Rate

Figure 5 shows the test results on the NR_{Si} at pH10 as a function reaction time for each temperature.

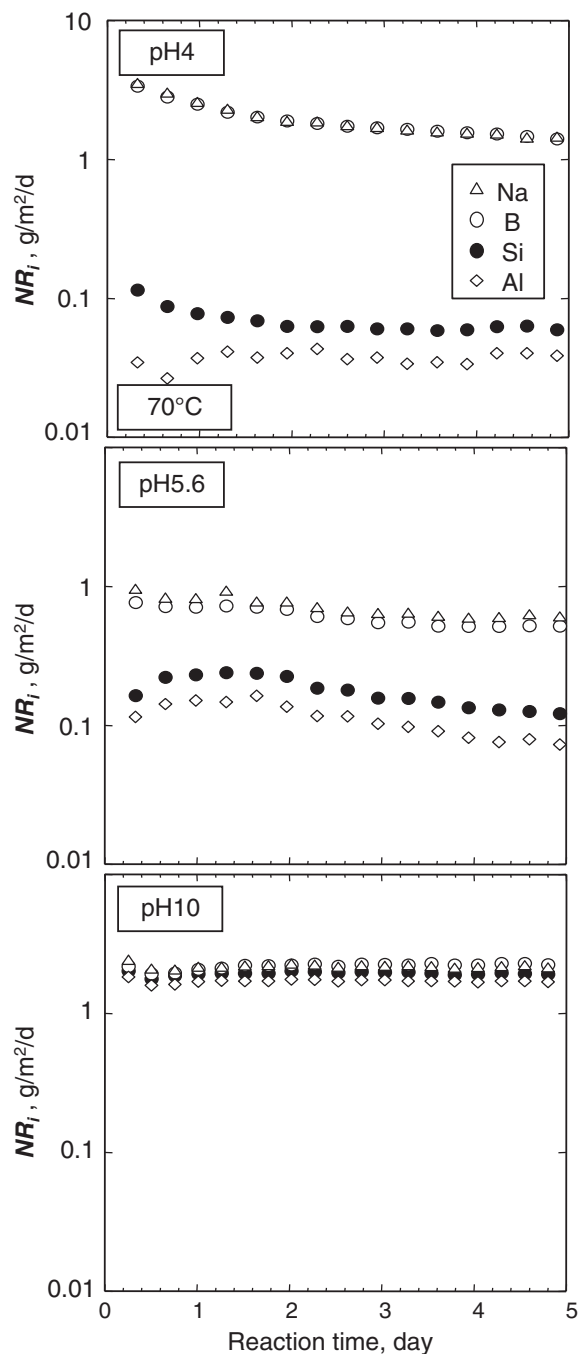


Fig. 4. Normalized dissolution rate of B, Na, and Al as well as Si at 70°C as a function of reaction time and pH.

Because the concentration of Si in the output solution was measured to be much less than the solubility of $\text{SiO}_2(\text{am})$ at any temperature, the value of r_0 was evalu-

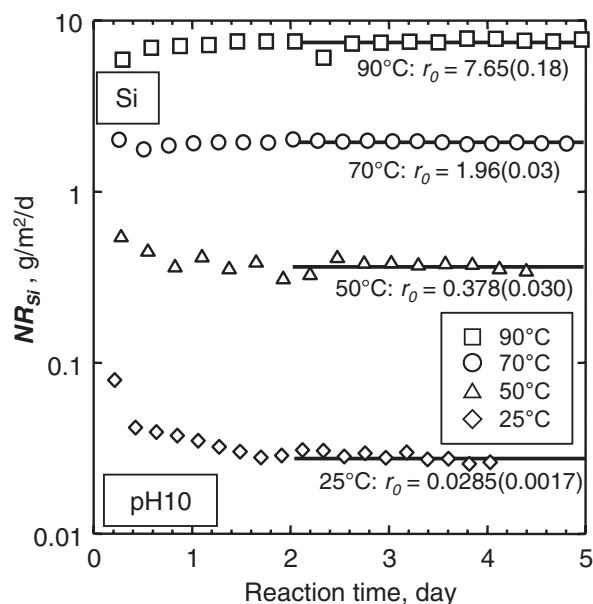


Fig. 5. Normalized dissolution rate of Si, NR_{Si} , at pH10 as a function of reaction time and temperature. The r_0 was evaluated for each temperature on the assumption that any data of NR_{Si} obtained at the test period of beyond 2 days indicate the r_0 with uncorrelated random errors. Numbers in parentheses represent the estimated standard deviation, 1σ .

ated for each temperature on the assumption that any data of NR_{Si} obtained at the test period of beyond 2 days indicates the r_0 with uncorrelated random errors. The estimated value of r_0 at pH10 is shown in Fig. 5 with the estimated standard deviation, 1σ , for each temperature. Arrhenius plot of the r_0 is shown in Fig. 6, where a good linear relation can be observed to give the apparent activation energy, E_{act} , of 77.4 kJ/mol. This value of E_{act} is similar to that of 76 kJ/mol given by our previous study for the initial dissolution of a Japanese reference glass of P0798 at pH10 measured using the MCFT method⁹ and that of 77 kJ/mol given by Jollivet for the initial dissolution of a French reference glass of SON68 in deionized water and clay-equilibrated groundwater measured using the SPFT method.¹⁵

Initial Dissolution Rate as a Function of pH and Temperature

The value of r_0 was evaluated at each pH and temperature in the above way, and the results are summa-

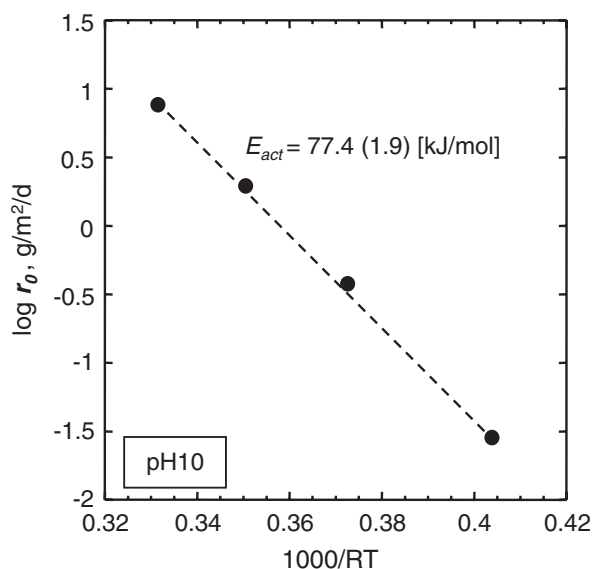


Fig. 6. Arrhenius plot of the r_0 at pH10. Error bars representing the estimated standard deviation, $\pm 1\sigma$, are located within symbols.

ri- zed systematically as a function of pH and temperature in Table III and in Fig. 7 in comparison with that of P0798 glass measured using the MCFT method in our previous study.⁹ The results indicated that the r_0 of ISG increases with temperature at any pH, and it has a “V-shaped” pH dependence with a minimum at around pH4 at any temperature, although P0798 glass has a “U-shaped” pH dependence with a minimum at around pH6.

The dissolution rate of ISG has been measured by Gin *et al.*¹⁶ using static dissolution tests with powdered glass specimen, and the r_0 at 90°C and pH9 was evaluated to be 1.7 [g/m²/d]. In the present tests, however, there are no data measured at 90°C and pH9 for direct comparison. Therefore, the r_0 at pH9 and 90°C was estimated by interpolation of the present data of pH dependence at 90°C assuming a linear relation between $\log r_0$ and pH in the pH range of 4–10. The results are shown in Fig. 8, and the r_0 was estimated to be 3.66 (SD of +2.76 and –1.57) [g/m²/d] at pH9 and 90°C, which value is almost consistent with that evaluated by Gin, but larger by a factor of nearly 2. The discrepancy between them can be supposed to arise partly from difference in the shape of glass specimen, coupon shaped specimen, and powdered one, that is, uncertainty in determination of the surface area for pow-

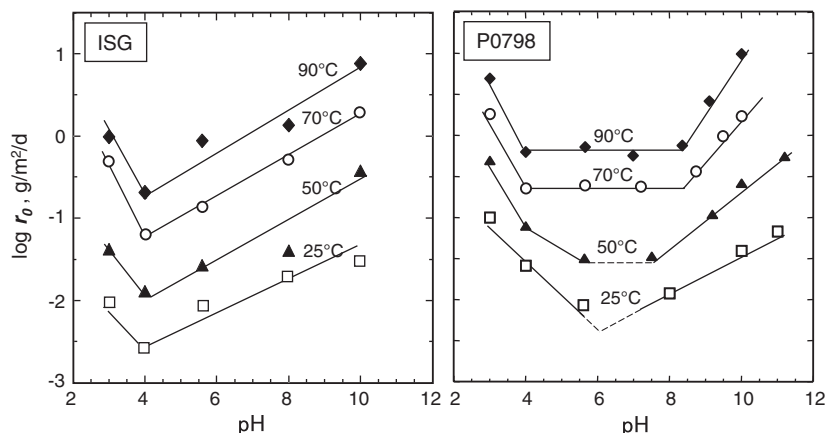


Fig. 7. The r_0 of ISG as a function of pH and temperature in comparison with that of P0798 glass.⁹

dered specimen. Regarding the effects of shape of glass specimen, Icenhower *et al.*¹⁷ compared the dissolution rate of French reference glass of SON68 between coupon shaped (monolith) specimen and powdered specimen using the SPFT test method, and reported that the rates of powdered glass evaluated by the geometric surface area normalization matched to those of monolith, and the rates by the BET surface area normalization were slower by a factor of 2 or 3. Because Gin's data of r_0 were evaluated by the B.E.T surface area normalization, which can be supposed to be lower than that by the geometric surface area normalization by a factor of 2–3 from comparison by Icenhower, the discrepancy between the present data and Gin's data can be suggested to arise mainly from the error of determination of the surface area.

From the present test results on temperature dependence of the r_0 shown in Fig. 7, the apparent activation energy of the initial dissolution was evaluated for each pH. The results of Arrhenius plot of r_0 are shown in Fig. 9, where a good or fair linear relation can be observed at any pH to give the apparent activation energy, E_{act} , of 61–68 [kJ/mol] at pH range of 3–8, and 77 [kJ/mol] at pH10. Figure 10 shows the E_{act} as a function of pH in comparison with that of P0798 glass evaluated in our previous study.⁹ The results shown in Fig. 10 indicate that the E_{act} for ISG is very close to that for P0798 glass at neutral to basic pH. At acidic pH, however, the E_{act} for ISG is larger than that for P0798 glass, although the E_{act} at pH3 has a relatively large uncertainty, that is, the E_{act} for P0798 glass decreases as pH changes from neutral to acidic, while

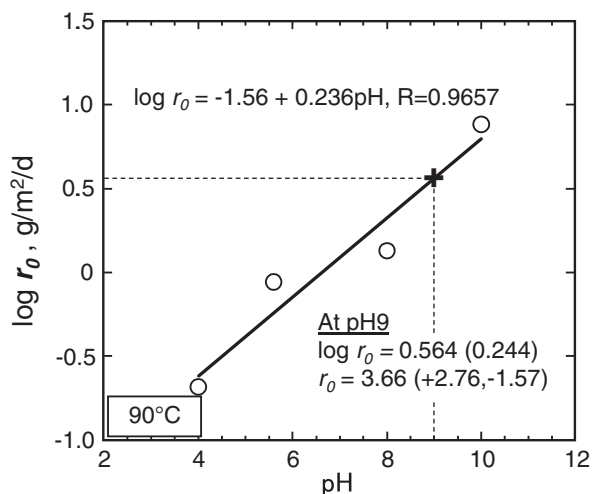


Fig. 8. Estimation of the r_0 at pH9 and 90°C by interpolation of the data of pH dependence assuming a linear relation between $\log r_0$ and pH in the pH range of 4–10. Error bars representing the estimated standard deviation, $\pm 1\sigma$, are located within symbols.

that the E_{act} for ISG is almost constant at pH range from neutral to acidic. These comparisons suggest that the initial dissolution of ISG proceeds by the same mechanism as P0798 glass at neutral to basic pH, but it may proceed by the different mechanism from P0798 glass at acidic pH. The E_{act} of 60–70 [kJ/mol], observed at acidic to neutral pH for the ISG and at only neutral pH for P0798 glass, is consistent with that of a surface-reaction controlled dissolution mechanism proposed for borosilicate glass and SiO_2 polymor-

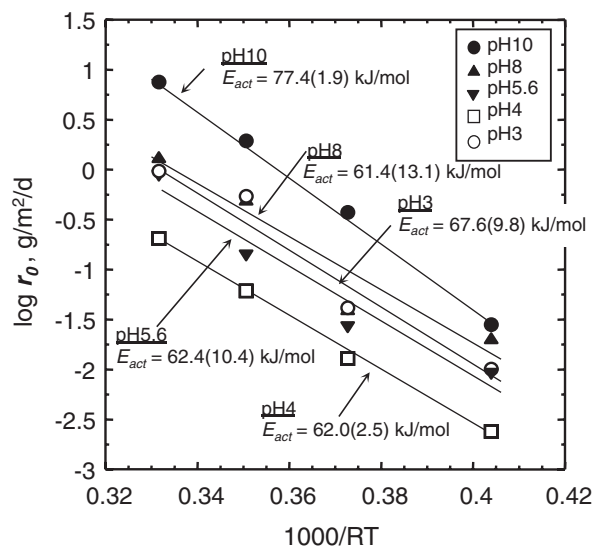


Fig. 9. Arrhenius plot of the r_0 at each pH. Numbers in parentheses represent the estimated standard deviation, 1σ .

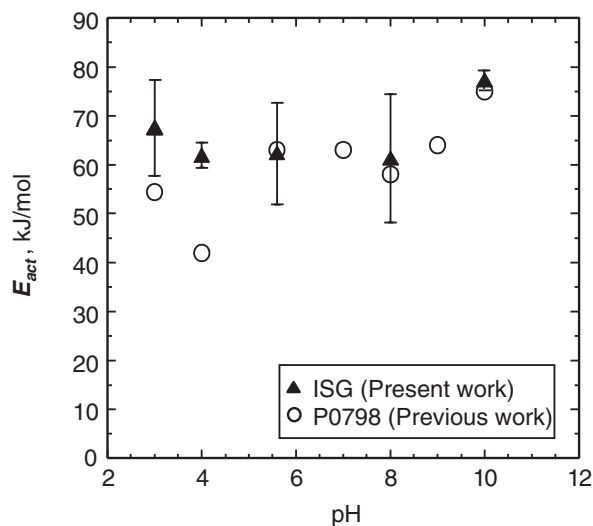


Fig. 10. Apparent activation energy for initial dissolution of ISG as a function of pH in comparison with that of P0798 glass.⁹ Error bars represent the estimated standard deviation, $\pm 1\sigma$.

phs.^{18–21} While, the E_{act} of around 50 [kJ/mol], observed at acidic pH for P0798 glass, is close to that of a diffusion-controlled dissolution mechanism proposed for the residual dissolution of some waste glasses^{22,23} and for diffusion of water or hydronium ion with

ion-exchange in sodium aluminosilicate glasses.²⁴ Therefore, it may be supposed that the initial dissolution of ISG proceeds controlled by a surface-reaction mechanism at acidic to neutral pH, although that of P0798 glass at acidic pH proceeds controlled partly by the diffusion process. The E_{act} of 70–80 [kJ/mol] observed at pH10 for both glasses, which value is slightly larger than that at neutral pH, suggests that another different process may affect the glass matrix dissolution at basic pH.

The mechanism to account for the difference in the pH and temperature dependence of r_0 between the ISG and P0798 glass is currently uncertain. However, the difference in the content of alkali metal elements in the glass can be supposed to be one of the potential reasons, because alkali metal elements break silica network partly in the glass and provide a pathway for diffusion of water or hydronium ion with ion-exchange. The chemical composition of P0798 glass is shown in Table I, in comparison with that of ISG. The ISG contains 19.1 cation mol% of alkali metals (only Na), while P0798 glass contains larger amount of alkali metals (Na, Li, Cs) of 26.3 cation mol%, and the certain difference between them can be supposed to cause differences in the dissolution mechanism and rate at acidic pH, that is, dissolution by a surface-reaction mechanism for ISG and that by a diffusion-controlled mechanism for P0798 glass as mentioned above.

Conclusions

Aqueous dissolution tests were performed for the International simple glass (ISG) using a newly developed microchannel flow-through (MCFT) test method to evaluate the initial dissolution rate of glass matrix, r_0 , precisely and systematically as a function of solution pH (3–10) and temperature (25–90°C). The test results indicated that the r_0 shows a “V-shaped” pH dependence with a bottom at around pH4 at any temperature, which differs from that of a Japanese reference glass of P0798, for which the r_0 showed a “U-shaped” pH dependence with a bottom at around pH6 in our previous study. The results also indicated that the r_0 increases with temperature according to an Arrhenius law at any pH, and the apparent activation energy evaluated from Arrhenius relation is 62–68 [kJ/mol] at pH range of 3–8, and 77 [kJ/mol] at pH10. The E_{act} for ISG is very close to that for P0798 glass at neutral to

basic pH; however, it is larger than that for P0798 glass at acidic pH, that is, the E_{act} for ISG is almost constant at pH range from neutral to acidic, although the E_{act} for P0798 glass decreases as pH changes from neutral to acidic. These results suggest that the mechanism of initial dissolution for ISG may be different from that for P0798 glass at only acidic pH.

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