WM2013 Conference, February 24 – 28, 2013, Phoenix, Arizona, USA

Fundamental Study on Temperature Dependence of Deposition Rate of Silicic Acid − 13270

Hayata Shinmura[*], Yuichi Niibori[*], and Hitoshi Mimura[*]

[*] Dept. of Quantum Science & Energy Engineering, Graduate School of Engineering, Tohoku University, 6-6-01-2 Aobayama, Aoba-ku, Sendai 980-8579 JAPAN
E-mail: shinmura@michiru.qse.tohoku.ac.jp

ABSTRACT

The dynamic behavior of the silicic acid is one of the key factors to estimate the condition of the repository system after the backfill. This study experimentally examined the temperature dependence of dynamic behavior of supersaturated silicic acid in the co-presence of solid phase, considering Na ions around the repository, and evaluated the deposition rate constant, k, of silicic acid by using the first-order reaction equation considering the specific surface area. The values of k were in the range of 1.0×10^{-11} to 1.0×10^{-9} m/s in the temperature range of 288 K to 323 K. The deposition rate became larger with increments of temperature under the Na ion free condition. Besides, in the case of Na ions 0.6 M, colloidal silicic acid decreased dramatically at a certain time. This means that the diameter of the colloidal silicic acid became larger than the pore size of filter (0.45 μm) due to bridging of colloidal silicic acid. Furthermore, this study estimated the range of altering area and the aperture of flow-path in various value of k corresponding to temperature by using advection-dispersion model. The concentration in the flow-path became lower with increments of temperature, and when the value of k is larger than 1.0×10^{-11} m/s, the deposition range of supersaturated silicic acid was estimated to be less than 20 m around the repository. In addition, the deposition of supersaturated silicic acid led the decrement of flow-path aperture, which was remarkable under the condition of relatively high temperature. Such a clogging in flow paths is expected as a retardation effect of radionuclides.

INTRODUCTION

Groundwater around the repository is affected by not only high alkalinity due to the cement materials used for the construction of the repository but also decay heat of radioactive wastes. In either case, such an altered groundwater increases the solubility of silicic acid, changing pH dramatically downstream by diluting with the surrounding groundwater of natural condition. This process leads the silicic acid supersaturated in the mixing-zone, altering the surfaces of

1

flow-paths around the repository through the polymerization and deposition processes (e.g., [1-4]). In other words, the dynamic behavior of the silicic acid is one of the key factors to estimate the condition of the repository system after the backfill.

To comprehend the temperature dependence of the deposition rate, this study examined the dynamic behavior of silicic acid in the range of 288 K to 323 K in the presence of the solid phase. Furthermore, we should consider saline groundwater around the repository. In this study, Na ions concentration was set in the range of 0 M to 0.6 M. These experimental results give the deposition rate-constants, k, of silicic acid by using the first-order reaction equation. Applying the values of k to the advection-dispersion model including the deposition rate, this study calculated numerically the range of altered area and the change of flow-path aperture.

EXPERIMENTAL

Procedures

The main experimental procedures are the same as the previous works reported by the authors [4-7]. That is, the polyethylene vessel with cover had a fluid volume of 250 ml. Nitrogen was passed through the vessel to avoid contacting with air. The silicic acid solution prepared by dissolving Na_2SiO_3 solution (water glass obtained from Wako Pure chemical Industries, Ltd) in distilled ultrapure water was put into the vessel and mechanically stirred with a polypropylene stirrer. Na_2SiO_3 solution was diluted to a given concentration (pH>10). The temperature of the solution was set to a given value within the range of 288 K to 323 K by using thermostat. The initial supersaturated concentration of soluble silicic acid was given by considering the relation between the solubility of silicic acid and temperature (the relation was based on Furnier's eq. [8]). As a solid phase, a weighed amount of the amorphous silica (the range of 0.1 g to 1.0 g) was poured into the vessel. (The detail of the solid sample is described later in next section.) Then, the pH of the solution was adjusted to 8 with an HNO_3 solution and a buffer solution mixing MES (2-morpholinoethanesulfonic acid, monohydrate) and THAM (trishydroxymethyl). Table I shows the experimental conditions. The Na ions were prepared from a NaCl solution.

The concentrations of both soluble silicic acid and colloidal silicic acid, and the amount of precipitated silicic acid were monitored. In order to determine the each concentration of soluble-silicic acid and colloidal form in the solution, this study used silicomolybdenum-yellow method and ICP-AES. That is, the soluble-silicic acid (monomeric or oligomeric silicic acid) was

defined as silicic acid reacting with molybdate reagent, giving siliciomolybdic acid and coloring yellow, and colloidal-silicic acid was defined as silicic acid in liquid phase except for soluble-silicic acid. The concentration of precipitated silica was defined as the initial concentration of soluble silica minus the total concentration of silicic acid in soluble and colloidal forms [6, 7].

Table I. Experimental conditions

Initial supersaturated concentration of silicic acid	4.8 mM, 10.0 mM
Addition amount of solid sample	0.1 g, 0.5g ,1.0 g
Na ions concentration	0 M, 0.06M, 0.6M
pH	8
Stirring rate	300 rpm
Pore size of membrane filter	0.45 μm
Temperature	288 K, 298K, 313K, 323K

Solid sample

The solid sample was purchased as silica powder ($SiO_2·0.23H_2O$) of 100 mesh-under from Mallinckrodt Co. Since small granules or coherent aggregates of submicron particles were contained on the powder, a size fraction of 74 of 149 μm in particle diameter was separated by sieving. Its specific surface area was estimated to 350 m^2/g by the BET method using nitrogen gas. If the specific surface area of parallel flat boards (as a simplified form of fracture) with aperture b (m) is approximately calculated by $2/b$, the amount of the amorphous silica, M (g), corresponding to the value of b, is estimated by the $2/b=Ma/V$, where V is the volume of the solution (m^3), and a is BET (N_2 gas) specific surface area (m^2/g). For example, when b=0.1 mm, M almost equals 0.01 g (a=350 m^2/g, V=250 ml). This equation may yield an estimate of the relation between the flow system and the batch test through a specific surface area. Furthermore, Chida et al [6] reported that the rock surface altered by the silicic acid forms an amorphous layer with slight thickness, even if its basement of the solid phase is crystalline. As an experimental approach, this study used amorphous silica particles on batch test as the solid phase, in order to simulate a large surface area observed in flow-paths such as fractures included in rock matrix.

RESULT AND DISCSSION

Figs. 1, 2 and 3 are some examples of the experiment results. The initial supersaturated concentration, C_{ini}-C_e, was set to 4.8 mM or 10 mM, where C_{ini} is the initial concentration of soluble silicic acid and C_e is the saturated concentration of silicic acid in the presence of amorphous silica. The vertical axis, f, in these figures, is the fractions of soluble silicic acid, colloidal silicic acid and precipitated silicic acid to the initial concentration of soluble silicic acid. In the case of 4.8 mM in initial supersaturated concentration, the concentration of soluble-silicic acid decreased with increment of the amount of the solid phase and the temperature. Then, colloidal silicic acid could not be detected in observed temperature, as shown in Fig. 1. By contrast, in the cases of 10 mM in initial supersaturated concentration, colloidal silicic acid can be remarkably observed (Fig. 2). In addition, colloidal silicic acid deposited under only the condition of relatively high temperature. That is, the initial supersaturated concentration and the temperature strongly affect the dynamic behavior of colloidal silicic acid. Furthermore, the fractions of the soluble and the colloidal silicic acid were quite different in those results of the added solid phase amount 0.1 g and the 1.0 g. This means that the specific surface area of solid phase also affects the formation of colloid silicic acid and the precipitation of the silicic acid to the solid phase. Besides, Fig. 3 shows the dependence of the dynamic behavior of silicic acid on Na ions concentration. Under the condition of 0.6 M in Na ions concentration, Fig. 3(c) shows that the colloidal silicic acid decreased drastically at a certain time. This indicates that Na ions bridge the colloidal silicic acid, whose apparent size exceeds the pore size of filter.

Since the specific surface area changes due to the deposition, this study focused on the initial gradient of f to time in order to evaluate the deposition rate of the silicic acid. Practically, by applying the first-order reaction equation to the initial gradient of f, the apparent rate-constants, k (m/s) under various conditions were estimated. The obtained rate-constants were summarized by the function of both the supersaturated concentration and the specific surface area, aM/V (1/m).
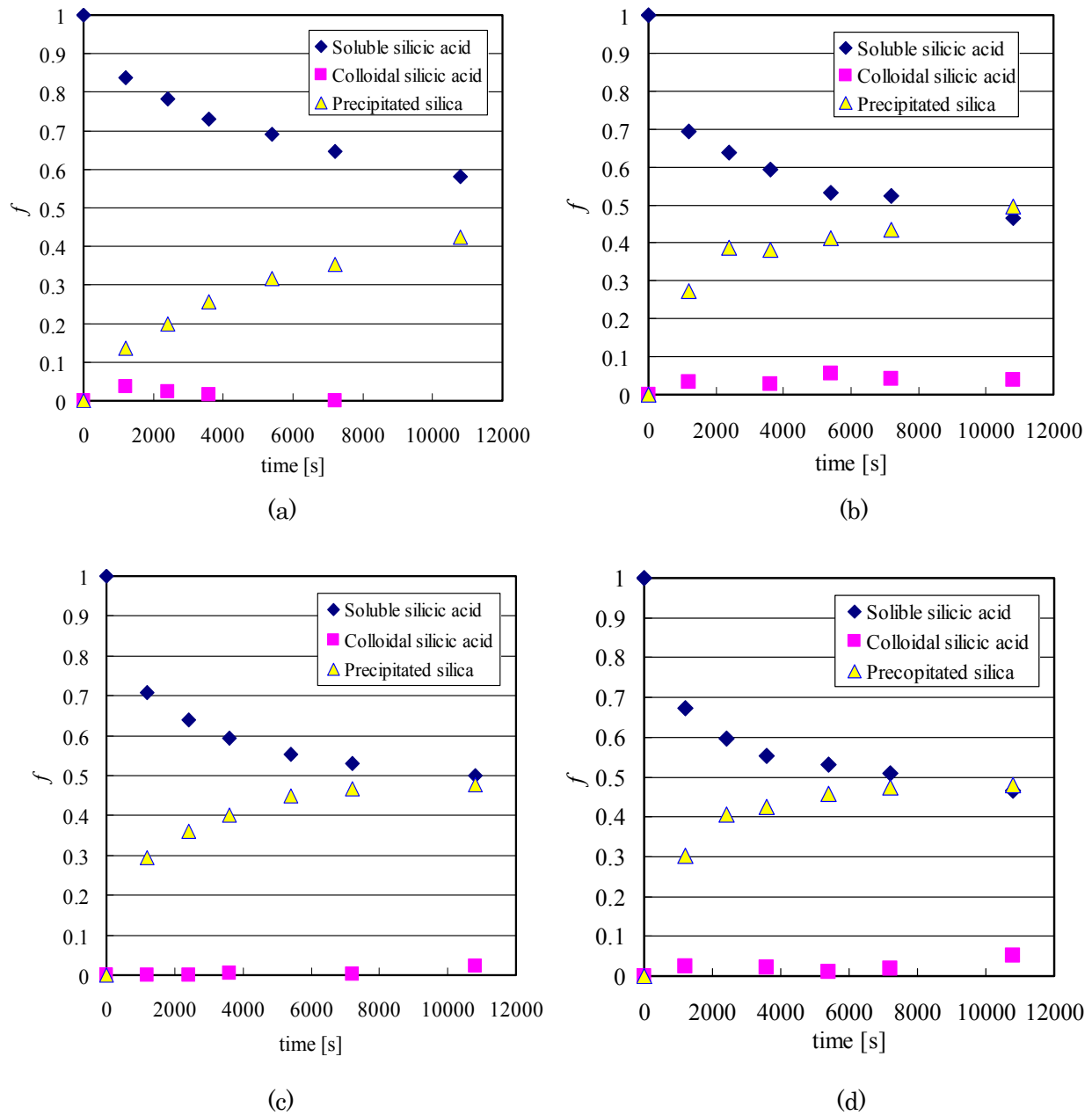
Fig. 1. The temperature dependence of deposition behavior of supersaturated silicic acid under the condition of 4.8 mM in initial supersaturated concentration.

((a) 288 K, (b) 298 K, (c) 313 K, (d) 323 K, Solid sample: Mallinckrodt silica powder, Pore size of filter: 0.45 μm, Amount of solid phase: 1.0 g, and Na ions: 0 M)
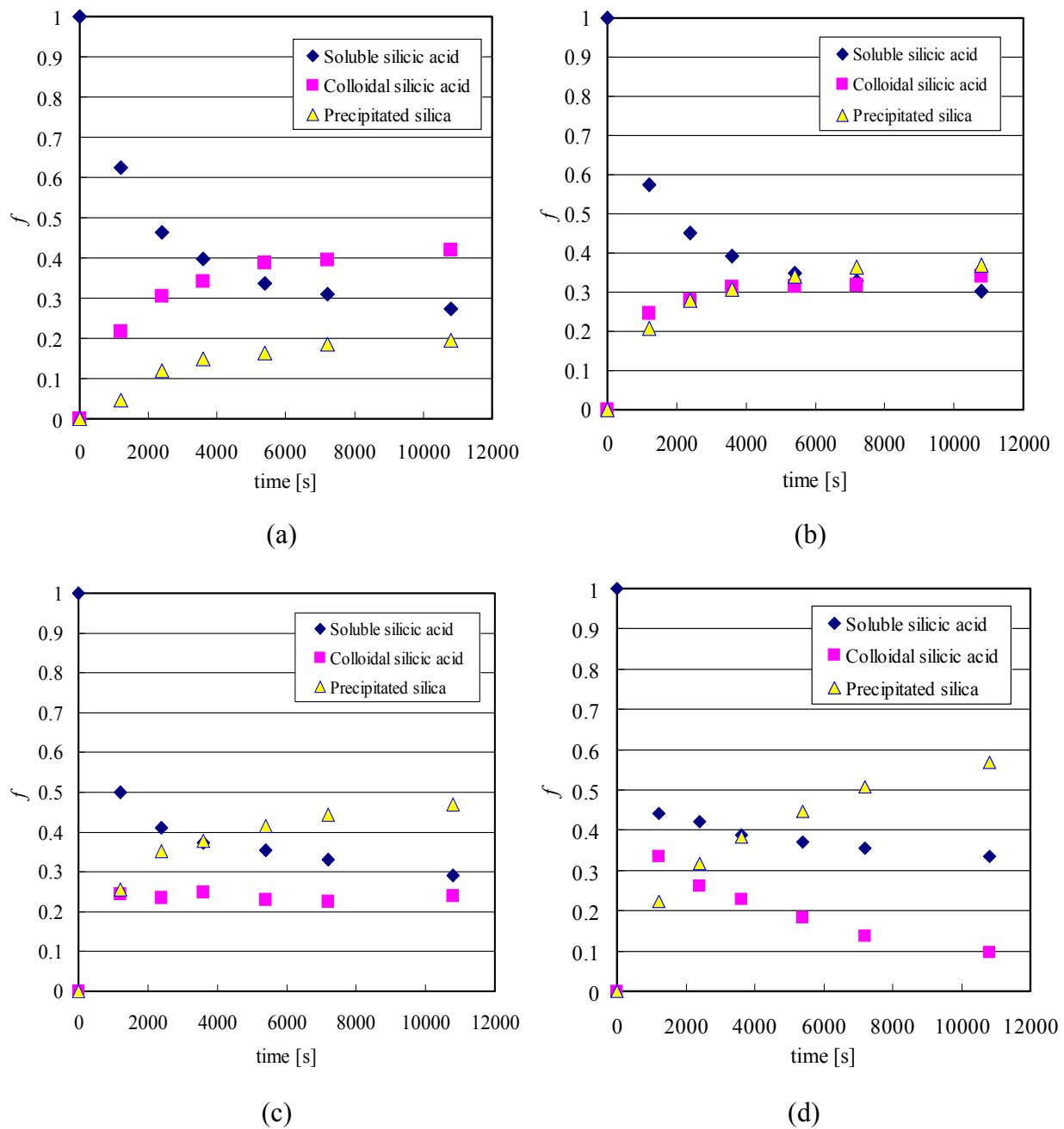
Fig. 2. The temperature dependence of deposition behavior of supersaturated silicic acid under the condition of 10 mM in initial supersaturated concentration.
((a) 288 K, (b) 298 K, (c) 313 K, (d) 323 K, Solid sample: Mallinckrodt silica powder, Pore size of filter: 0.45 μm, Amount of solid phase: 1.0 g, and Na ions: 0 M)
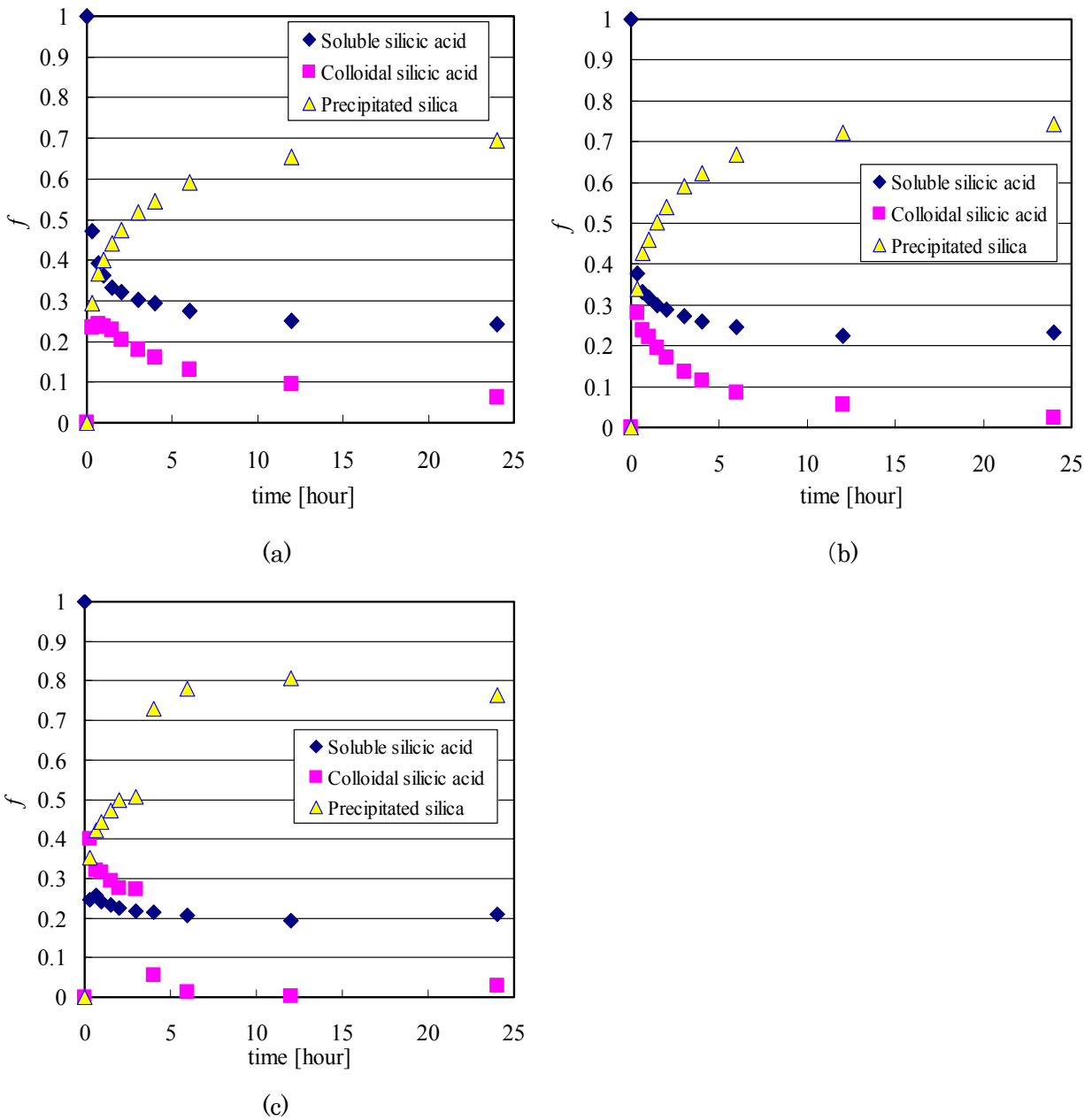
Fig. 3. The dependence of the deposition behavior on the Na ions concentration.
((a) 0 M, (b) 0.06 M, (c) 0.6 M, Initial supersaturated concentration: 10 mM, Solution temperature: 313 K, Solid sample: Mallinckrodt silica powder, and Pore size of filter: 0.45 μm)

Table II. The apparent rate-constants, k (m/s), of the deposition of supersaturated silicic acid (Na ions: 0 M)

Solution temperature (K)	288	298	313	323
Apparent Rate-constant, k (m/s)	1.21×10^{-11}	2.99×10^{-11}	3.14×10^{-11}	5.22×10^{-11}

Table III. The apparent rate-constants, k (m/s), of the deposition of supersaturated silicic acid (Solution temperature: 323 K)

Na ions concentration (M)	0	0.06	0.6
Apparent Rate-constant, k	5.22×10^{-11}	1.17×10^{-11}	5.52×10^{-11}

Now, consider the one-dimensional, advection-dispersion model including the deposition rate [10].

$$B\frac{\partial C_f}{\partial T} = -\frac{\partial C_f}{\partial X} + \frac{1}{P_{e_f}}\frac{\partial^2 C_f}{\partial X^2} - D_a C_f \qquad\qquad \text{(Eq.1)}$$

This formula is described by using non-dimensional form, i.e., $B=b/b^*$, $C_f=(C-C_e)/(C_{ini}-C_e)$, $T=t/t^*$ ($t^*=x_1/u_1$) and $P_{ef}=u_1x_1/D_f$ and $D_a=k\,t^*/b^*$, where x_1 is the characteristic length (length of flow path) (m), D_f is the dispersion coefficient (m^2/s), b is the aperture of flow-path (m), b^* is the initial aperture (m), and u_1 is the fluid flow velocity of groundwater (m/s). Eq. 1 assumes the approximation of pseudo-steady state for B (dimensionless aperture of flow-path) and the incompressibility of fluid under the condition of a constant pressure gradient in the interval of [0, x_1]. Then, the change of the aperture at an arbitrary x can be described by $-dB/dT=D_a\gamma C$, where $\gamma = (C_{ini}-C_e)/\rho_M$, ρ_M is a conversion factor (mol/m^3) (the density of the deposit (kg/ m^3) divided by the molar mass (kg/mol)). Then, the normalized over-all permeability K_P ($=k_p/k_{p0}$, where k_p (m^2) is approximated by $b^2/12$) yields.

$$K_p = 1/(\int_0^1 \frac{1}{B^2}dX). \qquad\qquad \text{(Eq. 2)}$$

Eq. (1) and $-dB/dT=K_R\gamma C$ was numerically solved with the FTCS (forward time central space) finite difference method. In discretizing the advection terms in Eq. (1), the first order upwind difference method was used. Here, the boundary conditions are the closed vessel boundary condition at $X=0$ and $\partial C/\partial X=0$ at $X=1$, and the initial conditions (at $T=0$) are $C=0$ and $B=1$ in the range of $0\leq X\leq1$.

This model has two non-dimensional parameters: The Peclet number, P_e, and the Damkohler number, D_a. Generally, the value of the Peclet number is smaller than 10^2 [4]. On the other hand, this study assumed u_1=2.5×10^{-7} m/s, x_1=100 m, A=10^4 1/m, b^*=1.0×10^{-4} m [1]. Fig.4 show the Arrhenius plots of the apparent deposition-rate-constant for each initial supersaturated concentration from the experimental results. In this model, the deposition rate constant, k, was used at that of 4.8 mM in initial supersaturated concentration. The value of k was corrected the error by Arrhenius plots, as shown in Table IV. Furthermore, the rate-constants of 4.8 mM exceeded those of 10 mM. This means that the remark deposit of silicic acid covered the solid surface, which in turn decreases the specific surface area.

Figs. 5 show the concentration in the flow-path and the aperture at x=0 in various value of k corresponding to temperature. As shown in Fig. 5, the concentration along a flow-path became lower when the temperature increased. Besides, as the value of k is larger than 1.0×10^{-11} m/s, the range of altering area was estimated less than 20 m around the repository. Furthermore, the aperture of flow-path became enough narrow with increment of temperature, expecting the clogging-effect in flow-path as a retardation effect of radionuclides. However, in case of small k conditions ($\approx$1.0×10^{-12} m/s), the range of altering area spreads broadly.

Table IV. The apparent rate-constants, k (m/s), of the deposition of supersaturated silicic acid corrected by Arrhenius plot.

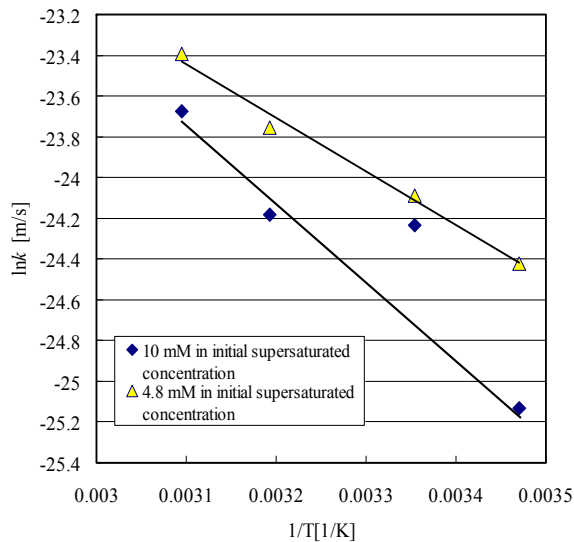| Solution temperature (K)	288	298	313	323
k corrected by Arrhenius plot (m/s)	2.47×10^{-7}	3.35×10^{-7}	5.12×10^{-7}	6.63×10^{-7}

Fig. 4. Arrhenius plots at each initial supersaturated concentration.

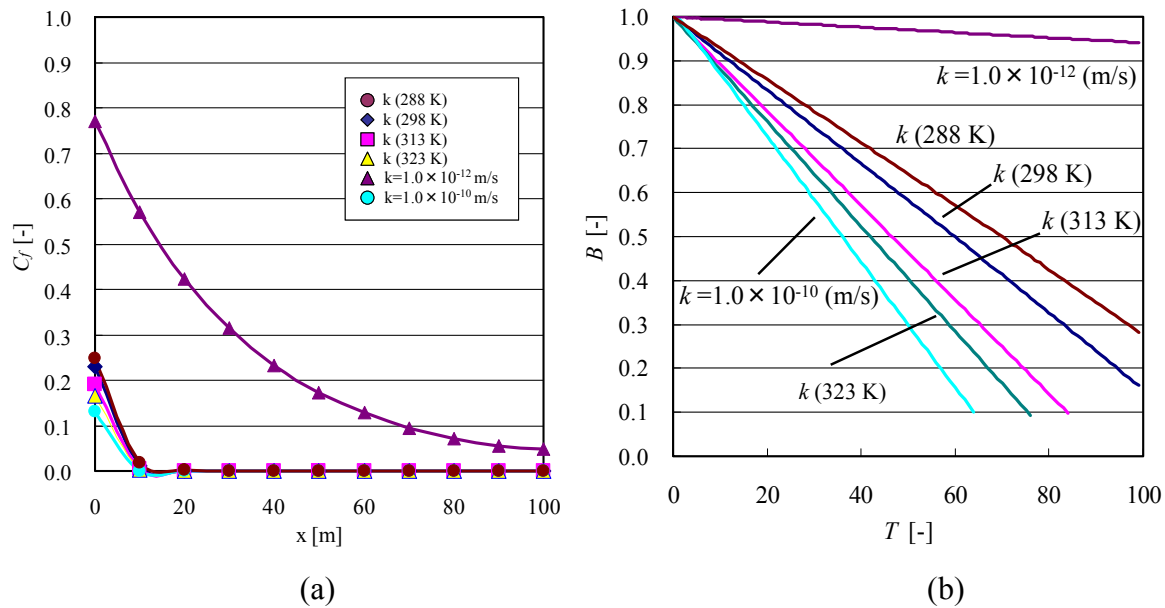(a)   (b)

Fig. 5. The results of calculation.(The concentration in flow-path (a) and the aperture at x=0 (b)).

Figs. 6 show the change of diameter of colloidal sillicic acid with time. At Na ion free condition, the diameter of colloidal sillicic acid is quite unstable to exactly detect the size distribution. This indicates the possibility that the particles were condensed rapidly in the process of filtration. On the other hand, under the conditions containing Na ions, the value of diameter is comparatively stable. In the case of Na ions 0.06 M, the diameter gradually became small. By contrast, in the case of Na ions 0.6 M, the diameter increased. The results are harmonic to the rate-constants shown in the Table III.
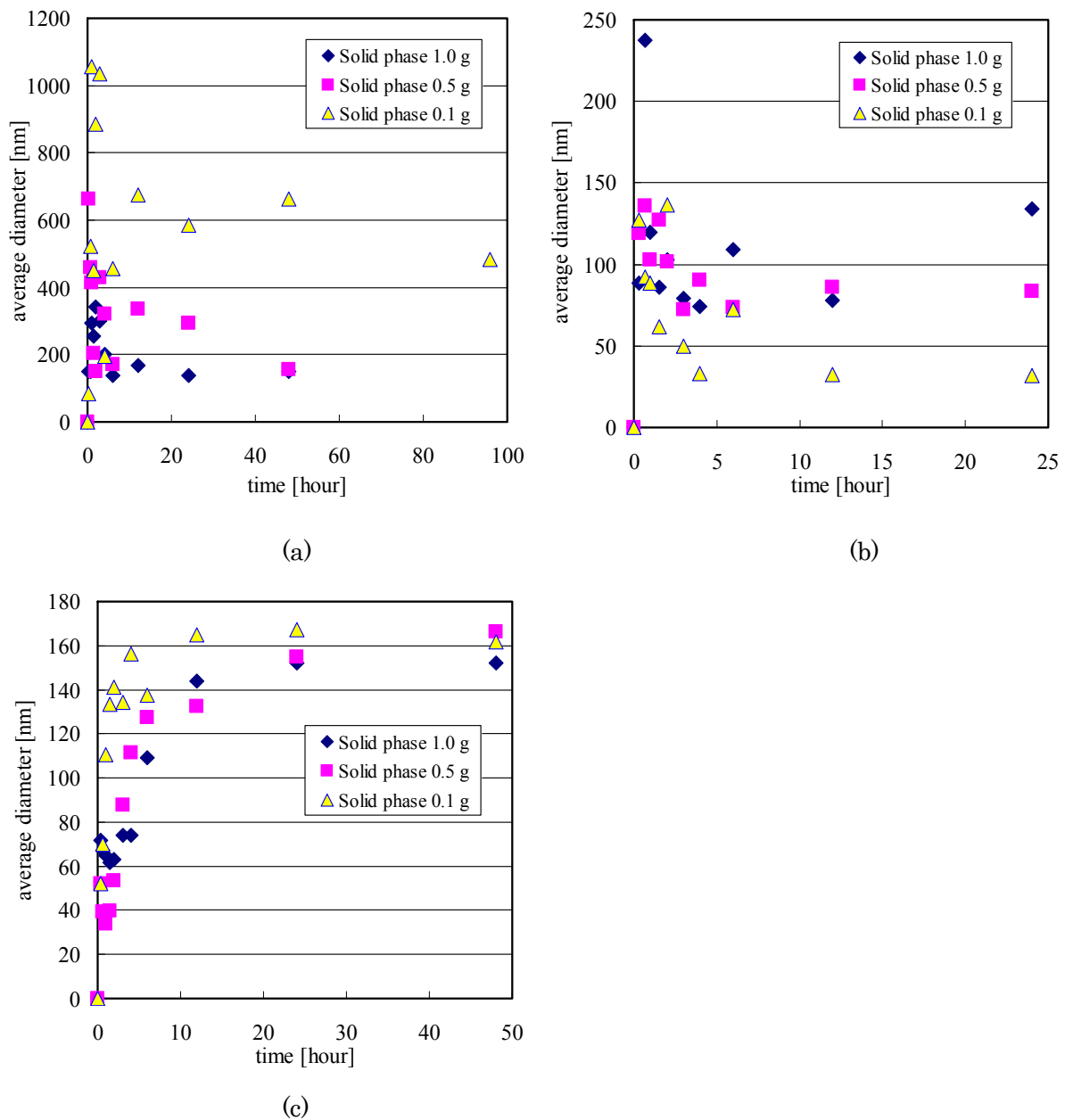
(a)

(b)

(c)

Fig. 6. The average diameter of colloidal silicic acid detected by ELSZ-2.

((a) Na 0 M, (b) 0.06 M, (c) 0.6 M, Initial supersaturated concentration: 10 mM, Solid sample: Mallinckrodt silica powder, Pore size of filter: 0.45 μm, Amount of solid phase: 1.0 g, and Solution temperature: 293 K).

CONCLUSIONS

This study examined the dynamic behavior of silicic acid in the co-presence of a solid phase considering the ground water temperature and Na ions around the repository. The apparent deposition rate-constant, k, became larger as temperature increased in Na ion free conditions. In case of Na 0.06 M conditions, the value of k exceeded that of Na free conditions. This suggests that the water activity decreased due to the hydration of Na ions, which in turn limited the solubility of soluble silicic acid compared to the value estimated by Furnier's eq. [8]. On the other hand, in case of Na 0.6 M conditions, the value of k was lower than that of Na 0.06 M conditions. This is because Na ions played a role also in bridging the colloidal silicic acid. Such a supersaturated solution undergoes an induced time to grow the colloidal silicic acid enough large to deposit. As the result, the initial deposition rate-constant of 0.6 M in Na ions concentration is estimated to be apparently small, compared to that of 0.06 M.

From the advection-dispersion model considering the deposition rate and the change of flow-path aperture, the range of altering area was less than 20 m around the repository when the value of k is larger than 1.0×10^{-11} m/s. Furthermore, it was confirmed that the deposition of supersaturated silicic acid narrows the aperture of flow-path, and that the time until the flow-path is blocked becomes shorter with increment of the temperature. In other words, such a clogging-effect in flow-path is expected as a retardation effect of radionuclides which is remarkable in higher temperature condition surrounding the repository. In order to understand in more detail the behavior of silicic acid in the presence of a solid phase, the distributions of pH around a repository and the effects of other metallic ions on the silicic acid also should be examined.

REFERENCES

1. JNC (Japan Nuclear Cycle development institute), "H12 Project to Establish the Scientific and Technical Basis for HLW Disposal in Japan, Supporting Report I, Geological Environment in Japan," Chapters V & VI (1999).
2. C. I. STEEFEL, P. C. LICHTNER, "Diffusion and reaction in rock matrix bordering a hyperalkaline fluid-filled fracture," *Geochim. Cosmochim. Acta*, **58**, 3595 (1994).
3. E. C. GAUCHER, P. BLANC, J. MATRAY, N. MICHAU, "Modeling diffusion of an alkaline plume in a clay barrier," *Applied Geochemistry*, **19**, 1505 (2004).
4. Y. NIIBORI, Y. KASUGA, H. YOSHIKAWA, K. TANAKA, O. TOCHIYAMA and H.

MIMURA, "An Experimental Approach on the Effect of Rock Alteration on Sorption Behavior," *Scientific Basis for Nuclear Waste Management XXIX (Material Research Society)*, **932**, 951 (2006).

5. N. TAMURA, Y. NIIBORI, K. IIJIMA, and H. MIMURA, "Dynamic behavior of silicic acid in the co-presence of the solid phase and Ca ions," *Proc. of WM2010*, Paper No.10120 (2010).

6. Y. NIIBORI, M. KUNITA, O. TOCHIYAMA and T. CHIDA, "Dissolution Rates of Amorphous Silica in Highly Alkaline Solution", *Journal of Nuclear Science and Technology*, **37**, 349 (2000).

7. T. CHIDA, Y. NIIBORI, O. TOCHIYAMA and K. TANAKA, "Dynamic Behavior of Colloidal Silica in the Presence of Solid Phase," *Scientific Basis for Nuclear Waste Management XXVI (Material Research Society)*, **757**, 497 (2003).

8. R. O. FOUNIER and J. J. Rowe, "The Solubility of Amorphous Silica in Water at High Temperature and High Pressure," *Amer. Mineralogist*, **62**, 1052 (1977).

9. T. CHIDA, Y. NIIBORI, O. TOSHIYAMA, H. MIMURA, K. TANAKA, "Deposition rates of polysilicic acid with up to 10^{-3} M calcium ions," *Applied Geochemistry*, **22**, 2810 (2007).

10. Y. NIIBORI, K. KOMATS and H. MIMURA**, "**Deposition of Calcium- Silicate-Hydrate Gel on Rough Surface of Granite from Calcium-rich Highly Alkaline Plume," *Scientific Basis for Nuclear Waste Management XXXV*, edited by Ricardo M. Carranza, Gustavo S. Duffó, Raul B. Rebak (Material Research Society Proceedings), **1475**, 349 (2012).

11. R.O.FOURNIER and W.L.MARSHALL,"Calculation of Amorphous Silica Solubilites at 25°C to 300°C and Apparent Cation Hydration Numbers in Aqueous Salt Solutions Using the Concept of Effective Density of Water," *Geochimica et Cosmochimica Acta*, 47,587-596(1983)

12. Y. TAKAHASHI, T.YOKOYAMA and T. TARUTANI, " Effect of the Concentraion of Sodium Chloride on the Polymerization of Silicic Acid," *Journal of the Geothermal Research Society of Japan*,**225**,235(1988)