

**Effects of pH on Deposition Rate of Supersaturated Silicic Acid around Geological Disposal System –  
15245**

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**ABSTRACT**

For the migration assessment of radionuclides around geological repository, it is important to estimate the dynamic behavior of silicic acid under a high alkalinity condition due to the cementitious materials for the construction of the repository. This study examined the pH dependencies of the deposition behavior of supersaturated silicic acid in the co-presence of solid phase. The parameters for the deposition experiments were as follow: the pH was set to 8, 9 and 10, the initial saturated concentration was set to 2-8 mM, the amount of amorphous silica (350 m<sup>2</sup>/g) as solid phase was set to 0.1-1.0 g. The experimental results showed that the initial supersaturated concentrations strongly affected the formation of colloidal silicic acid, increasing the deposition amount of silicic acid and decreasing the soluble silicic acid with time. In other words, the polymerization and the deposition of silicic acid simultaneously arose in these experiments. Furthermore, this study evaluated the apparent deposition rates of silicic acid by assuming the first-order reaction equation considering the specific surface area. As a result, the deposition rate constants,  $k$ , were in a narrow range of  $10^{-11}$  to  $10^{-10}$  m/s under all experimental conditions in this study. This means that the deposition rate constants do not depend both on pH-value (in the range from 8 to 10) and the initial concentration of supersaturated silicic acid. That is, the estimated deposition rate constants are useful in estimation of the deposition behavior of supersaturated silicic acid, such as the clogging in fractures (flow-paths) around the repository, even if the pH-value of groundwater gradually or dramatically changes.

**INTRODUCTION**

Cementitious materials for the construction of the repository of radioactive wastes would alter the groundwater up to pH 13[1]. Such high alkali groundwater is diluted with downstream natural groundwater (pH≈8). That is, the pH of the groundwater is dramatically changed around the repository system. Since silicic acid undergoes dissolution, polymerization, deposition and precipitation with the change in pH, the dynamic behavior of silicic acid is one of key factors for the performance assessment of the geological disposal system[2]. Especially, the precipitation and the deposition of silicic acid on solid phase may contribute to the retardation effect of radionuclide migration due to the clogging in flow-paths[3,4]. In order to comprehend such deposition behaviors of silicic acid around the repository, this study examined the effects of pH on the apparent deposition rates of supersaturated silicic acid in the co-presence of solid phase.

## EXPERIMENTAL

### Procedures

This study experimentally evaluated the deposition rate of colloidal (polymeric) and soluble silicic acid for estimating the altered area surrounding the repository. The main experimental procedures are the same as the previous works reported by the authors [3,4]. That is, Na<sub>2</sub>SiO<sub>3</sub> solution (water glass obtained from Wako Pure Chemical Industries, Ltd.) was diluted to a given concentration (pH>10). The initial supersaturated concentration of soluble silicic acid was given in Table I, and based on the solubility of silicic acid, i.e., 2.02 mM (298 K, pH 8), 2.30 mM (298 K, pH 9), 5.02 mM (298 K, pH 10). Pure amorphous silica (Silicic Acid (SiO<sub>2</sub>·0.23H<sub>2</sub>O)) was purchased as powder of 100 mesh-under from Mallinckrodt Co. Since micro granules or coherent aggregates of submicron particles were contained in the powder, a size fraction of 74 to 149 μm in particle diameter was separated by sieving. Its specific surface area was estimated as 350 m<sup>2</sup>/g by the BET method using nitrogen gas.

Table I is the experimental conditions. A weighed amount of the solid sample (amorphous silica powders) was poured into the polyethylene vessel. The vessel with cover had a fluid volume of 250 ml. Then, the pH of the solution was adjusted to 8, 9 or 10 with an HNO<sub>3</sub> solution and a buffer solution mixing MES (2-morpholinoethanesulfonic acid, monohydrate) and THAM (tris(hydroxymethyl)). Nitrogen was passed through the vessel to avoid contact with air. The temperature was kept constant within 298 K and it was mechanically stirred with a polypropylene stirrer.

Table I. The experiment conditions.

Initial supersaturated concentration of silicic acid	2, 4, 6, 8 mM
Addition amount of solid sample	0.1 g, 0.5g ,1.0 g
pH	8, 9, 10
Rate of stirring	300 rpm
Pore size of membrane filter	0.45 μm
Temperature	298 K

This study monitored the concentrations of each soluble silicic acid and colloidal (polymeric) silicic acid, and the amount of precipitated silicic acid. After aliquots had been filtered through the disposable membrane filter of 0.45 μm in pore size, the concentration of soluble silicic acid was determined by the silicomolybdenum-yellow method. In this study, the species of silicic acid in liquid phase were defined as soluble silicic acid and colloidal silicic acid. The concentration of soluble silicic acid was measured by the silicomolybdenum-yellow method that colors monomeric or oligomeric silicic acid only yellow with molybdate reagent. Then, the total concentration of silicic acid in liquid phase including both soluble silicic acid and colloidal form was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The deposition amount of silicic acid was defined as “the initial concentration of silicic acid” minus “the total concentration of silicic acid in liquid phase”[3,4].

## Solid Phase Sample

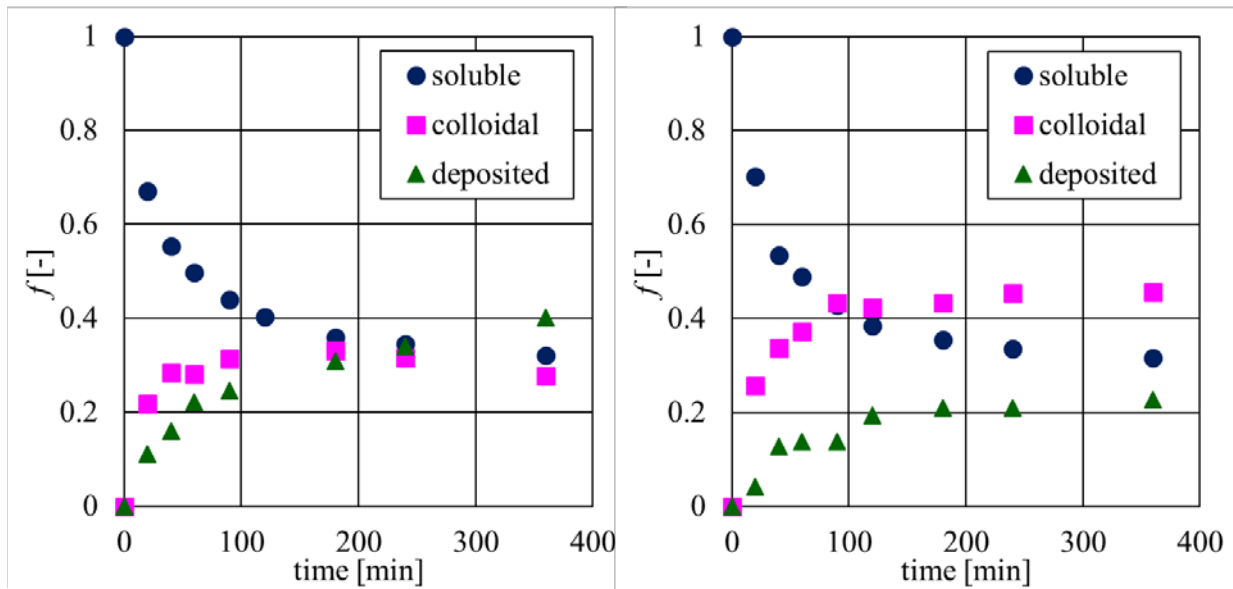
In general, flow-paths around the repository take the specific surface area larger than at least  $10^4$  (1/m). For example, if the flow-path is simply described by a parallel flat board, the specific surface area exceeds  $10^4$  when the aperture is less than 0.1 mm. Tamura et al. [4] have discussed the relation of the solid sample amount in batch experiments to an ideal flow-path. That is, when 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 weight amount of the amorphous silica,  $M$ , corresponding to the value of  $b$ , is estimated by the  $2/b=Ma/V$  (e.g., when  $b=0.1$  mm,  $M$  almost equals 0.01 g ( $a=350$  m<sup>2</sup>/g,  $V=250$  ml)). This equation yields an estimate of the relation between the flow system and the batch test through a specific surface area. Furthermore, Iler [5] has reported that the rock surface altered by the silicic acid are covered by an amorphous layer with slight thickness, even if its basement of the solid phase is crystalline. Besides, Chida et al. [6] examined the apparent solubility of soluble silicic acid in meta-stable state, using various silicate and silica minerals, from a given supersaturated condition. In the result, the solubility of soluble silicic acid controlled by each solid sample agreed with that by amorphous silica particles. As an experimental approach, this study also used amorphous silica particles in a batch test as the solid phase, in order to simulate a large specific surface area observed in flow-paths such as fractures included in rock matrix [7].

## RESULTS AND DISCUSSION

Figs. 1, 2 and 3 are the experiment results which the initial supersaturated concentration was set to 8 mM. The initial supersaturated concentration,  $(C_{ini}-C_e)$ , was set to 2 mM to 8 mM, where  $C_{ini}$  is the initial concentration of soluble silicic acid and  $C_e$  is the solubility of silicic acid in the presence of amorphous silica mentioned above. The vertical axis,  $f$ , in these figures is the fraction of soluble silicic acid, colloidal silicic acid and deposited silicic acid to the initial concentration of soluble silicic acid. As shown in Figs. 1-3, the amounts of both colloidal silicic acid and deposition increase as soluble silicic acid decreases with time. These whole tendencies did not depend on the initial supersaturated concentration. Regarding the deposition of silicic acid, the influence of the amount of solid phase were much larger than other parameters including pH. This means that the surface area is a predominant factor for the deposition of silicic acid. On the other hand, the fractions of soluble silicic acid for pH 10 were kept very high. These fraction values (about 0.55) are equivalent to about 6 mM, which is much higher than the solubility at pH 10 (2.95 mM). We need more detail investigation to understand such a certain kind of metastable state.

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 constants. Practically, by applying the first-order reaction equation to the initial gradient of  $f$  (calculated by three data next to time 0), this study estimated the apparent deposition rate-constants,  $k'$  (1/s) under various conditions. Since the apparent rate-constants were linear to specific surface area,  $a$ , we can obtain the rate-constant  $k$  (m/s) by using  $k' = ak$ , where  $a$  is specific surface area (1/m) defined by BET surface area (m<sup>2</sup>/g)  $\times$  weight amount of solid phase (g) / the solution volume (m<sup>3</sup>). Table II summarizes the obtained rate-constants as function of both the

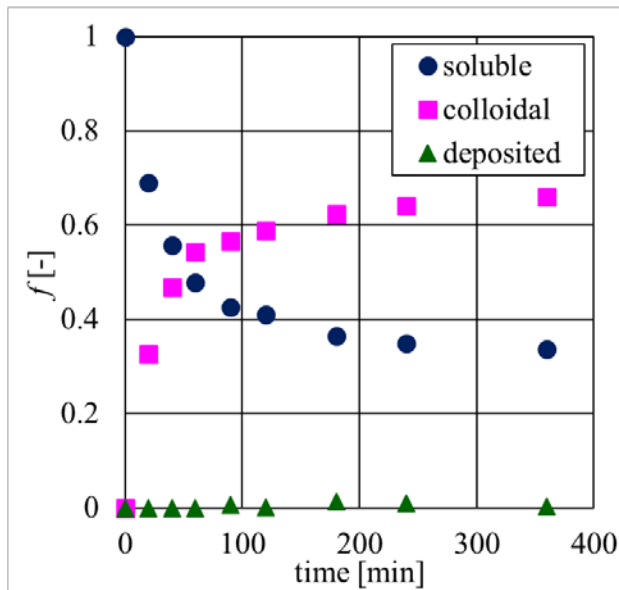
supersaturated concentration and pH. In the results, the deposition rates of silicic acid were in the narrow range of  $10^{-11}$  to  $10^{-10}$  m/s under all experimental conditions. This suggests that the deposition rate



constants of silicic acid do not depend on pH and the initial supersaturated concentration.

(a)

(b)



(c)

Fig.1. Deposition of silicic acid on solid phase. (pH 8)

(a) 1.0 g, (b) 0.5 g, (c) 0.1g (Initial supersaturated concentration: 8 mM, Solid sample: Mallinckrodt silica powder, pore size of filter: 0.45  $\mu\text{m}$ )

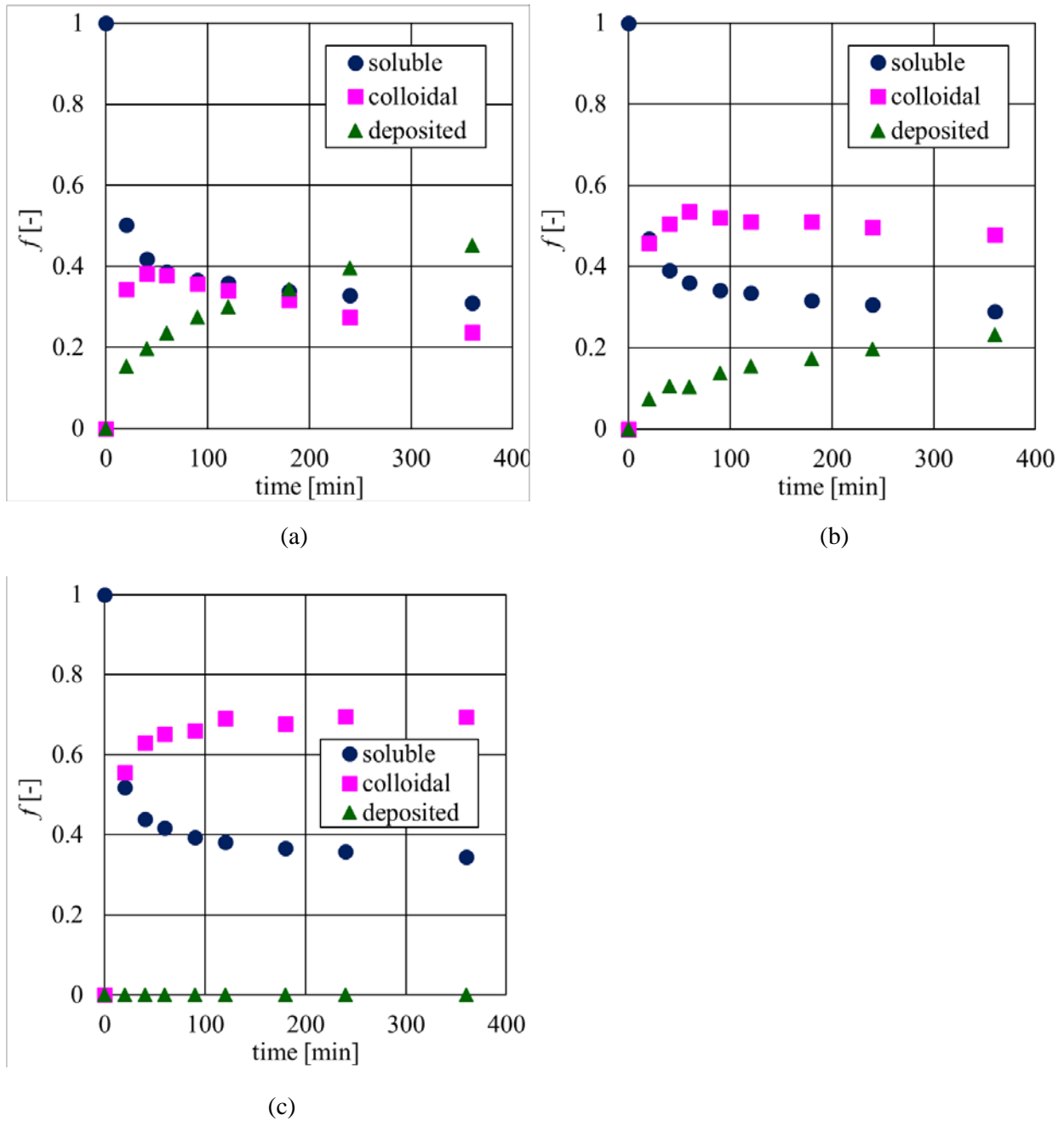
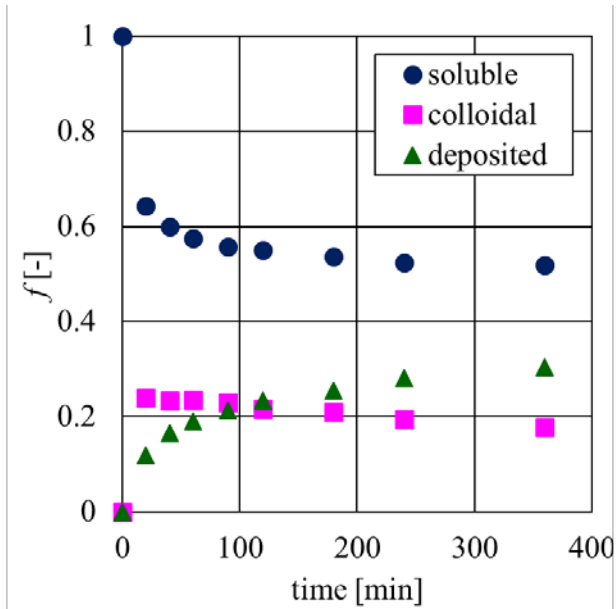
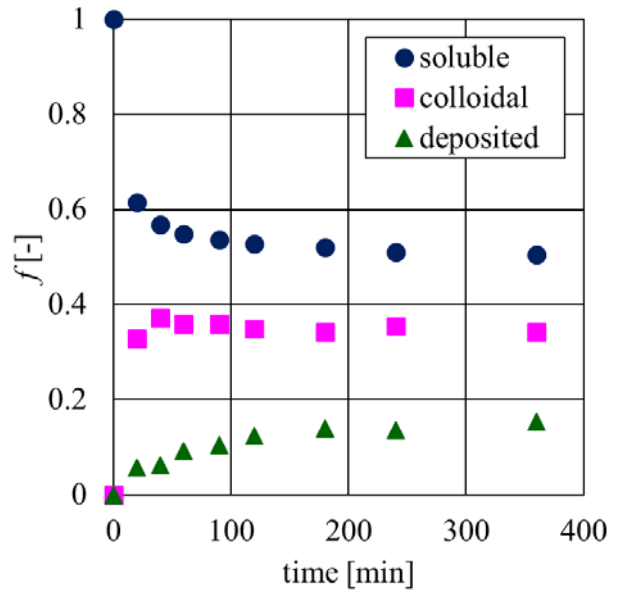


Fig.2. Deposition of silicic acid on solid phase. (pH 9)

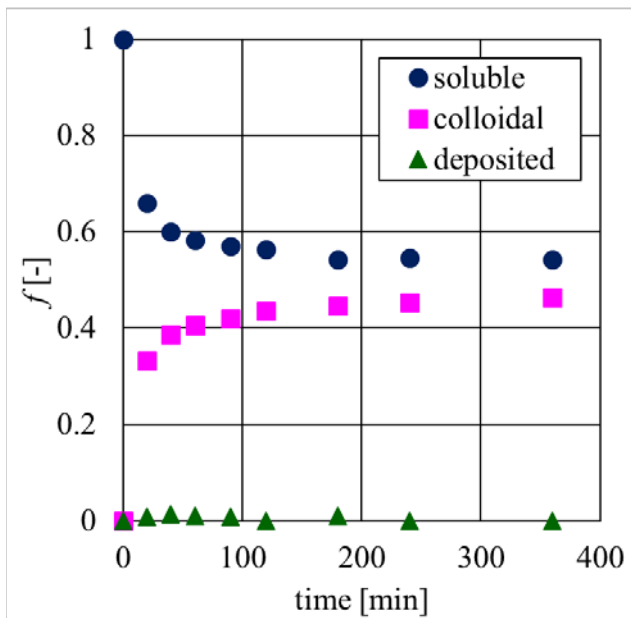
(a) 1.0 g, (b) 0.5 g, (c) 0.1g (Initial supersaturated concentration: 8 mM, Solid sample: Mallinckrodt silica powder, pore size of filter: 0.45  $\mu\text{m}$ )



(a)



(b)



(c)

Fig.3. Deposition of silicic acid on solid phase. (pH 10)

(a) 1.0 g, (b) 0.5 g, (c) 0.1g (pH 10) (Initial supersaturated concentration: 8 mM, Solid sample: Mallinckrodt silica powder, pore size of filter: 0.45  $\mu\text{m}$ )

Table II. Deposition rate-constant,  $k$  [m/s].

Deposition rate-constant $k$ [m/s]		pH		
		8	9	10
Initial supersaturated concentration [mM]	2.0	$4.25 \times 10^{-11}$	$6.70 \times 10^{-10}$	$8.05 \times 10^{-11}$
	4.0	$1.70 \times 10^{-10}$	$3.47 \times 10^{-11}$	$1.60 \times 10^{-11}$
	6.0	$4.38 \times 10^{-11}$	$1.15 \times 10^{-10}$	$7.59 \times 10^{-11}$
	8.0	$1.90 \times 10^{-10}$	$3.42 \times 10^{-11}$	$4.29 \times 10^{-11}$

Now, consider the one-dimensional, advection-dispersion model including the deposition rate [3,8].

$$B \frac{\partial C}{\partial T} = -\frac{\partial(BUC)}{\partial X} + \frac{1}{P_{ef}} \frac{\partial}{\partial X} (BD' \frac{\partial C}{\partial X}) - D_a C \quad (1)$$

This formula is described by using non-dimensional form, i.e.,  $B=b/b^*$ ,  $U=u/u^*$ ,  $C_f=(C-C_e)/(C_{ini}-C_e)$ ,  $T=t/t^*$  ( $t^*=x_1/u^*$ ) and  $P_{ef}=u^* x_1/D_f^*$ ,  $D'=D_f/D_f^*$  and  $D_a=kt^*/b^*$ , where  $x_1$  is the characteristic length (length of flow path) (m),  $D_f$  is the dispersion coefficient ( $\text{m}^2/\text{s}$ ),  $k$  is the deposition rate constant of silicic acid as defined in this study,  $b$  is the aperture of flow-path (m),  $u$  is Darcy flow velocity of groundwater (m/s), and the super subscript “\*” denotes the initial condition. 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  $[0, x_1]$ . When the volumetric flow rate is constant,  $BU$  in Eq. (1) is equal to 1. In addition, when  $D_f$  is approximated by  $\alpha u$  ( $\alpha$  is the dispersion length (m),  $\alpha=0.1x_1$ ), i.e.,  $\alpha u$  is assumed to be large enough than the diffusion coefficient,  $BD'$  in equation (1) also becomes 1. Then, the change of the aperture at an arbitrary  $x$  can be described by  $-dB/dT=D_a\gamma C$ , where  $\gamma = (C_{ini}-C_e)/\rho_M$ ,  $\rho_M$  is a conversion factor ( $\text{mol}/\text{m}^3$ ) (the density of the deposit ( $\text{kg}/\text{m}^3$ ) divided by the molar mass ( $\text{kg}/\text{mol}$ )). Then, the normalized over-all permeability  $K_p (=k_p/k_{p0}$ , where  $k_p$  ( $\text{m}^2$ ) is approximated by  $b^2/12$ ) yields.

$$K_p = 1 / \left( \int_0^1 \frac{1}{B^2} dX \right) \quad (2)$$

Eq. (1) and  $-dB/dT=D_a\gamma C$  were 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 pressure gradient is constant, assuming the change in flow velocity with the decrease of the aperture. The initial conditions (at  $T=0$ ) are  $C=0$  and  $B=1$  in the range of  $0 \leq X \leq 1$ . This model has two non-dimensional parameters: The Peclet number,  $P_{ef}$ , and the Damköhler number,  $D_a$ . Of them, the value of the Peclet number is 10 (because  $D_f^*$  is approximated by  $\alpha u^*$ , and  $\alpha=0.1$  as mentioned above). Furthermore, this study assumed  $u^*=5$  m/year,  $50$  m/year,  $x_1=100$  m,  $b^*=1.0 \times 10^{-4}$  m [9], and  $(C_{ini}-C_e)=0.1$  mM. These values determine the value of  $D_a$  by using the deposition rate constant  $k$  as shown in Table II.

Fig. 4 show the calculation results of the aperture of flow-path (at  $X=0$ ). As the deposition rate constant,  $k$ , the lowest value ( $k=1.60 \times 10^{-11}$  for pH 10) were selected for these calculation. As shown in Fig. 4, even in the case of the latest clogging, the aperture of flow-path is clogged after about 200 years by the deposition of silicic acid. Around the geological repository, the pH of groundwater gradually and dramatically undergoes the change in the range from 8 to 13 due to cementitious materials until thousands years later [10]. Under such a condition, the retardation effect of radionuclides may be caused by the clogging of flow-path with the deposition of the supersaturated silicic acid around the repository.

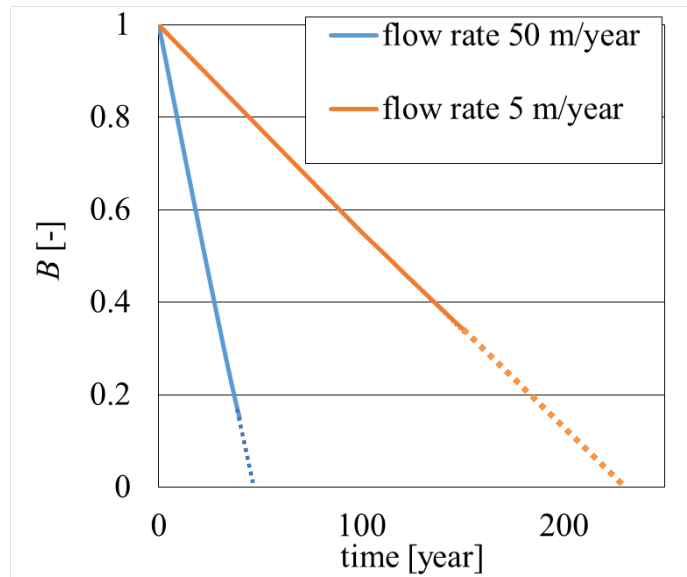


Fig. 4. The calculation results of the aperture at  $X=0$ . ( $k=1.60 \times 10^{-11}$  for pH 10). (Note that the value of  $B$  diverges in the numerical implementation, when  $B$  is approaching 0.)

## CONCLUSIONS

This study discussed the effects of pH on the deposition behavior of silicic acid in the co-presence of solid phase. In the results, the deposition rate constants of silicic acid were in the narrow range of  $10^{-11}$  to  $10^{-10}$  m/s for the pH in the range from 8 to 10 and the initial supersaturated concentrations. This means that the deposition rates of silicic acid under the condition of this pH range do not depend on the change in pH and the supersaturated condition of silicic acid. That is, such estimated deposition rate constants are applicable to the estimation of the clogging in flow-path and the alteration of solid surface with the deposition of silicic acid. The spatial distribution of supersaturated silicic acid around the geological repository would be also required in order to estimate more realistic clogging-effect.



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