

**Dynamic behavior of silicic acid in the co-presence of  
the solid phase and Ca ions – 10120**

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**ABSTRACT**

A main concern about cement materials for the construction of the repository is altering the groundwater to high alkalinity around the repository. Under such chemical condition, the behavior of the silicic acid is one of the key factors to estimate the initial condition of the repository system after the backfill. Since the solubility of silicic acid is extremely large in pH larger than 10, the silicic acid is supersaturated by mixing with the surrounding groundwater (pH 8).

Supersaturated silicic acid would produce the polymeric silicic acid even in the presence of a solid phase (i.e., the flow-path surface). Such polymeric silicic acid also deposits gradually onto the flow-path surface while flowing downstream from the repository. However, the precipitation (or deposition) alters the surface to an amorphous one, which in turn strongly affects the sorption behavior of radionuclides. To estimate the spatial spread of the altered surface around the repository, this study examined the dynamic behaviors of supersaturated silicic acid in the co-presence of the solid phase and Ca ions.

To determine the concentrations of both soluble silicic acid and its polymeric (colloidal) form in the solution, this study used the silicomolybdenum-yellow method and ICP-AES. As a silicate mineral, Mallinckrodt silicic acid powder ( $\text{SiO}_2 \cdot 0.23\text{H}_2\text{O}$ , specific surface area  $350 \text{ m}^2/\text{g}$ ) was used. A  $\text{Na}_2\text{SiO}_3$  solution was diluted to a given concentration as a sample solution (pH>10), then the pH value of the solution was adjusted to 8 in the co-presence of the solid phase and Ca ions (1.0 mM). The amount of solid phase was within the range of 0.1 g to 1.0 g. The concentrations of the soluble silicic acid, the polymeric silicic acid and Ca ions in the solution were monitored.

This study evaluated the decrease rate, using the first-order reaction equation considering the specific surface area. In the results, the apparent rate constant,  $k$ , was  $4.9 \times 10^{-11} \text{ m/s}$ , smaller than that under the Ca ion free condition ( $k=2.0 \times 10^{-10} \text{ m/s}$ ). This means that Ca ions obstruct the deposition of silicic acid onto the surface. Moreover, the polymeric silicic acid was obviously observed, although the polymeric silicic acid could not be detected under the Ca ion free condition when the initial supersaturated concentration of silicic acid was less than 5 mM. In addition, the concentration of Ca ions in the solution immediately decreased down to 0.4 in

fraction, due to the contact with the solid phase of  $\text{SiO}_2$ . After that, the fraction of Ca ions was kept at 0.4 in the solution. These suggest that Ca ions played two roles in producing the polymeric silicic acid in the presence of the solid phase. One is that Ca ions altered the surface of the  $\text{SiO}_2$  solid phase by producing CSH gel on the surface of the solid phase. Such alteration affects the chemical property of the surface, also changing the surface area. The other is that the remaining Ca ions in the solution played a role in producing polymeric silicic acid as a pseudo-colloid. (Contrarily, it was confirmed that, when the Ca ion concentration exceeds 10 mM, the supersaturated silicic acid immediately produces the bridged compound and drops on the surface.) To estimate the altered surface due to polymeric silicic acid, we need a more reliable model to estimate these roles of Ca ions at less than 1.0 mM in the presence of silicic acid of a relatively low concentration such as 5 mM.

## INTRODUCTION

In Japan, the high-level radioactive waste (HLW) generated by nuclear power plants is scheduled to be disposed of in an underground repository deeper than 300 m. It is necessary to study nuclide migration in the performance assessment of the repository system. In this nuclide migration, the retardation effect by the interaction of radionuclides and the host rock in the surroundings is expected. However, it is pointed out that a colloidal silicic acid may obstruct the sorption of radionuclides showing large influence on nuclide migration.

A large amount of cement material will be used to construct the repository and the use of such materials would alter the groundwater to high alkalinity ( $\text{pH} > 12$ ). Such groundwater of high alkalinity is gradually diluted with the surrounding groundwater of natural acidity ( $\text{pH} 8$ ), flowing downstream. Thus, it is thought that the area where the acidity of groundwater dramatically changes exists around the repository site (hereinafter referred to as the “alkali-front”).

The solubility of the silicic acid, supplied from silicate minerals that form the host rock, is known to be sensitive to the change in the acidity. That is, the solubility is very large in the alkaline range compared with the neutral range. Therefore, the silicic acid in the high alkaline water becomes supersaturated at the “alkali-front”, forming polymeric (colloidal) silicic acid and finally depositing on the surface of the rock. Such a precipitation (or deposition) alters the surface of the solid phase (i.e., the flow-path surface) to an amorphous type, which in turn may affect the sorption behavior of radionuclides (e.g., [1-4]). In order to estimate the spatial spread of the altered surface around the repository, this study examined the dynamic behaviors of supersaturated silicic acid in the co-presence of solid phase and Ca ions.

## EXPERIMENTAL

### Samples

$\text{Na}_2\text{SiO}_3$  solution (water glass obtained from Wako Pure Chemical Industries, Ltd.) was diluted to a given concentration, that is, 6.74 mM, as a sample solution ( $\text{pH} > 10$ ). Pure amorphous silica

(Silicic Acid ( $\text{SiO}_2 \cdot 0.23\text{H}_2\text{O}$ )) was purchased as powder of 100 mesh-under from Mallinckrodt Co. Since small granules or coherent aggregates of submicron particles were contained in the powder, a size fraction of 74 to 149  $\mu\text{m}$  in particle diameter was separated by sieving [5]. Its specific surface area was estimated as 350  $\text{m}^2/\text{g}$  by the BET method using nitrogen gas.

## Procedures

The experimental procedure is as follows [6-8]: Nitrogen was passed through the vessel to avoid contact with air. The polyethylene vessel with cover had a fluid volume of 245 ml. The silicic acid solution prepared by dissolving water glass in distilled ultrapure water was put into the vessel and mechanically stirred with a polypropylene stirrer. The temperature was kept constant within  $298 \pm 0.5$  K. A weighed amount of the amorphous silica (the range of 0.1 g to 1.0 g) was poured into the vessel. The Ca ion concentration was set to 1.0 mM (prepared from  $\text{Ca}(\text{NO}_3)_2$ ). Then, the pH of the solution was set to 8 with an  $\text{HNO}_3$  solution and a buffer solution mixing MES (2-morpholinoethanesulfonic acid, monohydrate) and THAM (tris(hydroxymethyl)). This study monitored the concentrations of both soluble silicic acid and colloidal (polymeric) silicic acid, and the amount of precipitated silicic acid.

## Measurement of silicic acid

In the experiment, the concentration of soluble silicic acid was determined by the silicomolybdenum-yellow method, after aliquots had been filtered through the disposable membrane filter of pore size 0.20  $\mu\text{m}$  or 0.45  $\mu\text{m}$ . In this study, soluble silicic acid (monomeric or oligomeric silicic acid) was defined as silicic acid reacting with molybdate reagent and coloring yellow, and polymeric silicic acid was defined as silicic acid in liquid phase except for soluble silicic acid. Its total concentration of silicic acid was measured by inductively-coupled plasma atomic emission spectrometry (ICP-AES). The concentration of precipitated silica is equal to the initial concentration of soluble silica minus the total concentration of silicic acid in soluble and colloidal forms. Therefore, to obtain the precipitated amount of silicic acid, this study used the following Eq. 1.

$$\begin{aligned} \text{Amount of precipitated silicic acid} &= \text{Initial amount of silicic acid} \\ &\quad - (\text{Amount of soluble silicic acid} + \text{Amount of colloidal silicic acid}). \end{aligned} \quad (\text{Eq. 1})$$

## RESULTS AND DISCUSSION

Figures 1 show an example of the dynamic behaviors of both soluble silicic acid and colloidal silicic acid, where the initial concentration of silicic acid was set to 6.74 mM, and the amount of solid sample (amorphous silica) was changed within the range of 0.1 g to 1.0 g. The initial supersaturated concentration,  $C_{\text{ini}} - C_e$ , was set to 4.8 mM, where  $C_{\text{ini}}$  is the initial concentration of soluble silicic acid (pH>10) and  $C_e$  is the solubility of soluble silicic acid (pH=8) in the presence of amorphous silica. The vertical axis,  $f$ , in Fig.1 is the fraction of soluble silicic acid, colloidal form and precipitated silica to the initial concentration of soluble silica. As shown in Fig.1, the

amount of colloidal silicic acid and precipitated silicic acid increased, while the amount of soluble silicic acid decreased. Moreover, the precipitation amount of the silicic acid has increased greatly with increments of the addition amount of the solid phase.

To evaluate the decrease rate of the soluble silicic acid, this study assumed one-order reaction considering the specific surface area:

$$r_{ini} = \left. \frac{dC_s}{dt} \right|_{t=0} = -kA(C_{ini} - C_e) \quad (\text{Eq. 2})$$

where  $t$  (s) is time,  $k$  is the apparent decrease-rate-constant (1/s),  $A$  is the specific surface area,  $C_s$  is the concentration of the soluble silicic acid and  $C_{se}$  is the solubility of soluble silicic acid (pH=8).

Figure 2 is the apparent decrease-rate-constants of  $k$ , respectively, where the specific surface area  $A$  is defined by  $aM/V$  ( $a$  is the BET (N<sub>2</sub> gas) surface area (m<sup>2</sup>/g),  $M$  is the addition amount of the solid phase (g), and  $V$  is the solution volume (m<sup>3</sup>)). As shown in Fig. 2, the rate constant in logarithm form is almost linear to the specific surface area.

If the specific surface area of a fracture with aperture  $b$  (m) is approximately calculated by  $2/b$ , the amount of the amorphous silica,  $M$ , corresponding to the value of  $b$  is estimated by the following Eq. 3.

$$\frac{2}{b} = \frac{M \times a}{V} \quad (\text{Eq. 3})$$

For example, when  $b=0.1$  mm,  $M$  almost equals 0.01 g ( $a=350$  m<sup>2</sup>/g,  $V=245$  ml). Of course, the practical fracture surface is not a parallel flat plate, but Eq. 3 makes 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 in a batch test as the basement of the solid phase, in order to simulate a large surface area shown in flow-paths.

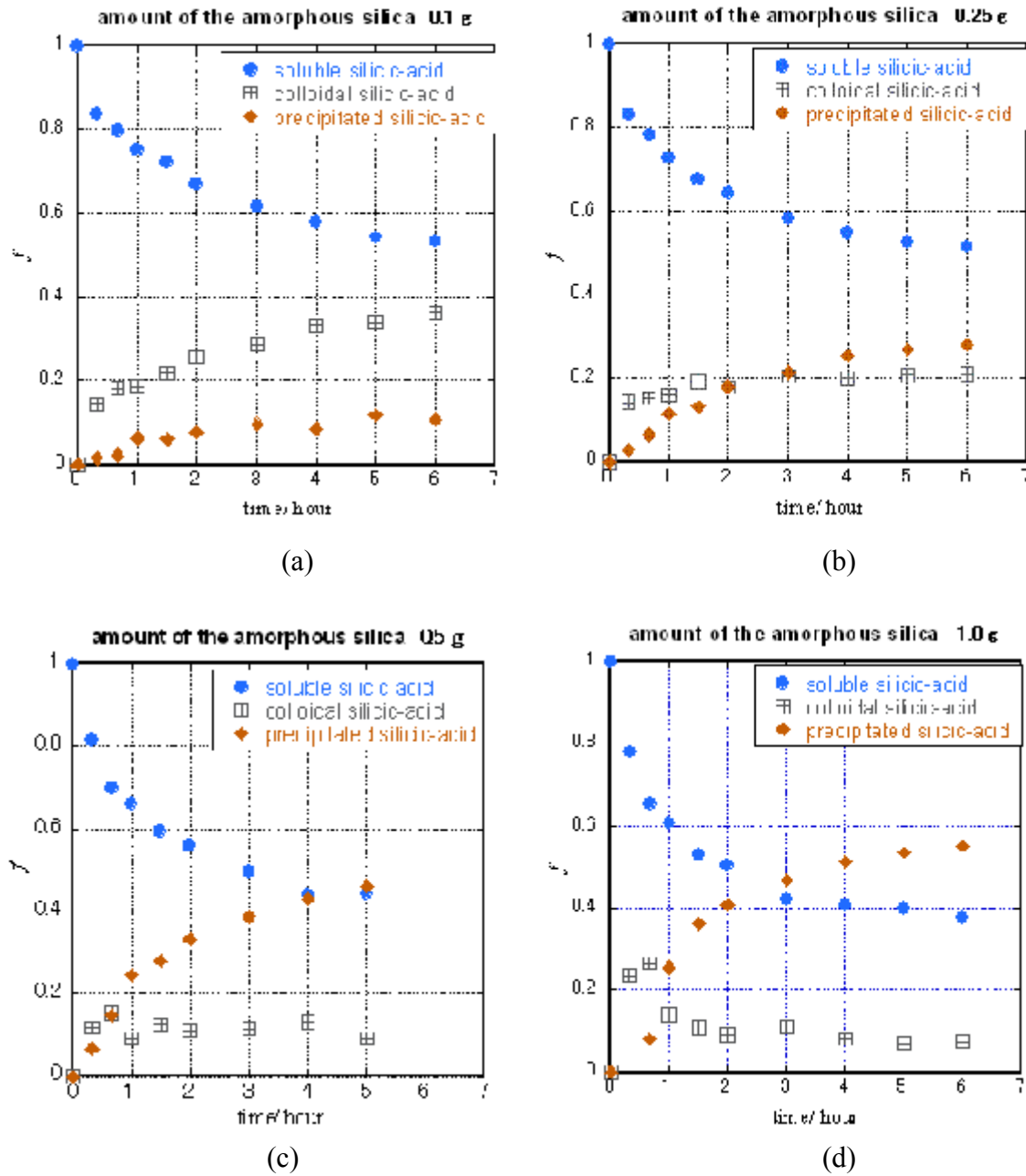


Fig.1. The dependence of the deposition behavior on the amount of the solid phase. (a) 0.10 g, (b) 0.25 g, (c) 0.50 g and (d) 1.0 g (Initial supersaturated concentration: 4.8 mM, Solid sample: Mallinckrodt silica powder, pore size of filter: 0.20  $\mu\text{m}$ )

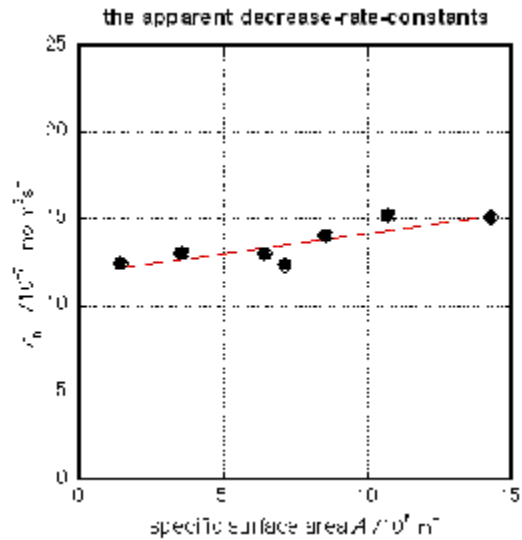


Fig.2. The relationship between the decrease rate constant of soluble silicic acid and specific surface area under the condition of Ca ions.

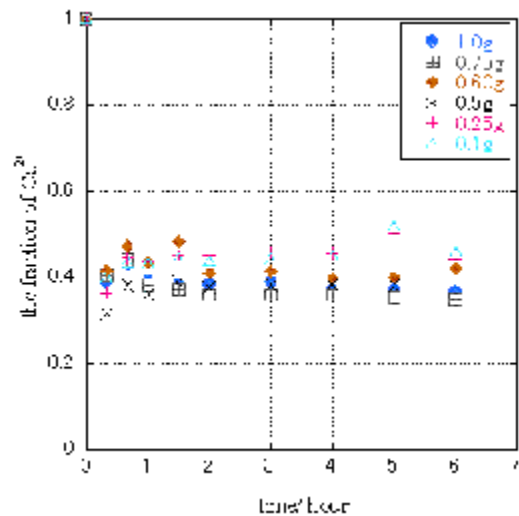


Fig.3. Temporal change of Ca ion fraction

From the result of Fig. 2, the apparent rate constant,  $k$ , was estimated to be  $4.9 \times 10^{-11}$  m/s, smaller than that under the Ca ion free condition ( $k=2.0 \times 10^{-10}$  m/s)[7, 8]. This means that Ca ions obstruct the deposition of silicic acid onto the surface. Moreover, the polymeric silicic acid was definitely observed, though the polymeric silicic acid could not be detected under the Ca ion free condition in  $C_{ini}-C_e < 5$  mM. Figure 3 shows the concentration of Ca ions in the solution. In the results, the concentration of Ca ions immediately decreased down to 0.4 in fraction, due to the contact with the solid phase of  $\text{SiO}_2$ . After that, the fraction of Ca ions was kept at 0.4 in the solution. The tendency did not depend on the addition amount of the solid phase.

These suggest that Ca ions played two roles affecting the behaviors of silicic acid in the presence of the solid phase. One is that Ca ions altered the surface of the  $\text{SiO}_2$  solid phase by producing CSH gel on the surface of the solid phase. Such alteration affects the chemical property of the surface, also changing the surface area. The other is that the remaining Ca ions in the solution played a role of forming polymeric silicic acid as a pseudo-colloid. (Contrarily, it was confirmed that, when the Ca ion concentration exceeds 10 mM, the supersaturated silicic acid immediately produces the bridged compound and drops on the surface.)

Figure 4 shows SEM images of the solid phase samples. As shown in Fig. 4(c), we can confirm a deposit on the surface of the solid phase. Usui et al. [9] reported that the deposit is calcium silicate hydrate (CSH) gels. In fact, such deposit was not confirmed under the Ca ion free condition. The deposit would decrease the surface area of BET by covering the solid surface [6].

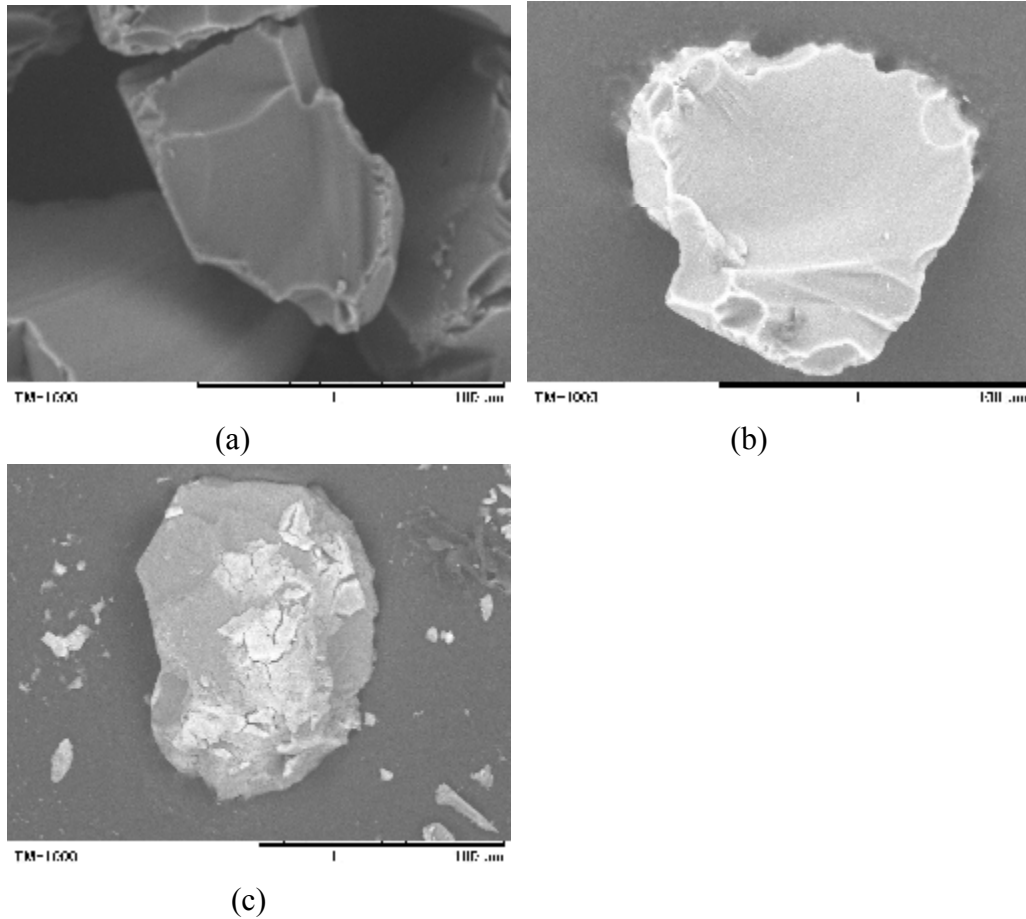


Fig. 4. SEM images of the solid phase sample ((a) Solid phase sample before the batch test, (b) Solid sample that has passed 4 hours after the start of the examination (0.75 g, 0.20  $\mu\text{m}$ ), and (c) Solid sample submerged for over 5 days in a silicic acid solution of the supersaturated condition.)

As mentioned above, the apparent rate constant of the soluble silicic acid under the Ca ion coexistence was about 1/4 smaller than that under the Ca ion free condition. However, this rate-constant seems large enough to limit the spatial region altered by the deposit of the soluble silicic acid. For example, consider the one-dimensional, advection-dispersion model including the precipitation rate of soluble silicic acid, as follows:

$$\frac{\partial C_s}{\partial T} = -\frac{\partial C_s}{\partial X} + \frac{1}{P_e} \frac{\partial^2 C_s}{\partial X^2} - D_a C_s. \quad (\text{Eq.4})$$

This formula is described in non-dimensional form, i.e.,  $C_s = (C - C_e) / (C_{ini} - C_e)$ ,  $T = t / t^*$  ( $t^* = x_1 \varepsilon / u_0$ ) and  $P_e = u_0 x_1 / D_e$  and  $D_a = x_1 A k / u_0$ , where  $x_1$  is the characteristic length (length of flow-path) (m),  $\varepsilon$  is porosity (-),  $D_e$  is the dispersion coefficient ( $\text{m}^2/\text{s}$ ) and  $u_0$  is the fluid flow velocity of groundwater (m/s). This model has two parameters: Peclet number,  $P_e$ , and Damkohler number,  $D_a$ . Generally, the value of the Peclet number is smaller than  $10^2$ . On the other hand, assuming

$u_0=1$  (m/year)  $=3.2 \times 10^{-8}$  (m/s),  $x_1=10$  m,  $A=10^6$  (1/m) [10] and  $k=2.0 \times 10^{-10}$ ,  $D_a$  is estimated to be larger than  $10^4$ . Table I indicates  $D_a$  estimates. Such a large value of  $D_a$  suggests that the altered range is sufficiently limited around the repository.

Table I.  $D_a$  estimated from  $k$  under each condition.

	Ca ion coexistence	Ca ion free
The apparent rate constant $k$	$4.0 \times 10^{-11}$	$2.1 \times 10^{-10}$
Damkohler number $D_a$	$1.25 \times 10^4$	$6.56 \times 10^5$

Furthermore we have to focus also on the dynamic behavior of the polymeric (colloidal) silicic acid in the presence of a solid phase. Chida et al. [7] reported that such polymeric silicic acid also gradually precipitates on the surface of the solid surface. However, in the results, the concentrations of polymeric silicic acid were relatively scattered compared to those of soluble silicic acid. Depending on the combination of the initial supersaturated concentration, the concentration of Ca ions and the addition amount of the solid phase, the behaviors seem different. Moreover, the behavior may also depend on the filter size used for classification into the polymeric silicic acid and the deposit amount of silicic acid.

Figure 5 shows the comparison of experimental results for filter pore sizes of 0.20  $\mu\text{m}$  and 0.45  $\mu\text{m}$ . As shown in the results, the effect of filter size on the dynamic behavior of silicic acid is small. These results mean at least that the size of colloidal silicic acid is smaller than 0.20  $\mu\text{m}$ . In other words, the size of precipitated silicic acid is larger than 0.45  $\mu\text{m}$ . Moreover, as shown in, e.g., the result of Fig.5(c), if the decrease rate constant of colloidal silicic acid is one tenth of that of soluble silicic acid, the value of the Damkohler number,  $D_a$ , proportionally becomes small. This suggests the altered surface area would spread, depending on the local flow-velocity of groundwater around the repository. In addition, since the colloidal silicic acid plays a role as a source to supply soluble silicic acid, we will need to monitor not only the decrease rate but also the size distributions of colloidal silicic acid.



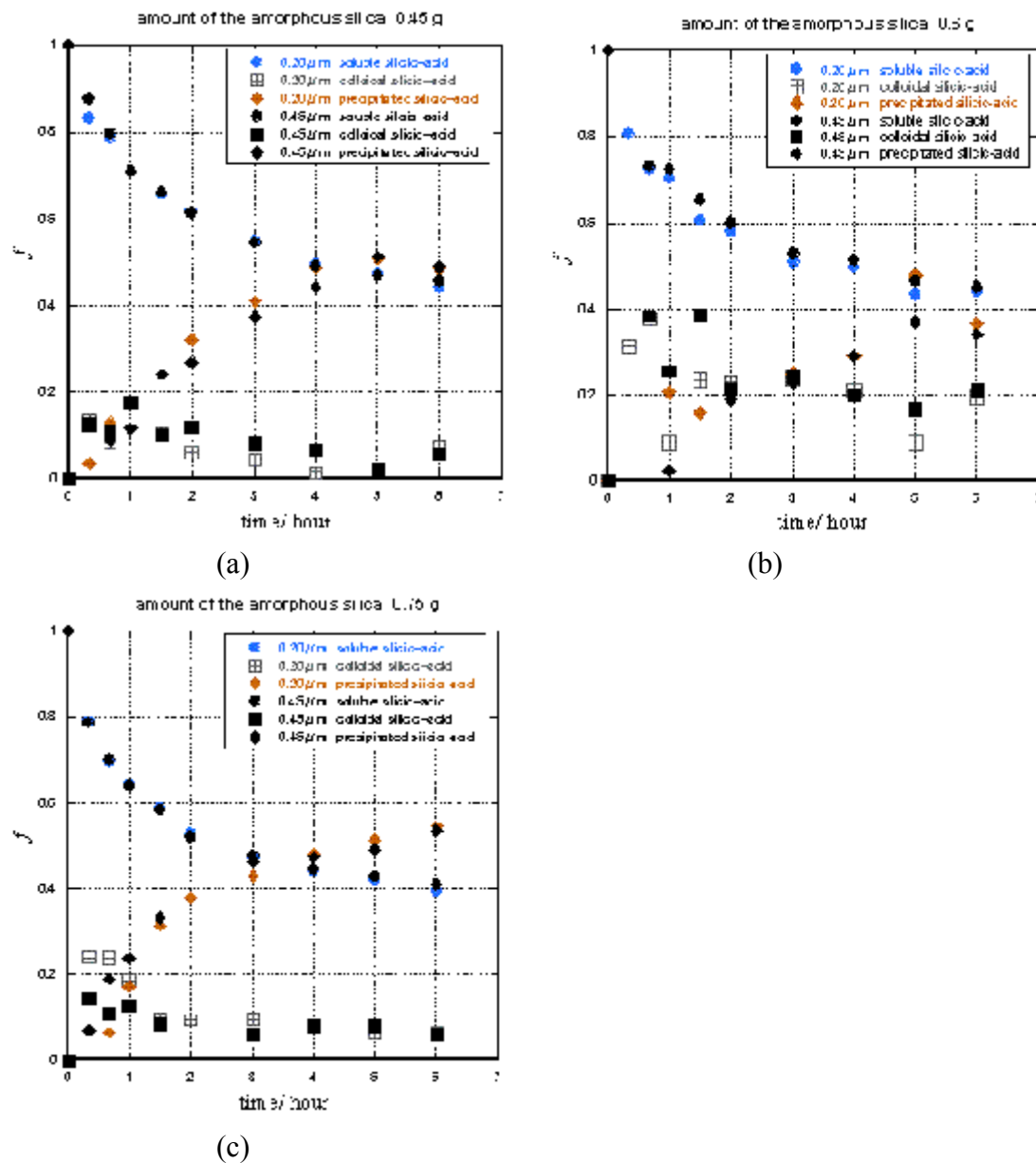


Fig.5. Comparison of the results of experiments with different filter pore sizes; 0.20 and 0.45 μm ((a) 0.45 g, (b) 0.6 g, and (c) 0.75 g).

## CONCLUSIONS

This study examined the dynamic behavior of silicic acid in the co-presence of a solid phase and Ca ions. In the results, the apparent deposition rate-constant,  $k$ , was  $4.9 \times 10^{-11}$  m/s, smaller than that under the Ca ion free condition ( $k=2.0 \times 10^{-10}$  m/s). This means that Ca ions obstruct the deposition of soluble silicic acid onto the surface. Moreover, the polymeric silicic acid was definitely observed, although the polymeric silicic acid could not be detected under the Ca ion free condition with less than 5 mM in the initial supersaturated concentration. These influences

of Ca ions suggest the possibility of expanding the spatial range altered by the silicic acid. To estimate the altered surface area due to polymeric silicic acid, we need a more reliable model to estimate these roles of Ca ions at less than 1.0 mM, even under the condition of low supersaturated concentration such as 5 mM.

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