

## Deposition Rates of Polymeric Silicic Acid onto the Surface of Silicate Minerals in the Co-presence of Ca Ions – 11378

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### ABSTRACT

The concentration of Ca ions in the groundwater predicted around a hypothetical repository of radioactive wastes in Japan is envisaged to be in the range from 1 mM to about 10 mM. Within this range, this study evaluated the deposition rate of polymeric silicic acid by using the first-order reaction equation considering the specific surface area. The smallest value of  $k$  was  $1.0 \times 10^{-12}$  m/s in the co-presence of Ca ions of 1 mM. While the deposition rate dramatically increased due to the bridging of colloidal silicic acid when the concentration of Ca ions was 10 mM, the rate-constant under the Ca free condition also exceeded that of Ca 1 mM. That is, Ca ions strongly affect the deposition rate of colloidal silicic acid around the repository. Furthermore, it was confirmed that the zeta potential can explain such a dynamic behavior of the colloidal silicic acid. Besides, this study estimated the Damköhler number,  $D_a (\equiv x_1 A k / u_0)$ , 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 dimensionless parameter controls the spatial range altered by the deposition of colloidal silicic acid around the repository. In the results, although the relative low concentration of Ca ions (<10 mM) obstructs the deposition of colloidal silicic acid, the obtained value of  $D_a$  suggested that the altered range is sufficiently limited around the repository when the flow-velocity of groundwater is around 1 m/year.

### INTRODUCTION

As in many other countries, it is assumed that groundwater around any future repository for radioactive wastes in Japan would become highly alkaline due to the use of cement-based structural materials [1]. Such altered groundwater is diluted with surrounding groundwater in the downstream region. Therefore, we should consider a chemical/physical alteration in the spatial domain dramatically changing pH (e.g., from 12 to around 8). Particularly, the silicic acid dissolves to the highly alkaline groundwater and then forms a supersaturated condition in the downstream region. Supersaturated silicic acid produces the polymeric silicic acid (colloidal-silicic acid) even in the presence of a solid phase (i.e., flow-path surface). Since the deposition rate is smaller than that of soluble silicic acid, the colloidal silicic acid deposits gradually onto the flow-path surface while flowing downstream from the repository. That is, such a low deposition rate of the colloidal silicic acid would alter the surface to an amorphous type, which in turn affects the sorption behavior of radionuclides (e.g., [1-4]) and the permeability of the flow paths. Therefore, the estimate of the spatial spread altered around the repository is very important in assessing the repository performance.

In a previous work [5], the authors examined the deposition rate-constant under the condition of 1 mM Ca ions. However, its concentration was insufficient to know the deposition behavior in a wider range of Ca ion concentration. Therefore, considering its concentration range in normal groundwater, i.e., from 1 mM to 10 mM, this study examined the deposition rate-constants of colloidal silicic acid defined by the first-order reaction equation under various conditions of co-presence of amorphous silica. Then, using the smallest rate-constant, the Damköhler number,  $D_a$ , was estimated in order to know the spatial range altered by supersaturated silicic acid. In its estimation processes of  $D_a$ , the realistic values (not only the rate-constant, but also, the fluid flow-velocity, the specific surface area of flow-paths and so on) are required. Hypothetical values used in this study were taken from Japan Nuclear Cycle's (now Japan Atomic Energy Agency's) H12 report [1].

## EXPERIMENTAL

### Procedures

This study experimentally evaluated the deposition rate of colloidal (polymeric) silicic acid necessary for estimating the altered area. 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 contact with air. The temperature was kept constant within  $298 \pm 0.5$  K and it was mechanically stirred with a polypropylene stirrer.  $\text{Na}_2\text{SiO}_3$  solution (water glass obtained from Wako Pure Chemical Industries, Ltd.) was diluted to a given concentration ( $\text{pH} > 10$ ). The initial supersaturated concentration of soluble silicic acid was given, based on the solubility of silicic acid, 1.94 mM (298 K, pH 8). 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. Its specific surface area was estimated as  $350 \text{ m}^2/\text{g}$  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 vessel. The Ca ions were prepared from  $\text{Ca}(\text{NO}_3)_2$ . Then, the pH of the solution was adjusted to 8 with an  $\text{HNO}_3$  solution and a buffer solution mixing MES (2-morpholinoethanesulfonic acid, monohydrate) and THAM (tris(hydroxymethyl)).

Table I. The experiment 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
Ca ions concentration	0.1 mM, 1.0 mM, 10 mM
pH	8
Rate of stirring	300 rpm
Pore size of membrane filter	0.20 $\mu\text{m}$ , 0.45 $\mu\text{m}$
Temperature	$298 \pm 0.5$ K

This study monitored the concentrations of each soluble silicic acid and colloidal (polymeric) silicic acid, and the amount of precipitated silicic acid. The concentration of soluble silicic acid was determined by the silicomolybdenum-yellow method, after aliquots had been filtered through the disposable membrane filter of 0.20  $\mu\text{m}$  or 0.45  $\mu\text{m}$  in pore size. 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 was defined as the initial concentration of soluble silica minus the total concentration of silicic acid in soluble and colloidal forms [5-7, 9].

### Solid sample

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,  $M$ , corresponding to the value of  $b$ , is estimated by the  $2/b=Ma/V$ . For example, when  $b=0.1$  mm,  $M$  almost equals 0.01 g ( $a=350$  m<sup>2</sup>/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] and Iler [10] 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 solid phase, in order to simulate a large specific surface area observed in flow-paths such as fractures included in rock matrix.

## RESULTS AND DISCUSSION

Figs. 1 and 2 are some examples of the experiment results. The initial concentration of silicic acid was set to 6.74 mM and 11.94 mM. In other words, the initial supersaturated concentration,  $C_{\text{ini}}-C_e$ , was set to 4.8 mM and 10 mM, where  $C_{\text{ini}}$  is the initial concentration of soluble silicic acid (pH>10) and  $C_e$  is 1.94 mM, the solubility of soluble silicic acid (pH=8, 298 K) in the presence of amorphous silica. The vertical axis,  $f$ , in Figs. 1 and 2, is the fraction of soluble silicic acid, colloidal form and precipitated silica to the initial concentration of soluble silica. From Figs. 1 and 2, it can be confirmed that the amount of the soluble silicic acid decreases immediately and the fractions of colloidal silicic acid and precipitated silicic acid were increasing with time. The precipitation of colloidal silicic acid started from the time the soluble silicic acid reached an equilibrium condition (meta-stable condition, approximately 2 mM higher than the solubility). However, the fractions of colloidal silicic acid and precipitated silica were quite different between the 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 strongly affects the formation of colloid silicic acid and the precipitation of the silicic acid to the solid phase. Furthermore, when the Ca ions are 10 mM, the rapid precipitation of colloidal silicic acid was observed. This suggests that the supersaturated silicic acid immediately forms the bridged compound with Ca ions and drops on the surface. (Contrarily, under the condition of the Ca ions lower than 1 mM, the Ca ions in the solution play a role of forming polymeric silicic acid as a pseudo-colloid and obstruct the immediate precipitation, although colloidal silicic acid does not exist under the Ca free condition with less than 5 mM in initial

supersaturated concentration [5].)

Since the specific surface area changes due to the precipitation, this study focused on the initial gradient of  $f$  to time in order to evaluate the decrease rate of the silicic acid. This study obtained the rate-constants,  $k$  (m/s) under various conditions by using the first-order reaction equation considering the supersaturated concentration and the specific surface area  $A$  (1/m) 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>)) [5].

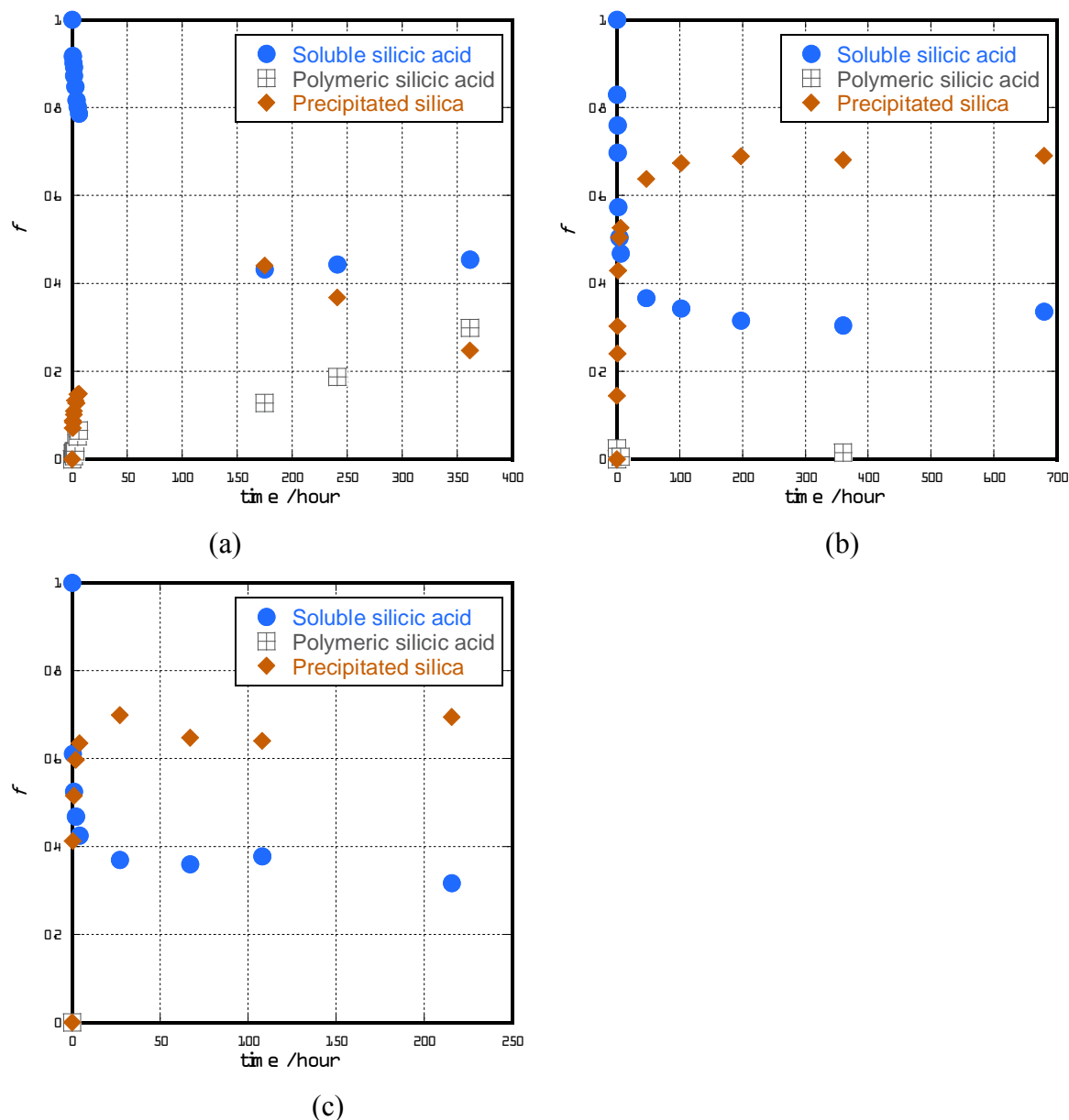


Fig.1. The deposition behavior on the amount of the solid phase.

(a) 0.10 g, (b) 1 g, (c) 1g (Ca 10 mM) (Initial supersaturated concentration: 4.8 mM, Solid sample: Mallinckrodt silica powder, pore size of filter: 0.20  $\mu$ m)

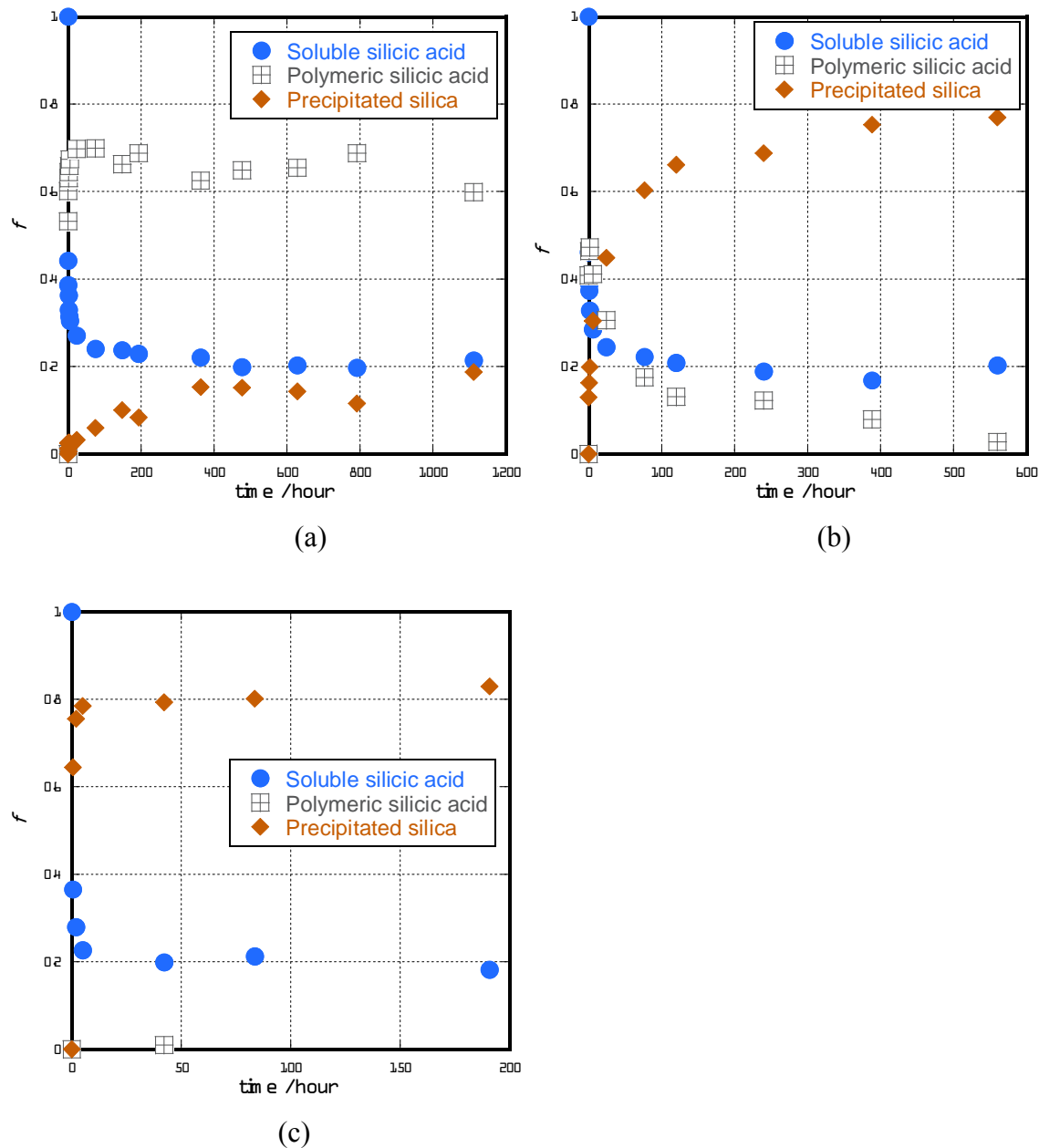


Fig.2. The deposition behavior on the amount of the solid phase.

(a) 0.10 g, (b) 1 g, (c) 1g (Ca 10 mM)

(Initial supersaturated concentration: 10 mM, Solid sample: Mallinckrodt silica powder, pore size of filter: 0.20  $\mu\text{m}$ .)

Table II shows the deposition rate-constants,  $k$ , under each condition of co-presence of amorphous silica powder. In the results, the deposition rate of both silicic acid,  $k$ , were in the range of  $10^{-13}$  to  $10^{-10}$  m/s even in the co-presence of Ca ions. A concentration of Ca ions in groundwater predicted around the repository is range from 1 mM to about 10 mM. Within this range, the smallest value of  $k$  was around  $1.0 \times 10^{-12}$  m/s in the co-presence of Ca ions of 1 mM, while the deposition rate

dramatically increased due to the bridging of colloidal silicic acid when the concentration of Ca ions was 10 mM. Therefore, although the Ca ions contribute to the precipitation of the silicic acid when the concentration of Ca ions is relatively high, they obstruct the precipitation when the concentration is lower (around 1 mM generally assumed in groundwater).

Table II.  $k$ , the deposition rate-constants.

Concn. of Ca ions [mM]	0	0.1	1.0	10
$k$ (m/s) of soluble silicic acid	$3.3 \times 10^{-11}$	$8.0 \times 10^{-11}$	$6.2 \times 10^{-11}$	$9.6 \times 10^{-11}$
$k$ (m/s) of colloidal silicic acid	$3.1 \times 10^{-12}$	$4.10 \times 10^{-13}$	$7.6 \times 10^{-13}$	$5.1 \times 10^{-12}$

Now, consider the one-dimensional, advection-dispersion model including the deposition rate [5]

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

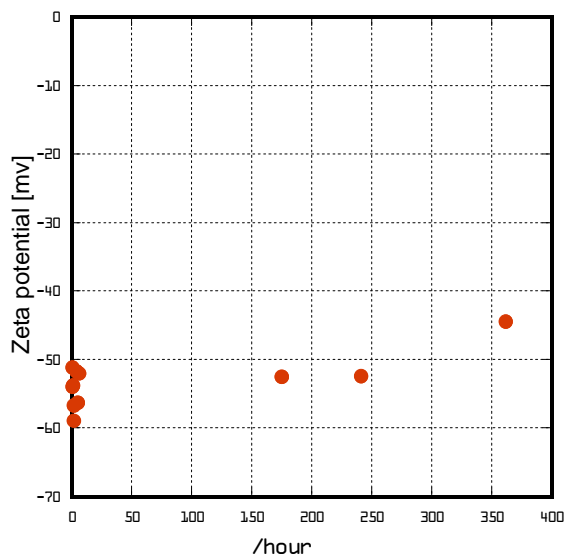
This formula is described by using non-dimensional form, i.e.,  $C_s = (C - C_e) / (C_{ini} - C_e)$ ,  $T = t / t^*$  ( $t^* = x_1 \varepsilon / u_0$ ) and  $P_e = u_0 x_1 / D_e$  and  $D_a = x_1 A k / u_0$ , where  $x_1$  is the characteristic length (length of flow-path) (m),  $\varepsilon$  is porosity (-),  $D_e$  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 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, assuming  $u_0 = 1$  (m/year)  $= 3.2 \times 10^{-8}$  (m/s),  $x_1 = 10$  m,  $A = 10^6$  (1/m) [8] and  $k = 2.0 \times 10^{-10}$ ,  $D_a$  is estimated to be larger than  $10^4$ . Such a large value of  $D_a$  suggests that the altered range is sufficiently limited around the repository. (The H12 report assumed 100 m as a characteristic distance from the repository to hypothetical fault connecting with aquifer [1]. This study used one-tenth of its distance as  $x_1 (= 10$  m).)

Table III indicates the values of  $D_a$  estimated by the deposition rate-constant of the colloidal silicic acid. The result indicates also that, when the flow-velocity is assumed as around 1 m/year, the altered range is sufficiently limited around the repository, except for less than 1 mM in Ca ions concentration.

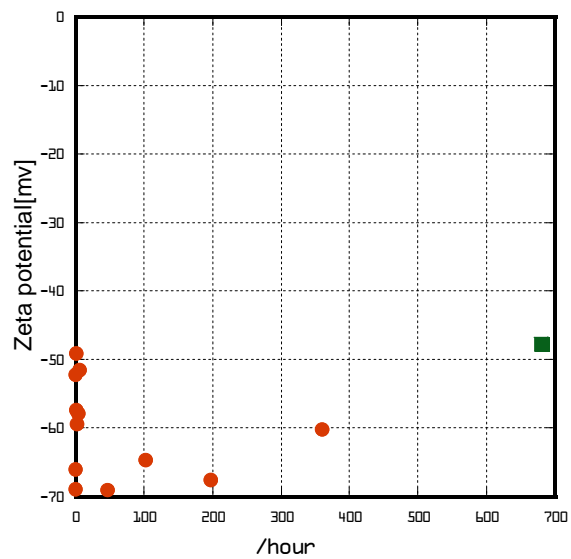
Table III.  $D_a$  estimated from  $k$  under each condition.

Conc. of Ca ions [mM]	0	0.1	1.0	10
Damkohler number $D_a$	$1.0 \times 10^4$	$2.5 \times 10^4$	$1.9 \times 10^4$	$3.0 \times 10^4$
Damkohler number $D_a$	$9.5 \times 10^2$	$1.3 \times 10^2$	$2.4 \times 10^2$	$1.6 \times 10^3$

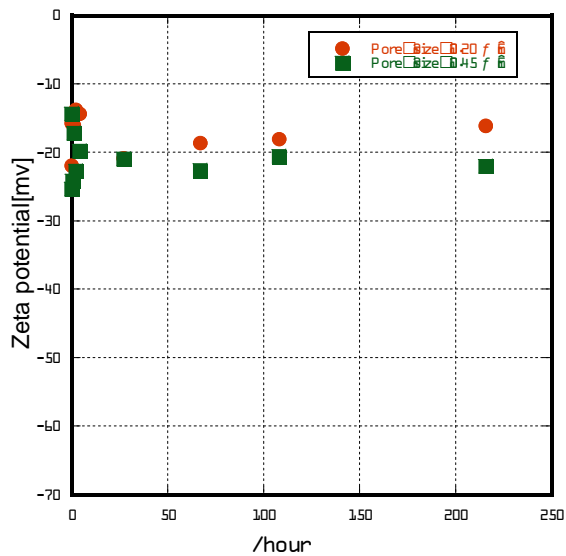
Figs. 3 and 4 show the changes of zeta potential with time. In the results, zeta potential was kept about -50 mV to -60 mV under Ca free condition, and its tendency did not depend on the additional amount of the solid phase or initial supersaturated concentration. However, the zeta potential under the condition of 10 mM Ca ions indicated a relatively large value, i.e., -20 mV. This means that Ca ions and silicic acid are obviously agglutinated.



(a)



(b)

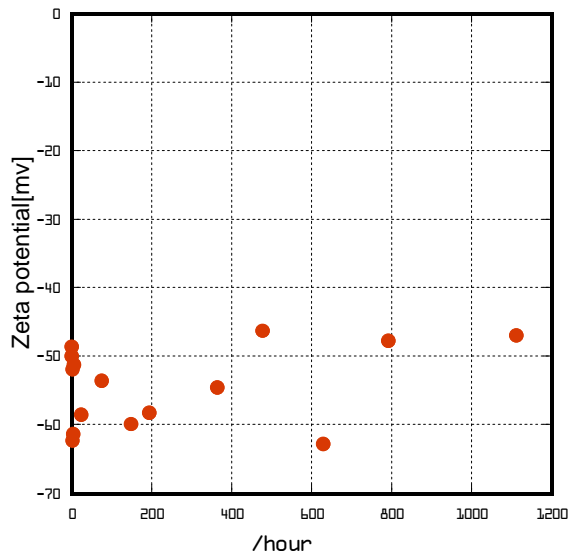


(c)

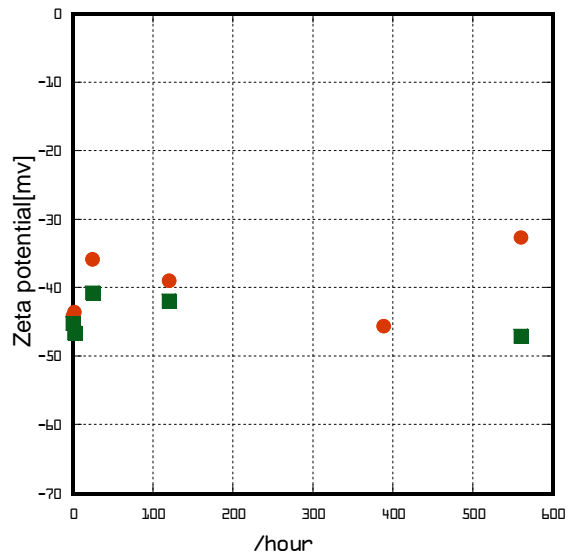
Fig.3. Transition of zeta potential.

(a):0.10 g , (b):1 g , (c):1g (Ca 10mM)

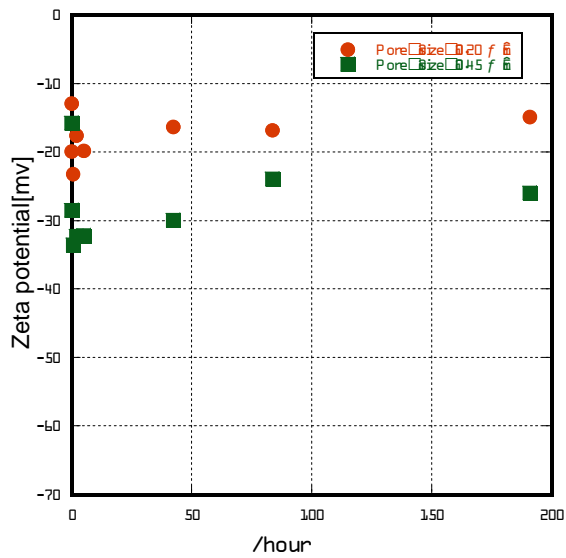
(Initial supersaturated concentration: (a) (b) (c): 4.8 mM)



(d)



(e)



(f)

Fig.4. Transition of zeta potential.  
 (d):0.10 g , (e):1 g , (f):1g (Ca 10 mM)  
 (Initial supersaturated concentration: (d) (e) (f):10 mM)



## CONCLUSIONS

This study examined the dynamic behavior of silicic acid in the co-presence of a solid phase and Ca ions. The apparent deposition rate-constant,  $k$ , was  $7.6 \times 10^{-13}$  m/s in a Ca ion concentration of 1 mM which was smaller than the apparent deposition rate-constant when the Ca ions concentration was 10 mM ( $k=5.1 \times 10^{-12}$  m/s). This means that the low concentration of Ca ions obstruct the deposition of soluble silicic acid onto the surfaces of solid phases. Such an influence of Ca ions suggested the possibility of spreading the spatial range altered by the silicic acid. However, the concentration range of Ca ions in normal groundwater (around 1 mM or larger) limits the altered spatial spread. Furthermore, the zeta potential was consistent with the dynamic behavior of the colloidal silicic acid. To understand in more detail the behavior of colloidal silicic acid in the presence of a solid phase, the distributions of pH and temperature around a repository and the effects of Al ions on the colloidal silicic acid also should be examined.

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