

Deposition Behavior of Supersaturated Silicic Acid on Ca-type Bentonite in Geological Disposal System – 16033

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ABSTRACT

For backfilling tunnels in geological disposal systems, the degradation of the low permeability of Na-type bentonite by ion-exchanging to Ca-type is a concern. The deposition of silicic acid around a repository with the dramatic change in pH due to the use of cement causes the clogging of the flow-path and pore space. Such effect may contribute to a more effective barrier performance for radionuclide migration in the backfill. As a first step to clarifying the clogging effect in the backfill, this study examined the deposition of supersaturated silicic acid on Ca-type bentonite. In the deposition experiments, the supersaturated silicic acid solution (250 ml, 4-10 mM, pH>10) was poured into a polyethylene vessel containing Ca-type bentonite (2.5-10.0 g). The deposition of silicic acid was started by setting the pH to 8. As a result, supersaturated silicic acid significantly deposited on Ca-type bentonite under all experimental conditions of supersaturated silicic acid concentration. The experimental results showed that the deposition rate-constants were in the order of 10^{-11} m/s. Our previous study showed the clogging effect in rocks by using numerical simulation with the same order rate-constants. These findings suggest that the deposition of supersaturated silicic acid on Ca-type bentonite causes the retention of low permeability and the retardation effect for radionuclides by the clogging effect in backfilled tunnels.

INTRODUCTION

Na-type bentonite is one of the main closure components used for tunnel backfill of geological repositories because of its low permeability. However, most Na-type bentonite is changed to Ca-type bentonite by Ca-rich groundwater leached from the cementitious materials used for the construction of repositories. Since the permeability of Ca-type bentonite exceeds that of Na-type, such alteration may deteriorate the retardation effect of radionuclide migration [1]. On the other hand, highly alkaline groundwater (up to pH 13), which is altered by alkaline components leached from cementitious materials, dissolves silicate minerals due to the increase in the solubility of silicic acid [2]. As high alkaline groundwater is diluted by mixing with natural groundwater (pH 8), the solubility of silicic acid gradually decreases. Such a spatial change of the solubility produces supersaturated silicic acid, which might form colloidal silicic acid and/or deposit the silicic acid on the solid phase such as bentonite [3, 4]. Therefore, it is expected that long-term deposition of supersaturated silicic acid will greatly change the spatial properties in backfill. In particular, deposition on the surface of the flow-path (or pore space) in

the bentonite probably contributes to the decrease in the permeability, inducing a higher retardation effect of radionuclide migration. To gain more fundamental knowledge about the clogging effect for flow-paths in backfill with the deposition of supersaturated silicic acid on Ca-type bentonite, this study estimated the specific surface area [m^2/g] of bentonite and deposition rate-constants [m/s], k , from the deposition experiments of supersaturated silicic acid by using Ca-type bentonite as the solid phase.

EXPERIMENTAL

Solid phase sample

Ca-type bentonite was prepared by exchanging sodium ions of Na-type bentonite with calcium ions [5]. As Na-type bentonite, Kunigel-VI was purchased from Kunimine Industries Co., Ltd. For the ion-exchange reaction, Na-type bentonite was immersed in 1 M CaCl_2 solution (10 g/L) with stirring mechanically for 24 hours. This ion-exchange process was repeated four times with replacing the CaCl_2 solution. After the ion-exchange, bentonite samples were washed with ultra-pure water for cleaning extra CaCl_2 , and dried in an oven at 383 K. The particle size of Ca-type bentonite was adjusted to a size fraction of less than 75 μm in particle diameter by sieving. Furthermore, sufficient ion-exchange of Ca-type bentonite was confirmed by measuring the cation exchange capacity (CEC) of before-and-after bentonite samples [6].

The specific surface area of Ca-type bentonite was measured by Ethylene Glycol Mono-ethyl Ether (EGME) method [7]. EGME method measures the specific surface area of mainly clay minerals, which have a layered structure, by adsorbing EGME on samples. Ca-type bentonite was dried in an oven at 383 K for 24 hours, and the dried sample was weighed (about 1 g). This dried sample was mixed with 4 mL of EGME, and left in atmosphere for 1 hour. The EGME-mixed sample was put into desiccators with 100 g of dried CaCl_2 powder and 20 mL of EGME respectively. After 1 hour with vacuuming, the EGME-mixed sample was weighed every 1 hour until the weight of the sample became constant for estimating the retention amount of EGME. The specific surface area (SSA) was calculated by the following equation:

$$\text{SSA} [\text{m}^2 / \text{g}] = \frac{\text{the weight of retained EGME} [\text{g}]}{0.000371 [\text{g} / \text{m}^2] \times \text{the weight of dried sample} [\text{g}]}$$

Here, the value of 0.000371 is the theoretical specific surface area for complete unimolecular layer surface coverage. By the above procedure, the initial specific surface area of Ca-type bentonite was estimated to be 423 m^2/g (the average of three measurements). The specific surface area of the sample after the deposition experiment was also estimated by the same procedure.

Procedures of deposition experiments

The deposition experiments of silicic acid in this study followed basic procedures reported in our previous study [8]. The initial supersaturated concentrations of silicic acid were given in the range from 4 mM to 10 mM by diluting Na₂SiO₃ solution (water glass obtained from Wako Pure Chemical Industries, Ltd.). The weighed amount of Ca-type bentonite was also given in the range from 2.5 g to 10.0 g. The temperature of the solution was set to 298 K by using a thermostat. After pouring the bentonite into the silicic acid solution (250 ml, pH > 10), the pH of the solution was set to 8. The concentrations of soluble silicic acid and colloidal forms were monitored during 6 hours under nitrogen atmosphere. The aliquot was centrifuged in order to separate the solid phase and liquid phase by using a 0.45- μ m membrane filter. Table I summarizes the experimental conditions.

Table I. Experimental conditions

Initial supersaturated concentrations of silicic acid [mM]	4, 6, 8, 10
Addition amount of solid sample [g]	1.0, 2.5, 10.0
pH	8
Rate of stirring [rpm]	300
Pore size of membrane filter [μ m]	0.45
Temperature [K]	298

Measurements and analysis

In this study, three species of silicic acid were defined as soluble silicic acid, colloidal silicic acid and deposition on Ca-type bentonite [3, 8]. The concentration of soluble silicic acid in the liquid phase was quantified by the silicomolybdenum-yellow method, which can detect mainly monomeric or oligomeric species only, and the total concentration of silicic acid in the liquid phase was quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES. SPS7800, Seiko Instruments Inc.). Then, the concentration of colloidal silicic acid was calculated from the measurement results of the silicomolybdenum-yellow method and ICP-AES. The deposition on Ca-type bentonite was calculated from the results of ICP-AES and the initial concentration of silicic acid. Finally, the deposition rate-constants [m/s], k , were calculated from the deposition rates and specific surface area by using a first-order reaction equation as described later.

RESULTS AND DISCUSSION

Deposition of silicic acid on Ca-type bentonite

Figure 1 shows the experimental results for the amount of Ca-type bentonite of 5.0 g and the initial supersaturated concentrations of 4, 6, 8 and 10 mM. The vertical axis, f , in these figures is the fraction of soluble silicic acid, colloidal silicic acid and deposition to the initial concentration of soluble silicic acid. As shown in Fig. 1, the

decrease in soluble silicic acid and the increase in deposition and colloidal silicic acid were confirmed to be significant under these experimental conditions, and such a tendency was observed also under all other experimental conditions. Notably, the deposition amount exponentially increased at the early stage of the experiments under a relatively high supersaturated concentration, then the deposition rate dramatically increased after several minutes. Such deposition behavior may result from the change in the surface area of the solid phase because, in general, deposition rates strongly depend on the surface area of the solid phase.

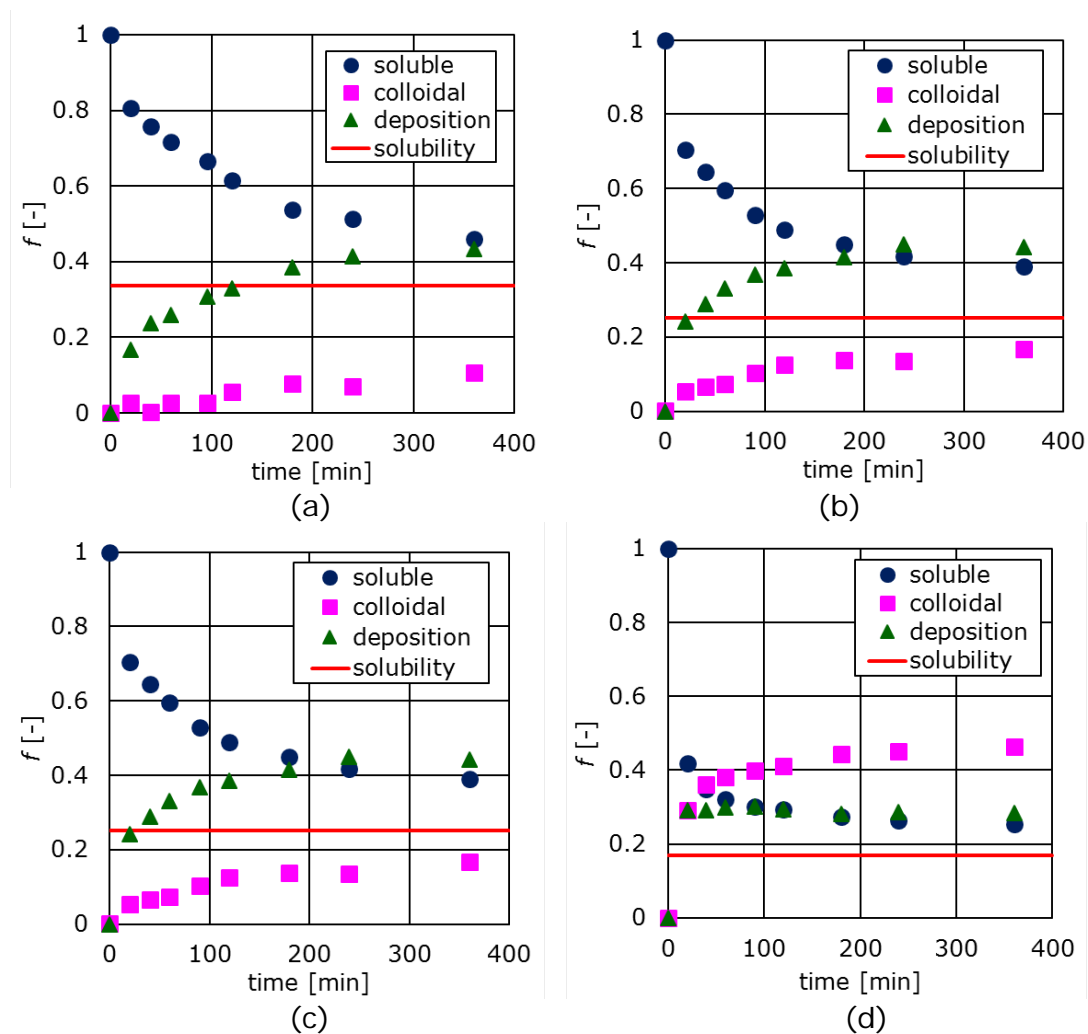


Fig. 1. Deposition of silicic acid on solid phase (Initial supersaturated silicic acid is (a) 4 mM, (b) 6 mM, (c) 8 mM, (d) 10 mM. Amount of Ca-type bentonite is 5.0 g.)

Fig. 2 shows the change over time in the specific surface area of Ca-type bentonite for the deposition experiment (initial supersaturated silicic acid: 6 mM, Ca-type bentonite: 5.0 g). As shown in Fig. 2, the specific surface area decreased immediately after starting the experiment, then became constant approximately. However, Ca-type bentonite after the deposition of silicic acid retained the large specific surface area (about 300 m²/g), even if the specific surface area became less than the initial one (423 m²/g). Besides, the decrease in the deposition rate

might be caused by the selective deposition of silicic acid on the edge site of bentonite materials [9]. In other words, this means that it is necessary to estimate both the deposition rate-constant on the Ca-type bentonite surface (initial reaction from 0 to 40 min) and on deposit products (subsequent reaction from 20 to 60 min). Therefore, we estimated both deposition rate-constants and adopted the conservative value of the deposition rate-constants for clogging effect.

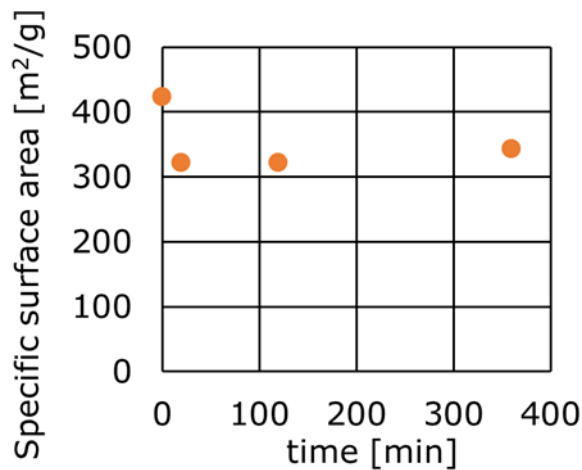


Fig. 2 Change in specific surface area for deposition experiments. (Initial supersaturated silicic acid: 6 mM, Ca-type bentonite: 5.0 g)

Deposition rate-constants

For the estimation of deposition rate-constants, k , the simple following Eq. (1) is assumed at the early stage of the deposition experiments,

$$-\frac{df}{dt} = kA(f - f_e) + k_c^+(f - f_e)^n - k_c^-f_c^m \quad , \quad (1)$$

where A is the specific surface area [$1/m$], defined by the EGME surface area [m^2/g] \times weight amount of the solid phase [g] / the solution volume [m^3], f , f_e and f_c are the fractions of the soluble silicic acid, the solubility of soluble silicic acid and the colloidal silicic acid to the initial concentration of soluble silicic acid, respectively, k , k_c^+ and k_c^- are the deposition rate constant, the formation rate constant of colloidal silicic acid, and the decomposition rate constant of colloidal silicic acid, n and m are arbitrary reaction orders and t is time [s]. While the polymerization rate of colloidal silicic acid and the depolymerization rate are more complicated with the nucleation, the growth and the decomposition processes, the apparent formation rate of colloidal silicic acid is

$$\frac{df_c}{dt} = k_c^+(f - f_e)^n - k_c^-f_c^m \quad . \quad (2)$$

Since the fraction of the deposition on the solid phase, f_d , is defined by

$$f_d = 1 - f - f_c , \quad (3)$$

the deposition rate yields

$$\frac{df_d}{dt} = \frac{d(1 - f - f_c)}{dt} = -\frac{df}{dt} - \frac{df_c}{dt} = kA(f - f_e) \quad (4)$$

That is, the deposition rate is equivalent to *the decrease rate of the soluble silicic acid* minus *the formation rate of the colloidal silicic acid*. From Eqs. (1) to (3), Eq. (4) is obtained as follow:

$$r_{ini} = \left. \frac{df_d}{dt} \right|_{ini} = kA(1 - f_e) , \quad (5)$$

where r_{ini} is the initial deposition rate [1/s] of $t=0$. This study estimated its value by using two kinds of the gradients. That is, the one is the case (I) including $f_d=0$, and another is the case (II) excluding $f_d=0$. For A , the same value (423 m²/g) of the specific surface area both $t=0$ and 20 min is used due to assessing the deposition rate-constants conservatively. The apparent deposition rate-constants [m/s], k , were estimated by Eq. (4) as shown in Table II.

Table II. Apparent deposition rate-constants, k [m/s]

Initial supersaturated silicic acid (mM)		4	6	8	10
Deposition rate-constant (m/s), k	Case (I)	1.73×10^{-11}	2.74×10^{-11}	2.81×10^{-11}	4.01×10^{-11}
	Case (II)	4.45×10^{-12}	2.16×10^{-12}	7.74×10^{-12}	8.61×10^{-12}

Table II shows that the values of the initial deposition rate-constants ($t=0$) were in the same order (10^{-11} m/s) under all experimental conditions of initial supersaturated silicic acid. This means that the deposition rate-constants of silicic acid for Ca-type bentonite hardly depend on the initial supersaturated concentration of soluble silicic acid. Furthermore, these initial deposition rate-constants were almost the same as those for the deposition on silicate mineral reported in our previous study, in which we showed a clogging effect with the deposition of silicic acid in a fracture (flow-path) of rock matrix. Here, for example, consider the one-dimensional, advection-dispersion model including the deposition rate of soluble silicic acid on the Ca-type bentonite. The model has a key non-dimensional parameter, i.e., Damköhler number, $D_a = x_1 ak/u_0$, where x_1 is the characteristic length (length of flow-path), and u_0 is the fluid flow velocity of underground water. Assuming $u_0 = 1$ [m/year] = 3.2×10^{-8} [m/s], $x_1 = 10$ m, $a = 10^6$ [1/m] [10] and $k = 10^{-11}$ m/s, the value of D_a exceeds 10^3 . And the subsequent deposition rate-constants were estimated to be in the order of 10^{-12} , the value of D_a exceeds 10^2 . Such large values of D_a mean that the deposition is a

dominate process of mass transfer with groundwater flow. That is, it is expected that the deposition of silicic acid on Ca-type bentonite under the supersaturated condition will clog pore space in the backfill even if the permeability of bentonite materials themselves degrades after the closure of the repository.

CONCLUSIONS

This study examined the deposition behavior of supersaturated silicic acid on Ca-type bentonite. The deposition experimental results showed a decrease in the concentration of soluble silicic acid and an increase in the deposition on Ca-type bentonite. In particular, the deposition amount dramatically increased at the early stage of the experiments under the condition of higher supersaturated concentration (e.g., 8 mM or 10 mM), and the deposition rates became much smaller after several minutes. These results suggest that the surface area of the bentonite sample was apparently altered to a small one immediately by the deposition of supersaturated silicic acid particularly on the edges of the layered structure of the bentonite. The initial deposition rate-constants [m/s] were estimated to be in the order of 10^{-11} for all the experiments of this study. Taking these findings together with the previous analysis results for rocks, these deposition rate-constants would be large enough to clog the flow-path in the backfill. And the subsequent deposition rate-constants were estimated to be in the order of 10^{-12} . Even if the clogging effect is estimated using the value of 10^{-12} conservatively, there are the adequate values of D_a as with the initial deposition rate-constants for the retardation effect of radionuclide migration. This means that the deposition of supersaturated silicic acid on Ca-type bentonite also brings such a clogging effect in the backfilled tunnels, which plays an important role in the retardation effect of radionuclide migration.

REFERENCES

1. JNC (Japan Nuclear Cycle development institute), "H12 project to establish the scientific and technical basis for HLW disposal in Japan, Supporting Report III, Geological Environment in Japan," (1999).
2. Japan Nuclear Cycle Development Organization Institute and The Federation of Electric Power Companies of Japan, "Second progress report on research and development for TRU waste disposal in Japan", JNC-TY1400-2005-013, Chapter VI (2005).
3. H. Shimura, Y. Niibori, K. Iijima, and H. Mimura, "Fundamental study on temperature dependence of deposition rate of silicic acid," Proc. of WM2013, Paper No.13270 (2013).
4. 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).
5. T. Kozaki et al., "Self diffusion of sodium ions in compacted sodium montmorillonite," nuclear technology, 121, (1997)
6. Japanese Society of Soil Science and Plant Nutrition, "The Analysis of Soil Environment," pp. 218-219, Hakuyusha Co., Ltd., Tokyo, Japan (1997).

7. M. Eltantawy and P.W. Arnold, "Reappraisal of ethylene glycol mono-ethyl ether (EGME) method for surface area estimations of clays," *Journal of Soil Science*, 24, No.2 (1973).
8. T. Sasagawa, T. Chida and Y. Niibori, "Effects of pH on deposition rate of supersaturated silicic acid around geological disposal system," *Proc. of WM2015*, Paper No.15245 (2015).
9. M. Holmboe, S. Wold and T. Petterson, "Effects of the injection grout silica sol on bentonite," *Physics and Chemistry of the Earth*, **36**, (2011).
10. Y. Niibori, Y. Kasuga, H. Kokubun, K. Iijima, and H. Mimura, "Dependence of the dynamic behavior of supersaturated silicic acid on the surface area of the solid phase", *Scientific Basis for Nuclear Waste Management XXXII*, edited by R.B. Rebak, N.C. Hyatt, D.A. Pickett (*Mater. Res. Soc. Symp. Proc.*), **1124**, 319-324 (2009).

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