A Calculation of Spatial Range of Colloidal Silicic Acid Deposited Downstream from the Alkali Front*

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Abstract

A high alkali domain spreads out due to the use of cement materials for the construction of the repository of radioactive wastes. Sudden change of pH at this alkali front produces colloidal silicic acid (polymeric silicic acid) in addition to the deposition of supersaturated monomeric silicic acid onto the fracture surface of flow-pathway. The colloidal silicic acid also deposits with relatively small rate-constant in the co-presence of solid phase. Once the flow-path surface is covered with the amorphous silica, the surface seriously degrades the sorption behavior of radionuclides (RNs). Therefore, so far, the authors have examined the deposition rates of supersaturated silicic acid. This study summarized the deposition rate-constants defined by the first-order reaction equation under various conditions of co-presence of amorphous silica powder. Then, using the smallest rate-constant (1.0×10^{-12} m/s in the co-presence of calcium ions of 1 mM) and a simulation code, COLFRAC-MRL, the spatial range of colloidal silicic acid deposited downstream from the alkali front was estimated. The results suggested the clogging caused by the deposition of colloidal silicic acid in flow-path. The altered spatial range in the flow-path was limited to around 30 m in fracture and to several centimeters in rock matrix.

Key words: Radioactive Waste Repository, High pH Plume, Alteration, Colloidal Silicic Acid, Deposition Rate

1. Introduction

The cement-based structural materials (e.g., cement grout) are required for the construction of the repository of radioactive wastes located under the groundwater table. Such cement materials would produce high alkali plume ⁽¹⁾⁻⁽³⁾, dramatically changing pH downstream by diluting with the surrounding natural groundwater (pH≈8) as shown in Fig. 1. Hereinafter, such a large change of pH is referred to as "alkali front", in this study. Since the solubility of silicic acid remarkably increases with pH>9 ^{(4),(5)}, the change of pH from e.g., 12 to 8 undergoes a supersaturated condition of silicic acid.

Chida et al. ^{(6),(7)} reported that at the alkali front colloidal silicic acid (polymeric silicic acid) was produced even if in the presence of the solid phase, in addition to the deposition of supersaturated monomeric silicic acid. Furthermore, the colloidal silicic acid also deposited, as amorphous silica, with relatively small rate-constant. That is, the range altered by colloidal silicic acid becomes spatially wider than that by supersaturated monomeric

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silicic acid. Since flow-path surface covered with the amorphous silica seriously degrades the sorption behavior of radionuclides ⁽⁸⁾, the flow rate of groundwater and the deposition rate of supersaturated silicic acid are key parameters to estimate the spatial spread of altered flow-path surface.

This study summarizes the deposition rate-constants of supersaturated silicic acid defined by the first-order reaction equation in the presence of solid phase. Then, using the smallest rate-constant and fluid flow velocity, the spatial range of colloidal silicic acid deposited downstream from the alkali front is estimated. The smallest rate-constant would yield its widest range altered by the supersaturated silicic acid around the repository.

Fig. 1 An illustration of alkali front caused by the use of cement-based structural materials for the repository.

2. Experimental

2.1 Procedures

So far, the authors have evaluated the deposition rate constants of supersaturated silicic acid ^{(7), (9)-(12)}. The experimental procedure is as follows:

The silicic acid solution prepared by dissolving water glass (Na_2SiO_3 solution obtained from Wako Pure Chemical Industries, Ltd.) in distilled ultrapure water was put into the polyethylene vessel with cover (solution volume, 245 ml) and mechanically stirred with a polypropylene stirrer at 300 rpm. (There was no difference between 300 rpm and 400 rpm in estimate of the deposition rates of both soluble silicic acid and colloidal silicic acid). In the vessel, the concentration of silicic acid was given in the range of up to 10 mM ($\text{pH} \approx 12$). To avoid contact with air, nitrogen was passed through the vessel. A weighed amount of the solid phase (amorphous silica powders within the range of 0.1 g to 1.0 g) was poured into the vessel. Then, the pH of the solution was set to 8 with an HNO_3 solution and a buffer solution mixing MES (2-morpholino-ethanesulfonic acid, monohydrate) and THAM (tris-(hydroxymethyl)). The temperature was kept constant within 298 ± 0.5 K.

In the procedure mentioned above, the solid surface is immediately covered with amorphous silica deposited from mainly supersaturated monomeric silicic acid. Then, the colloidal silicic acid gradually deposits on such an altered surface of the solid phase, as shown in Fig. 2(a). However, in an open system such as the near field around the repository, colloidal silicic acid would flow downstream with groundwater, depositing on flow-path surfaces not altered by the deposition of soluble silicic acid, as shown in Fig. 2(b). Therefore, this study tried to contact the colloidal silicic acid more directly with solid phase. That is, after adjusting pH from 12 to 8, producing the colloidal silicic acid from supersaturated silicic acid and curing for 12 hours, the solid sample was poured in the solution. This study confirmed through some preparatory experiments that its curing time is enough to apparently stabilize the concentration of colloidal silicic acid in solid phase free system.

2.2 Solid Sample

It is well-known that 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. In order to simulate such a large specific surface area, the amorphous silica particles were used as solid phase in this study. The solid sample was pure amorphous silica ($\text{SiO}_2 \cdot 0.23\text{H}_2\text{O}$)⁽¹³⁾ purchased as Wako-gel C-200 from Wako Pure Chemical Industries, Ltd. and separated to a size fraction of 74–149 μm particle diameters by sieving. Its specific surface area was 450 m^2/g BET (N_2 gas).

Furthermore, the amorphous silica as a solid sample simulates a thin layer of amorphous silica on the silicate minerals under the supersaturated conditions of silicic acid. Iler⁽¹⁴⁾ pointed out that the deposition of silicic acid easily forms amorphous layer on the silicate minerals. In fact, 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 results, the solubility of soluble silicic acid controlled by each solid sample agreed with that by amorphous silica particles. In addition, Niibori et al.⁽⁸⁾ found (through the sorption experiments of Eu in the co-presence of soluble silicic acid, colloidal silicic acid and the silica samples) that the apparent solubility of soluble silicic acid slightly dropped in a short time-period when each solid sample of silica was poured in the meta-stable solution of soluble silicic acid and colloidal silicic acid. This suggested that such a contact with solid phase also slightly shifted the equilibrium of soluble and colloidal silicic acids in solution.

Therefore, even if the solid sample is poured in the solution after attaining to a pseudo steady-state of the colloidal silicic acid with no solid phase, the solid surface is slightly altered in a short time-period. However, the degree altered by the initial deposition of supersaturated silicic acid would be different, depending on the experimental procedures. That is, it is predicted that the timing of contact with solid sample in this study, in comparison with the previous procedure, decreases the degree altered on the solid surface.

(a) Previous works

(b) This work

Adjusted pH from 12 to 8, and cured colloidal silicic acid for 12 hours. Then, contacted colloidal silicic acid with solid sample.

Fig. 2 The difference of the experimental procedures for the contact of the colloidal silicic acid and the solid phase. (In the case (a), the supersaturated soluble silicic acid deposits (covers) on the solid surface (amorphous silica powders), then the colloidal silicic acid gradually deposits on the solid surface. In the case (b), after producing the colloidal silicic acid and curing it for a given time, the colloidal silicic acid contacts the solid phase.)

2.3 Determination of the Concentrations of Silicic Acid

In the experiments, the concentrations of both soluble silicic acid and colloidal (polymeric) silicic acid, and the amount of precipitated silicic acid were monitored. Here, 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 deposited silica was defined as the original concentration of soluble silicic acid minus the total concentration of silicic acid in soluble form and colloidal form, where the original concentration means the concentration of soluble silicic acid prepared in the solution of pH 12.

3. Experimental Results

Figure 3 shows the experimental results, where the vertical axis f is the fractions of soluble silicic acid, colloidal form and precipitated silica to the concentration of soluble silicic acid prepared with pH=12. Since the colloidal silicic acid produces before pouring solid phase into the vessel, the initial fraction of the soluble silicic acid becomes less than 1.0 at $t=0$ (the timing when solid sample was poured in the solution). In Fig.3, the “Original concentration of supersaturated silicic acid (9 mM or 6 mM)” means the *supersaturated* concentration of soluble silicic acid prepared in the solution of pH 12 (i.e., before producing colloidal forms). As mentioned in 2.2, Fig. 3 also showed the shift of equilibrium of soluble silicic acid due to the addition of the solid phase to the solution (i.e., the fraction of soluble silicic acid slightly dropped at $t=0$). Then, the soluble silicic acid immediately attained to the meta-stable concentration (≈ 2.2 mM) slightly higher than the solubility of silicic acid at 1.9 mM (pH8) ⁽⁴⁾. On the other hand, the decrement rate of colloidal silicic acid strongly depended on the amount of solid phase (the surface area).

Fig. 3 The changes of the fractions of the soluble silicic acid, the colloidal silicic acid and the deposited (precipitated) silicic acid. (These experiments were carried out in the experimental procedures shown in Fig. 2 (b)).

This study forced on the change of colloidal-silicic acid concentration at this meta-stable state of soluble silicic acid. In this period, the decrease in the amount of colloidal silicic acid is equal to that deposited on the solid surface.

Figure 4 shows the apparent rate-constant k' (1/s) defined by

$$-\frac{df_c}{dt} = k' f_c, \quad (1)$$

where f_c is the fraction of colloidal silicic acid, and t is time (s). k' includes the specific surface area. For the fitting, the data of f_c were used in $|df_s/dt| < 0.003$ (1/h), where f_s is the fraction of soluble silicic acid ⁽⁶⁾. As shown in Fig. 4, the apparent rate-constant was linear to specific surface area. Therefore, we can obtain the rate-constant k (m/s),

$$k' = ak, \quad (2)$$

where a is specific surface area (1/m) defined in this study by the BET surface area (m²/g) × weight amount of solid phase (g) / the solution volume (m³). In Fig. 4, the curing time 0 hour means the experimental result obtained in the previous procedure as shown in Fig. 2 (a). From the results, the values of k were 3.66×10^{-12} m/s and 2.50×10^{-12} m/s for the curing time of the colloidal silicic acid 0 and 12 hours, respectively. While the difference in the apparent rate-constants may suggest the slight change of the solid surface due to the initial deposition (at $t=0$) of supersaturated silicic acid, these values agreed within the range of from 2.50×10^{-12} m/s and 3.66×10^{-12} . Furthermore, the original supersaturated concentration of silicic acid at least in the range less than 10 mM did not affect the rate-constant. In this study, hereinafter, k is referred to as deposition rate constant. Besides, Tamura et al. ⁽¹²⁾ also examined the apparent rate-constant of colloidal silicic acid (i.e., 3.1×10^{-12} m/s) under the experimental condition of the curing time 0 hour. The value is almost similar to that of this study.

Fig. 4 Relations of the apparent deposition rate-constant, k' (1/s), and the specific surface area. (The curing-time means the time taken before contacting the colloidal silicic acid with the solid phase. The apparent rate-constants, k' , of "Curing time 0 hour" were obtained through the previous experimental procedures as shown in Fig. 2(a), and the k' of "Curing time 12 hours" were done through the procedure shown in Fig. 2(b).)

Table 1 is the summary of the deposition rate-constants estimated in the same way as mentioned above. Here k_m is the deposition rate-constant of soluble silicic acid. As shown in Table 1, the rate-constant of colloidal silicic acid is two-orders of magnitude smaller than that of soluble silicic acid. Furthermore, when Ca ions are 1 mM, the rate-constant is smallest, as shown in Table 1.

On the other hand, Chida et al. ⁽⁷⁾ reported that, when Ca ions exceeded 10 mM, the colloidal silicic acid instantly precipitates by forming a bridged component of the colloidal silicic acid with Ca ions. Tamura et al. ^{(11), (12)} explained that these behaviors were due to two roles of Ca ions. That is, one is the surface alteration due to the produce of CSH (Calcium Silicate Hydrate) on the solid surface. Such an alteration would decrease the local surface area, changing the chemical property of the surface. The other is that the remaining Ca ions in the solution contribute to form the pseudo-colloid. In order to produce the pseudo-colloid large enough to precipitate immediately, Ca ions need to exceed 10 mM in this system.

Table 1 Summary of the deposition rate-constant of colloidal silicic acid, k (m/s).

Initial colloidal silicic acid	Ca ions	k (m/s) Colloidal silicic acid	k_m (m/s) Soluble silicic acid*	Remarks
free	free	$3.66(\pm 0.57) \times 10^{-12}$	$5.89(\pm 2.60) \times 10^{-11}$	Kokubun et al. ⁽⁹⁾ , Tamura et al. ⁽¹²⁾
free	free	-	$2.10(\pm 0.10) \times 10^{-11}$	Niibori et al. ⁽¹⁰⁾
adjusted	free	$2.50(\pm 0.07) \times 10^{-12}$	-	This work
free	1 mM	$3.44(\pm 2.44) \times 10^{-12}$ (The smallest value: 9.98×10^{-13})	$4.29(\pm 0.58) \times 10^{-11}$	Evaluated from the initial rate of the data reported by Chida et al. ⁽⁷⁾ .

*: k_m (m/s) is the deposition rate-constants of the soluble silicic acid shown for comparing those of colloidal silicic acid.

(Both rate-constants of k and k_m were evaluated from each relation of the apparent rate-constants and the specific surface area as shown in Fig. 4.)

4. Spatial Range Deposited Downstream

At JAEA Tokai R&D Center, Nuclear Fuel Cycle Engineering Laboratories, the authors calculated the spatial range deposited by colloidal silicic acid downstream from an alkali front, using a computation code, COLFRAC-MRL ⁽¹⁵⁾ and the smallest rate-constant of the colloidal silicic acid ($\approx 1.0 \times 10^{-12}$ m/s).

Figure 5 illustrates the calculation system of this study. The code COLFRAC-MRL can treat various cases including the sorption of radionuclide onto colloid and solid surface. This study focused on the transport of colloidal silicic acid. That is, the advection, the dispersion and the deposition rate in a fracture (thin, parallel flat board with aperture $2b$ (m)) were considered in the calculation. Here, the aperture is assumed to be constant. In addition, the diffusion from the flow-path into rock matrix and the deposition rate in the matrix were evaluated. Then, the dimensionless mass balance equation in a fracture is controlled by two dimensionless parameters, Peclet number, P_e , and the Damköhler number, D_a ^{(10), (12)}:

$$P_e = \frac{z_1 u_0}{D_e}, \quad (3)$$

$$D_a = \frac{z_1 a k}{u_0}, \quad (4)$$

where z_1 is the characteristic length (length of flow-path) (m), u_0 is the fluid flow velocity of groundwater (m/s) and D_e is the dispersion coefficient (m^2/s). In Eq. (4), ak is an apparent rate-constant, corresponding to Eq. (2). Generally, the dispersion coefficient is approximated by $\alpha u_0 + D_m$, where α is longitudinal dispersivity (m) and D_m is molecular diffusion coefficient (m^2/s). As $\alpha u_0 \gg D_m$, D_e is simply αu_0 . Then, Eq. (3) becomes $P_e = z_1/\alpha$. Now considering $z_1 = 100$ m and $\alpha = 0.1 z_1$ ⁽¹⁶⁾, we obtain $P_e = 10$. Here, the value of z_1 was based on a basic scenario of H12 report ⁽²⁾. Therefore, the critical parameter becomes just only the Damköhler number for the mass transport in a fracture.

Furthermore, in the rock matrix, COLFRAC-MRL can consider the diffusion from the fracture and the deposition rate. Its mass balance equation is controlled by the Peclet number and Damköhler number of rock matrix: $P_{eM} = \varepsilon z_1 u_0 / D_{Ma}$ and $D_{aM} = z_1 a_M k / (\varepsilon u_0)$, where D_{Ma} is diffusion coefficient, ε is porosity and a_M is specific surface area in the rock matrix (1/m). Here, this code assumes D_{Ma} , ε and a_M to be constant, respectively. This study defined the dimensionless time, $T (= t/t^*)$, where t is time (s) and t^* is the characteristic time ($= z_1/u_0$). Therefore, also in the mass balance equation in the rock matrix (i.e., diffusion equation with the rate of one-order reaction), the Peclet number and Damköhler number of rock matrix are

defined. From H12 Report (JNC, 1999) (except for the deposition rate-constant, k , of colloidal silicic acid), this study gave some practical values to these parameters as a basic case. Table 2 is the parameter values set in the calculation.

Fig. 5 The calculation system for estimating the concentration distribution of the colloidal silicic acid (In a fracture, one-dimensional mass balance equation of the colloidal silicic acid considering the advection, the dispersion and the deposition rate is used. In addition, the diffusion from the fracture to rock matrix and the deposition rate are considered in the rock matrix.)

As shown in Table 2, the specific surface area, a , and the hydraulic conductivity, K , are related to the aperture of fracture b . Furthermore, the apparent deposition rate-constant, k' , is also linked to a through Eq. (2). In the calculation of this study, the deposition rate-constant, k (not k'), was fixed to 1.0×10^{-12} m/s. The Damköhler number of fracture, D_a , based on Table 2 and $k=1.0 \times 10^{-12}$ m/s is 8.0 ($P_e=10$ as mentioned above). Then, the Damköhler number and the Peclet number of rock matrix are $D_{aM}=4.0 \times 10^4$ and $P_{eM}=8.0 \times 10^5$, respectively. About the boundary condition, the concentration of colloidal silicic acid fed at $x=0$ and $z=0$ was set to a constant value (Dimensionless concentration=1). The other boundary conditions were described by each normal derivative, $\partial C/\partial n=0$.

Table 2 Parameters used in the calculation of basic case except for the deposition rate-constant⁽²⁾.

Parameter	Value
<i>Fracture</i>	
characteristic length (z_1)	100 m
aperture ($2b$)	1.0×10^{-4} m
specific surface area ($a(=1/b)$)	1.0×10^4 1/m
gradient of hydraulic head (∇h)	-0.01
hydraulic conductivity ($K(=T_R/2b)$) ^{*)}	2.5×10^{-5} m/s
flow velocity (m/s) u_0 ($= -K \nabla h$)	2.5×10^{-7} m/s
longitudinal dispersivity (α)	10 m
dispersion coefficient ($D_e \approx \alpha u_0$)	2.5×10^{-6} m ² /s
<i>Rock Matrix</i>	
porosity (ϵ)	0.02
diffusion coefficient (D_{Ma})	3.0×10^{-12} m ² /s
specific surface area ($a_M(=10^2 a)$)	1.0×10^6 1/m

^{*)} T_R : Transmissibility (m²/s) ($2b=2\sqrt{T_R}$)

Figure 6 shows the calculation results of the basic case, where Fig. 6(a) is two-dimensional (x - z) concentration distribution of colloidal silicic acid existing in liquid phase, Fig. 6(b) is the concentration distribution in the fracture with time (year), and Fig. 6(c) is the concentration distribution in the rock matrix (at $z=0$). Once the flow path surface is covered (altered) with the amorphous silica due to the deposition of silicic acid, it would take more time than several million years in order to crystallize the surface of the solid phase⁽⁸⁾, even if the time to attain to the steady state was within around 6 years in the calculation of Figs. 6(b) and 6(c). However, as shown in Fig. 6(b), the deposition area (e.g., assumed in the range of $0.05 \leq C \leq 1.0$) is limited to around 20 m from alkali front ($z=0$). (Since the deposition rate is described by one-order equation with the concentration of colloidal silicic acid, the deposition of colloidal silicic acid appears only in the range of its concentration >0 .) Furthermore, the deposition range in rock matrix was limited to several centimeters.

Figure 7 shows some examples of the steady state in the concentration distribution of the colloidal silicic acid. Table 3 is the parameter set of each case. These results suggested that the altered spatial range from alkali front is limited to several ten meters. While at the present stage in Japan the total amount of cement-based materials for the construction of the repository is not clarified, this code cannot consider the clogging of the fracture (i.e., the change of fracture aperture) due to the deposition. However, Fig. 7 shows that within at least these ranges the continuous deposition of colloidal silicic acid (described by the deposition rate-constant and the concentration of colloidal silicic acid (in liquid phase)) would lead to the clogging of flow-path (fracture) as reported by Mäder et al.⁽¹⁷⁾, by Soler & Mäder⁽¹⁸⁾ and by Komatsu et al.⁽¹⁹⁾. Therefore, the radionuclides (RNs) released from the repository move through other flow-paths not altered by the deposition.

Fig. 6 The calculation results of the basic case shown in Table 2. (The feed-point of colloidal silicic acid (alkali front): $x=0, z=0$.) (a): The steady state of the concentration distribution (x - z) of colloidal silicic acid, (b) the concentration change in the fracture, and (c) the concentration change in the rock matrix at $z=0$.)

Fig. 7 Two-dimensional concentration distribution of the colloidal silicic acid in the steady state of each case. (The scale bar. of the concentration is the same as shown in Fig. 6(a). Case (a) is the same to the basic case in Fig. 6(a), and the other cases are based on the parameters shown in Table 3.)

Table 3 Parameters of each case of Fig. 7. (Basic case (a) is based on Table 2. Each underline shows the difference from the basic case (a).)

Parameters	Case (a)	Case (b)	Case (c)	Case (d)	Case (e)	Case (f)
<i>Fracture</i>						
Aperture ($2b$)*	1.0×10^{-4} m	<u>2.0×10^{-4} m</u>	<u>0.5×10^{-4} m</u>	1.0×10^{-4} m	1.0×10^{-4} m	1.0×10^{-4} m
<i>Rock Matrix</i>						
Diffusion coefficient (D_{Ma})	3.0×10^{-12} m ² /s	3.0×10^{-12} m ² /s	3.0×10^{-12} m ² /s	<u>3.0×10^{-11} m²/s</u>	<u>3.0×10^{-11} m²/s</u>	3.0×10^{-12} m ² /s
Specific surface area (a_M)	$10^2 a$	$10^2 a$	$10^2 a$	$10^2 a$	<u>$10^2 a \times 5$</u>	<u>$10^2 a \times 5$</u>

* Through the relations shown in Table 2, the fracture aperture, $2b$, links the specific surface area of fracture (a), the hydraulic conductivity of fracture (K), the flow velocity of fracture (u_0), the dispersion coefficient ($D_e \approx au_0$), and the specific surface area of matrix ($a_M (=10^2 a)$).

5. Conclusions

Since the deposition rate of colloidal silicic acid is smaller than that of soluble silicic acid, the colloidal silicic acid would flow downstream with groundwater, depositing on flow-path surfaces not altered by the deposition of soluble silicic acid. Therefore, this study examined the dynamic behavior of the colloidal silicic acid contacted directly with solid phase. That is, after adjusting pH from 12 to 8, producing the colloidal silicic acid from supersaturated silicic acid and curing for 12 hours, the solid sample was poured into the vessel. The results showed that the initial condition of the solid surface did not so affect the apparent rate-constant at least in the range less than 10 mM in supersaturated silicic acid. Furthermore, the apparent rate- constants, k' (1/s), showed good linearity to the specific surface area ($=a$ (1/m)) under the isotherm condition of 293K. Therefore, the gradient of k' (1/s) to a (1/m) can yield the rate-constants k (m/s) through $k'=ak$.

Through summarizing the deposition rate-constants of supersaturated silicic acid, the smallest value of k was 1.0×10^{-12} m/s in the co-presence of calcium ions of 1 mM.

Furthermore, in JAEA, the authors calculated spatial ranges altered by colloidal silicic acid, using a simulation code, COLFRAC-MRL, considering the deposition rate, the advection-dispersion in single fracture, and the diffusion to rock matrix. The practical values of various parameters, such as fracture aperture, surface area of micro pores in rock matrix and so on, except for the deposition rate-constant were quoted from H12 report of JNC⁽²⁾. The calculation results suggested the clogging caused by the deposition of colloidal silicic acid in flow-path. The altered spatial range in the flow-path was limited to around 30 m in fracture and to several centimeters in rock matrix. Although the deposition of colloidal silicic acid affects the sorption of RNs in rock matrix, such a deposition of silicic acid plays a role of physical barrier by decreasing the permeability of fracture. Therefore, on the whole, the deposition of colloidal silicic acid would lead to the retardation effect of the migration of RNs released from the repository.

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