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STUDY ON THE POLYMERIZATION OF SILICIC ACID IN RELATION TO SILICA SCALING

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ABSTRACT

The process of polymerization of silicic acid in aqueous solution can be divided into three steps: (1) a reaction between monosilicic acids, (2) a reaction between monosilicic and polysilicic acids, and (3) a reaction between polysilicic acids. The pH value giving maximum rate of polymerization was different among three reactions, and was shifted to lower pH value with increasing temperature.

Silicic acid adsorbed on iron(III) hydroxide rapidly polymerized, and the rate of polymerization was rapid in the pH range 8 - 10 and increased with increasing temperature. Hard and glassy silica was formed by the adsorption of silicic acid on iron hydroxide from geothermal water.

The rate of reaction between polysilicic acids was accelerated by the addition of alkyltrimethylammonium bromides (ATAB). On the other hand, ATAB did not practically affect the rate of reactions between monosilicic acids and between monosilicic and polysilicic acids. Although the rate of reaction between polysilicic acids increased with increasing temperature, the rate became very much faster by the addition of cetyltrimethylammonium bromide.

INTRODUCTION

Geothermal discharge waters from geothermal power plants are generally supersaturated with respect to silica, and deposition of silica in drains and channels is an important practical problem. It is thought that the polymerization of silicic acid is responsible for the formation of silica scale. It is therefore necessary to study the process of polymerization of silicic acid.

This paper describes (1) polymerization of silicic acid in aqueous solution, (2) polymerization of silicic acid adsorbed on iron(III) hydroxide and (3) polymerization of silicic acid in the presence of alkyltrimethylammonium salts.

POLYMERIZATION OF SILICIC ACID IN AQUEOUS SOLUTION

Introduction

Polymerization of silicic acid in geothermal waters has been studies [1-3]. The rate of polymerization is measured by monitoring the decrease in the concentration of silicic acid by colorimetry. However, no information is available on the change in particle sizes of polysilicic acids with time by colorimetry.

Gel chromatography is useful for the study of the polymerization of silicic acid [4], because the change in elution curves for polysilicic acid with time reflects a mechanism of the particle growth of polysilicic acids [5].

The process of polymerization of silicic acid is divided into three steps [6].

(1): A reaction between monosilicic acids.

(2): A reaction between monosilicic and polysilicic acids.

(3): A reaction between polysilicic acids.

The term "monosilicic acid" here indicates the molybdate reactive silicic acid species unless otherwise specified, while the term "polysilicic acid" indicates molybdate unreactive silicic acid species, for convenience.

The first step of the polymerization is due to Reaction (1) and then Reactions (2) and (3) may occur. If it can be assumed that, in the early stage of polymerization, the decrease in the concentration of monosilicic acid in solutions of various pH is due mainly to Reaction (1), it may be possible to obtain the relationship between the rate of Reaction (1) and the pH.

When the concentration of monosilicic acid is higher than the solubility of amorphous silica at given pH and temperature, monosilicic acid generally polymerizes, but the rate of polymerization depends on the concentration of monosilicic acid. In a solution with an adequate concentration of monosilicic acid, Reaction (1) does not occur within a certain period of time. Therefore, when monosilicic acid solution in which Reaction (1) does not occur within a certain period of time is mixed with a polysilicic acid solution and the concentration of monosilicic acid decreases with time from the moment of mixing the solutions, it is concluded that the decrease in the concentration of monosilicic acid is due mainly to Reaction (2).

When the concentration of monosilicic acid is close to the solubility of amorphous silica at given pH and temperature, Reactions (1) and (2) do not virtually occur. As Reaction (3) proceeds regardless of the presence of monosilicic acid, the effect of pH on the reaction between polysilicic acids can be measured by gel chromatography from the change in elution curves for silicic acid in the solutions of various pH values.

Gel chromatography is a method for separating solute molecules according to their size, larger molecules being eluted faster than smaller molecules. The elution volumes of molecules are correlated with their molecular weight (size). A distribution coefficient, K_{av}, for a given gel in gel chromatography is defined as follows [7]:

$$K_{av} = (V_e - V_o)/(V_t - V_o) \qquad (1)$$

where V_o is the void volume, V_t the total bed volume, and V_e the elution volume. Here, V_o, V_t and V_e are easily measured. As K_{av} value is correlated to V_e, it is a measure of molecular size and decreases with increasing particle size.

In this work, the effect of pH and temperature on the rate of Reactions (1), (2) and (3) was studied by colorimetry and gel chromatography.

Effect of temperature on the polymerization between polysilicic acids at pH 7.

Sample solution containing 225 ppm (SiO_2) polysilicic acid and monosilicic acid, of which the concentration is nearly equal to the solubility of amorphous silica at given temperature, was prepared and adjusted to pH 7. After standing for 1 h, silicic acid was chromatographed on Sephadex G-100 column [5]. The amounts of silicic acid in the fractions were measured by atomic-absorption spectrometry. As the concentration of monosilicic acid is close to the solubility of amorphous silica, Reactions (1) and (2) do not occur, but only Reaction (3) proceeds. Under these conditions, Reaction (3) was measured. The elution curves for polysilicic acid in solutions after standing for 1 h at various temperatures are shown in Fig. 1. The elution curve for polysilicic acid in the solution at 2°C did not change within 1 h. This elution curve represents the distribution of particle sizes of polysilicic acid in the initial solutions at various temperatures. The results show that the rate of reaction between polysilicic acids increases with increasing temperature.

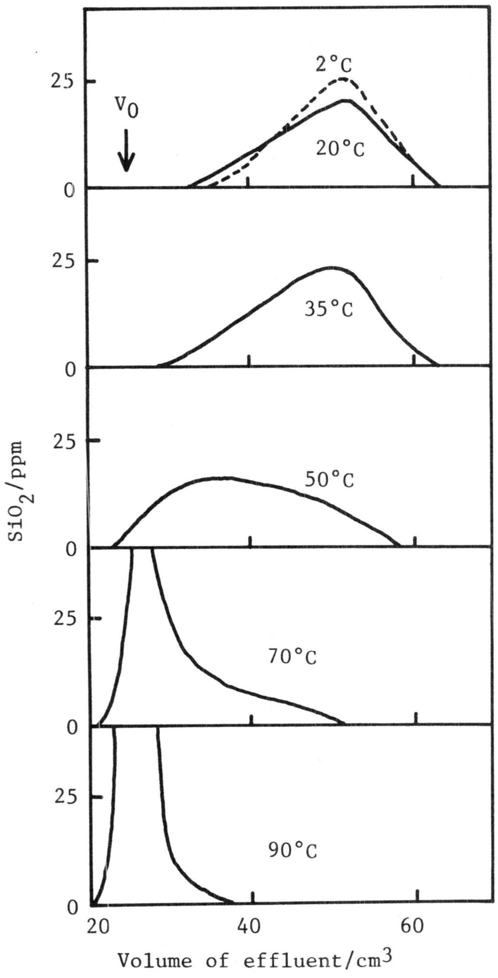

Fig. 1 Elution curves after 1 h for polysilicic acid in solutions of pH 7 at various temperatures.

The reaction between monosilicic acids.

The kinetics of polysilicic acid formation obtained by monitoring the concentration of monosilicic acid as functions of time and pH at 20° and 90°C is shown in Fig. 2. As it can be assumed that the decrease in the concentration of monosilicic acid is due mainly to the formation of polysilicic acid by Reaction (1) in the early stage of polymerization, the pH values of the maximum of the decrease in the concentration of monosilicic acid after 90 min at 20°C and 10 min at 90°C may close to the pH values at which the rate of polymerization is maximal, respectively. The pH giving maximum rate of polymerization slightly shifted to a lower pH with lapse of time. This may be due to the effect of polysilicic acid formation by Reaction (2). The results indicate that Reaction (1) is most rapid at around pH 9.3 at 20°C and pH 8.1 at 90°C, respectively.

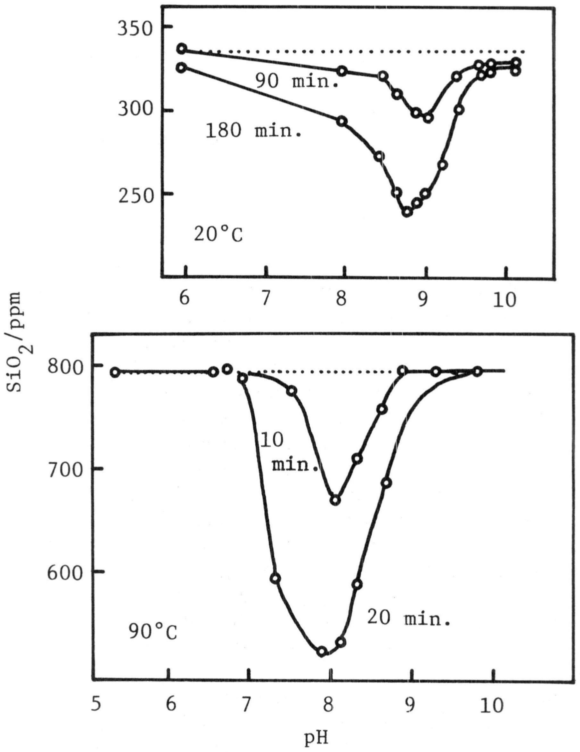

Fig. 2 Variation of the concentration of monosilicic acid as a function of pH. Dotted lines show the concentration of monosilicic acid in the initial solutions.

The reaction between monosilicic and polysilicic acid.

When monosilicic acid solutions of 330 ppm at 20°C and 590 ppm at 90°C were adjusted to the pH range of 2.0 - 9.5, the concentration of monosilicic acid did not decrease within 30 min at 20°C and 15 min at 90°C, respectively. If polysilicic acid solution is mixed with these monosilicic acid solutions and the concentration of monosilicic acid decreases from the moment of mixing, it may be concluded that the decrease in the concentration of monosilicic acid is caused by the reaction between monosilicic and polysilicic acids. The procedure for the determination of Reaction (2) has been done under these conditions. The results are shown in Fig. 3. The decrease in the concentration of monosilicic acid is maximal at around pH 8.6 at 20°C and pH 7.5 at 90°C, respectively.

The reaction between polysilicic acids.

Sample solution containing polysilicic acid and monosilicic acid, of which concentration is close to the solubility of amorphous silica at given pH and temperature, was prepared. After standing for desired time, silicic acid was chromatographed. K_{av} value of polysilicic acid was calculated from equation 1. The relationship between K_{av} value and pH at 20°C and 90°C is shown in Fig. 4. It appears that the K_{av} value of polysilicic acid is minimal at around pH 6.8 at 20°C and pH 6.1 at 90°C, respectively. The results show that the rate of reaction between polysilicic acids is most rapid at these pH values.

Conclusion

The pH values, at which Reactions (1), (2) and (3) are most rapid, are listed in Table 1. The pH value giving the maximum rate of each Reaction was shifted to a lower pH value with increasing temperature. It was concluded that, above about pH 4, the polymerization due to Reactions (1), (2) and (3) proceeds mainly a reaction between ionized and un-ionized silanol groups [6].

Table 1. The pH values that the reactions between monosilicic acids, between monosilicic and polysilicic acids and between polysilicic acids are most rapid.

Temperature (°C)	pH		
	Monomer and monomer	Monomer and polymer	Polymer and polymer
2	9.5	8.9	7.0
20	9.3	8.6	6.8
50	8.5	8.0	6.7
90	8.1	7.5	6.1

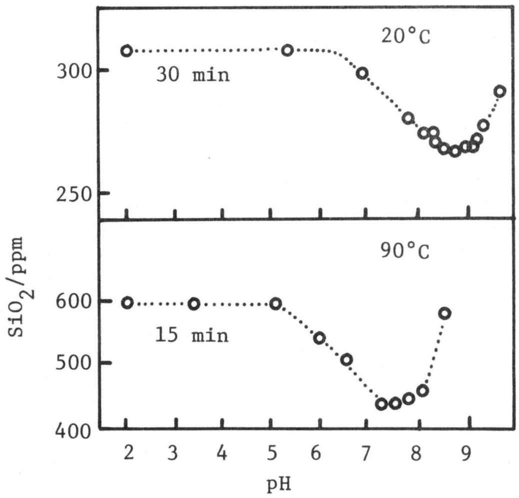

Fig. 3 Change in the concentration of monosilicic acid with pH after given time when polysilicic acid was added to monosilicic acid solutions.

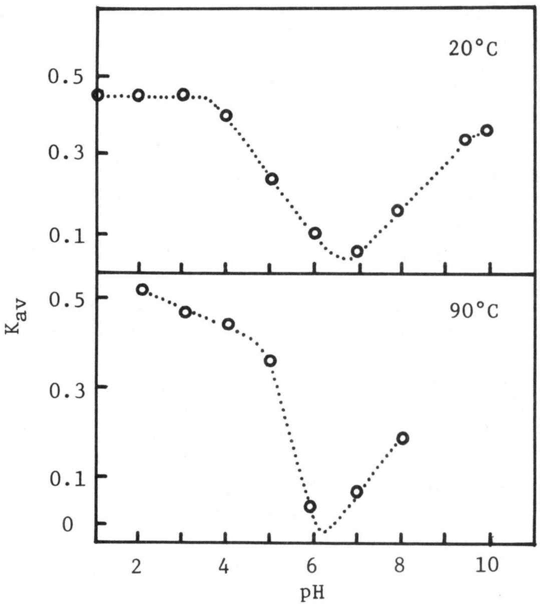

Fig. 4 Plot of K_{av} against pH.

POLYMERIZATION OF SILICIC ACID ADSORBED ON IRON(III) HYDROXIDE

Introduction

Silica scales formed from geothermal waters generally contain a large amount of iron compared with iron content of geothermal waters. Silicic acid adsorbed on iron hydroxide rapidly polymerizes in a short period of time [8]. It is supposed that iron hydroxide may play a role in the formation of silica scales.

In this work, the adsorption of silicic acid on iron hydroxide and the polymerization of adsorbed silicic acid were studied.

Adsorption of monosilicic acid on iron hydroxide and the formation of low-molecular-weight silicic acid species.

Monosilicic acid solution (30 or 40 ppm) was adjusted to the desired pH at given temperature and a known amount of iron hydroxide was then introduced into the solution. The suspension was stirred vigorously. After 30 min, the suspension was filtered through membrane filter having pores of 0.1 μm. The concentration of monosilicic acid in the filtrate was determined and the amount of silicic acid adsorbed on iron hydroxide was calculated. Silicic acid adsorbed on iron hydroxide was trimethylsilylated [9] and trimethylsilyl derivatives of silicic acids were determined by gas chromatography [10]. The mole ratio of monosilicic acid and iron hydroxide in the initial solution is expressed as Si/Fe(MR).

Fig. 5 shows relationship between the amount of silicic acid adsorbed on iron hydroxide (expressed as Si/Fe mole ratio) and pH. The maximum adsorption with respect to pH occurred at pH around 9 - 10.

Fig. 6 shows the proportion of low-molecular-weight silicic acid species existing on iron hydroxide as a function of pH. Proportion is given by

$$\text{Proportion}(\%) = 100(P_i/\Sigma P_i) \qquad (2)$$

where Pi is the peak intensity of the i-th species on gas chromatogram. Dimer ($Si_2O_7^{6-}$), linear trimer ($Si_3O_{10}^{8-}$) and cyclic tetramer ($Si_4O_{12}^{8-}$) other than monomer (SiO_4^{4-}) were formed at any pH in the range 6 to 12. Although monosilicic acid concentration in the initial solution is very low and monosilicic acid never polymerizes, it is noteworthy that monosilicic acid adsorbed on iron hydroxide from such solutions polymerizes.

Effect of temperature on the formation of low-molecular-weight silicic acid species is shown in Fig. 7. The proportion of monomer decreased and that of dimer increased with increasing temperature. Decrease in the proportion of trimer + tetramer at 50°C may be due to the formation of higher-molecular-weight silicic acid species which can not be determined by gas chromatography.

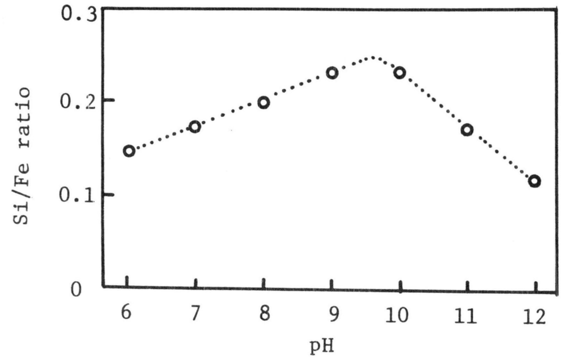

Fig. 5 The effect of pH on the amount of silicic acid adsorbed on iron hydroxide after 30 min.
Initial monosilicic acid concentration: 40 ppm (SiO_2).
Si/Fe(MR): 0.33.

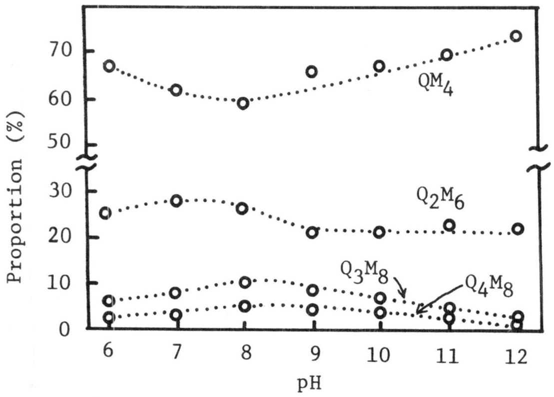

Fig. 6 Variation of proportion of low-molecular-weight silicic acid species existing on iron hydroxide as a function of pH.
Initial monosilicic acid concentration: 40 ppm (SiO_2).
Si/Fe(MR): 0.33.

Polymerization of adsorbed silicic acid.

Monosilicic acid solution (300 ppm) was adjusted to the desired pH at given temperature and a known amount of iron hydroxide was then introduced into the solution. The suspension was stirred vigorously. After 5 h, the suspension was filtered through membrane filter having pores of 0.1 μm. The iron hydroxide on the membrane filter was dissolved with dilute hydrochloric acid, the resulting solution being filtered. The amounts of monosilicic acid (Si(M)), total silicic acid (Si(T)) and iron ion in the filtrate were measured. Silicic acid in the filtrate was chromatographed on Sephadex G-25 column [8]. The results are shown in Figs. 8, 9 and 10. Si(M)/Si(T) ratio indicates the degree of polymerization of silicic acid adsorbed on iron hydroxide. The results shown in Fig. 8 indicate that the polymerization of adsorbed silicic acid is rapid in the pH range 8 - 10.

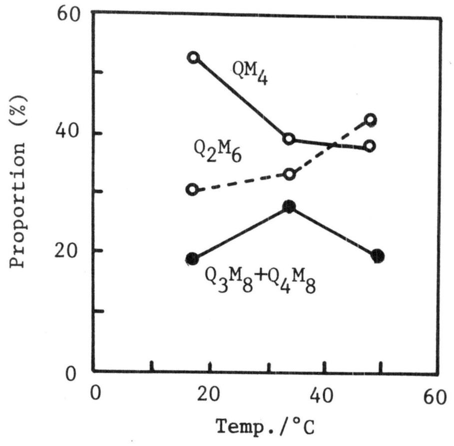

Fig. 7 Change with temperature of proportion of low-molecular-weight silicic acid species existing on iron hydroxide.
Initial monosilicic acid concentration: 30 ppm (SiO_2).
Si/Fe(MR): 0.25.

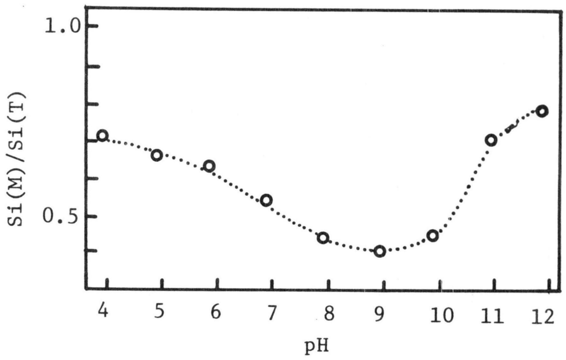

Fig. 8 Effect of pH on the degree of polymerization of silicic acid adsorbed on iron hydroxide after 5 h.
Si/Fe(MR): 0.63. Temperature: 25°C.

Elution curves for silicic acid are shown in Fig. 9. The dotted line is the elution curve for monosilicic acid. From the elution curves we see that the growth of polymers is most rapid at pH 9.

Fig. 10 shows the effect of temperature on the polymerization of adsorbed silicic acid. Si(M)/Si(T) ratio decreased with increasing temperature. This means that the rate of polymerization increases with increasing temperature.

Adsorption of silicic acid on iron hydroxide from geothermal water.

An iron hydroxide was introduced into a flask

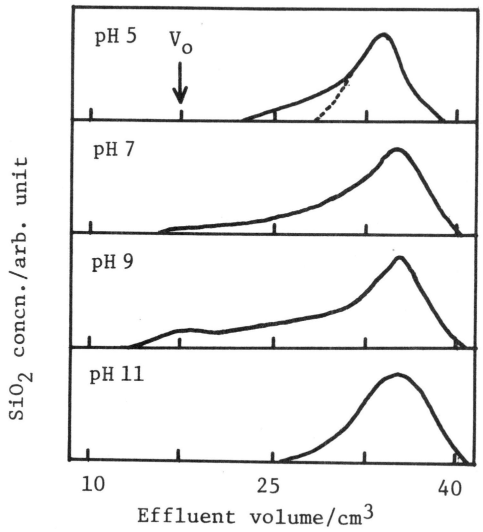

Fig. 9 Gel chromatograms for silicic acid adsorbed on iron hydroxide at various pH after 5 h.
Si/Fe(MR): 0.63. Temperature: 25°C.

and the geothermal water from Otake No. 9 well, Oita Prefecture, was flowed through the flask with flow rate of 1 l/h. Silicic acid in the geothermal water (about 600 ppm SiO_2, pH 8.3, 90°C) was almost monomeric form. After 2 days, the iron hydroxide was separated from the geothermal water and dissolved with hydrochloric acid. A large amount of hard and glassy silica was obtained. Scanning electron microscope photograph of silica is shown in Fig. 11. X-ray diffraction diagram of silica is shown in Fig. 12. The diagram shows a broad peak at around $2\theta = 21 - 22°$.

Conclusion

The rate of adsorption of monosilicic acid on iron hydroxide was most rapid at pH 9 and silicic acid adsorbed rapidly polymerized in the pH range 8 - 10. The rate of polymerization of adsorbed silicic acid increased with increasing temperature. Hard and glassy silica was formed by the adsorption of silicic acid on iron hydroxide from geothermal water.

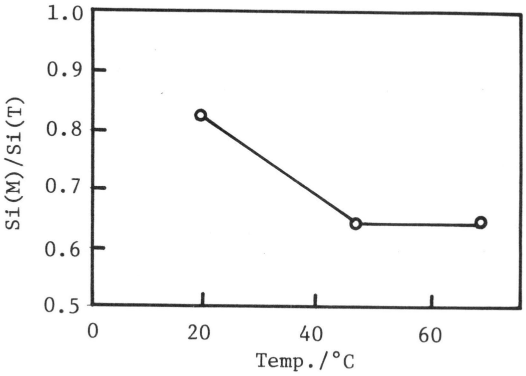

Fig. 10 Effect of temperature on the degree of polymerization of silicic acid adsorbed on iron hydroxide after 5 h.
Si/Fe(MR): 0.25.

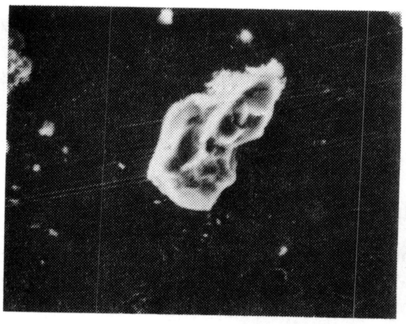

Fig. 11 Scanning electron microscope photograph of silica.

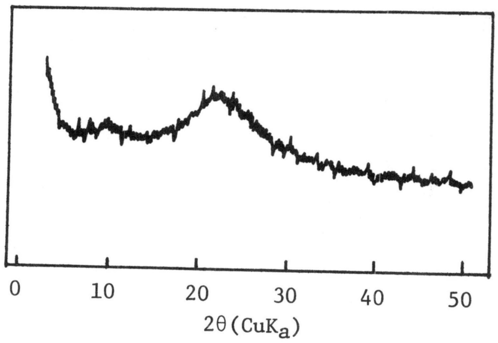

Fig. 12 X-ray diffraction diagram of silica.

POLYMERIZATION OF SILICIC ACID IN THE PRESENCE OF ALKYLTRIMETHYLAMMONIUM SALTS

Introduction

Organic compounds have been tested for controlling the scale formation or to remove the polysilicic acid from geothermal waters. Iler summarizes the studies of the interaction of organic compounds with silica [11]. However, the process of polymerization of silicic acid in the presence of organic compounds has not been studied.

In this work, the effect of alkyltrimethylammonium bromides as model compound on the polymerization of silicic acid was studied.

Experimental

Monosilicic acid solution was prepared by dissolving silica gel with sodium hydroxide solution.

Alkyltrimethylammonium bromides (ATAB) used were tetramethylammonium bromide (TMAB), lauryltrimethylammonium bromide (LTAB) and cetyltrimethylammonium bromide (CTAB).

ATAB solution (5 ml) was added to monosilicic acid solution (500 ml, 600 ppm SiO_2) to give the desired concentration of ATAB and pH of the solution was adjusted to 8. The solution was stirred vigorously with magnetic stirrer. Periodically, an aliquot of sample solution was pipetted and filtered through membrane filter having pores of 0.45 μm in order to separate the precipitated silica. The amount of monosilicic acid in the filtrate was determined by colorimetry and the silicic acid was then chromatographed on a Sephadex G-100 column. The amounts of silicic acids in the fractions were measured by atomic absorption spectrometry. The polymerization of silicic acid in the solution without ATAB was also examined.

Results

Polymerization of silicic acid in the presence of ATAB. Fig. 13 shows the variation with time of elution curves for silicic acid in the solution without ATAB. The peaks on the right are due to monosilicic acid and those on the left to polysilicic acid. Particle sizes of polysilicic acids increased with time. Polysilicic acids larger in size than 0.45 μm did not form within 24 h. Each elution curve for polysilicic acid is called the reference elution curve for convenience.

Fig. 14 shows the elution curves after 24 h for silicic acid in solutions with 10^{-4}M ATAB. The polymerization of silicic acid was not affected in the presence of 10^{-4}M TMAB, because the elution curve in the presence of TMAB is almost the same as the reference elution curve. Bar graphs in the figure show the relative amounts of precipitated silica. The amount of precipitated silica in the presence of CTAB is larger than that in the presence of LTAB. The polymerzation of silicic acid was accelerated by the presence of LTAB and CTAB.

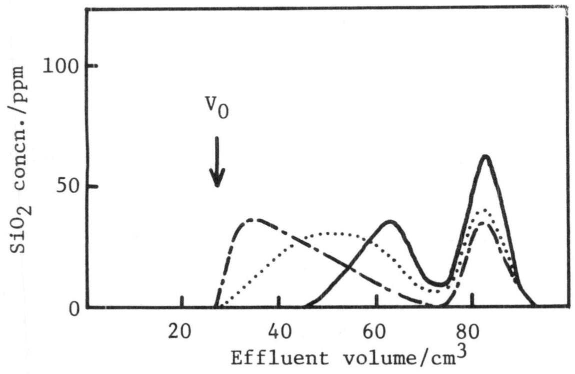

Fig. 13 Variation with time of the elution curves for silicic acid in solution of pH 8. —— 0.5 h, --- 5 h, —·— 24 h.

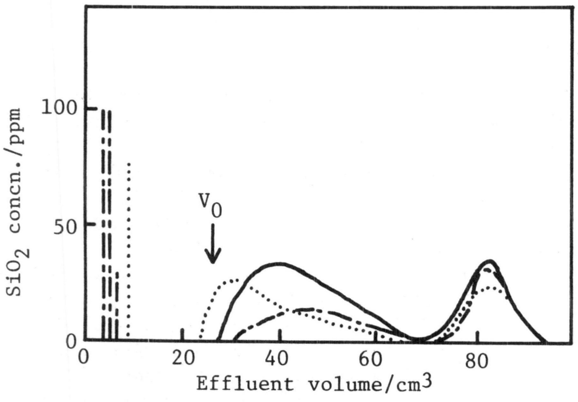

Fig. 14 Elution curves after 24 h for silicic acid in solutions in the presence of ATAB at pH 8. —— TMAB, --- LTAB, —·— CTAB: 10^{-4}M.

Effect of concentration of ATAB. At ATAB concentration range of 10^{-3} - 10^{-7}M, the polymerization of silicic acid was examined. Fig. 15 shows the elution curves after 5 h for silicic acid. The elution curve for polysilicic acid at TMAB concentration of 10^{-3}M shifted to the left compared with the reference elution curve, indicating that the rate of particle growth of polysilicic acid is accelerated by TMAB. At LTAB concentration range of 10^{-3} - 10^{-5}M and at CTAB concentration range of 10^{-3} - 10^{-6}M, silica was precipitated. The amount of precipitated silica decreased with decreasing concentration of LTAB and CTAB. At ATAB concentration of 10^{-7}M, ATAB did not affect the polymerization of silicic acid.

Fig. 16 shows the variation with time of monosilicic acid concentration in solutions with and without ATAB. The rate of decrease in monosilicic acid concentration in solutions with ATAB was almost the same as that in the solution without ATAB. The results indicate that ATAB hardly affects the reactions between monosilicic acids and between monosilicic and polysilicic acids. The results shown in Figs. 15 and 16 indicate that ATAB accelerates the reaction between polysilicic acids.

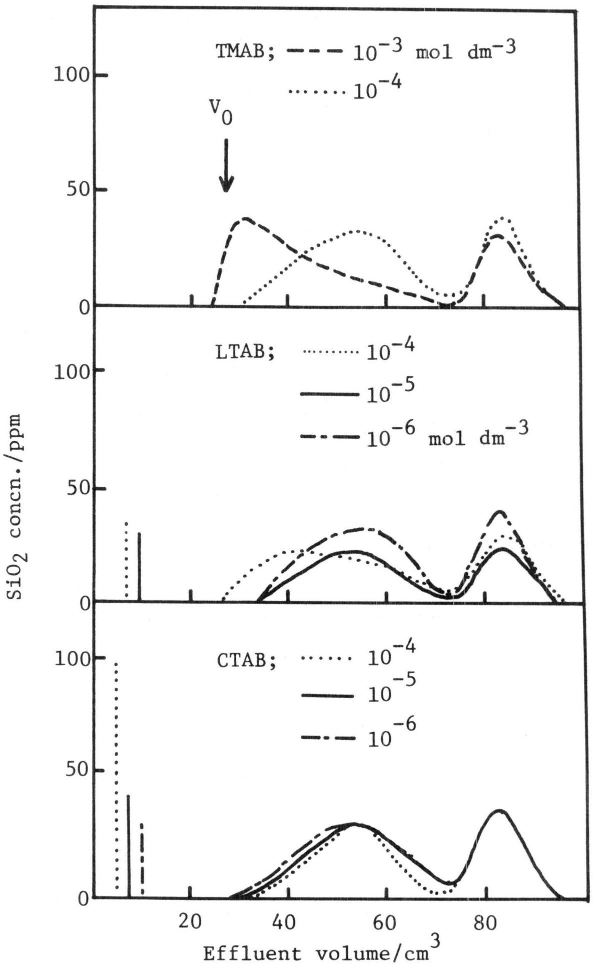

Fig. 15 Elution curves after 5 h for silicic acid in solutions of various ATAB concentrations at pH 8.

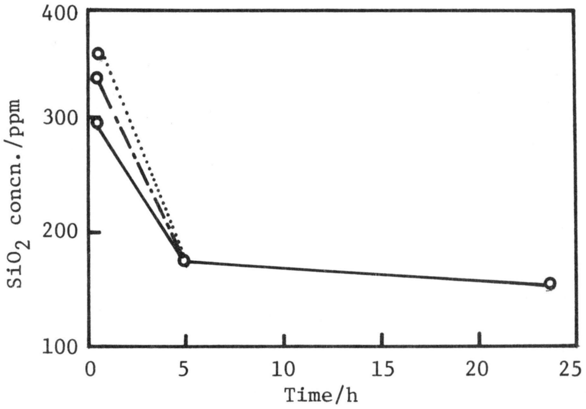

Fig. 16 Variation with time of monosilicic acid concentration in solutions in the presence of ATAB at pH 8.

Effect of temperature. The effect of temperature on the polymerization of silicic acid at CTAB concentration of 10^{-4}M was examined. Monosilicic acid solution of which concentration is 450 ppm (SiO_2) higher than the solubility of amorphous silica at given temperature was used.

Fig. 17 shows the variation of ratio of the amount of precipitated silica (Si(P)) and the amount of silicic acid in initial solution (Si(I)) as functions of time and temperature. The Si(P)/Si(I) ratio, which is a measure of the amount of precipitated silica, increased with increasing temperature.

Fig. 18 shows the variation of ratio of monosilicic acid concentration (Si(M)) and total silicic acid concentration (Si(T)) in the filtrate as functions of time and temperature. Since the difference of Si(M) and Si(T) can be regarded as the amount of polysilicic acid in the filtrate, Si(M)/Si(T) ratio is an indicator of the amount of polysilicic acid. Si(M)/Si(T) ratio decreased with time at 25°C. At 50°C, Si(M)/Si(T) ratio decreased in one hour and then increased with time. At 83°C, Si(M)/Si(T) ratio was nearly unity. This means that polysilicic acids formed rapidly grow and the most part of polysilicic acids are precipitated. The results indicate that although the rate of reaction between polysilicic acids increases with increasing temperature [12], the rate becomes very much faster in the presence of CTAB.

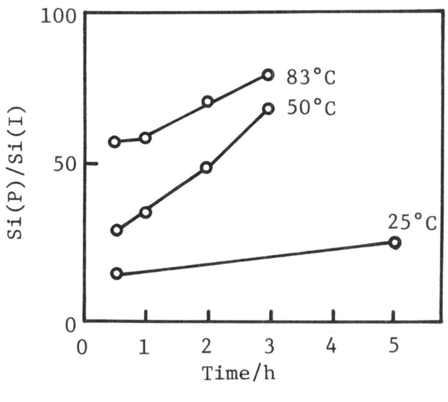

Fig. 17 Variation with time of the amount of precipitated silica at various temperatures.
CTAB concentration: 10^{-4}M.
pH: 8

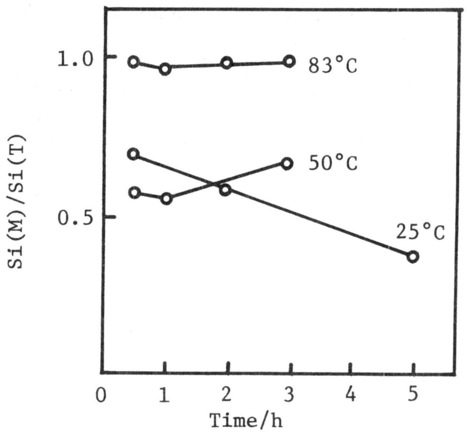

Fig. 18 Variation with time of the amount of polysilicic acid in the filtrates at various temperatures.
CTAB concentration: 10^{-4}M.
pH: 8.

Polymerization of silicic acid in geothermal water in the presence of ATAB. Geothermal water (552 ppm SiO_2, pH 8.3, 90°C) from Otake No. 9 well was collected and kept at 90°C. The water sample immediately after sampling is designated as 0-h sample and the water sample after standing for 3 h is designated as 3-h sample. The elution curves for silicic acid in both samples are shown in Fig. 19. The concentration of monosilicic acid (Si(M)) and that of total silicic acid (Si(T)) are shown in Table 2. Silica did not precipitate after 3 h.

LTAB and CTAB were added to both samples to give the concentration of 10^{-4}M respectively. The solutions were stirred vigorously. After 30 min, the sample solutions were filtered through membrane filter having pores of 1.0 μm, and Si(M) and Si(T) in the filtrates were determined. The results are shown in Table 2. As the concentration of polysilicic acid in 0-h sample was low (Table 2) and particle sizes of polysilicic acids were small (Fig. 19), no precipitation of silica occurred by the addition of LTAB and CTAB. On the other hand, as the concentration of polysilicic acid in 3-h sample was high and particle sizes of polysilicic acids were large, almost all polysilicic acid were precipitated by the addition of LTAB and CTAB.

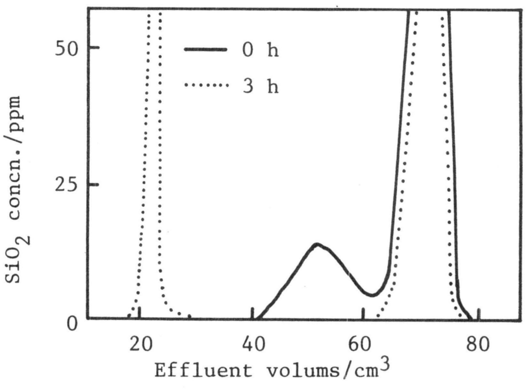

Fig. 19 Elution curves for silicic acid in 0-h and 3-h samples collected from Otake No. 9 well.

Table 2. Effect of ATAB on the precipitation of silica from 0-h and 3-h samples (Otake No. 9 well water; 10^{-4}M ATAB).

ATAB	0-h sample		3-h sample	
	Si(M) (ppm SiO_2)	Si(T) (ppm SiO_2)	Si(M) (ppm SiO_2)	Si(T) (ppm SiO_2)
None, Control	536	552	375	551
LTAB	523	545	379	381
CTAB	519	533	358	351

Conclusion

Effect of ATAB on the polymerization of silicic acid was examined. ATAB did not practically affect the rate of reactions between monosilicic acids and between monosilicic and polysilicic acid. On the other hand, the rate of reaction between polysilicic acids was accelerated by the addition of ATAB. Although the rate of reaction between polysilicic acids increased with increasing temperature, the rate became very much faster by the addition of CTAB. The polymerization of silicic acid in geothermal water in the presence of ATAB was studied.

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