HOKKAIDO UNIVERSITY

Title	Fundamentals in the Use of Activated Silica in Water Purification
Author(s)	Okura, Takeshi; Goto, Katsumi; Murai, Minoru
Citation	Memoirs of the Faculty of Engineering, Hokkaido University, 11(1), 25-39
Issue Date	1960-03-30
Doc URL	https://hdl.handle.net/2115/37817
Type	departmental bulletin paper
File Information	11(1)_25-40.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Fundamentals in the Use of Activated Silica in Water Purification

By

Takeshi OKURA, Katsumi GOTO,
and Minoru MURAI

(Received January 12, 1960)

Abstract

Polymerization of silica in water solution has been studied with special interest to its use in water purification as coagulation aid. It has been inferred that the particle size for the most active silica lies at about 20 Å or below. Mechanism of precipitation of aluminum hydroxide in the presence of colloidal silica has also been discussed.

Introduction

Highly colored or turbid water is frequently met with in Hokkaido, where peat bogs are widely distributed. The removal of color or turbidity of water is usually accomplished by coagulation, settling and filtration. The most widely used coagulant is aluminum sulfate. The coagulation is best carried out at the most favorable pH value. With aluminum sulfate, the optimum point varies over a range from about 5.0 to 6.8 for most waters. However, there are many cases where good flocculation is not obtained by the addition of aluminum sulfate alone. Such circumstances occur especially in winter time.

Activated silica is reported to be frequently useful as a coagulation aid in these cases. It is also reported that the addition of activated silica broadens the pH range at which good flocculation is obtained, and considerably reduces the dosage of aluminum sulfate.

Since Baylis[1] first published the use of polymerized silica in 1937 in water purification to aid coagulation of colloidal matter with aluminum sulfate, numerous investigations[2~8] have been carried out on the use and preparation of this material. The polymerized silica or the colloidal silica used for this purpose is usually called the "activated" silica. Its use has already become standard practice in many municipal and industrial water purification plants.

The activated silica is prepared from sodium silicate by activation with

such chemicals as sulfuric acid, ammonium sulfate, chlorine, carbon dioxide, and aluminum sulfate. The activation reaction is believed to be the neutralization of sodium silicate, leading to polymerization of silicate ions.

Our recent works on silica[9] have shown that colloidal silica is produced in various states of solution, depending on the conditions of activation. Even when the same chemicals are used to produce colloidal silica, the state of solution varies with such variables as the molecular ratio of the activant to silicate, the rate of addition of activant, temperature, and aging time. Merrill[8] describes that polymerized silica produced from sodium silicate by treatment with ion-exchange resin in the hydrogen form has little activity as coagulation aid. It is very interesting to consider that the inactivity is related to the different state of polymerization.

In spite of its great importance, however, few works have been made to establish a method for characterizing the form of silica in water. Consequently, little attention has been called to the correlation of the activity of polymerized silica with its state of solution. On the other hand, our recent works[9] have suggested that the state of solution of silica can be described at least in part by the viscosity and the rate of solution of silica particles in hydrofluoric acid. It is now possible therefore to find the form of silica which is most active as coagulation aid.

Little had been known also on the form of aluminum added to the water, until K. Goto et al.[10] proposed a method for the determination of monoaluminum ion in the presence of polymeric forms of aluminum ion. This method enables the authors to study the solubility behavior of aluminum salt in water.

The Nature of Silicate Solution

The properties of colloidal silica are widely varied depending on the conditions of its preparation. A right understanding of the nature of silicate solution is therefore essential to a better use of acitivated silica in water purification.

When a solution of soluble silicate, which is always strongly alkaline, is neutralized by acid, the silicate ion decomposes to silicic acid. Silicic acid is soluble only to an extent of about 100 to 200 mg./l. as SiO_2 at ordinary temperatures[10~15]. Thus, the solubility of monomeric form of silica (monosilicic acid and monosilicate ion) increases steeply as the pH increases above a certain point as will be seen in Fig. 1. However, the silica present beyond the solubility never forms a precipitate but polymerizes to form colloidal or polymerized silica.

The formation of polymerized silica can be regarded as taking place in

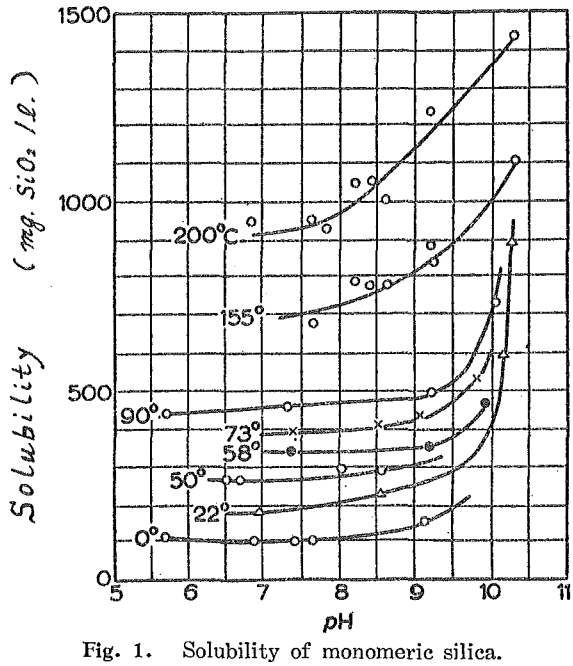


Fig. 1. Solubility of monomeric silica.

two stages. In the first, initially formed silicic acid, $Si(OH)_4$, condenses into colloidal particles. In dilute solution, further slow increase in particle size is the only subsequent change. Under certain conditions, however, these primary particles are able to condense together to give a very open and continuous structure. When the aggregation proceeds further, the network structure extends throughout the medium, thus bestowing a certain degree of rigidity upon it.

In both stages, the mechanism is fundamentally the same, that is, condensation to form Si–O–Si links. Therefore, colloidal particles of silica and silica gel is schematically shown

$$Si(OH)_4 \xrightarrow{\text{Polymerization}} \text{Colloidal particles (Sol)}$$

$$\xrightarrow{\text{Aggregation}} \text{Aggregates of primary particles}$$

$$\xrightarrow{\text{Further aggregation}} \text{Network structure (Gel)}$$

It is generally accepted that the condensation of silanol groups takes place most rapidly in neutral solution[16], the conclusion being derived from measurements

of gelation time[17~19] and other properties[20,21]. It is questionable, however, whether or not the gelation time could be used as a measure of the rate of condensation as far as there is no proof that silanol groups condense together always to form the same structure with no regard to pH.

It has been shown in our previous[9] paper that in basic solution, while the reactivity of polymerized silica to hydrofluoric acid decreases with aging time, no measurable change takes place in the viscosity. Contrary, the reactivity remains high in neutral or acid media, but the viscosity increases rapidly. This appears to indicate that there is no direct connection between the gelation time and the rate of condensation of silanol groups.

An increasing solubility of silica with pH should also be taken into account. The concentration of silica capable of undergoing polymerization, or the degree of supersaturation of monomeric form of silica may be low in a basic medium where most of the silica is in the form of highly soluble silicate ion.

K. Goto[22] has thus investigated the rate of condensation from measurements of the rate of disappearance of monomeric silica over the range of pH's from 7 to 10 and on the assumption that the condensation is of third order with respect to the monomeric form of silica present in excess of the solubility value. The results indicate that the logarithm of the reaction constant increases linearly with pH, as is shown in Fig. 2.

Rate of dissolution of silica particles is also a function of pH as will be seen in Fig. 3.

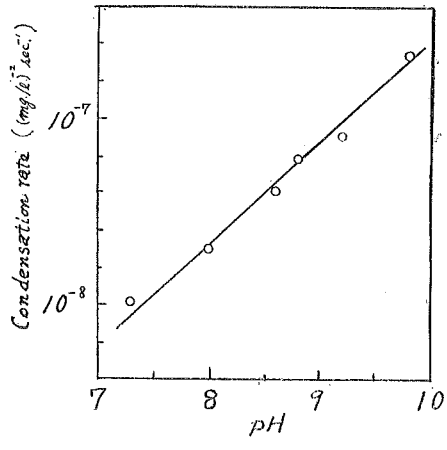


Fig. 2. Rate of condensation of monosilicic acid.

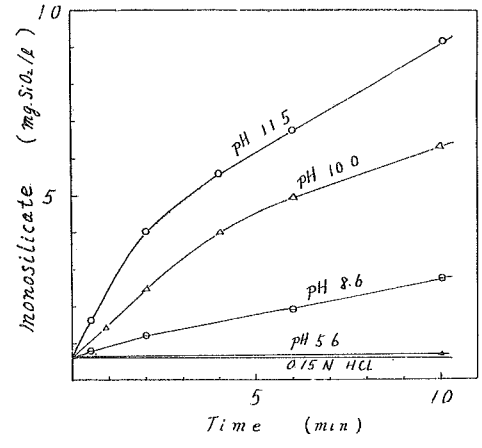


Fig. 3. Dissolution of colloidal silica particles at various pH values. Total SiO_2, 18.5 mg./l.; pH adjusted with Na_2CO_3 and $NaHCO_3$.

The increasing rate of dissolution and of condensation with pH may facilitate a primary particle, in basic solution, to dissolve and then deposit on the surface of another particle. It may be reasonably assumed, therefore, that the growth of primary particles takes place more easily in basic medium than in acid one.

Colloidal silica has an isoelectric point at pH 2–3, above which double-layer repulsion between primary particles of silica increases with pH, minimizing the collision of particles to take place in basic solution. Silicic acid would polymerize, therefore, in basic media to form descrete particles of silica rather than aggregates of primary particles. On the other hand, it would form aggregates of smaller primary particles in neutral or acid solution, in which double-layer repulsion is not sufficiently strong to prevent collision of particles, but the tendency to form Si–O–Si links still plays a role. The most rapid gelation of silica in slightly acid or neutral solution will be easily understood from the above considerations. The foregoing discussion indicates that two extreme cases arise in the form of polymerized silica. These are shown in Figs. 4 A and B.

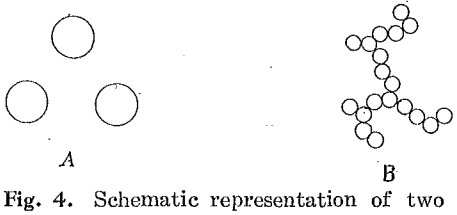


Fig. 4. Schematic representation of two types of colloidal silica particles.

According to Einstein, relative viscosity of a colloidal solution is expressed by the equation

$$\eta_{rel} = 1 + 2.5\,\varphi \qquad (1)$$

where η_{rel} is the relative viscosity and φ the fraction of total volumes occupied by the particles.

If the apparent hydrodynamic volume, V, or the volume immobilized by 1 g. of particles is used instead of φ, equation (1) becomes

$$\eta_{rel} = 0.0025\,CV \qquad (2)$$

where C is the concentration of particles in grams per liter, and V is expressed in ml./g.

If silica would polymerize to form particles as shown in Fig. 4 B, the apparent hydrodynamic volume of particles would greatly increase, while the decrease in specific surface area would be rather small. On the other hand, if polymerization takes place in such a way in which aggregation is minimized, the specific surface area would decrease considerably, but the specific hydrodynamic volume will remain almost unaltered, or it rather decreases since the fraction of the volume of hydrated water on silica surfaces decreases with the

growth of particles. It may be reasonable, therefore, to express the form of activated silica by the specific surface area and the specific hydrodynamic volume.

Solubility Behavior of Aluminum

A proper understanding of the solubility behavior of aluminum is essential for the best use of aluminum salt as coagulant. One of the present authors[23] has found that aluminum dissolves in water as monomeric ion up to the concentration expressed by the following equations:

$$\log S = 5.732 - 2.00\,\mathrm{pH} \quad \text{(on the acid side)}$$

$$\log S = 1.056\,\mathrm{pH} - 13.050 \quad \text{(on the alkaline side)}$$

where S is the concentration of monomeric form of aluminum in moles per liter and designated hereafter as the solubility of aluminum ion. Fig. 5 shows the solubility of aluminum ion as calculated from the above equations.

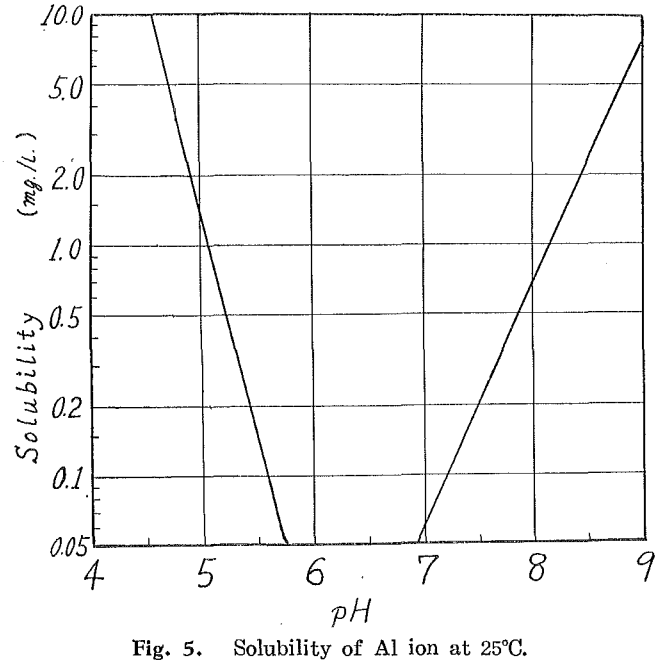
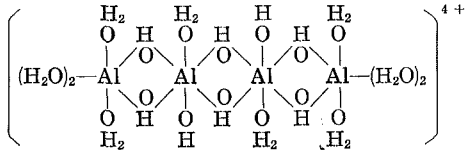


Fig. 5. Solubility of Al ion at 25°C.

In many cases, however, much aluminum is found in solution beyond the solubility given above. This is true especially at pH 4.5 to 6 (Fig. 6), and is attributed to the formation of polynuclear hydroxo-aquo-aluminum ions, such as[24]:



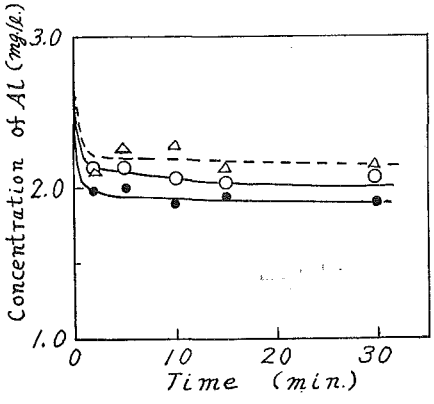


Fig. 6. Changes in the concentration of aluminum capable of passing through filter paper.

—△·····△— pH 5.40
—○——○— pH 6.10
—●——●— pH 6.41

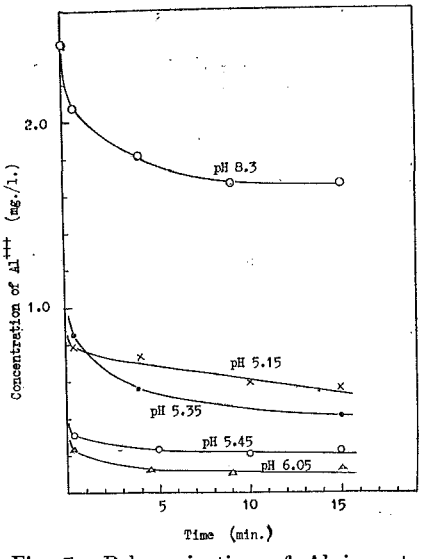


Fig. 7. Polymerization of Al ion at 25°C. Initial concn. of Al^{+++}, 2.42 mg./l. ; pH adjusted with NaOH ; $AlCl_3$ was used.

Formation of polynuclear species of aluminum ion takes place quite rapidly as will be seen in Fig 7, in which the curves have been obtained by neutralyzing a solution of aluminum salt with alkali and by measuring the change taking place thereafter in the concentration of monomeric form of aluminum by the method described in our earlier paper[10].

The optimun pH for the coagulation of water with aluminum salt lies in most cases at pH 5–6, where polynuclear hydroxo-aquo-aluminum ions are quite stable and readily formed. It is very interesting to consider the possibility that the aluminum ion added to the water undergoes polymerization to form highly charged polynuclear ions and these are the active forms as coagulant.

It is also interesting in the the use of aluminum salt that sulfate ion reacts with polynuclear hydroxo-aquo-aluminum ions to form a precipitate, and considerably modifies the solubility of aluminum ion by shifting the monomer-polymer equilibrium toward the polymer side. Sulfate is also known to act as coagulation aid[8].

The Form of Silica Most Active as Coagulation aid

Dissolution Rate as a Measure of the Specific Surface Area

Although several methods have been reported on the determination of specific surface area of particles in colloidal silica sols, none is capable of being applied to activated silica sols. Recently, however, K. Goto[25] has proposed a new method based on the rate of dissolution of particles in a dilute solution of hydrofluoric acid. This method is simple and rapid, requiring only about 4 mg. of SiO_2 to be tested.

Colloidal silica is dissolved under the conditions given in Table I. Ten-milliliter portions of this solution are taken at definite intervals in beakers

TABLE I. Conditions for the Measurement of Dissolution Rate

Concentration of sodium fluoride	300 mg./l. with respect to F-ion.
Concentration of hydrochloric acid	0.12 N
Temperature	25.0°C
Concentration of silica particles	around 20 mg./l. as SiO_2.

containing 0.5 ml. of aluminum chloride solution (30 mg. Al/ml.), which prevents the dissolution reaction from taking place further. To each beaker is added 0.5 ml. of ammonium molybdate solution (10% w/v). Intensity of the developed color is determined after 6 or 8 min. at a wave length of 430 mμ. The amount of monosilicic acid formed is calculated from the color intensity and is plotted against the time elapsed between the start of the dissolution reaction and the mixing with aluminum chloride. Since the plot lies on a straight line in most cases over a wide range of time, the dissolution rate

$$\frac{\text{Initial rate of increase in the concentration of monosilicic acid (mg./l./min.)}}{\text{Initial concentration of colloidal } SiO_2 \text{ (mg./l.)}}$$

is easily obtained from the slope. The relationship between the dissolution rate and the specific surface area as determined by Sears' titration procedure[26] is shown in Fig. 8. Particle size can be calculated, on the assumption that colloidal silica particles are spheres having a specific gravity of 2.2, from the equation

$$r = 13600/A$$

where r is the radius of particles in Å and A the specific surface area in sq. meters per gram.

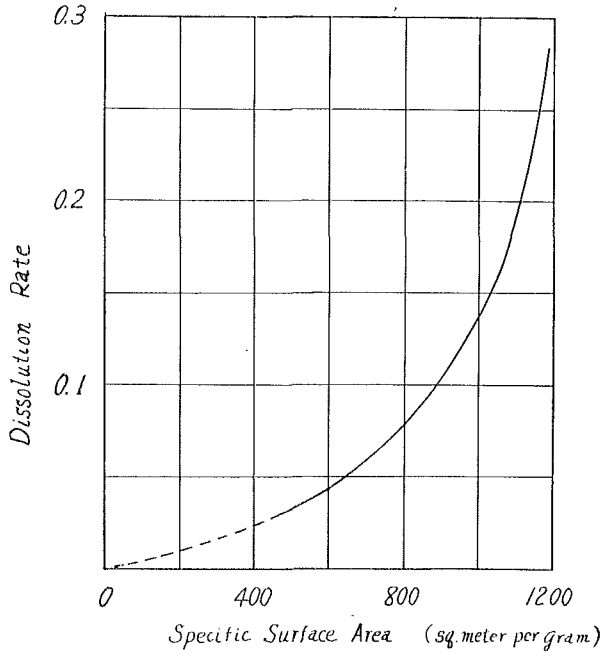


Fig. 8. Relationship between the specific surface area and the dissolution rate.

Preparation and Properties of Activated Silica

Two types of silica sols were prepared in the present investigation. The first was prepared by ion-exchange. A dilute solution of sodium silicate containing about 1% SiO_2 was passed through a column of strongly acid ion-exchange resin in the hydrogen form. Since the polymerization of silica is very slow in acid medium small amounts of sodium silicate were added to maintain a proper pH value of 8–9. The resulting mixture was aged for various periods of time. Sols of colloidal silica having larger particle sizes were prepared by aging at higher temperatures. The sol prepared by the ion-exchange method is called hereafter the "ion-exchanged sol". The sodium silicate used in the present investigation was the one having a molar ratio of Na_2O : SiO_2 of about 1 : 3.

The other type of colloidal silica is the so called "Baylis sol"[1,3] and was prepared by the following procedure. A dilute solution of sodium silicate containing about 3.0 per cent of SiO_2 was mixed with an equal volume of sulfuric acid (0.33 N) to obtain a solution containing about 1.5 per cent SiO_2 and having an alkalinity of 1140 to 1250 mg./l. of equivalent calcium carbonate.

By this process about 86 per cent of the initial alkalinity was neutralized. The pH of this mixture was about 8.5. This mixture was aged at this concentration for short periods of time and then diluted to about 0.6 per cent silica to prevent gelation.

Changes in the form of silica on aging were studied by measuring the dissolution rate and the specific hydrodynamic volume of silica particles. The results for ion-exchanged sol and for Baylis sol are shown in Figs. 9 and 10, respectively. It is apparent that the dissolution rate decreases more rapidly at

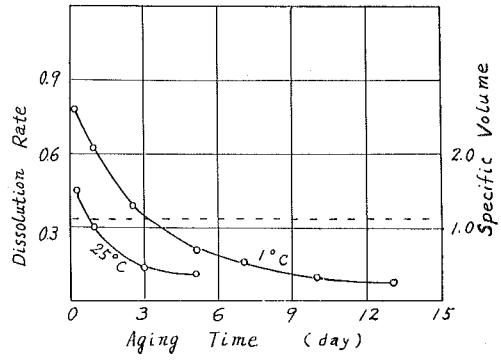


Fig. 9. Changes in dissolution rate and specific hydrodyamic volume during the aging of ion- exchanged sol.
—○—○— dissolution rate;
..... specific volume.

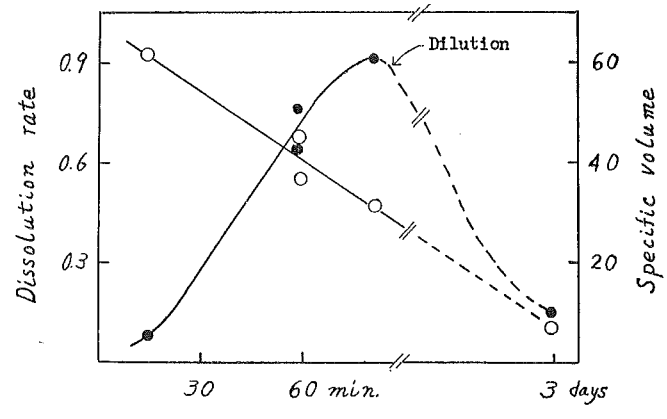


Fig. 10. Changes in dissolution rate and specific hydrodynamic volume during the aging of Baylis sol.
○ dissolution rate; ● specific volume.

higher temperatures than at lower temperatures. For ion-exchanged sols, dissolution rate is reduced to about 0.15 in 3 days at 25°C., while more than a week is required to attain the same value at 1°C. These results appear to indicate that the aging at higher temperature yields sols consisting of larger primary particles.

The specific volume of particles in the ion-exchanged sol is kept constant at about 1.1, which is close to the theoretical value of 0.45 calculated on the assumption that silica particles are not hydrated. It is therefore apparent that the secondary aggregation of primary particles is insignificant in this sol and that the aging brings about only the growth of primary particles.

In the case of the Baylis sol, however, the specific volume increases very rapidly until the sol is diluted to 0.6 per cent of silica. When the sol is diluted, the specific volume rather decreases but remains higher than for the ion-exchanged sol. It is probable that a high concentration of sodium sulfate in the Baylis sol reduces the zeta potential of the primary particles formed, and thus causes the condensation to occur between primary particles to form loose network structures. When the sol is diluted, these network structures are broken in part, rendering more compact structures or dense particles to be formed.

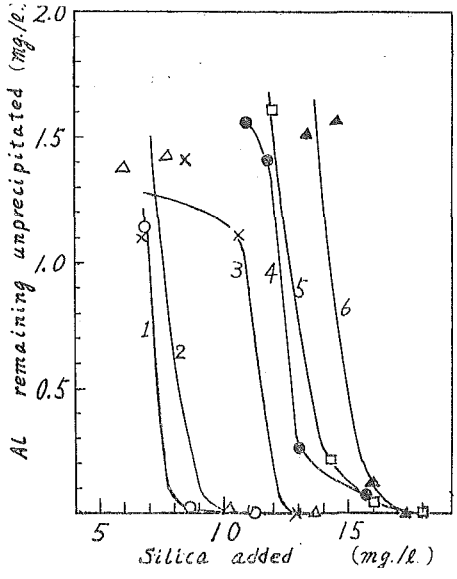


Fig. 11. Effect of ion-exchanged sol on the coagulation of aluminum hydroxide. pH, 6.5±0.2; temp, 10°C; initial concentration of Al, 2.6 mg./l.

Characteristics of colloidal silica

	Dissolution rate	specific volume
1	0.778	1.1
2	0.667	1.1
3	0.449	1.1
4	0.247	1.1
5	0.110	1.1
6	0.085	1.1

Effects of Various Forms of Silica on the Coagulation of Aluminum Hydroxide

Five hundred-ml. portions of distilled water were taken in 500-ml. beakers and stirred with a jar tester. While continuing the stirring at about 100 r.p.m., aluminum chloride and various colloidal silica sols were added. The pH of each mixture was adjusted with NaOH to 6.2±0.2. After 15-minutes' stirring at 90 r.p.m., the mixture were filtered with a Toyo filter paper

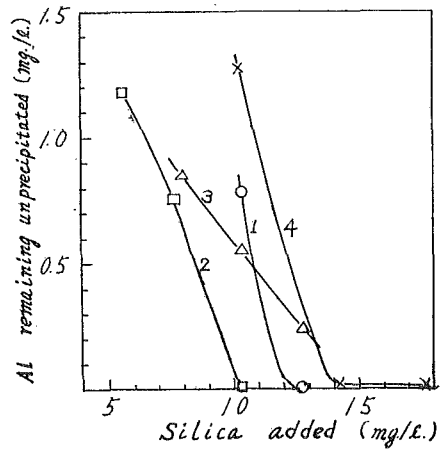


Fig. 12. Effect of Baylis sol. pH, 6.2±0.2; temp., 10°C; initial concentration of Al, 2.6 mg./l.

	Characteristics of silica	
	Dissolution rate	specific volume
1	0.893	5.1
2	0.666	48.7
3	0.452	61.0
4	0.094	8.5

No. 5 A (pore size is said to be 15×10^{-3} m.m.) and the filtrates were analysed for total aluminum concentration. The results were shown in Figs. 11 and 12. It is very interesting to note in these figures that the coagulation of aluminum hydroxide does not take place unless the concentration of silica is raised above a certain critical value.

With ion-exchanged sol, about 8 mg. of silica was sufficient to precipitate aluminum when the dissolution rate of silica is 0.778, whereas 16 mg was required when the dissolution rate is 0.085. In the range studied, it was revealed that the activity of ion-exchanged sol decreases as the particle size increases. Effect of colloidal silica having a particle size smaller than those used in the above tests was not studied because of difficulty of its preparation. It has been shown in our previous paper[8], however, that monosilicic acid has little activity (see Fig. 13). Although higher dissolution rate cannot be interpreted in terms of particle size, the particle size of the most active silica seems to lie at 20 Å or below. The activity of the Baylis sol could not be explained by the size of primary particles alone, as will be seen in Fig. 12. Secondary aggregation of primary particles seems to play some roles.

It is quite interesting to point out that contrary to Merrill's view[3], ion-exchanged sol and Baylis sol have about the same activity, as will be apparent from the comparisons between the curves in Figs. 11 and 12. When a solution of sodium silicate is treated with ion-

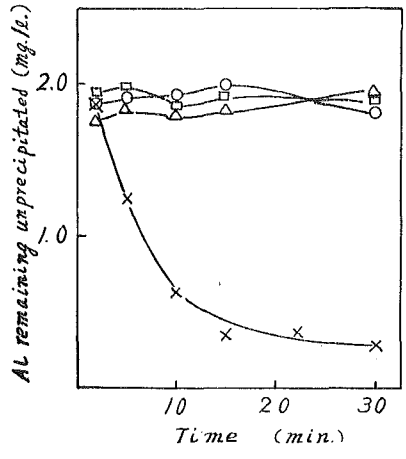


Fig. 13. Effect of monomeric silica. pH, 6.2±0.2; initial concentration of Al, 2.6 mg./l.; concentration of added in mg./l., □ 0, △ 10, ○ 20, and × 50.

exchange resin, its pH is decreased to as low as 3, at which polymerization of silica proceeds very slowly, as has been pointed out already. It seems quite probable that Merrill has aged the sol at such a low pH value and thus could not obtain an active sol.

The Role of Activated Silica in the Coagulation Aluminum Hydroxide

Effect of the concentration of colloidal silica on the coagulation of aluminum hydroxide and of colloidal silica itself is shown in Fig. 14. Aluminum hydroxide is precipitated within the same pH range as that for colloidal silica.

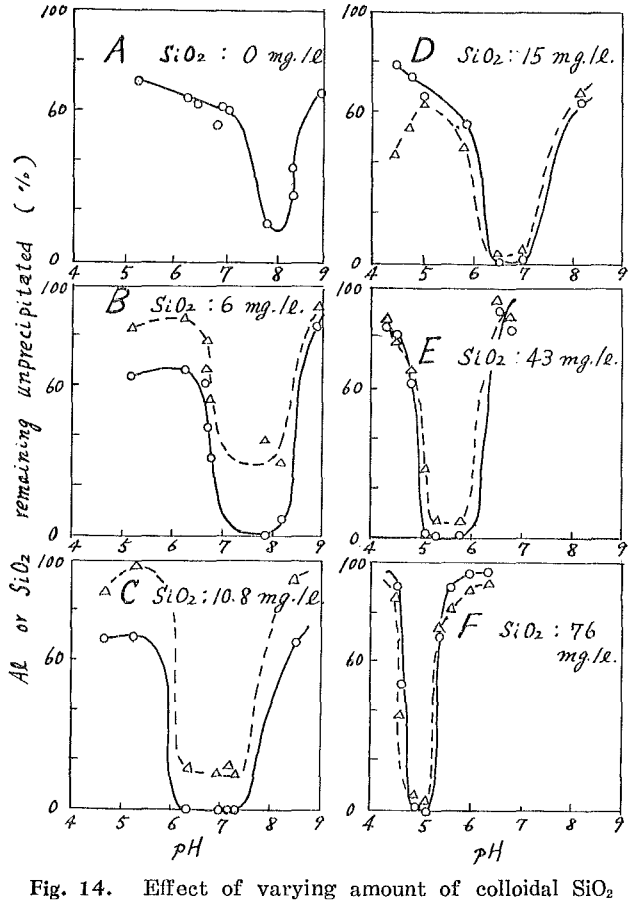


Fig. 14. Effect of varying amount of colloidal SiO_2 (specific surface area, 1100 sq. m./g.)
○ Al, △ SiO_2 in the solution filtered 10 min. after pH adjustment.

This range shifted towards the acid side as the concentration of added silica increased. A close examination of Fig. 14 also reveals that the coagulating effect of activated silica at a fixed pH increases with the increase in its concentration, passing a maximum, and then rapidly decreases again as the concentration of the silica further increases beyond a certain critical point. In other words, activated silica rather prevents the coagulation of aluminum hydroxide when the former is added in larger amounts. These characteristics of coagulation of silica and aluminum hydroxide appear to show the mutual coagulation taking place between these particles, owing to neutralization of their charges by the other.

A larger amount of activated silica is required at a lower pH value to produce good coagulation of aluminum hydroxide. This may be explained as follows: Silanol groups on the surface of polymerized silica dissociate to a higher degree at higher pH or the silica particle is highly charged negatively in basic medium. A smaller amount of these particles may be sufficient to neutralize the positive charges of aluminum hydroxide. At lower pH values, where dissociation of surface silanol groups is low, larger amounts are required to neutralize the charges of aluminum hydroxide. The increasing positive charge on aluminum hydroxide with decreasing pH may also be connected with the amount of silica required to produce coagulation.

It is very interesting to consider that the effect of colloidal silica is due to the following mechanism. Aluminum ion has a tendency to form highly polymerized hydroxoaquo ions in slightly acid or neutral solution. However, an increasing charge with increasing degree of polymerization of these ions prevents further polymerization from taking place in slightly acid solution. A similar situation may arise for silicate ions. The situation is somewhat different in the presence of silica. The charges of polymerized aluminum ion and of silica are neutralized by each other. This minimizes the electrical repulsion between particles, and causes these particles to associate together.

Acknowledgment

The authors wish to express their thanks to Professors Y. Uzumasa, G. Okamoto, and I. Kayma for their advice and encouragement and to Ebara Manufacturing Co. for a jar tester. The authors are also indebted to the Asahi Glass Foundation for the Promotion of Researches in Chemical Industries for the financial aid.

References

1) J. R. Baylis: *J. Amer. Water Wks. Assoc.*, **29**, 1355 (1937).
2) C. R. Henry: *ibid.*, **50**, 61 (1958).
3) R. C. Merrill: *Ind. Eng. Chem.*, **40**, 1355 (1948).
4) V. W. Langworthy: *J. Amer. Water Wks. Assoc.*, **50**, 56 (1958).
5) F. R. Jackson: *Wat. & Wat. Engng.*, **62**, 473 (1958).
6) L. L. Klinger: *J. Amer. Water. Wks. Assoc.*, **47**, 175 (1955).
7) R. Iwatsuka: *J. Japan Waterworks and Sewarage Assoc.*, No. 260, 24 (June, 1956).
8) T. Okuro, K. Goto and T. Komatsu: *Bull. Faculty of Eng. Hokkaido Univ.*, No. 17, 119 (1957).
9) T. Okura, K. Goto, and T. Komatsu: *Bull. Chem. Soc. Japan*, **31**, 139 (1958).
10) K. Goto, H. Ochi and T. Okura: *Bull. Chem. Soc. Japan*, **31**, 783 (1958).
11) K. Goto: *J. Chem. Soc. Japan, Pure Chem. Sect.*, **76**, 1364 (1955).
12) G. Okamoto, Okura and K. Goto: *Geochem. et. Cosmochim. Acta*, **12**, 123 (1957).
13) G. B. Alexander, W. M. Heston and R. K. Iler: *J. Phys. Chem.*, **58**, 453 (1954).
14) K. B. Krauskopf: *Geochim. et Cosmochim. Acta*, **10**, 1 (1956).
15) D. E. White, W. W. Brannock and K. J. Murata: *ibid.*, **10**, 27 (1956).
16) I. Iwasaki, T. Tarutani, T. Katsura and H. Arino: *J. Chem. Soc. Japan, Pure Chem. Sect.*, **75**, 857 (1954).
17) W. D. Dreadwell: *Trans. Faraday Soc.*, **31**, 297 (1935).
18) R. C. Merrill and R. W. Spencer: *J. Phys. & Coll. Chem.*, **54**, 806 (1950).
19) I. A. Heald, K. D. Coates and J. E. Edwards: *J. Appl. Chem.*, **5**, 806 (1950).
20) A. P. Brady, A. G. Brown and H. Huff: *J. Coll. Sci.*, 8, 252 (1953).
21) S. A. Greenberg: *J. Poly. Sci.*, **27**, 523 (1958).
22) K. Goto: J. Phys. Chem., **60**, 1007 (1956); *J. Chem. Soc. Japan, Pure Chem. Sect.*, **77**, 957 (1956).
23) K. Goto: *J. Chem. Soc. Japan, Pure Chem Sect.*, **81**. 349 (1960)
24) K. F. Jahr u. A. Brechlin: *Z. anorg. allgem. Chem.*, **270**, 257 (1952).
25) K. Goto: *Bll. Chem. Soc. Japan*, **31**, 900 (1958).
26) C. W. Sears, Jr,: *Anal. Chem.*, **28**, 1981 (1956).