Study on behavior of silicic acid in ion exchange resin and efficient treatment of water resources

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to OH type anion exchange resin on the efficient water treatment

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Chapter 1 General Introduction

1.1. Background

Various factors such as population growth, industrial development, and climate change have warned that water resources will be scarce in the future. The amount of water in rivers and lakes that are relatively accessible to humans is only about 0.01% of the earth's water (Igor., 1998). Due to the uneven distribution of demand and supply, it is difficult to say that the resources for water demand are already sufficient.

Against this background, the United Nations Sustainable Development Goals (SDGs) 's Goal 6 aims to ensure access to water and sanitation and sustainable management for all by 2030. Among them, "6.4, 6.a" aims to maximize water use efficiency (UN Document, A/70/L.1, 2015).

In water treatment, various technologies using functional materials such as ion exchange resins and reverse osmosis (R.O.) membranes have already been used, while considering the maximization of water use efficiency (Antony et al., 2011 and Calmon, 1986). These technologies are selected according to the purpose, for example, for beverages or cleaning. Moreover, the cost-minimum technology is selected so that the processing is not expensive.

The ion exchange method is one of the most popular deionization / adsorption methods used as one of the means for water treatment. A cation exchange resin or anion exchange resin is packed into an ion exchange tower in layers to adsorb and remove various unnecessary ions in water.

At the time of adsorption, the cation exchange resin releases H^+ ions and the anion exchange resin releases OH^- ions, so that the ions finally become H_2O. The ion exchange resin can be repeatedly used by alternately performing a load process of adsorbing unnecessary ion and a regeneration process of returning ions adsorbed with a concentrated acid or alkali to H^+ ions or OH^- ions. Ion exchange reaction is an equilibrium reaction (equation 1～3), and the change in free energy is very small at about 5.7 kJ / mol (1.36 kcal / mol). This value is only about half of the activation energy required for the methyl group to rotate (Kanzaki et al., 2001). The ion exchange method does not require a large amount of energy unlike the reverse osmosis membrane treatment, and has a great advantage that water treatment can be performed reasonably by repeatedly using the ion exchange resin.

However, the actual ion exchange unit cannot fully utilize this advantage. This is because energy is used by heating in the regeneration process, which is a desorption reaction of ions. The cause is the ion exchange of silicic acid ($Si(OH)_4$). Other anions such as chloride ions can be replaced with OH^- ions by only applying a high concentration of NaOH that can ignore the selectivity in the regeneration process. But, further heating (energy) is actually required to elute the silicic acid from the ion exchange resin. It is known that if the loading step and the regeneration step are repeated without heating, silicic acid remains in the resin layer, leading to problems such as poor quality of treated water.

Ion exchange resins can be used repeatedly for several years if oxidation of the resin structure does not occur, but with this problem, the ions cannot be removed within a few

months and the service life ends (Osmun et al., 1951, Guowei et al., 1988 and Zaganiaris et al., 1992). This phenomenon that silicic acid cannot be sufficiently eluted has been attributed to the fact that the silicic acid adsorbs on the OH^- type resin is polymerized in the pores of the resin particles to form polysilicic acid. It is pointed out that although the concentration of silicic acid in the treated raw water is less than the solubility of amorphous silica, polymerization occurs in the resin and the elution of silicic acid is hindered (Guowei et al., 1988 and Meyers, 1999). In order to operate the ion exchange tower optimally and to treat water efficiently, it is important to further investigate the detailed mechanism of the polymerization and utilize the ion exchange based on the polymerization mechanism of silicic acid.

Cation exchange resin $R\text{-}SO_3^-\ H^+\ +\ Na^+\ \rightleftharpoons\ R\text{-}SO_3^-\ Na^+\ +\ H^+$ $\cdots(1)$

Anion exchange resin $R\text{-}N(CH_3)_3^+\ OH^-\ +\ Cl^-\ \rightleftharpoons\ R\text{-}N(CH_3)_3^+\ Cl^-\ +\ OH^-$ $\cdots(2)$

$$H^+\ +\ OH^-\ \rightleftharpoons\ H_2O \qquad \cdots(3)$$

R : Main chain structure

Equation (1)～(3)　: Formula of ion exchange reaction in water treatment

1.2. Previous researches

1.2.1. Empirical knowledge and chemical engineering analysis

Figure 1.1. shows the flow of reagents used in the loading process and the regeneration process of a general ion exchange tower. In the ion exchange column, the cations are removed from the solution by replacement with H^+, and then the anions are removed by replacement with OH^-. In the tower of anion exchange resin, sulfate ions, nitrate ions, chloride ions, and carbonate ions are removed, and then silicic acid is also removed as silicate anion. The order of ion removal depends on the ion selectivity. Ion exchange resins made by any manufacturer show the same order of ion removal if they are general ion exchange resins. The silicic acid is removed in the layer of the OH^- type ion exchange resin after passing through the ion exchange resin layer adsorbing ions that are preferentially removed, such as sulfate ions and chloride ions.

It is thought that there are two possible cases in the process of silicic acid polymerization in the ion exchange tower as below.

(A) Polymerization in ion-exchange resin that hinders regeneration.

(B) Polymerization outside the ion-exchange resin, which occurs when the waste liquid containing silicic acid during regeneration moves to the discharge side and the pH becomes acidic.

The both polymerization processes are important issues in terms of efficient treatment of water resources. As a trouble, (B) is likely to attract attention because it leads to blockage of the resin tower. However, this problem can be almost solved by keeping the pH of the recycled waste liquid on the alkaline side. (Figs. 1.2. and 1.3.)

In water treatment, (A) has empirically been known. The ion exchange reaction of ions in the ion exchange tower can be expressed by three mathematical formulas in terms of chemical engineering. They are the mass balance equation, the transfer velocity equation, and the ion exchange equilibrium equation. (Fig. 1.4.) Based on these formulas, a calculation consisting of simultaneous three formulas was performed with silicic acid as a monovalent anion $(Si(OH)_3O^-)$. The leakage curve (breakthrough curve) showing the time-dependent change of the silicic acid concentration at the outlet of the ion exchange column shifts in the direction of earlier time than the actual leakage curve. (Fig. 1.5.) This is nothing less than the fact that more silicic acid than expected was adsorbed in the ion exchange column. This model can accurately reproduce the leakage curve for other anion components. (Fig. 1.6.) From this result, it can be considered that silicic acid is not ion-exchanged as monovalent ion with respect to the ion-exchange group. Silicic acid is ion-exchanged with a valence of less than 1, supporting the situation of polymerization.
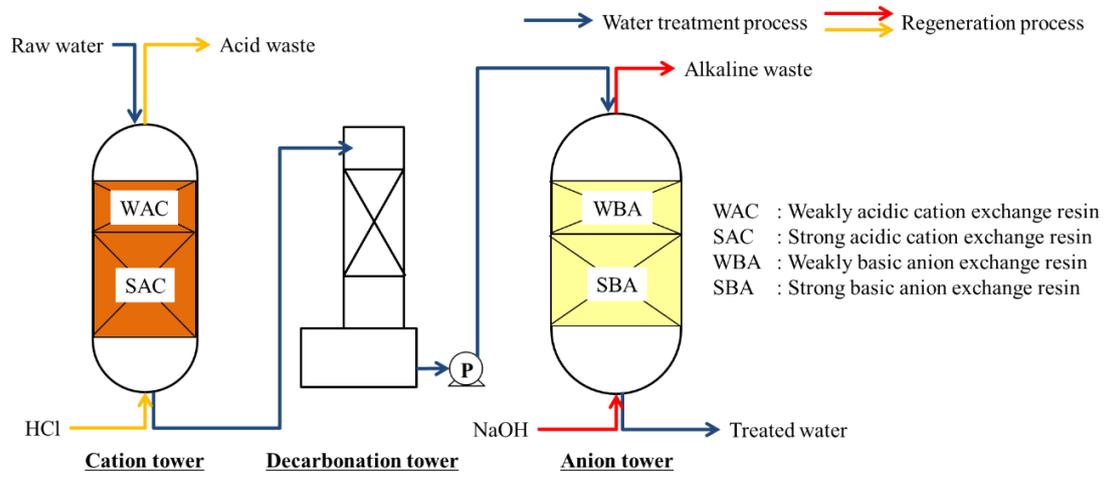
Fig.1.1. General ion exchange water treatment unit and process
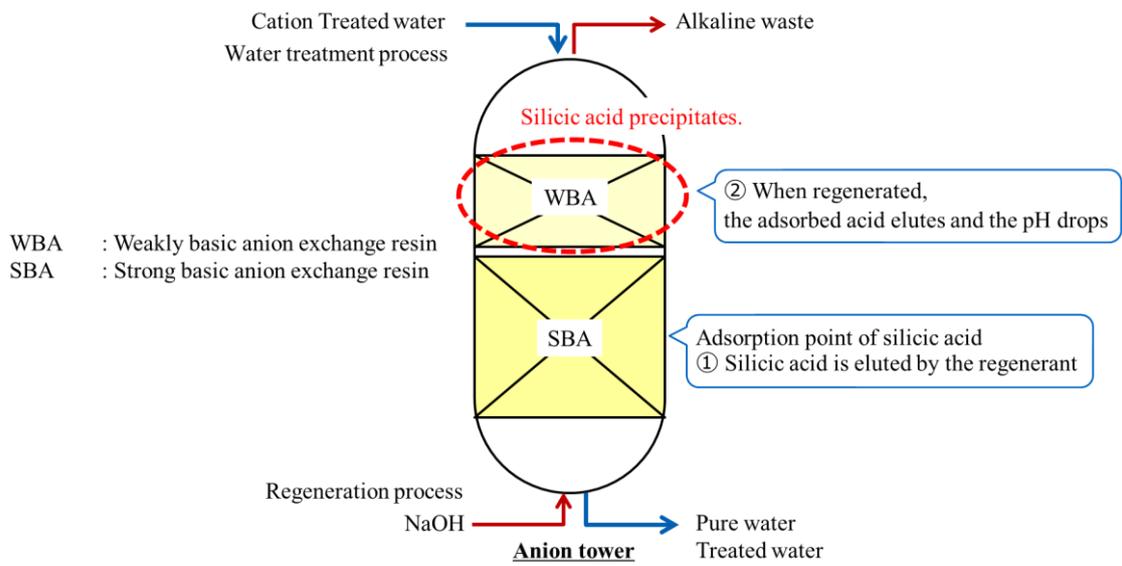
Fig.1.2. Polymerization point of silicic acid in regeneration waste containing silicic acid
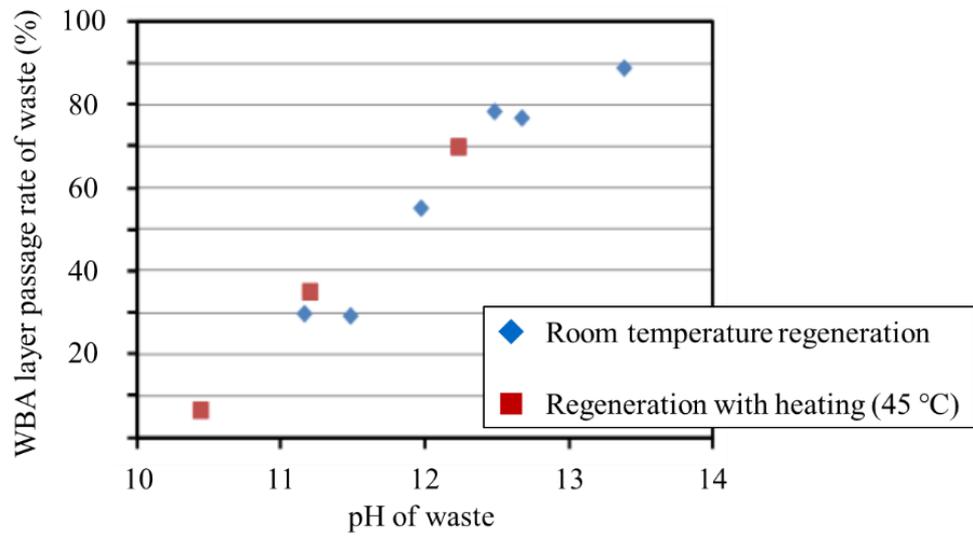
Fig.1.3. WBA layer passage rate of regeneration waste

Mass balance $\varepsilon \dfrac{\partial C}{\partial t} + u \dfrac{\partial C}{\partial z} + \gamma \dfrac{\partial q}{\partial t} = 0$

Moving speed $\gamma \dfrac{\partial q}{\partial t} = K_F a_v (C - C^*)$

$y_A = \dfrac{K_{OH}^A [A]}{K_{OH}^A [A] + K_{OH}^B [B] + K_{OH}^C [C] + [OH^-]}$

$y_B = \dfrac{K_{OH}^B [B]}{K_{OH}^A [A] + K_{OH}^B [B] + K_{OH}^C [C] + [OH^-]}$

$y_C = \dfrac{K_{OH}^C [C]}{K_{OH}^A [A] + K_{OH}^B [B] + K_{OH}^C [C] + [OH^-]}$

$y_{OH} = \dfrac{[OH^-]}{K_{OH}^A [A] + K_{OH}^B [B] + K_{OH}^C [C] + [OH^-]}$

t : time
z : distance from inlet
ε : porosity
γ : bulk density
u : raw water line velocity
q : resin concentration
$K_f a_v$: overall mass transfer capacity coefficient
C : concentration in liquid phase
C^* : concentration in water phase equilibrium with q
K : Selection coefficient

Adsorption equilibrium formula

Extended Langmuir equation of four components by A, B, C, OH

Fig.1.4. Model formulas of ion exchange reaction in chemical engineering

Fig.1.5. Comparison of experimental (blue plots) and calculated (green line) breakthrough
curves　of silicic acid

Fig.1.6. Comparison of experimental (dark blue plots) and calculated (orange line)
breakthrough curves of carbonic acid

1.2.2. Use of NMR in chemical state analysis

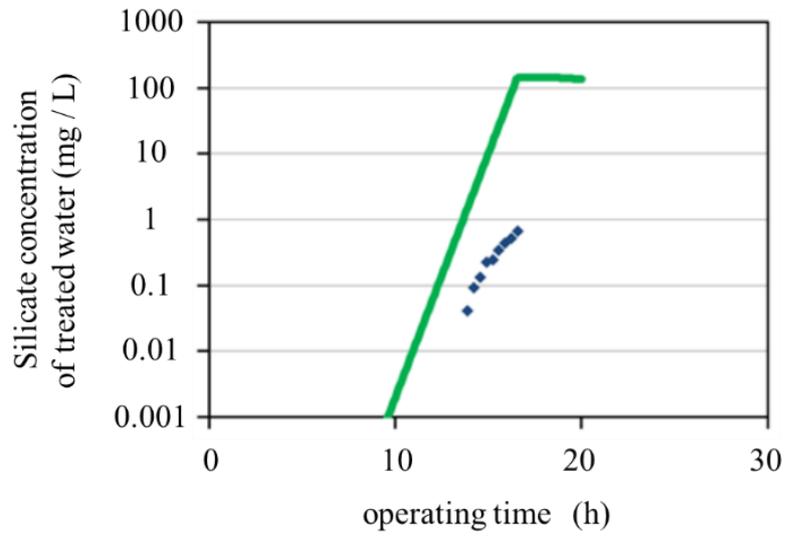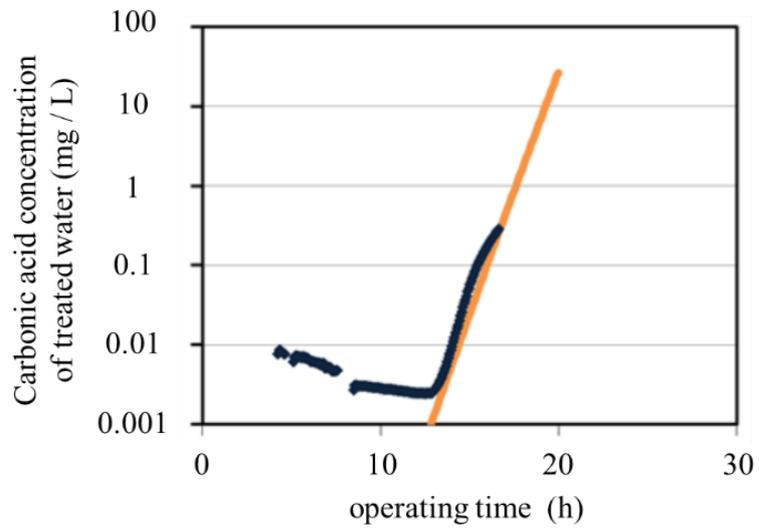It is necessary to correctly grasp change in the state of silicate ions during the polymerization inside the ion exchange resin. In order to understand the process of change in detail, it is necessary to obtain information before and after the changes. Therefore, an analytical method that directly observes speciation of the ion both in water and inside the ion exchange resin is useful.

Miyazaki et al. (1996) performed ^{31}P NMR of phosphorus species adsorbed on a strongly basic ion exchanger as a method for directly observing the chemical state of substances. It has been reported that NMR gives quantitative information on the chemical species adsorbed on the ion exchange resin (Miyazaki et al., 1996). Miyazaki et al. and Yoshimura et al. also reported the results of analysis of the interaction of boric acid with polysaccharides and their crosslinked polymers (Sephadex gels) (Yoshimura et al., 1996 and Miyazaki et al., 2003).

Lipmma et al. first reported the chemical shift of silica and silicate minerals in solid-state NMR (Lipmma et al., 1980). Kirkpatrick et al. used NMR for silica and silicate minerals has also been previously investigated but did not focus on ion-exchange resins (Kirkpatrick et al., 1985). Gallup analyzed the chemical states of Si and Al in silica scales formed at geothermal power plants by the ^{29}Si-MASNMR and ^{27}Al-MASNMR and reported that aluminum replaced the Si site of the silica lattice and existed as tetrahedral coordinated aluminum (Gallup, 1997). In addition, Yokoyama et al. examined change in chemical state of Al^{3+} when silicic acid was adsorbed to aluminum hydroxide and found that the coordination number of Al^{3+} changed from 6 to 4 with increasing the amount of silicic acid adsorbed (Yokoyama et al., 1997). Yokoyama et al. studied bonding mode of Al^{3+} to chelate resin (Chelex 100) and found that Al^{3+} first combines with iminodiacetate ligand to form chelate complex and after the adsorption it combines to carboxyl group as monodentate ligand (Aramaki et al., 2004). Like this, the NMR has been shown to be effective as a direct observation of chemical state of species adsorbed to ion exchange resins.

1.3. Chemical state of silicic acid in water

Before clarifying the behavior of silicic acid in an ion exchange resin, the chemical state of silicic acid in water before being adsorbed on the ion exchange resin should be clarified.

It is generally known that silica polymerization occurs when the concentration of silicic acid exceeds the solubility of amorphous silica at a given physicochemical condition. The solubility of silicic acid is the sum of monosilicic acid and monosilicate ions, and monosilicic acid is formed by the dissolution reaction of silica in water ($SiO_2 + 2H_2O \rightarrow Si(OH)_4$). Solubility is almost constant in the range of pH 2-8, and the only dissolved species is monosilicic acid (Iler, 1979). To confirm this directly, ^{29}Si MAS NMR of silicic acid solution was measured as a preliminary study.

^{29}Si NMR sensitivity is low because of a low abundance ratio (5 %) of ^{29}Si in nature compared to ^{28}Si which is non-sensitive nuclei. ^{29}Si concentrated silica gel was purchased from the Japan Isotope Association and used to prepare solutions containing silicic acid for the experiment. The ^{29}Si-enriched silica gel was fused with sodium carbonate, the melt was dissolved in ultrapure water, and the Si concentration was determined by spectrophotometry. Based on this concentration, a 100 ppm (SiO_2) sodium silicate solution was prepared by diluting the above solution with ultrapure water. The sodium silicate solution was passed through an H^+ type cation exchange resin column to remove sodium ions and prepare a silicic acid solution. The solution was diluted to 50 mg/L before measurement. The ^{29}Si MAS NMR spectra were recorded at ambient temperature on a JEOL NMR spectrometer ECA 400 owned by Kyushu University. Figure 1.7 shows the NMR spectrum of a ^{29}Si silicic acid aqueous solution. The NMR spectrum confirmed a single peak indicating monosilicic acid.

As for the chemical state of silicic acid in water, there is a previous study using mass spectrometry (Ariga et al., 2015). Therefore, the solution that was monosilicic acid in NMR Figure 1.7 was used as it was, and the measurement by ESI-MS was performed as in the previous study. Further, in order to confirm that 29Si silicic acid is not special, the same measurement was performed by adjusting 28Si silicic acid solution.

Mass spectrometry of the silicic acid solution was measured by JMS-T100LP 4G owned by JEOL. According to a pamphlet of ESI-MS, the measurements can be performed while maintaining the dissolved state of ions in a mass spectrometer. However, in principle, as a high voltage is applied at the same time, the desolvation of the droplets proceeds at high temperature. Under this condition, a chemical reaction of species may occur in the process of desolvation. Therefore, it cannot be said that the chemical state of the target species does not change. (Fig. 1.8) The cold spray (CSI) method is an ionization method that slows the desolvation rate by lowering the temperature of the introduced gas and performs ionization together with the solvent. Therefore, in this study, the ionization of silicic acid using the CSI method was also examined. The measurement conditions are shown in Table 1.1. The temperature of the desolvation chamber is 280 °C for normal ESI and 5 °C for CSI. The method of introducing the sample was the infusion method with high sensitivity, and the nebulizer was washed with ultrapure water before introduction of sample.

Usually, in mass spectrometry, a spectrum having the same peak intensity ratio as the isotope abundance ratio is obtained at each mass. In the case of Si in nature, the isotope abundance ratio of 28Si and 29Si is about 20: 1. Also, the purity of 29Si concentrated silica gel was about 95%, and the remaining 5% was 28Si. At this time, the abundance ratio of 28Si and 29Si is about 1:20. However, when the obtained peaks were analyzed, no peaks corresponding to the isotopic abundance ratio could be confirmed even for the monomer. The results were also the same for the CSI method, which examined ionization with water molecules.

Table 1.2 shows the mass number and chemical formula of silicic acid to be detected by mass spectrometry. As an example, Figure 1.10 shows the ESI-MS spectrum of the dimer region of silicic acid. For the dimer example, the peak ratio of m/z 173 and 175 should be 20:1 for 28Si silicic acid and 1:20 for 29Si silicic acid. It can be reasonably concluded that ionization of silicic acid is very difficult with ESI-MS.
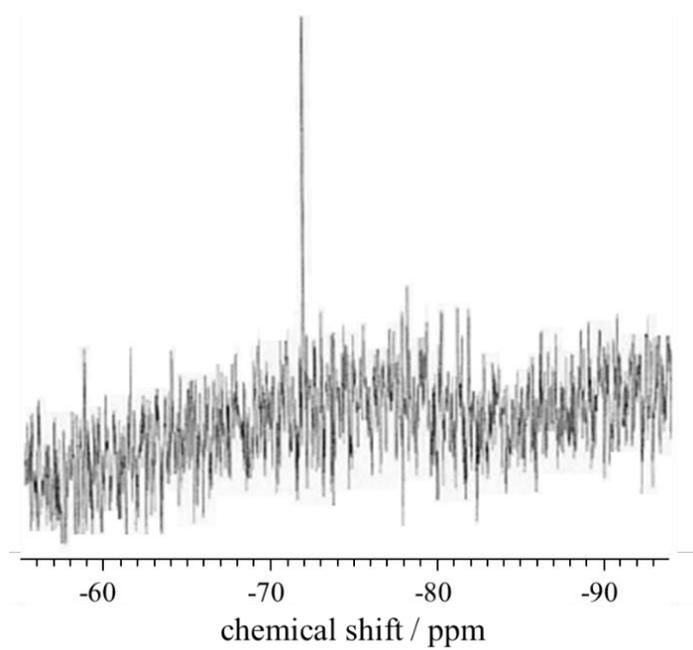
Fig.1.7. ^{29}Si MAS NMR spectrum of silicic acid in water.

Table 1.1. ESI-MS measurement conditions

Desolvation temperature	280 °C / 5 °C
Spray gas temperature	40 °C
Needle voltage	-2,000 V
Orifice voltage	-40 V
Ion guide peak-to-peak voltage	150 V
Mass range	m/z 10 – 1,000
Spectrum recording interval	0.4 sec.
Sample introduction method	Infusion method
Liquid transfer rate	20 μL / min
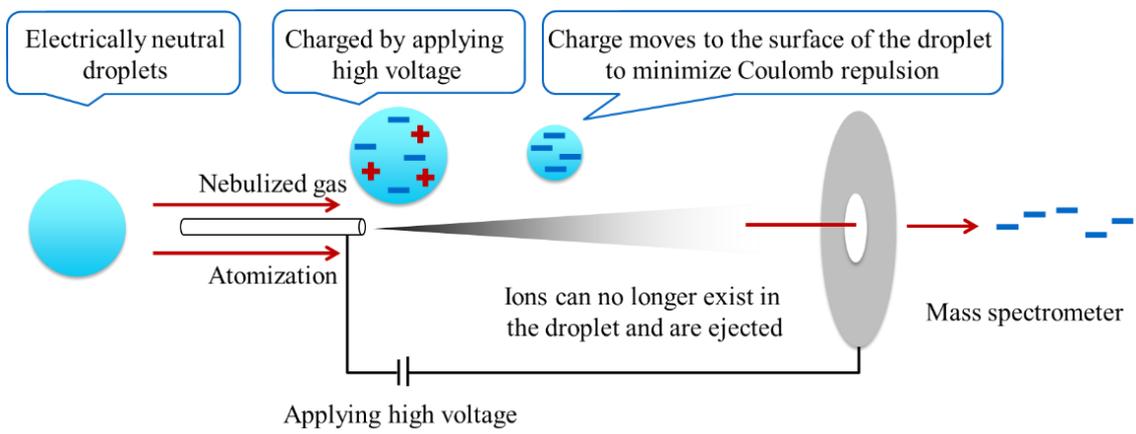
Fig.1.8. Desolvation process in ESI-MS

Table 1.2. Chemical species of silicic acid expected to be detected by mass spectrometry

| | *m/z* | | |
form	28Si	29Si	species
monomer	95	96	$[Si(OH)_3O]^-$
	113	114	$[Si(OH)_3O(H_2O)]^-$
	131	132	$[Si(OH)_3O(H_2O)]^-$
dimer	173	175	$[Si_2(OH)_5O_2]^-$
	191	193	$[Si_2(OH)_5O_2(H_2O)]^-$
	209	211	$[Si_2(OH)_5O_2(H_2O)_2]^-$
trimer	233	236	$[Si_3(OH)_5O_4]^-$
	251	254	$[Si_3(OH)_7O_3]^-$, $[Si_3(OH)_5O_4(H_2O)]^-$
tetramer	293	297	$[Si_4(OH)_5O_6]^-$
	311	315	$[Si_4(OH)_7O_3]^-$

Fig.1.9   ESI-MS spectrum in the dimer region of silicic acid.
The presence of monomer could not be determined.

1.4. Purpose of the thesis

The purpose of this research is to clarify and control the polymerization conditions of silicic acid in ion exchange resin, by directly observing changes in the chemical state of silicic acid, in order to make the treatment of raw water containing silicic acid more efficient. Previous studies have proposed the polymerization of silicic acid in ion exchange resins based on indirect analysis. However, the essence is not understood, and 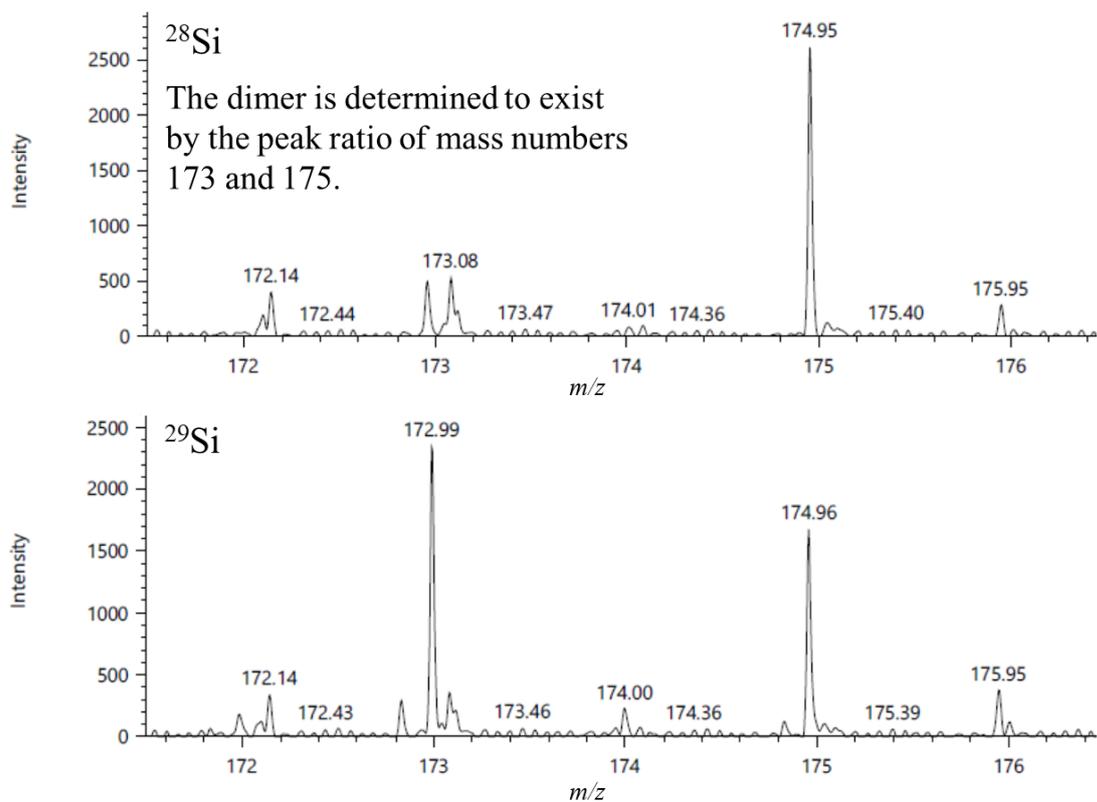it is difficult to propose a truly efficient water treatment. In water treatment, equipment is often operated empirically based on uncertain information. If the essence is understood and the process is optimized, operating costs may be reduced.

The paper consists of 4 chapters.

In Chapter 1, the outline of this study and the chemical state of silicic acid in water were explained. Chemical engineering analysis results indirectly indicate that silicic acid is polymerized. When the chemical state of silicic acid in water is confirmed by NMR, only monosilicic acid can be confirmed.

Chapter 2 describes the investigation of the elution mechanism of silicic acid in ion exchange equipment, focusing on the behavior of silicic acid in ion exchange resins. The chemical state of silicic acid in the ion exchange resin can be directly observed by NMR. According to the results of examining the elution mechanism of silicic acid from the viewpoints of ion selectivity experiment and changes in chemical state, it is effective to control the degree of polymerization of silicic acid in order to improve the efficiency of water treatment by ion exchange.

Chapter 3 describes the effect of the presence of coexisting ions and the structure of the ion exchange resin on the degree of polymerization of silicic acid. Even with unsaturated adsorption, silicic acid polymerizes to form Si-O-Si bonds. Therefore, silicic acid ideally controls the amount of highly polymerized Si-O-Si bonds during adsorption.

In order to prevent the formation of highly polymerized Si-O-Si bonds, it was clarified that it is effective to remove strongly acidic ions before removing silicic acid and use a low-crosslinking type I anion exchange resin.

Chapter 4 describes prospects for solutions, focusing on recent challenges in water treatment, based on the results of the whole research. Furthermore, it was summarized that understanding the environment in which silicic acid is likely to elute can improve efficiency such as reducing ion removal costs.

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Chapter 2 Chemical state and behavior of silicic acid adsorbed on ion exchange resin

2.1. Introduction

   Ion exchange method is often used to purify natural water such as river water and groundwater. Natural water contains silicic acid ($Si(OH)_4$), and its concentration is 10-20 mg/L as SiO_2 by chemical weathering of rocks. Silicic acid is removed by OH^- type strong base anion exchange resin tower. However, OH^- type resins can remove silicic acid to very low concentrations, but empirically the silicic acid discharge from the resin tower during the regeneration process is not completed without heating. This is in contradiction with the equilibrium reaction in which the free energy change of ion exchange is estimated to be only about 5.7 kJ/mol (1.36 kcal/mol). Incomplete regeneration process of silicic acid eventually leads to silicic acid leakage during removal process, shortening the resin life cycle (Osmun et al., 1951, Guowei et al., 1988 and Zaganiaris et al., 1992). Unraveling the mechanism behind the incomplete dissolution of silicic acid is a priority in the water treatment field. As a study investigating this problem, this chapter describes the direct observation of silica adsorbed in ion exchange resins. Furthermore, the elution mechanism of silicic acid is discussed based on the experiment of ion selectivity and the change of chemical state, and the result is described.

2.2. Experimental

All samples were prepared with ultrapure water.

・Preparation of ^{29}Si-based silicic acid solution

^{29}Si NMR sensitivity is low because of a low abundance ratio (5 %) of ^{29}Si in nature compared to ^{28}Si which is non-sensitive nuclei. ^{29}Si concentrated silica gel was purchased from the Japan Isotope Association and used to prepare solutions containing silicic acid for the experiment. The ^{29}Si-enriched silica gel was fused with sodium carbonate, the melt was dissolved in ultrapure water, and the Si concentration was determined by spectrophotometry. Based on this concentration, a 100 ppm (SiO_2) sodium silicate solution was prepared by diluting the above solution with ultrapure water. The sodium silicate solution was passed through an H$^+$ type cation exchange resin column to remove sodium ions and prepare a pure monosilicic acid solution without coexisting ions. The solution was diluted to the desired concentration before use.

・Preparation of ^{28}Si-based silicic acid solution

The sodium silicate solution was prepared by dissolving analytical grade $Na_2SiO_3 \cdot 9H_2O$ in ultrapure water. A pure monosilicic acid ($Si(OH)_4$) solution without coexisting ions is prepared by passing a 100 ppm (SiO_2) sodium silicate solution through an H$^+$ type cation exchange resin column to remove sodium ions. Stock solutions of monosilicic acid were diluted to the desired concentration before use.

・Adsorption of silicic acid by the batch experiment.

The OH$^-$ type resin (1 cm^3) was added to the monosilicic acid solution (100 cm^3) at a lower concentration than 100 ppm (SiO_2). The suspended solution was shaken by a shaker, and after 2 h, it was filtered with a 0.45 μm membrane filter. The silicic acid concentration of the filtrate was spectrophotometrically determined to estimate the adsorption proportion of silicic acid. The adsorbed water of the anion exchange resin remained on the filter was removed using a filter paper. The OH$^-$ type resin adsorbing silicic acid was immediately ground to a powder using an agate mortar and was stored in a bottle with a sealed stopper for the measurement of the ^{29}Si MAS NMR spectrum.

・Measurement of ^{29}Si magic angle spinning (MAS) NMR spectra.

Powder of the OH$^-$ type resin adsorbing silicic acid was placed in a zirconia rotor (diameter: 7 mm). The ^{29}Si MAS NMR spectra were recorded at ambient temperature on a JEOL NMR spectrometer ECA 400 owned by Kyushu University. The observation frequency was 79.43 MHz, the repetition time was 10 sec, and the spinning frequency of the zirconia rotor was 5 kHz. The ^{29}Si MAS NMR spectra were analyzed using software (Origin ver 7) to estimate the peak intensity of each peak.

・**Preparation of columns.**

The strong base anion exchange resin used in this study is SA10AOH (OH⁻ type, Mitsubishi Chemicals). The ion exchange capacity of this resin is 1.29 meq/L-Resin. The swollen resin (781 cm³) was packed in an acrylic column (inside diameter: 40 mm, length: 1000 mm) . Spacers (250 μm mesh) were put at the bottom and upper parts of the column to support the resin and to prevented the outflow of resin.

・**Adsorption of silicic acid by the column experiment.**

Silicic acid solution containing Cl⁻ions (0.6 mmol/L) was introduced from the upper part of the column with a constant flow rate (0.83 L/min). The amount of silicic acid adsorbed was controlled by changing the concentration of silicic acid (4～30 ppm SiO_2) and the volume of the silicic acid solution introduced. The adsorption proportion of silicic acid (%) ((mol of silicate ion)/(ion exchange capacity) × 100) was in the range of 10 to 45 %.

・**Desorption of silicic acid by the column experiment.**

After the adsorption of silicic acid, ultrapure water was introduced from the bottom of the column at a flow rate of 1 L/min to stabilize the resin condition. Next, to eliminate silicic acid, each solution was introduced from the bottom of the column at a flow rate of 0.21 L/min. The concentration and the volume of each reagent solution are as follows: 2% NaOH solution (1.55 L), 1% HCl (4.54 L), 1.4% H_2SO4 (8.68 L), 2.5% $NaHCO_3$ (4.2 L), 0.1 % HCl (45.4 L), and 1 % NaCl (7.31 L). After the solutions were passed through the column, ultrapure water was introduced for 30 min at a flow rate of 0.21 L/min until the pH of the effluent from the column reached neutral value. From the beginning of the introduction of each reagent solution to eliminate silicic acid, the effluent from the column was collected to determine the elution proportion of silicic acid ((the amount of silicic acid eluted)/(the total amount of silicic acid adsorbed) ×100). The silicic acid concentration in each effluent was determined by a spectrophotometric method based on the formation of molybdosilicic acid.

2.3. Results and Discussion

2.3.1. Effect of elution reagents on the elution behavior of silicic acid (column experiment).

Industrial water is usually prepared by passing groundwater and/or river water through a column packed with both an H^+ type cation exchange resin and an OH^- type anion exchange resin. Silicic acid is usually removed by the OH^- type anion exchange resin (functional group: $R_4-N^+ OH^-$). Silicic acid, which is an electrically neutral molecule, dissociates an H^+ to form $Si(OH)_3O^-$ (monomeric silicate ion). The adsorption of $Si(OH)_3O^-$ to the OH^- type resin can be represented by reaction (1).

$$R_4-N^+ OH^- + Si(OH)_3O^- \rightarrow R_4-N^+ \ ^-OSi(OH)_3 + OH^- \ (1)$$
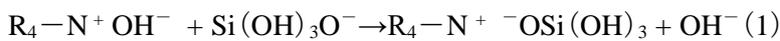
Adsorption is the ion exchange reaction between the OH^- ion of the functional group in the resin and the $Si(OH)_3O^-$ ion in solution. The adsorption of $Si(OH)_3O^-$ depends on the selective coefficient (Ali et al., 2004). In general, the order is as follows: $SO_4^{2-} > Cl^- > HCO_3^- > Si(OH)_3O^- > OH^-$. Consequently, $Si(OH)_3O^-$ can be adsorbed to only the OH^- type resin. On the other hand, reaction (2) is expected to occur in the regeneration of the column based on the order of selective coefficients against $Si(OH)_3O^-$.

$$R_4-N^+ \ ^-OSi(OH)_3 + Xn^- \rightarrow R_4-N^+ Xn^- + Si(OH)_3O^- \ (2)$$
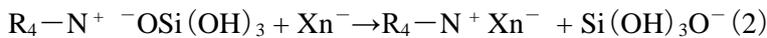
Here, Xn^- are OH^-, Cl^-, HCO_3^-, and SO_4^{2-}. As the elution reagents of $Si(OH)_3O^-$ from the column, 1.4 % sulfuric acid, 1 and 0.1 % hydrochloric acid, 2 % sodium hydroxide solution, 1 % NaCl solution and 2.5 % sodium hydrogen carbonate solution were applied in this study. Each solution passed through the column packed with an OH^- type resin adsorbing silicic acid (adsorption proportion of silicic acid: 10 %).

Figure.2.1. shows the elution proportion of silicic acid from the column for each elution reagent. Despite the larger selective coefficients for SO_4^{2-}, Cl^-, and HCO_3^- than that for $Si(OH)_3O^-$, only the 2 % NaOH solution was a successful elution reagent, and the 1 % HCl and 2.5 % NaHCO$_3$ solution were insufficient. Sulfuric acid, 0.1 % HCl, and 1 % NaCl solution were not very successful elution reagents. These results strongly suggest that silicate ion adsorption is the anion exchange reaction as written in reaction (1), whereas the desorption (elution) is different from reaction (2).
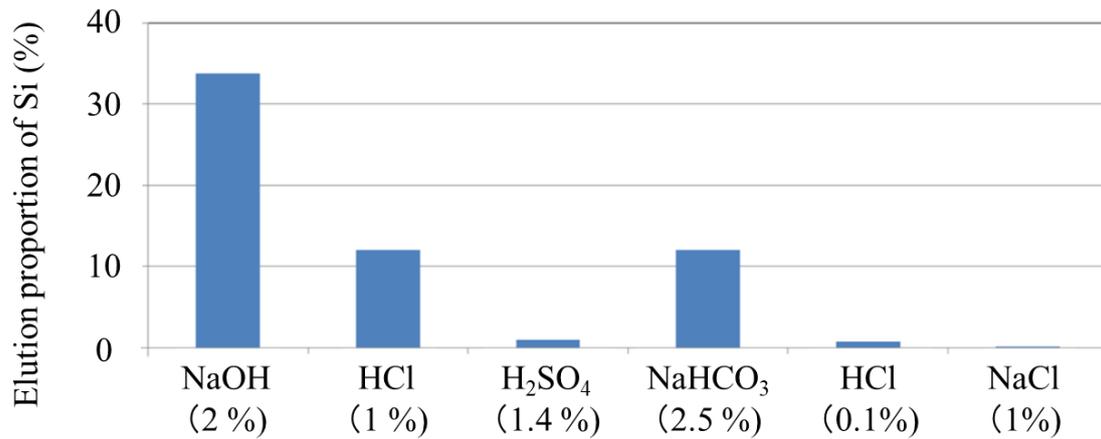
Fig.2.1. Elution proportions of silicic acid (Si) from a strong base anion exchange column when each elution reagent was introduced. Adsorption proportion of silicic acid: 10 %. Adsorption and elution experiments were performed at 25°C.   Elution reagents (introduced volume / L): 2 % NaOH solution (1.55), 1 % HCl (4.54), 1.4 % H2SO4 (8.68), 2.5 % NaHCO3 solution (4.2), 0.1 % HCl (45.4), and 1 % NaCl (7.31).

2.3.2. Chemical state of silicic acid adsorbed to an OH⁻ type resin (batch experiment).

To examine the existing state of adsorbed silicic acid, ^{29}Si MAS NMR spectra for silicic acid adsorbed to an OH⁻ type resin were measured. Various OH⁻ type resin samples with different amounts of silicic acid adsorbed were prepared using silicic acid solutions with different concentrations by batch experiments. The amount of silicic acid adsorbed was estimated from differences in silicic acid concentrations before and after adsorption. The adsorption amount is represented as the adsorption proportion. Fig.2.2. shows the ^{29}Si MAS NMR spectra. In the ^{29}Si NMR results, the polymerization mode of silicic acid (formation of Si-O-Si bonds by the condensation reaction between Si-OH bonds) is expressed using the symbol of Q^n (n=0 – 4: number of Si-O-Si bond in a $Si(OH)_4$ molecule) As shown in Fig. 1.7, only a peak for silicic acid in water was observed, but it could be observed as various Q^n states for silicons adsorbed on the ion exchange resin. This is the first example of directly confirming the polymerization of silicic acid in an ion exchange resin.

Q^0 is a monomeric silicate ion, Q^1 is a dimeric silicate ion, Q^2 is a polysilicate ion with a linear structure, Q^3 is a polysilicate ion with a planar structure, and Q^4 is a polysilicate ion with a three dimensional network structure. The Q^n structure can be assigned depending on the chemical shift value relative to a TMS (tetramethylsilane, $(CH_3)_4Si$) standard: Q^0: approximately -70 ppm, Q^1: approximately -80 ppm, Q^2: approximately -90 ppm, Q^3: approximately -100 ppm, and Q^4: approximately -110 ppm. In Fig. 1.9, the numbers on the right side indicate the adsorption proportion of silicic acid. Even at an adsorption proportion of 6 %, Q^1 and Q^2 structures were observed. Fig. 2.2 shows the variation in the peak intensity with the adsorption rate of silicic acid. By increasing the adsorption rate, the peak intensity assigned to the Q^0 and Q^1 structures abruptly decreased, while, the peak intensity assigned to the Q^3 structure abruptly increased (The three samples from the bottom of Fig. 2.2. were prepared from ^{29}Si enriched silicic acid solution, while the top sample was prepared using a typical silicic acid solution with natural abundance of ^{29}Si. Therefore, the sensitivity is lower.). These results clearly indicate that silicic acid adsorbed to an OH⁻ type resin can polymerize even at an unsaturated adsorption of silicic acid (the amount of silicic acid adsorbed is lower than the ion exchange capacity) to form polysilicic acid. Here, it should be emphasized that more silicic acid than the ion exchange capacity can be adsorbed to an OH⁻ type resin.

In Fig.2.2., the top spectrum indicates a case of supersaturated adsorption of silicic acid (adsorption proportion is 180 %). This indicates that another silicic acid may also combine with $Si(OH)_3O^-$ adsorbed on a functional group via an ion exchange reaction through the condensation reaction, and the polymerization reaction may continuously proceed. In the ^{29}Si NMR spectra of an alkaline silicate solution and an organic ammonium silicate solution, many peaks appear in the Q^2 and Q^3 regions due to formation of multiple silicate oligomers with different structures (Harris et al., 1981 and 1983, Kinrade et al., 1998, and Feimy et al., 2006). Unlike the polymerization of silicic acid in an aqueous solution, the ^{29}Si MAS NMR spectra for silicic acid adsorbed to an OH⁻ type resin are relatively simple because of fewer peaks. This result suggests that the polymerization reaction may be controlled by structure regulation

in a molecular scale space within the pore of the resin particle. In Fig. 2.3, no Q^4 structure was detected when the adsorption proportion was 6, 12 and 35 %. This is a specific feature of the polymerization of silicic acid adsorbed to an OH^- type resin. On the other hand, when the adsorption proportion was 180 %, a Q^4 structure was observed at approximately -110 ppm, although with a slight peak intensity. Bai et al reported the polymerization of silicic acid adsorbed to an Al-type chelate resin and the formation of silica (Q^4 structure) around the resin particle (Bai et al., 2012).
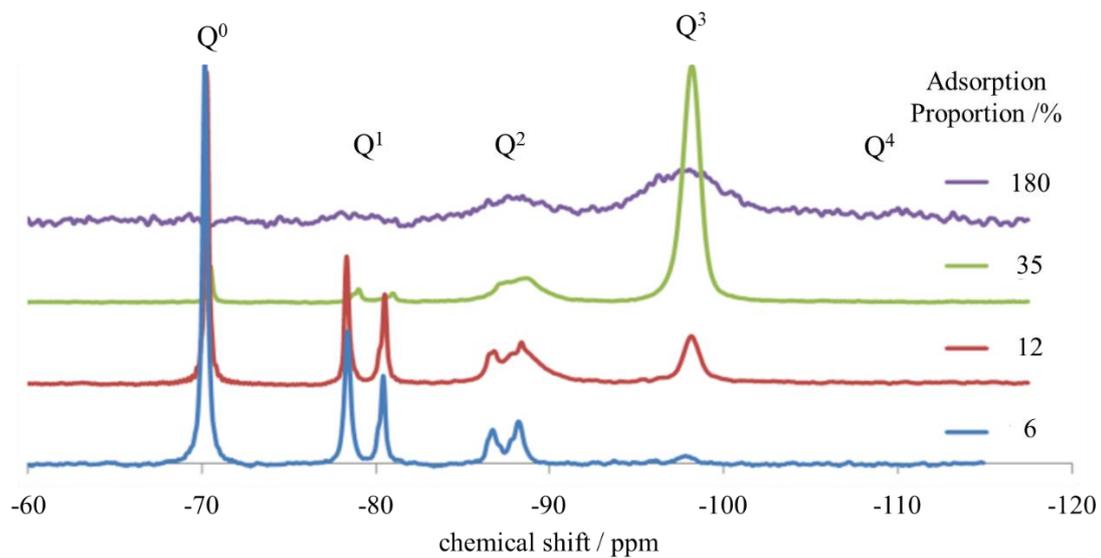
Fig. 2.2　^{29}SiMASNMR spectra for silicic acid adsorbed to OH type anion exchange resins. Adsorption proportions of silicic acid: 6, 12, 35, 180%.
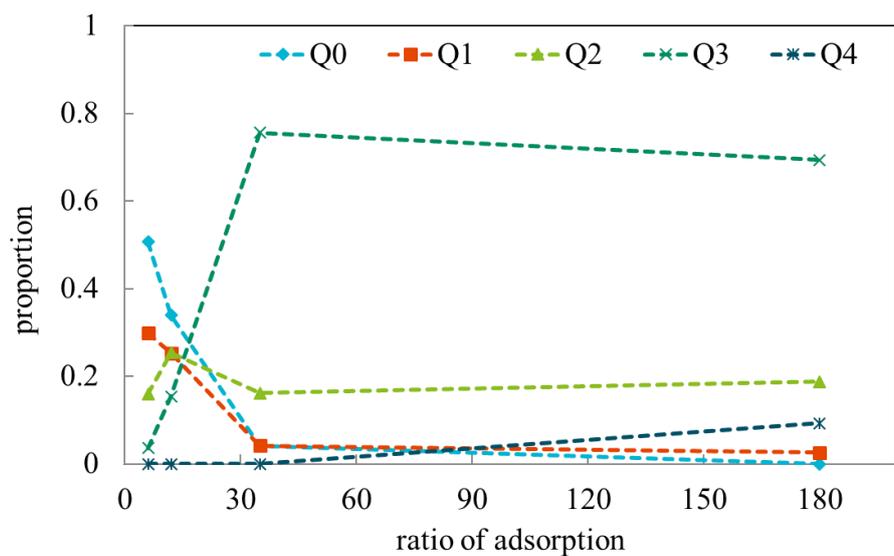
Fig.2.3. Variation of each Q^n structure proportion with adsorption rate of silicic acid. Each peak intensity was calculated for the ^{29}Si MAS NMR spectra in Fig. 2.2.

2.3.3. Effect of NaOH concentration on elution proportion (column experiment).

In Fig. 2.1, only the sodium hydroxide solution is valid as an elution reagent of silicic acid from an OH^- type resin column. In Fig. 2.2, it was first demonstrated that silicic acid adsorbed to an OH^- type resin can polymerize even when the amount of silicic acid adsorbed is unsaturated. These results suggest that although $Si(OH)_3O^-$ may be desorbed by the ion exchange reaction with the OH^- ion, the elution of polysilicate ions from the OH^- type resin is caused by the hydrolytic decomposition of polysilicate ions with alkali. The solubility of silica increased with increasing pH because of the ionization of silicic acid (Iler, 1979). Therefore, the effect of NaOH concentration on the elution proportion was examined. NaOH solution as the elution reagent passed through the column packed with an OH^- type resin adsorbing silicic acid (adsorption proportion of silicic acid: 10 %). Fig.2.3. shows the variation in the elution proportion of silicic acid with NaOH concentration (1, 2 and 5 %). The elution proportion increased in the NaOH concentration range of 1 % to 2 % but the proportion at 5 % NaOH was almost the same that at 2 % NaOH. This may be due to slower diffusion of the 5 % NaOH solution to the inside of the pore of the resin particle than that of 1 and 2 % NaOH solutions.
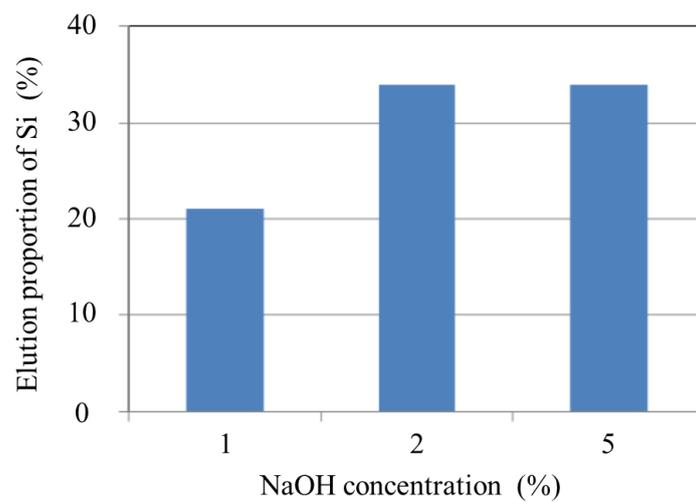
Fig.2.4. Variation of elution proportions of silicic acid with NaOH concentration as an elution reagent. NaOH concentration: 1, 2 and 5 %.　Adsorption proportion of silicic acid: 10 %. Adsorption and elution experiments were performed at 25℃

2.3.4. Effect of temperature of NaOH solution on elution proportion (column experiment).

  The dissolution of silica (polysilicic acid) is accelerated with increasing temperature (Iler, 1979 and Shimada et al., 1982). A 2 % NaOH solution was used as the elution reagent and its temperature was changed to examine whether the elution proportion of silicic acid increased. The column temperature (elution solution) was maintained using a water jacket in which water with a constant temperature flows around a column. The NaOH solution at different temperatures was passed through the column packed with OH^- type resin adsorbing silicic acid (adsorption proportion of silicic acid: 10 %). Figure.2.5. shows the variation in the elution proportion of silicic acid with temperature of 2 % NaOH solution as the elution reagent. In the temperature range from 25 to 45 °C, the elution proportion of silicic acid increased, but the proportion decreased at 55 °C. According to a previous study, an optimum temperature exists for the polymerization of silicic acid in solution at a given pH and silicic acid concentration (Shimada et al., 1982). The retardation of elution of silicic acid at 55 °C may be due to repolymerization of silicic acid or silica deposition during the elution (Zaganiaris et al., 1992).
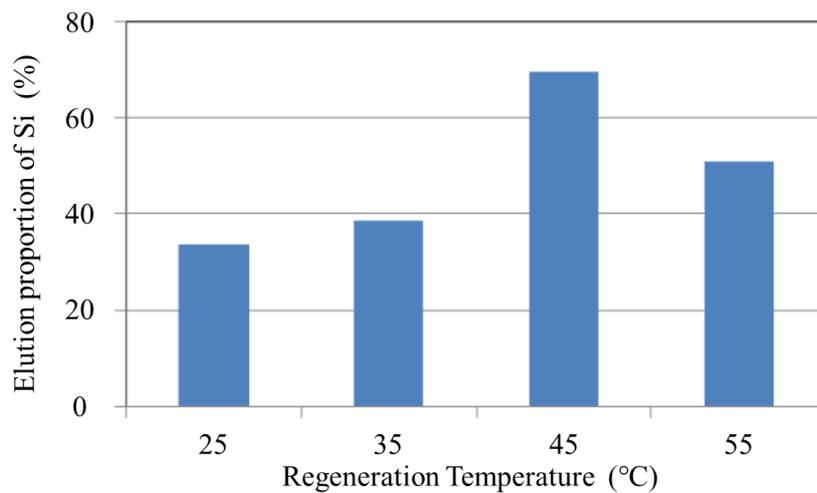
Fig.2.5. Variation of elution proportions of silicic acid with temperature of NaOH solution as an elution reagent. The adsorption experiment was performed at 25°C. Adsorption proportion of silicic acid: 10 %. Temperature of NaOH solution: 25, 35, 45 and 55 °C. NaOH concentration: 2 %.

2.3.5. Effect of adsorption proportion of silicic acid on elution proportion (column experiment).

In Fig. 2.2., the polymerization mode of silicic acid adsorbed to an OH^- type resin depends on the amount of silicic acid adsorbed (adsorption proportion). The elution proportion of silicic acid from the OH^- type resin column is expected to depend on the polymerization mode. OH^- type resin columns with different adsorption proportions of silicic acid adsorbed were prepared using silicic acid solutions with different concentrations (adsorption proportion: 10, 25 and 45 %). Figure.2.5. shows the variation in the elution proportion of silicic acid with the adsorption proportion. A 2 % NaOH solution was used as the elution reagent. By increasing the adsorption proportion, the elution proportion of silicic acid decreased, suggesting that the dissolution rate of polysilicic acid may be slower with increased polymerization of silicic acid adsorbed to the OH^- type resin.
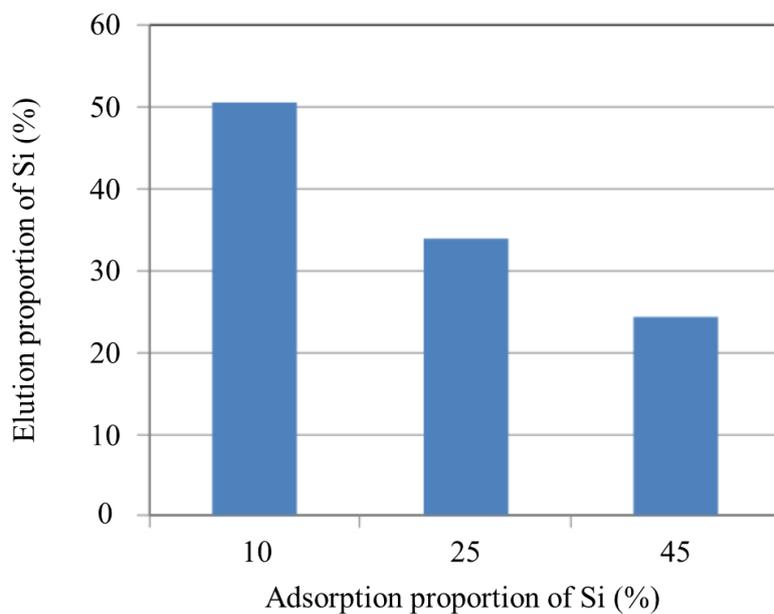
Fig.2.6. Variation in the elution proportions of silicic acid with the adsorption proportion of silicic acid (10, 25 and 45 %). NaOH concentration: 2 %. Adsorption and eution experiments were performed at 25°C.

2.3.6. Elution behavior of silicic acid from an OH^- type resin (batch experiment).

To examine the elution behavior of silicic acid with different Q^n structures, an OH^- type resin adsorbing silicic acid (adsorption proportion of silicic acid: 9.8 %) was prepared. Immediately after filtration, the resin on the filter (5 cm^3) was immersed in a 1 % NaOH solution (500 cm^3) for 5 min. Before and after the NaOH treatment, ^{29}Si MAS NMR spectra for silicic acid adsorbed to the OH^- type resin were measured. As shown in Fig.2.7., the peak intensities of the Q^0, Q^1 and Q^2 structures after treatment (blue line) were considerably decreased compared with those before the treatment (orange line), while the peak intensity for the Q^3 structure only slightly decreased. Based on this finding, the result in Fig. 2.7 can be explained as follows: silicic acids with Q^0, Q^1 and Q^2 structures are easily eluted by 1 % NaOH solution treatment, while silicic acid with a Q^3 structure is barely eluted. The result in Fig.2.7 corresponds well with the results in Fig.2.6.
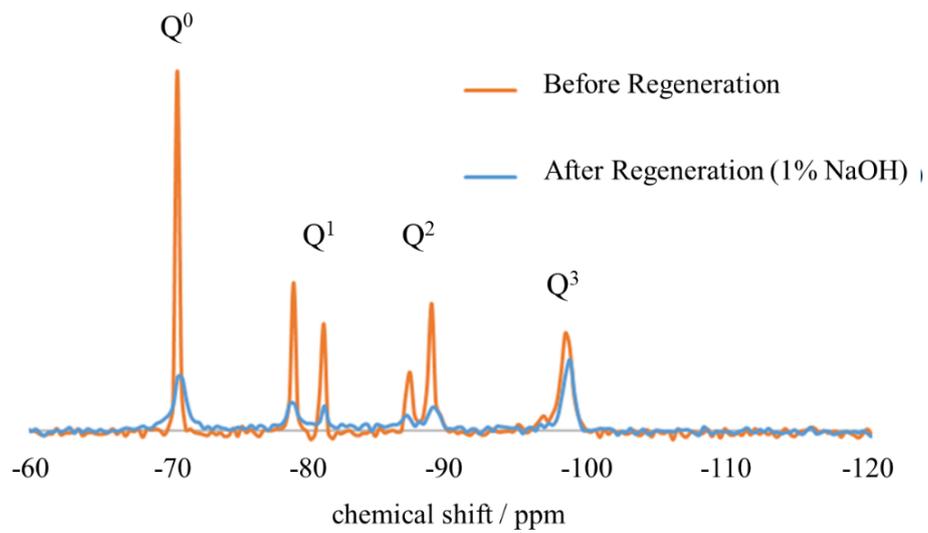
Fig.2.7. ^{29}Si MAS NMR spectra for silicic acid adsorbed to OH$^-$ type anion exchange resin before and after the treatment with 1 % NaOH solution. Before the NaOH treatment, the adsorption proportion of silicic acid was 9.8 %. Adsorption and elution experiments were performed at 25℃.

2.3.7. Effect of waiting time after adsorption of silicic acid on elution of silicic acid (column test)

Considering the results so far, there is a close relationship between the chemical state of silicic acid and the ease of elution. Therefore, considering that the chemical state may change with time, it was first confirmed whether the elution rate of silicic acid differs depending on the waiting time from the end of adsorption of silicic acid to the start of regeneration of the ion exchange resin column.

First, the silicic acid solution was passed through a column filled with an OH type ion exchange resin to adsorb silicic acid. The adsorption rate of silicic acid on the exchange group was 10%. Next, the regeneration operation was performed under each condition immediately after the end of adsorption and 20 hours after the end of adsorption. Figure 2.8 shows the difference in dissolution rate. The elution rate decreases with the passage of time. Considering the results obtained so far, it is possible that the Si-O-Si bond indicated by the Q^3 structure in the NMR of silicic acid is increased.
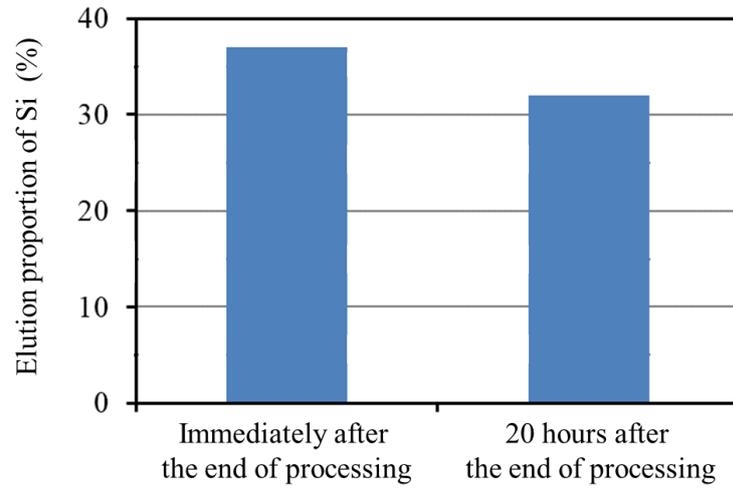
Fig.2.8. Comparison of the elution ratio of silicic acid due to the difference in time after the adsorption of silicic acid. Adsorption proportion of silicic acid: 10 %. NaOH concentration: 2%. Adsorption and adsorption experiments were performed at 25℃.

2.3.8. Change in NMR relaxation time of ^{29}Si nuclei as a measure of existing state of silicic acid adsorbed to OH$^-$ type resin (batch experiment).

In Fig. 2.9, the effect of delay time, which is a parameter on the NMR measurement, on the S/N ratio of the spectrum is shown. The sample was an OH$^-$ type resin adsorbing silicic acid (adsorption proportion: 10 %). By increase in the delay time from 10 seconds to 30 seconds, the S/N ratio of the spectrum was significantly improved despite the smaller accumulation number of the measurement. In particular, the peak intensity attributed to Q^3 near -90 ppm and Q^4 near -110 ppm increased. This means that the larger n, the longer the NMR relaxation time of ^{29}Si nuclei.

In order to discuss change in the relaxation time, an anion exchange resins with adsorbed silicic acid as shown in Table 2.1 were prepared. Samples 1 and 2 were prepared for the purpose of confirming the results in Fig.2.6 in detail. This enable to discuss the relationship among the amount of silicic acid adsorbed to OH$^-$ type resin and size of the polysilicic acid formed and the NMR relaxation time. Also, from the comparison of sample 2 and sample 3, the results in Figure 2.8 due to the difference in waiting time after silica adsorption can be considered.

Figure 2.10 shows the ^{29}Si MAS NMR spectra for the sample 1 when the delay time was varied from 1 s to 120 s. The spectra for the sample 1 showed all peaks from Q^0 to Q^4 due to the adsorption of a large amount of silicic acid. Figure 2.11 shows the same spectra for the sample 2. The spectra for the sample 2 had poor spectral quality due to a small amount of silicic acid adsorbed. In Fig. 2.11, the peak of Q^0 appeared at a delay time of 1.5 s, and the peak intensity became constant after 8.8 s. The Q^3 peak began to appear at a delay of 8.8 s and the peak intensity continued to increase up to 120 s.

On the other hand, for the spectra of the sample 1, the peak of Q^0 appeared at a delay time of 1 s, and the peak intensity became constant after 8.8 s. In the Q^3 peak, the intensity increased from 2.4 s to 32 s and then remained constant for 120 s.

From this comparison between the results in Figs.2.10 and 2.11, it was revealed that ^{29}Si nuclei having different relaxation times were present as the amount of silicic acid adsorbed increased. As the amount of silicic acid adsorbed increases, the environment inside the pores of the ion exchange resin changes, and peaks derived from ^{29}Si with different relaxation times appear. This means that the existing state of polysilicic acid becomes complicated due to the increase in the amount of silicic acid adsorbed. The results in Fig.2.7 show that silicic acid species having a complicated structure (for example, Q^3 structure rather than Q^0) is difficult to elute from the resin. The comparison of results in Figs.2.10 and 2.11 agrees well with the result of Fig.2.6.

In Figure 2.12, the peak due to Q0 appeared from the delay time of 3.1 seconds, and the peak intensity became constant after 9.3 seconds.The Q3 peak began to appear with a delay time of 4.4 seconds and the peak intensity increased to a delay time of 41 seconds.The peak symmetry of sample 3 was relatively good.However, in Sample 2, the peak symmetry was low.The Q3 peak for Sample 2 started to appear with a delay of 13.6 seconds and increased to

120 seconds.This suggests that the polymerization state of silicic acid changed significantly during the storage period of 3 days to 3 months. Table 2.2 shows the relaxation times for each sample. Sample 2 has a very small peak due to Q4. The relaxation time of Q3 was 23 seconds for sample 3 and 32 seconds for sample 2. This shows an increase in the size of the Q3 state in Sample 2 compared to Sample 3.

This means that the silicic acid structure inside the resin becomes complicated with the lapse of time after the adsorption of silicic acid without the supply of silicic acid. The comparison between results of Figs.2.11 and 2.12 support the result of Fig.2.8, considering that it is difficult to elute silicic acid with a complicated structure from the resin.

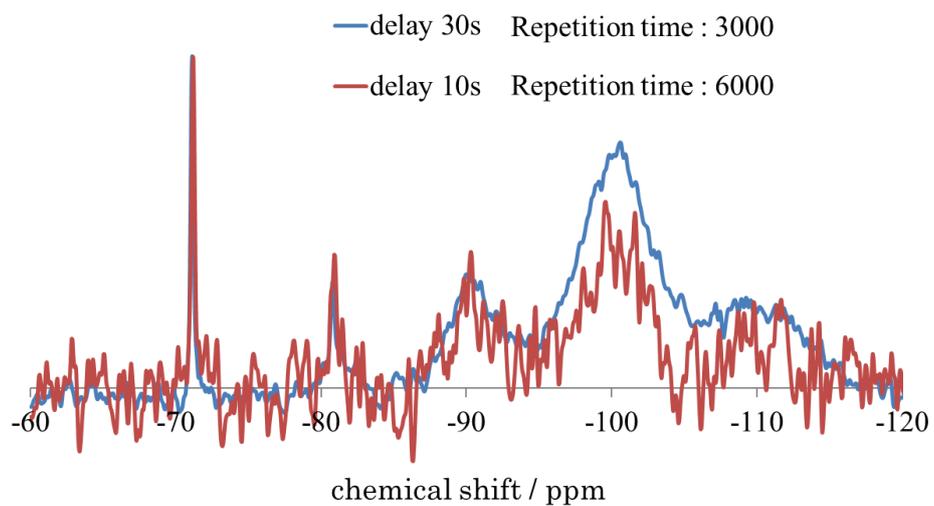Fig.2.9. ^{29}Si MAS NMR spectra for the sample measured under delay times of 10 s and 30 s. (adsorption proportion: 10 %, preservation period: 7 days)

Table.2.1. Sample for studying relaxation time

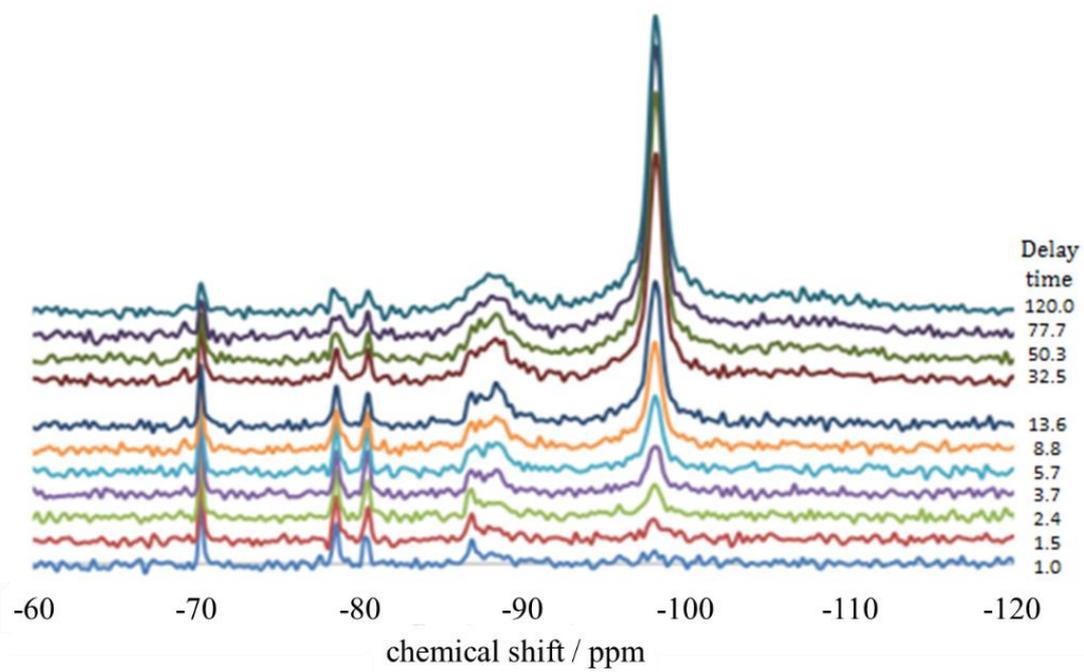|	Sample 1	Sample 2	Smple 3
Adsorption proportion (%)	35	12	12
Preservation period	3 months	3 months	3 days
Repetition time	160	160	128
Delay time (s)	1-120	1-120	1-60

Fig.2.10. ^{29}Si MAS NMR spectra for the sample 1   Delay time: 1 s – 120 s.
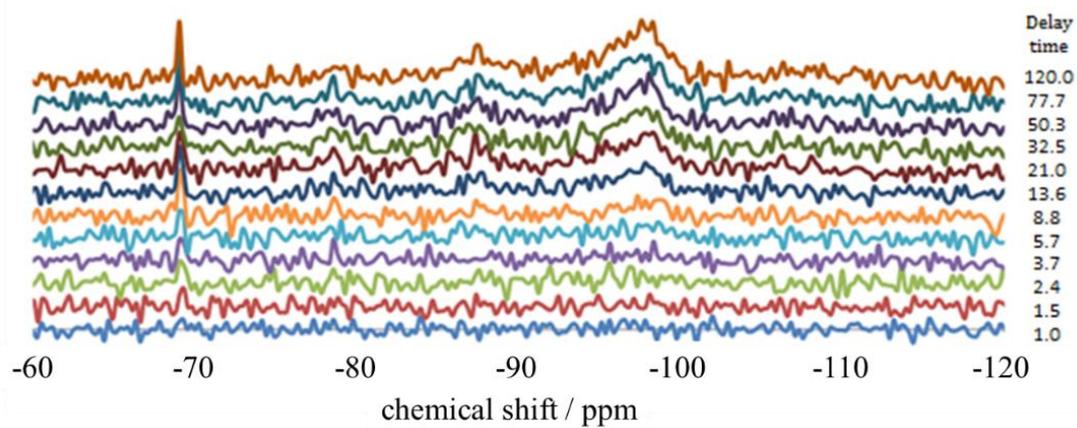
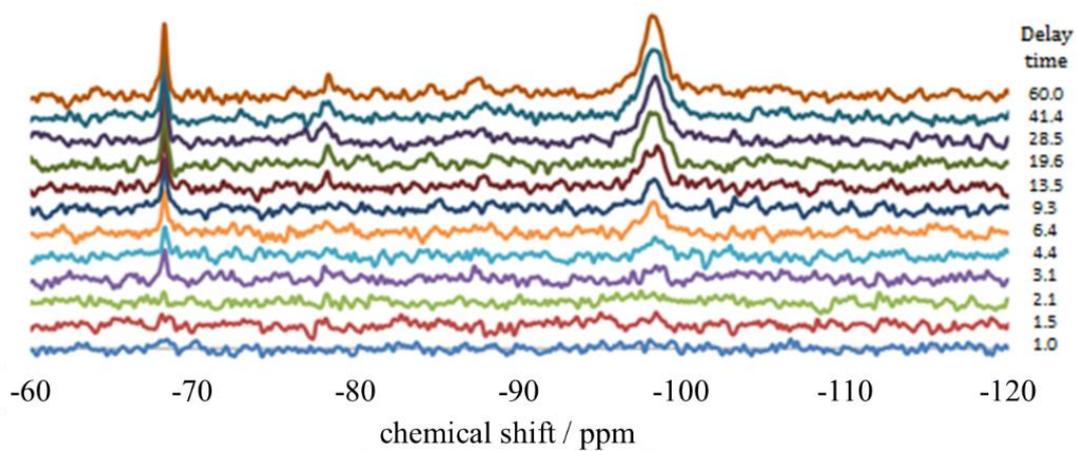Fig.2.11. ^{29}Si MAS NMR spectra for the sample 2   Delay time: 1 s – 120 s.

Fig.2.12. ^{29}Si MAS NMR spectra for the sample 3   Delay time: 1 s – 60 s.

Table.2.2. Comparison of relaxation times of samples 2 and 3

Structure	Sample 2	Sample 3
Q^0	6.19	8.11
Q^1	8.65	8.87
Q^2	21.2	18.9
Q^3	32	23.0
	32	22.5
Q^4	58.8	

2.4. Conclusion

$Si(OH)_3O^-$ is adsorbed via an ion exchange reaction with the OH^- ion in the OH^- type anion exchange resin. As shown in Figs.2.1, 2.2, and 2.3, $Si(OH)_3O^-$ adsorbed to an OH^- type anion exchange resin polymerizes to form polysilicate ions. It should be emphasized that the adsorbed silicic acid polymerized even at an unsaturated adsorption of silicic acid against the adsorption capacity.

For the desorption of silicic acid (monomeric $Si(OH)_3O^-$ and polysilicate ions), only a NaOH solution was a successful elution reagent. Monomeric $Si(OH)_3O^-$ adsorbed to an OH^- type resin is most likely desorbed by an ion exchange reaction with the OH^- ion. On the other hand, the desorption of polysilicate ions (elution of silicic acid) from an OH^- type resin column does not occur through an ion exchange reaction but by the partial hydrolytic decomposition of polysilicate ions by an attack of the OH^- ion to the siloxane bond ($\equiv$Si-O-Si$\equiv$). Polysilicate ions with Q^1 and Q^2 structures are easily eluted from resin columns, whereas silicic acid with a Q^3 structure is barely eluted. It can be understood that the empirical rule that heating is required in water treatment of silicic acid with an ion-exchange resin provides energy required for attack of OH^- ion to siloxane bond ($\equiv$Si-O-Si$\equiv$).

Due to the complexity of the silicic acid form and its effect on regeneration, if the resin column is regenerated before the complex polysilicate ions with Q^3 structure or more are generated, the silicic acid adsorbed on the ion exchange resin will be easily eluted. It is clear that it is important to control the degree of polymerization of silicic acid in order to improve the efficiency of water treatment by ion exchange.

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Chapter 3 Effect of adsorption condition of silicic acid to OH type anion exchange resin on the efficient water treatment

3.1. Introduction

In Chapter 2, it became clear that silicic acid polymerizes even if the amount of silicic acid adsorbed is below the adsorption capacity of the ion exchange resin. This fact makes it difficult to elute silicic acid from the ion exchange resin. In other words, if the polymerization of silicic acid can be controlled, the elution of silicic acid can be also easily accomplished.

Even under insaturated adsorption, silicic acid polymerizes to form Si-O-Si bonds. Therefore, it is ideal to control the amount of Si-O-Si bonds having a high degree of polymerization during the adsorption of silicic acid.

In contrast to the previous chapter discussing changes in chemical state only with silicic acid, this chapter directly observes and discusses the chemical state of silicic acid under conditions closer to actual water treatment conditions. It also considers ways to improve the efficiency of water treatment.

Since silicic acid has a small selectivity coefficient at the anion exchange resins, the adsorption is impeded in the coexistence of ions having higher selectivity such as chloride and sulfate ions. However, adsorption occurs at a constant ratio rather than zero. Fig.3.1. shows a model of the ion exchange adsorption zone by simulating an actual ion exchange tower (Mitsubishi Chemicals, 1998). After sulfate ions, nitrate ions, chloride ions, and carbonate ions are in equilibrium, finally silicic acid forms an adsorption zone. Although the inlet side is in an equilibrium state, since the ion exchange reaction is an equilibrium reaction, silicic acid is also adsorbed on the ion exchange resin on which coexisting ions are adsorbed.

Therefore, it was confirmed whether the chemical state of silicic acid was affected by coexisting ions, and whether coexisting ions could control the chemical state was investigated.

From another viewpoint other than coexisting ions, the influence of the structure of the ion exchange resin must be considered. Ion-exchange resins show the same selectivity if they have the same basic structure, but they are sold by various manufacturers. Moreover, it is unlikely that all water treatments will use the same from the same manufacturer. In many cases, the detailed structure of the ion exchange resin is a secret item of each manufacturer and is not disclosed. However, crosslinkage is relatively known and indicates how bridging the ion exchange resin matrix. A high crosslinkage means that the space around the ion exchange group is narrow, and a low crosslinkage means that the space around the ion exchange group is wide.

Therefore, in order to investigate the influence of the resin structure on the structure of the adsorbed silicic acid, ion exchange resins from the same manufacturer with different crosslinkages were prepared, and changes in the adsorbed structure of silicic acid were investigated. Difference of the crosslinking of ion exchange resins is considered to affect size and environment of space inside of ion exchange resin particle. It suggests that adsorption of silicic acid to the OH- type ion exchange resin and its polymerization may be changed depending on the difference in crosslinking of the ion exchange resin.
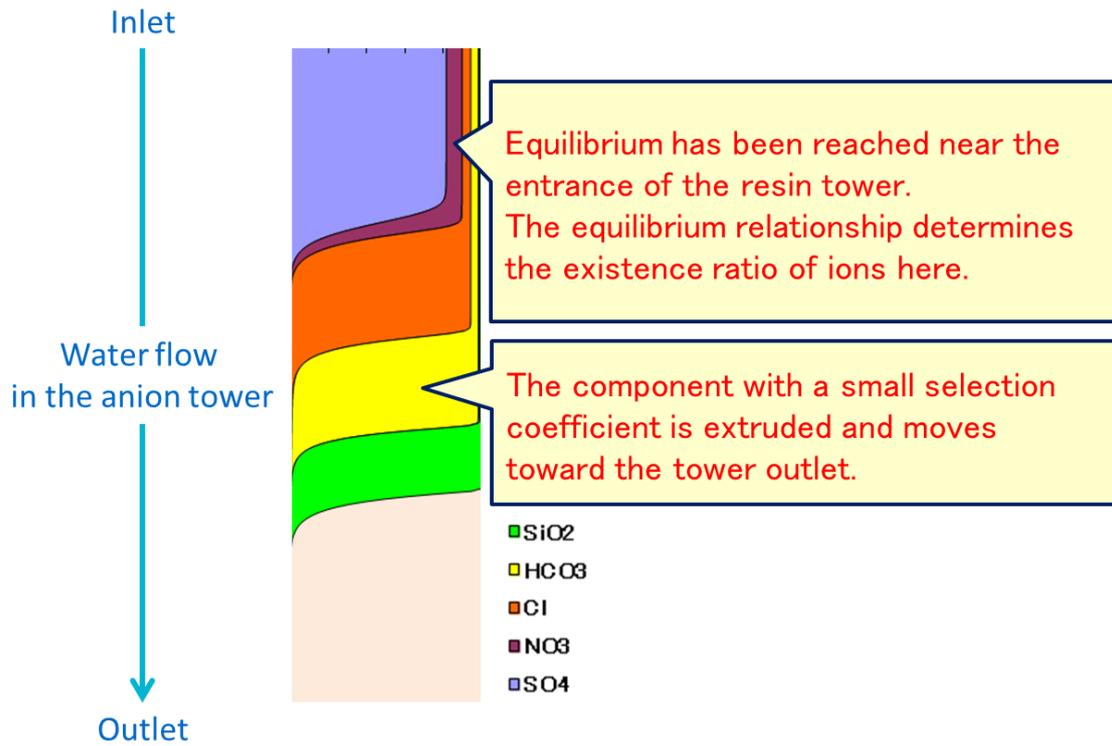
Fig.3.1. Schematic diagram of ion exchange adsorption zone

3.2. Experimental

・Preparation of ion exchange resin with coexisting ions (batch test)

SA10AOH (OH⁻ type, Mitsubishi Chemical) 100 cm^3 was immersed in hydrochloric acid or sulfuric acid adjusted to a dilute concentration to prepare an ion exchange resin with coexisting ions adsorbed. The amount of coexisting ions was changed by changing the concentrations of hydrochloric acid and sulfuric acid. The Cl type / OH type ratio and the SO$_4$ type / OH type ratio were calculated by measuring the adsorbed amount by measuring the solution after immersion by ion chromatography.

・Silicic acid adsorption test to ion exchange resin with coexisting ions. (batch test)

500 cm^3 of silicic acid solution adjusted to 8.3 mg-Si / L was prepared, and 5 cm^3 of anion exchange resin with adjusted amount of coexisting ions was added. The solution was shaken with a shaker, and after 2 h, filtered through a 0.45 μm membrane filter. The concentration of silicic acid in the filtrate was measured by spectrophotometry to determine the adsorption rate of silicic acid. For the anion exchange resin remaining on the filter, surface adsorbed water was removed with filter paper. The OH⁻ type resin having adsorbed silicic acid was immediately crushed into powder using an agate mortar and stored in a bottle with a stopper for ^{29}Si MAS NMR spectrum measurement. Table 3.1 shows a list of the prepared ion exchange resins.

・Preparation of ion exchange resins with different crosslinked proportions of resin

It is well known that ion exchange resins have different ion selective coefficients as shown in Table 3.2 depending on the different crosslinked proportions (Mitsubishi Chemicals, 1998 and Bonner et al., 1957). First, resins with different crosslinkages from the same manufacturer were prepared. Next, silicic acid was adsorbed from the solutions with the same concentration to these in the same method as in the batch test in Chapter 2.2 to prepare ion exchange resins with adsorbed silicic acid at various crosslinked proportions. Generally, when the crosslinked proportions is high, the water content of the ion exchange resin decreases and the physical strength increases. Increasing the crosslinked proportions means fixing the space around the ion-exchange group and increasing the number of electrically bound water molecules.

・Adsorption of silicic acid in the presence of coexisting ions (column experiment)

A silicic acid solution (0.2 mmol/L) containing Cl⁻ions (0.6 mmol/L) was introduced at a constant flow rate (0.83 L/min) from the top of a φ40 mm acrylic column. In the actual ion exchange treatment, a weak basic anion exchange resin (hereinafter referred to as WBA) remove Cl⁻ ions, and then a strong basic anion exchange resin (hereinafter referred to as SBA) remove silicic acid. In order to simulate the actual water treatment, water was passed in the order of WBA to SBA in the experiment. The amount of WBA was set under two conditions of 500 mL and 1000 mL. When WBA was 500 mL, the flow rate conditions were adjusted so that Cl⁻ ions would be adsorbed on SBA. The amount of silicic acid adsorbed was adjusted to be 5

g-SiO$_2$ / L-SBA regardless of the amount of WBA.

· Relationship between the number of repeated adsorption and desorption of silicic acid and the elution ratio (column test)

After the silicic acid adsorption operation, ultrapure water was introduced from the bottom of the column at a flow rate of 1 L/min to stabilize the resin state. Then a 2% -NaOH solution was introduced from the bottom of the column at a flow rate of 1.55 L, 0.21 L/min to desorb the silicic acid. After the solution passed through the column, ultrapure water was passed for 30 minutes at a flow rate of 0.21 L/min until the pH of the effluent from the column reached a neutral value. From the beginning of the chemical injection to regenerate the ion exchange resin (remove silicic acid), all the effluent from the column was collected and the elution proportion of silicic acid was calculated (((elution amount of silicic acid) / (adsorption amount of silicic acid)) x 100).

The silicic acid concentration in each effluent was determined by spectrophotometry based on the formation of molybdosilicic acid. In order to clarify the influence of silicic acid elution in the ion exchange column depending on the presence or absence of coexisting ions, adsorption and desorption were repeated to confirm the change in elution proportion with respect to the number of repetitions.

Table 3.1. Adsorption ratio of silicic acid on adjusted coexisting ion adsorption resin

| Coexisting | | Silicic acid adsorption ratio (%) | | |
Ion type	ratio(%)	For exchange capacity	For OH type part	
OH	100	2.1	2.1	
Cl	28	2.1	3.0	
Cl	55	2.1	4.6	
Cl	86	0.7	5.2	
SO$_4$	33	2.1	3.1	
SO$_4$	67	-	-	It fluctuates and cannot be calculated
SO$_4$	79	0.7	3.4	

OH is adsorbed on the ion-exchange group where Cl and SO$_4$ are not adsorbed.

Table 3.2. Selectivity coefficients of some cations against cation exchange resins with various crosslinkage.

Crosslinkage (%)		4	8	16
Selectivity Coefficients	Li$^+$	1.00	1.00	1.00
	H$^+$	1.32	1.27	1.47
	Na$^+$	1.58	1.98	2.37
	K$^+$	2.27	2.90	4.50
	Ca^{2+}	4.15	5.16	7.27
	Ba^{2+}	7.47	11.5	20.8

3.3. Results and Discussion

3.3.1. Adsorption of silicic acid to ion-exchange resin with adsorbed coexisting ions and its existing state

Figures 3.2 and 3.3 are the ^{29}Si MAS NMR spectra of the resins shown in Table 3.1. At lower Cl /OH or SO_4/OH ratios, almost the same spectra as the 100% OH type were obtained. On the other hand, ^{29}Si MAS NMR spectra were not observed at high Cl/OH or SO_4/OH ratios. This is probably because the adsorption of silicic acid was suppressed.

The chemical shift reflects the effect of electron density around the target atom. In the anion exchange resin, the ion exchange group attracts electrons. The power to attract electrons is the strength of basicity. The properties of such an ion exchange resin can be confirmed from the chemical shift (Eguchi, 2015).

Table 3.3 and Fig.3.4 show the chemical shifts of Q^0 and Q^1 that can be seen from Figures 3.2 and 3.3. As the number of coexisting ions increases, Si shifts to the higher magnetic field side, indicating that the electron density is higher. In other words, the basicity of the ion exchange resin is reduced. The initial adsorption of silicic acid is ion exchange. Due to the decrease in basicity, it may be more reasonable to polymerize silicic acid with each other than to adsorb silicic acid by ion exchange.

There is no significant difference in the amount of silicic acid adsorbed to either the 100% OH type or 55% Cl type in Fig.3.2 and Table 3.1, but the peaks of Q^2 and Q^3 can be observed in the 55% Cl type. This indicates that the coexistence of chloride ions in the resin promotes the polymerization of silicic acid. In the 55% Cl type resin, the number of silicate ions that can be adsorbed by ion exchange is reduced by replacing the OH type portion with Cl type. This means that the same amount of silicic acid as 100% OH type resin is dispersed in the adsorption site where 55% Cl type resin is low. With 55% Cl type resin, it is considered that the number of contacts between silicic acids increases and causes a state such as aggregation, which accelerates polymerization (Akinaga, 2017).

In the case of SO_4 type resin, the adsorption of silicic acid is considered to be suppressed more than that of Cl type. As shown in Table 3.1, the adsorption rate of silicic acid on 67% SO4 type decreased with time. An NMR spectrum similar to that of the 55% Cl type resin was expected, but the promotion of polymerization could not be confirmed. The sulfate ion is strongly hydrated in the ion exchange resin, and its hydration number is larger than that of chloride ion and hydroxide ion (Okada et al., 2009). It is considered that the bulky structure and the hydration effect occupy a wider space than the OH and Cl type parts in the resin, inhibit the diffusion of silicate ions, and suppress the polymerization of silicic acid.
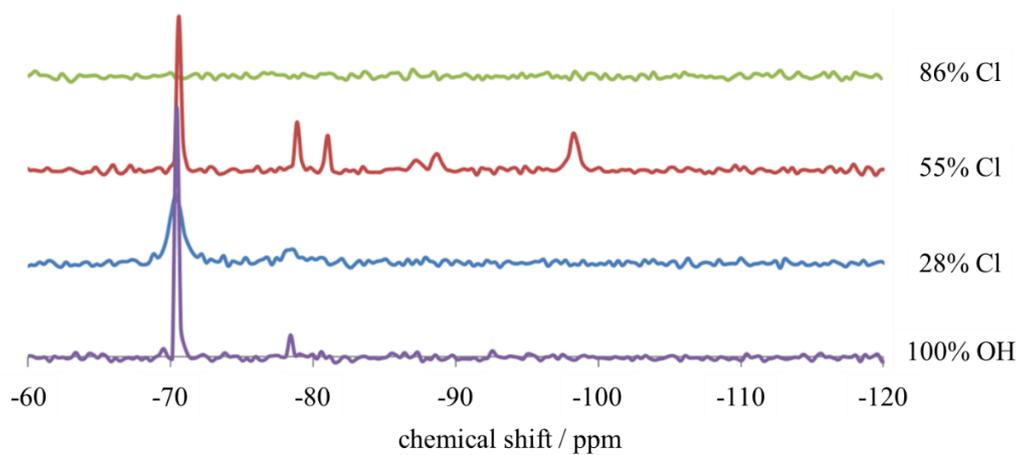
Fig.3.2. ^{29}Si MAS NMR spectra of silicic acid adsorbed to resin with Cl$^-$ ions.
Numerals in the right side: occupation proportion of Cl$^-$ ion against total adsorption capacity.
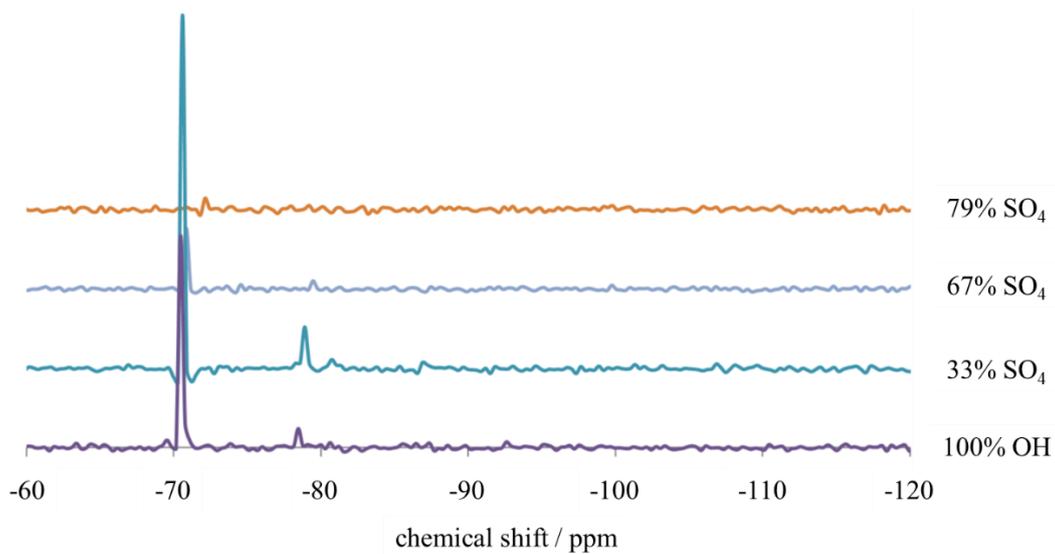Other adsorption sites are occupied by OH$^-$ ions.

Fig.3.3. ^{29}Si MAS NMR spectra of silicic acid adsorbed to resin with SO_4^{2-} ions.
Numerals in the right side: occupation proportion of SO_4^{2-} ion against total adsorption capacity.
Other adsorption sites are occupied by OH^- ions.

Table 3.3. Adsorption ratio of coexisting ions and chemical shift

Ion type	Coexisting ratio(%)	Chemical shift for 100% OH type resin		
		Q^0	Q^1	(ppm)
OH	100	-	-	
Cl	28	+ 0.106	-	
Cl	55	− 0.154	− 0.461	
SO_4	33	− 0.154	− 0.461	
SO_4	67	− 0.400	− 1.322	
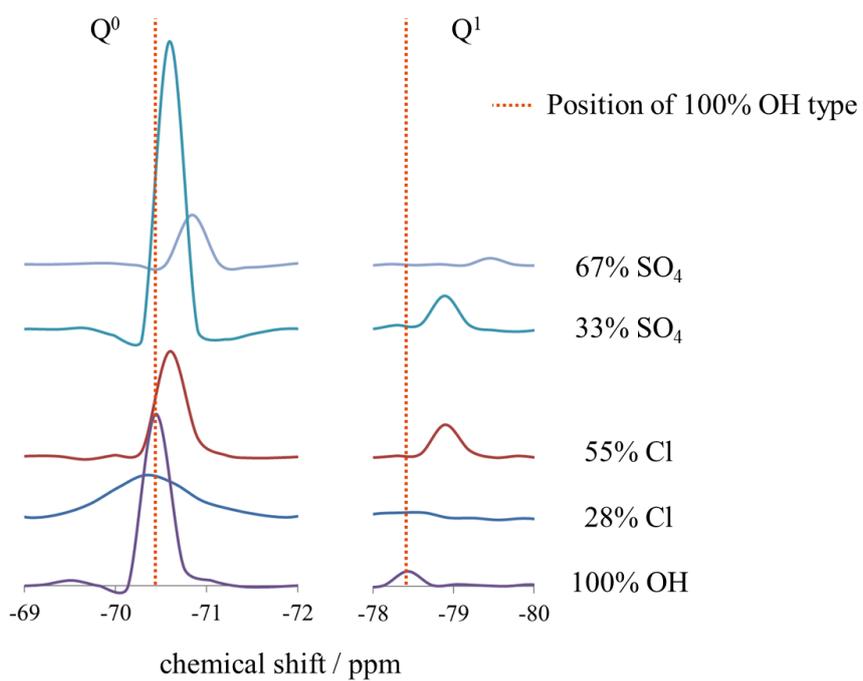
Fig.3.4. Enlarged view of chemical shift: Q^0 and Q^1 of ^{29}Si MAS NMR spectra with and without coexisting ions

3.3.2. Effect of crosslinkage of ion exchange resin on polymerization of silicic acid adsorbed

As shown in Table 3.4, five different ion exchange resins were prepared. A schematic diagram of the ion exchange resin and crosslinkage is shown in Figure 3.5. Crosslinkage is one of the factors that determine the space volume around the ion-exchange group. Samples 1 to 4 have trimethylammonium as the exchange group, and these are called type I resins. The structural difference between Samples 1-4 is the proportion of cross-linking to resin structure. Sample 5 is a type II ion exchange resin that has dimethylethanol ammonium as the exchange group. Type II resin has slightly larger exchange groups and slightly less basicity than Type I resin. The ^{29}Si MAS NMR spectra of silicic acid adsorbed on these resins are shown in Fig.3.5. The proportion of the Q^0 to Q^4 structures in Fig.3.5 is shown in Figs.3.6 and 3.7.

From the Fig.3.6, it is clear that the chemical shift values of the monomer and the polymerized silicic acid also vary depending on the type of resin. Comparing samples 2, 3, and 4 with the same exchange capacity but different proportions of crosslinking, Q^0 peak shifts toward the lower magnetic field as the crosslinking increases, indicating that the electron density of Si decreases. That is, the chemical shift values show a higher shielding effect in the order of lower proportions of crosslinking. Further, the lower proportions of crosslinking, the smaller the influence of the exchange group acting on Si, and the lower the basicity of the resin.

Focusing on the Q^3 peak, the shape of the peak became sharper as the proportions of crosslinking increased. Especially in sample 4, the symmetry of Q^3 peak was good, and was assigned to one peak in peak fitting. It is considered that this is because the pore size becomes smaller due to the increase in the degree of cross-linking and the spatial constraint becomes larger. For this reason, the diversity of polymerized species of silicic acid is reduced. The small pore size also leads to the short distance between the silicic acid and the exchange group, and it is consistent with the fact that the higher the crosslink, the greater the influence of the exchange group. It is considered that this is also applicable to the reason that Q^4 is observed in the spectra of samples 1 and 2 with low degree of crosslinking (degree of crosslinking 2% and 5%).

From the comparison of the relative peak intensities in the Fig.3.7, the peak intensity due to Q^3 is higher for the higher proportions of crosslinkage. Since it has been experimentally confirmed that all the silicic acid in the solution used for immersion is adsorbed, it can be said that the Q^3 structure is large in quantity. It can be considered that the diffusion path of ions is limited to some extent, the diversity is reduced, and the Q^3 structure easily grows.

In Fig.3.8, the NMR spectra of Type I (sample 3) and Type II (Sample 5) having the same proportions of crosslinking were compared. From the chemical shift of Q^0, it can be seen that type II has a higher electron density in Si and is less affected by ion-exchange groups. From the chemical shift of Q^3, type II has a smaller electron density of Si and is more affected by ion exchange groups. Type II resin uses dimethyl ethanol ammonium as an exchange group in order to increase the regeneration efficiency. The monomer shows a chemical shift in line with

this idea. However, from the chemical shift of the polysilicic acid, it was considered that type I resin is easier to elute polysilicic acid during the regeneration of the column compared with type II resin.

The relative intensity of Q^3 in the Fig.3.8 is lower in type II resin than in type I. For the relative intensity of Q^2, it is greater in type II. Also, the sum of Q^1 to Q^3 is more in type II. Assuming that the same proportions of cross-linking means the same spatial volume, the bulkiness of the ion-exchange groups may have an effect and polysilicic acid may be difficult to grow in type II. On the other hand, when a polysilicic acid is formed in a limited space, it is considered that the polysilicic acid approaches an electrostatic region that is strongly influenced by the exchange group and may occupy a part of space around the exchange groups. If the phenomena may occur, the diffusion of necessary chemicals for the regeneration of the column is deteriorated and the efficiency of the regeneration is lowered.

Table 3.4 Characteristics of the ion exchange resin used in the experiment.

resin sample	1	2	3	4	5
framework	styrene-divinylbenzene copolymer				
exchange group	trimethylammonium(type I)				dimethylethanol ammonium(type II)
resin type	gel type				
Crosslinkage (equivalence of D.V.B.) / %	2	5	7	11	7
total capacity / meq cm^{-3}－R	0.85	1.3	1.3	1.3	1.3
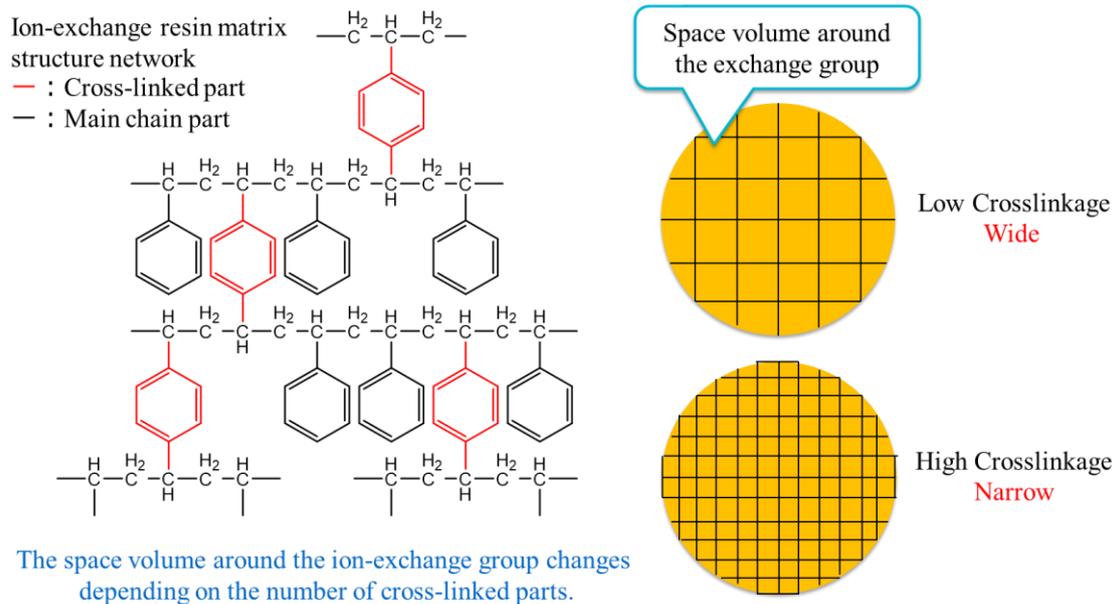
Fig. 3.5. Schematic image and meaning of crosslinkage
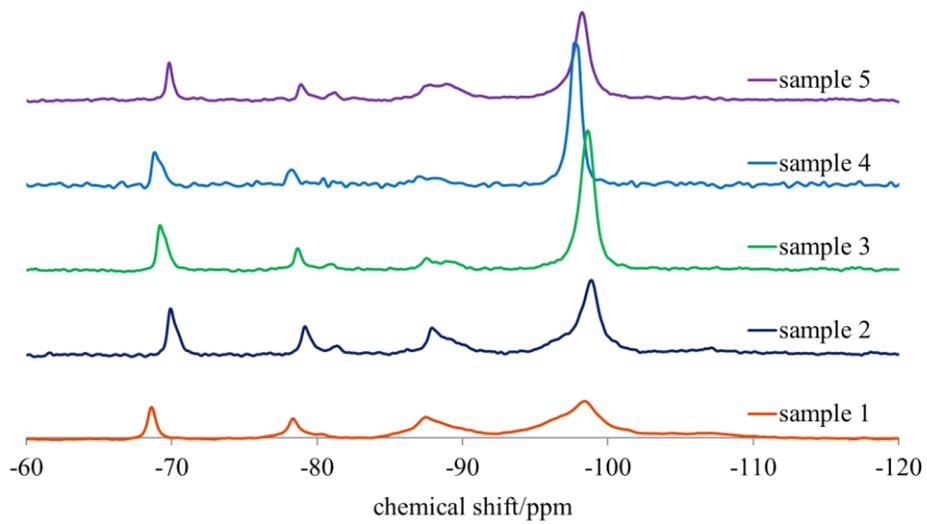
Fig.3.6. ^{29}Si NMR spectra of various resin types.
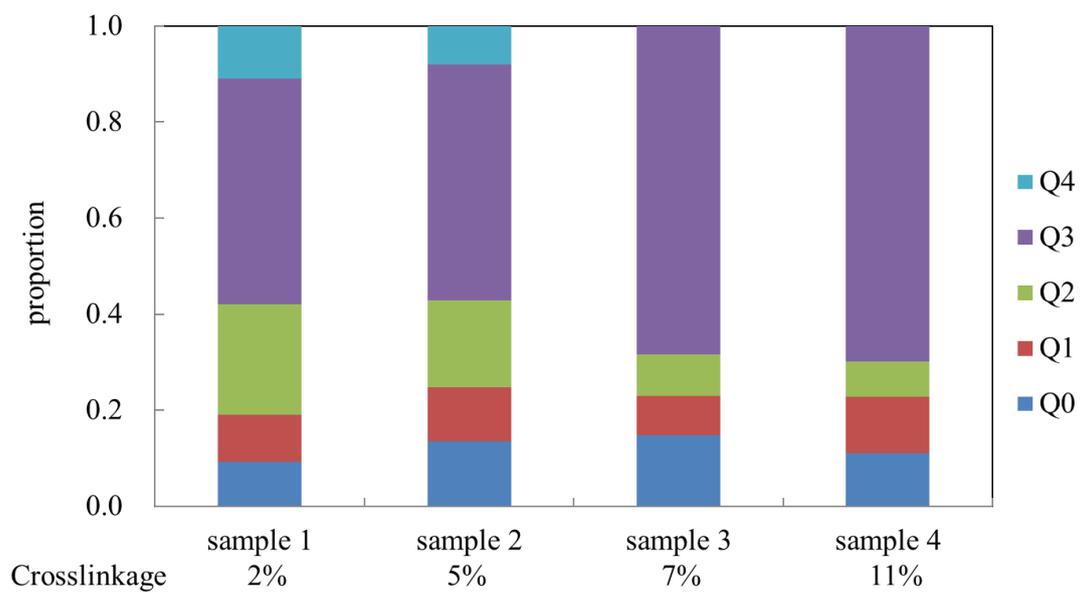
Fig.3.7. Comparison of Q^0 to Q^4 ratios of type I anion exchange resins with different crosslinkage
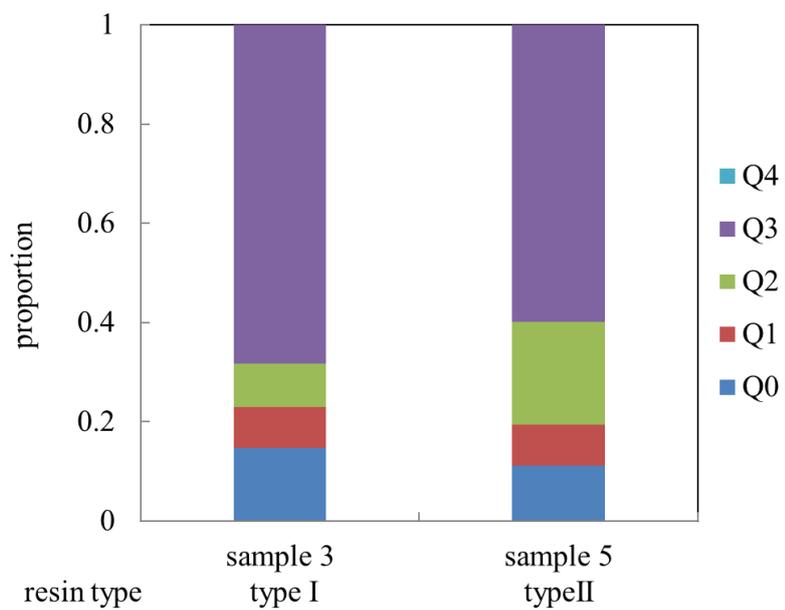
Fig.3.8.　Comparison of Q^0 to Q^4 ratio between type I and type II anion exchange resins with the same crosslinkage

3.3.3. Effect of coexisting ions on regeneration (column test)

Figure 3.9 shows the change in the elution proportion of silicic acid during regeneration when Cl^- was loaded together with silicic acid. The loading and regeneration tests were repeated 10 times. Comparing the case with a large amount of WBA and the case with a small amount of WBA, it was shown that when the amount of WBA was 500 mL (smaller amount), the silicic acid remained in the resin column and the elution proportion did not exceed 100% due to the small amount of WBA.

WBA is a weakly basic anion exchange resin that has dimethylammonium as texchange groups and has the effective adsorption property of chloride ions but cannot adsorb silicic acid. When the amount of WBA was small, the adsorption of silicic acid in the presence of chloride ions occurred in SBA, and when the amount of WBA was large, only silicic acid was adsorbed in SBA without coexisting ions. Prior removal of chloride ions with WBA facilitates elution of silicate ions..

Figure 3.10 shows the simulation result for the chloride ion load on SBA. The simulation visualizes the adsorption zone of chloride ion and silicic acid based on the variation of the ion concentration with time at the resin layer outlet. It shows the state when the water flow is completed. In the case of 500 mL of WBA, chloride ion is loaded in the SBA layer, while in the case of 1000 mL of WBA, chloride ion is hardly loaded in the SBA layer.
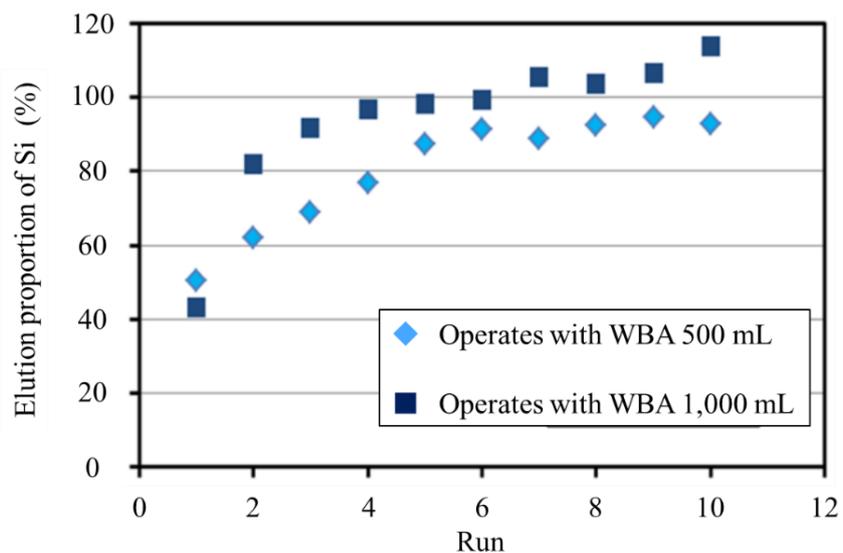
Fig.3.9. Changes in elution proportion of silicic acid when the adsorption of constant amount of silicic acid and its desorption were repeated 10 times.

WBA amount: ■ 1000 mL, ◆ 500 mL.

Adsorption proportion of silicic acid: 10 %. NaOH concentration: 2%. Adsorption and desorption experiments were performed at 25℃.
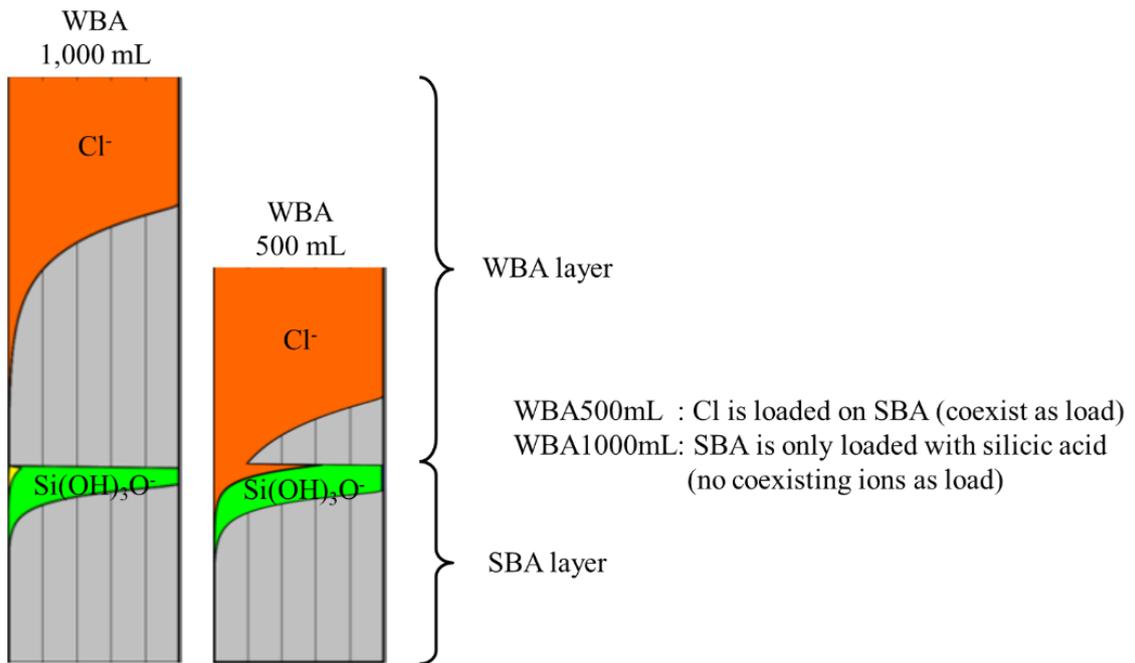
Fig.3.10. Schematic image of chloride ion loading on SBA (Simulation calculation result)

Text in figure:

WBA
1,000 mL

Cl⁻

WBA
500 mL

Cl⁻

$Si(OH)_3O^-$

$Si(OH)_3O^-$

WBA layer

WBA500mL : Cl is loaded on SBA (coexist as load)
WBA1000mL: SBA is only loaded with silicic acid
(no coexisting ions as load)

SBA layer

3.3.4. Effect of water content in ion exchange resin on polymerization of silicic Acid

The fact that the environment surrounding silicic acid affects the polymerization of silicic acid means that the state of water molecules around the silicic acid ion also influences the polymerization of silicic acid. As a previous study of ion exchange resins, the state of water around the ions is often discussed. Table 3.5 shows the hydration number for each ion in the reported anion exchange resin (Kaltbeitzel et al., 2007). It is also reported that the water in the ion exchange resin can be divided into two groups: one is bound waters (hydration water of the exchange group) which are strongly affected by the exchange group and another is free waters that can move relatively freely (Habuchi et al., 2001). From the volume change of the ion exchange resin, it is known that the anion exchange resin expands most and has the highest water content when the counter ion of the ion exchange group is OH^- (Mitsubishi Chemicals, 1998). The OH^- ion of the OH type ion exchange resin has only three hydration numbers, but it is considered that there is a large amount of free water due to its high water content.

Comparing Figs. 2.11 and 2.12, it was already shown that silicic acid forms a highly polymerized Si-O-Si bond depending on the time elapsed from the end of the adsorption operation. The fact that the Si-O-Si bonds increase despite the fact that the silicic acid is not supplied externally means that the silicic acid moves and polymerizes inside the resin.

Figs. 3.11 and 3.12 show how the ^{29}Si MAS NMR spectrum of silicic acid adsorbed to a resin having 55% Cl type ion exchange groups and 100% OH type ion exchange groups changed over a long period of time. First, the S / N deteriorated in both NMR spectra. The 55% Cl type has almost the same amount of silica adsorption as the 100% OH type, but the Q^4 structure can be detected at around -110 ppm. In the 100% OH type, relatively easy-to-regenerate Si-O-Si bonds such as Q^0, Q^1 and Q^2 remain after waiting for 3 months. On the other hand, in the 55% Cl type, Q^0, Q^1 and Q^2 decreased, and Q^1 was particularly remarkable. It can be seen that the adsorption of coexisting ions promotes the polymerization of silicic acid.

It is generally said that when the amount of free water is large, the fluidity of ions in the ion exchange resin is high. However, even if a sufficient reaction time of 3 months was given, the silicic acid adsorbed on the 55% Cl type resin, which had a small amount of free water, proceeded with the polymerization. This suggests that silicic acid once adsorbed is not eluted and diffused to polymerize without silicic acid supplied from the outside. There is a possibility that the adsorbed silicic acid will polymerize within the range where it can move with the exchange group. Of course, the narrower the range, the easier the silicic acids come into contact with each other. These results can be reflected in the operation of the ion exchange tower. For example, as already shown in Chapter 2, the ion-exchange unit should be shut down after the regeneration operation to prevent the regeneration of silicic acid from making regeneration difficult. In particular, the risk is higher when adsorbed with coexisting ions.

Table 3.5.   Hydration number of each ion in the ion exchange resin

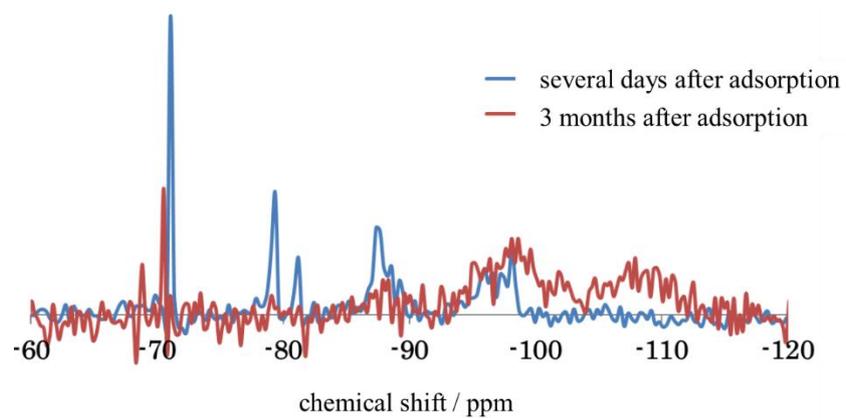| Ion	Hydration number
OH^-	3.0
Cl^-	2.4
SO_4^{2-}	8

Fig.3.11　^{29}Si MAS NMR spectra of silicic acid adsorbed on 55% Cl type resin after left for several days and 3 months after adsorption experiment of silicic acid
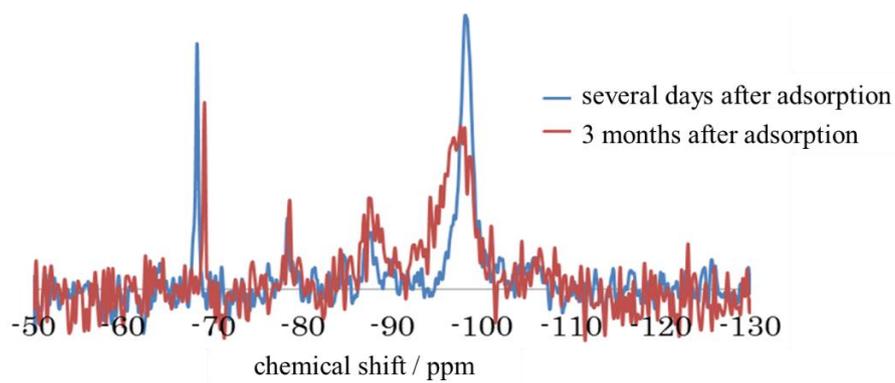
Fig.3.12. ^{29}Si MAS NMR spectra of silicic acid adsorbed on 100% OH type resin after left for several days and 3 months after adsorption experiment of silicic acid

3.3.5. Effect of anion exchange resin structure on regeneration (column test)

The silicic acid adsorbed on the low cross-linked resin formed Si-O-Si bonds in various chemical states. The silicic acid adsorbed on the highly cross-linked resin formed a highly polymerized Si-O-Si bond in a certain chemical state. Further, according to the result of the chemical shift, the ion exchange group of the highly crosslinked resin is strongly adsorbed on the silicic acid. Considering these results, it was expected that the silicic acid adsorbed on the highly crosslinked resin would not easily elute during regeneration. Therefore, the resin columns with different amounts of silicic acid adsorbed were prepared, and the elution ratios were compared using a 2% NaOH solution as a regenerant. Figure 3.13 shows a comparison of the silicic acid elution rates. When the adsorption amount is large, the difference in elution rate is small, but as expected, the highly crosslinked resin has a lower elution ratio of silicic acid.

Type II resin has less space around the exchange group than Type I resin. However, as can be seen in Figure 3.8 , Type I has more Si-O-Si bonds with a high degree of polymerization. Therefore, it was predicted that when polysilicic acid grows on the type II resin, it is difficult to elute during regeneration. Therefore, OH type resin columns were prepared with the same silicic acid adsorption rate using type I and type II resins, and the elution ratios were compared using 1% or 5% NaOH solution as a regenerant. Figure 3.14 shows expectedly that the elution proportion of silicic acid is low in case of the type II resin (sample 5) compared with that in case of type I resin (sample 3). The tendency of the elution rate did not change even if the NaOH concentration was changed. Type II resin is generally said to be easily regenerated, but it is difficult to decompose even Si-O-Si bonds that do not have a high degree of polymerization. This is probably because the diffusion of the regenerant is hindered. It was also found that the ease of elution was not determined only by the degree of polymerization of the Si-O-Si bond.
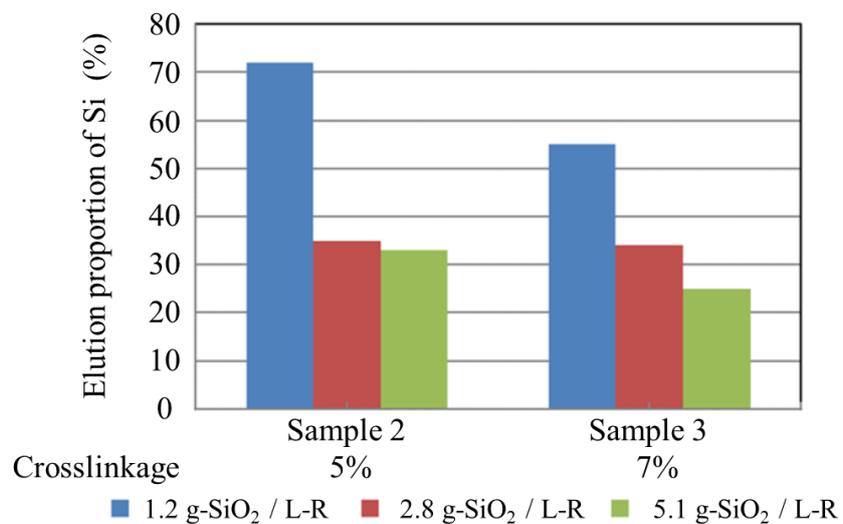
Fig.3.13. Adsorption amount and elution rate of silicic acid in ion-exchange resins with different crosslinkage. 2% NaOH was used as a regenerant at 25°C.
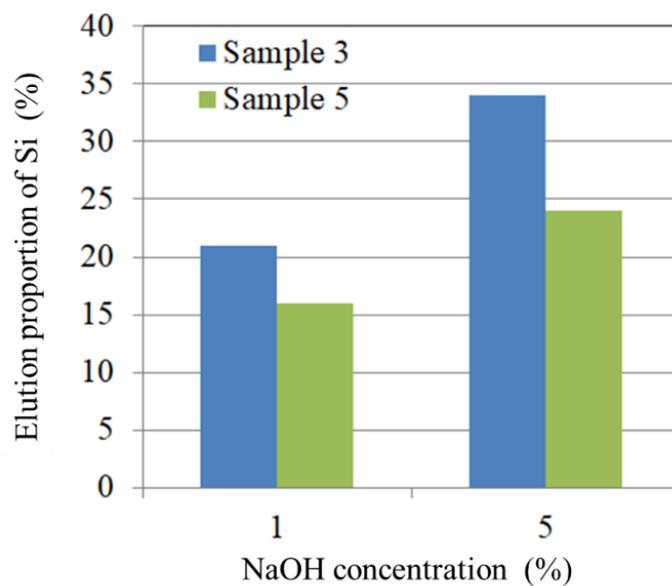
Fig.3.14. Comparison of the elution proportion of silicic acid between OH⁻ type ion exchange resins with different exchange groups (sample 3: trimethylammmonium, sample 5: dimethylethanolammonium). NaOH concentration: 1 and 5 %. Adsorption proportion of silicic acid: 10 %. Adsorption and elution experiments were performed at 25℃

3.4. Conclusion

In this chapter, we directly observed and discussed the chemical state of silicic acid under conditions close to actual water treatment conditions. Without coexisting ions, silicic acid polymerization is inhibitory. According to the results of the change in the chemical state of silicic acid, the more coexisting ions were present, the higher the degree of polymerization of Si-O-Si bond was formed. Based on this fact, silicic acid can be intentionally and easily eluted by removing the strong acid ions, which tend to become coexisting ions, with the weakly basic anion exchange resin layer in advance. It was also found that the presence of coexisting ions promotes the progress of polymerization and makes elution difficult when the apparatus stands by with silicic acid adsorbed.

According to the result of directly observing the formation of Si-O-Si bond by changing the structure of the ion-exchange resin, the ion-exchange resin with lower cross-linking is more efficient for regeneration of the ion-exchange resin column. A low crosslinkage means a large space around the exchange group. However, this result is premised on the action of the regenerant. By comparing the ion exchange groups of the type I and type II anion exchange resins with the same degree of cross-linking, it was confirmed that regeneration of type II with a narrow space around the ion exchange group was inefficient. This effect is thought to be due to the ease of diffusion of regenerated chemicals.

The existing state of silicic acid in these ion exchange resins can well explain the tendency of regeneration (elution rate) of silicic acid in the ion exchange column. The more grown and complicated polysilicic acid, the more difficult it is to regenerate. In this study, selecting a type I anion exchange resin with 5% crosslinkage and using WBA to remove strongly acidic ions was the most efficient water treatment.

From the above mentioned, the elution of silicic acid can be efficient by suppressing the formation of Si-O-Si bond, having a high degree of polymerization by monitoring the chemical state of silicic acid.

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Chapter 4 Outlook and Summary

4.1. Problems in recent water treatment

Based on the results of the whole research, the focus will be on the recent challenges of water treatment. When water treatment requires complete removal of silicic acid, the combination of RO technology and ion exchange technology is reasonable for effective silicic acid removal. A typical example is a production of ultrapure water used in the semiconductor industry.

In the semiconductor industry, the devices, which are cleaned by the ultrapure water, have become smaller and smaller in size and they are now discussing single-nano-order structures. When discussing the structure in this order, the effects of ions and fine particles as impurities are enormous. If a trace amount of them is present in the ultrapure water, they will impair the electrical characteristics and make it impossible to manufacture. Ideally, ultrapure water is theoretical (completely pure) H_2O.

In the ion exchange method, the difference in ion concentration between the water phase and the resin phase is the driving force for ion exchange. Ions are removed at the difference between the initial concentration and the equilibrium concentration even at a dilute concentration. Therefore, it is used for finishing ion removal in ultrapure water production. Ion exchange resins are one of the key functional materials in the ultrapure water production system in the latter half of the system after most of the ions have been removed. It is necessary that no ions be detected on the order of pg / L in ultrapure water for advanced semiconductors, and almost all metal ions are less than 10 pg/L.

The detection limit of silicic acid in ultrapure water is 50 ng/L, which is higher than that of metal ions, but low enough for practical use. When the produced ultrapure water is analyzed, it is below the lower limit of analysis in most cases, and there is no problem with the silicic acid concentration. Figure 4.1 shows an example of ultrapure water production system with each functional material and unit of the primary pure water system and secondary pure water system. By using such a system, it can be confirmed that the silicic acid concentration after the treatment is below the detection limit of the analysis.

However, according to a recent report on the composition of fine particles (Tanaka et al., 2015), Si occupies 50% of the element ratio of the fine particles collected at the inlet/outlet of the last ultrafiltration membrane (UF) of the ultrapure water production system (Figure 4.2). Silicic acid, which can be a silicon source, reaches the UF after being carefully removed by ion exchange and RO. Nevertheless, the compound containing silicon is captured as fine particles.
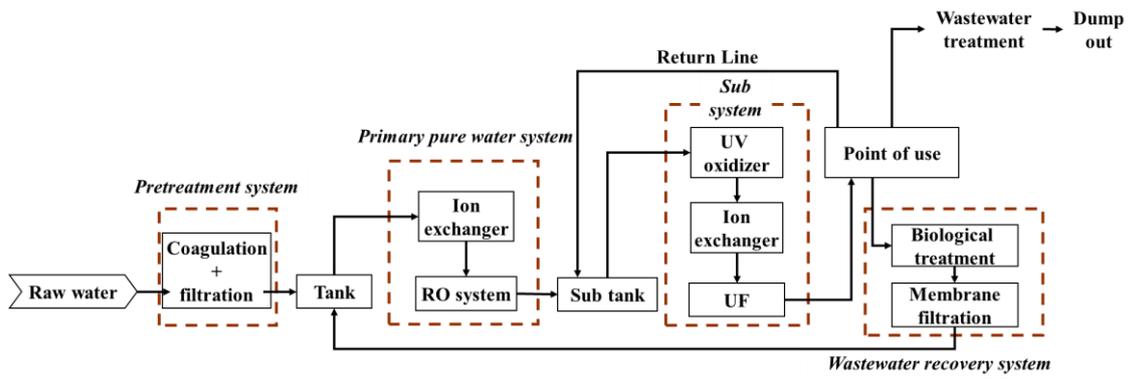
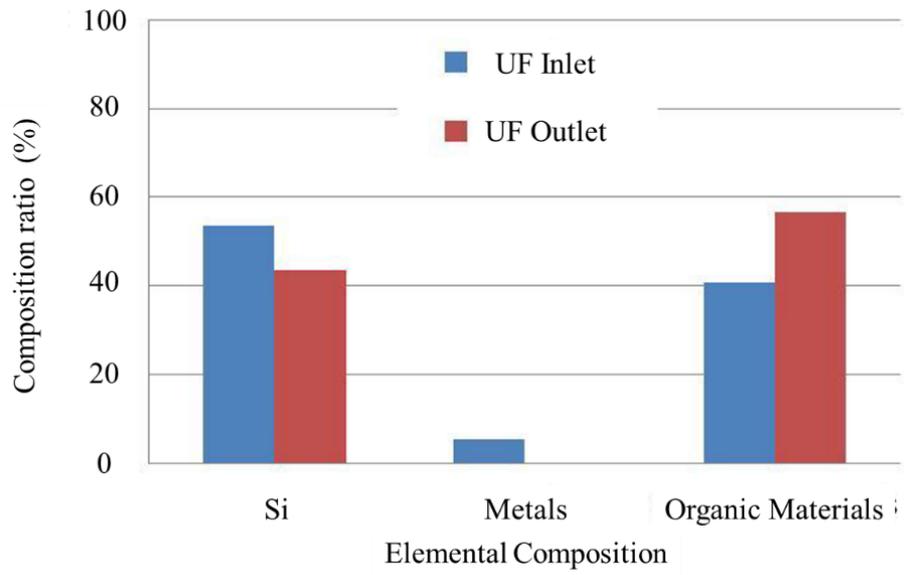Fig.4.1. An example of ultrapure water production system

Fig.4.2. Analytical result of fine particle composition before and after ultrafiltration membrane

4.2. Reduction of silicic acid risk in ultrapure water production

Where did the particles collected in the ultrapure water production end unit come from? The specific location is still unknown. However, if the aim is to produce higher purity ultrapure water, then the potential problems need to be minimized. This research shows that the polymerization of silicic acid often occurs inside of anion exchange resins. The silicic acid occupies only a few percent of the ion exchange groups by ion exchange adsorption of silicate ion, the polymerization of silicic acid begins. It seems to be almost impossible to prevent the polymerization. In addition, as shown in Fig.4.1, there is an ion exchanger closest to the UF where silicon was detected.

As already shown in Chapter 3, it is essential to quickly desorb after adsorption of silicic acid to prevent troubles due to silicic acid. Electrodeionization (EDI) is a method in which the ions adsorbed on the ion exchange resin in the device are immediately replaced with H and OH ions by electricity. Ions are moved in the direction perpendicular to the flow of water by the electrodes sandwiching the resin layer and discharged as concentrated water.

Fig. 4.3 shows an image of EDI equipment and ion removal. Ions are carried by the electric current and do not remain in the ion exchange resin. Therefore, there is a possibility that the silicic acid can be discharged without being polymerized.

Fig. 4.4 shows the change in the number of fine particles with time in treated water using a conventional ion exchange tower. The number of fine particles fluctuated due to chemical regeneration and changes in flow rate. The number of particles in water treated by EDI was 10 to 20 particles/mL (@ 0.05 μm), which was always almost constant number. Although EDI is not ideal in this result, it is clear which ion removal device has higher risk. It is necessary to deal with the possibility that silicic acid remains in the resin, polymerizes, and comes out in water in an equilibrium reaction. Also, if the effective charge density of polysilicic acids decreases and reaches to non-ionized state due to the quality of the water supplied, the polysilicic acid may leave out of the resin.

As mentioned above, the place where fine particles are generated and the presence or absence of contaminants are unknown. It is possible to conclude that the cause of the particles containing silicon is not due to ion exchange if the clarification progresses. However, at this time, it is necessary to carefully consider the risk of becoming fine particles and consider a method for removing silicic acid in ultrapure water production.

Thus, the consideration based on the change in the speciation of silicic acid gives an indication to the recent problem solving of water treatment. Of course, in order to completely solve the problem, consideration from various perspectives and deepening of technology are necessary. However, by continuing this study, it is possible to develop water treatment ideally and efficiently.
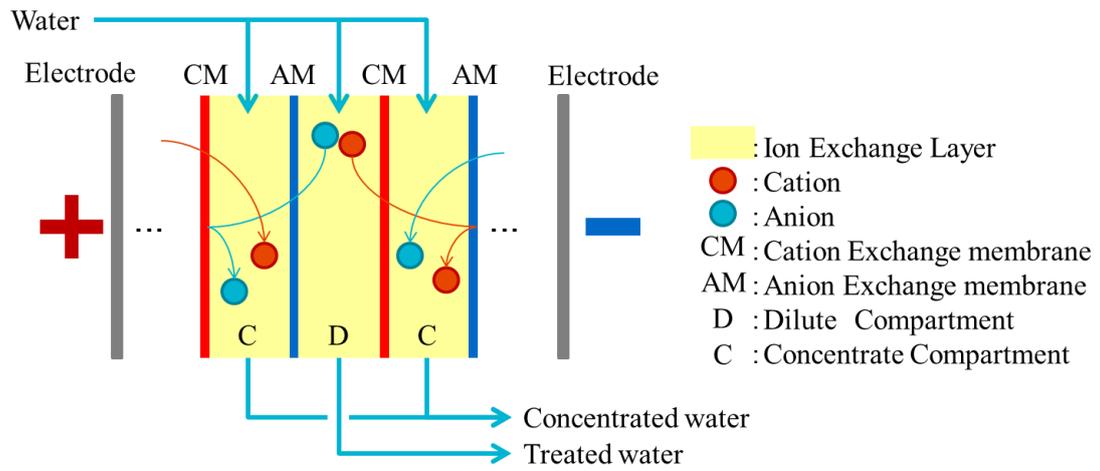
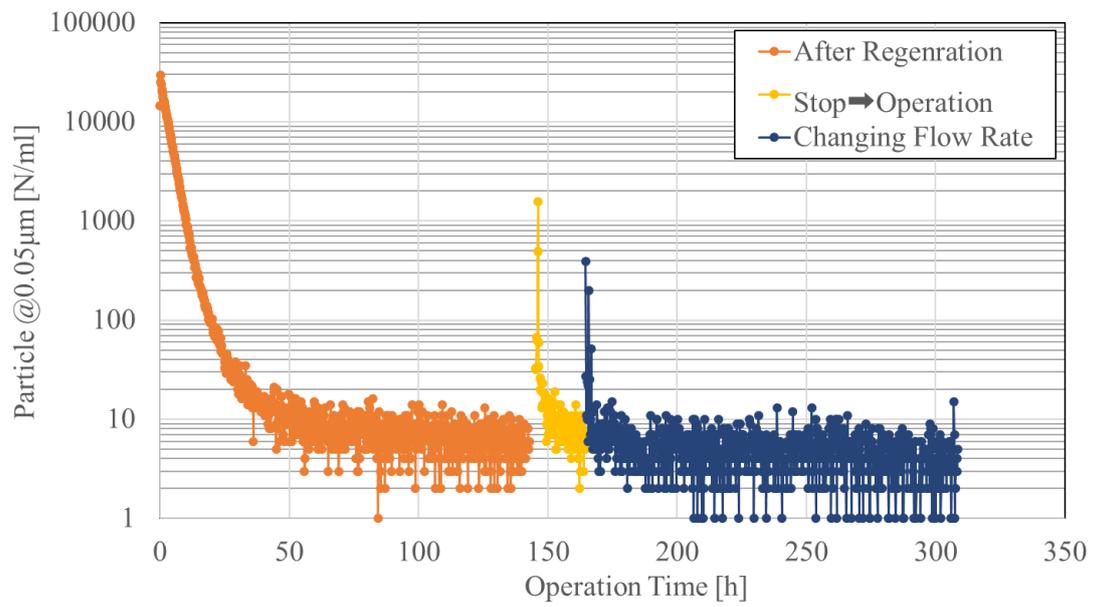Fig.4.3.　Schematic image of structure of EDI equipment and ion removal

Fig.4.4. Variation of number of fine particles at the outlet of the ion-exchange tower with time passage

4.3. Summary and conclusion

The ion exchange method is one of the most popular deionization / adsorption technologies used as one of the means for water treatment and making it efficient can contribute to the effective use of water resources. The ion exchange reaction is an equilibrium reaction and has the advantage that the change in free energy is small, but the adsorption and desorption of silicic acid are not simple equilibrium reactions, and desorption requires heating. Various studies have suggested that silicic acid is polymerized (Guowei et al., 1988). Polymerization of silicic acid makes water treatment difficult.

The purpose of this research is to clarify the polymerization conditions of silicic acid in ion exchange resin by directly observing change in the existing state of silicic acid, to control the polymerization, and to make the treatment of raw water containing silicic acid more efficient. In the studies so far, the polymerization of silicic acid has indirectly been suggested. Proposals for water treatment have been made based on this information, but the chemical state of silicic acid and water treatment have not yet been directly linked to improve efficiency (Meyers, 1999).

The outline and challenges of the research were shown in Chapter 1. The NMR results show that silicic acid in water appears as the only monosilicic acid peak.

In Chapter 2, ^{29}Si MAS NMR showed that various Si-O-Si bonds were formed in the ion exchange resin. This is the first example of a direct observation of the polymerization of silicic acid in an ion exchange resin. Elution of silicic acid from the ion exchange resin requires energy (heating) that is not normally required in the ion exchange reaction. Combining this empirical operation with the change in the chemical state of silicic acid, it was shown that the elution reaction of silicic acid adsorbed on the ion-exchange resin involves the decomposition of the siloxane bond ($\equiv$Si-O-Si$\equiv$).

The silicic acid in the ion exchange resin is polymerized even if it is adsorbed at a saturated concentration or less. This fact suggests that it is necessary to decompose polysilicic acid regardless of the amount adsorbed. In order to accelerate this decomposition reaction, heating is necessary for the regeneration process of the ion exchange resin column. Further, according to the NMR before and after the elution operation, the Si-O-Si bond having a high degree of polymerization is hardly decomposed. In order to improve the efficiency of water treatment by ion exchange, it is necessary to control the degree of polymerization of silicic acid.

In Chapter 3, the efficient elution method of silicic acid was considered from the viewpoint of controlling the degree of polymerization of silicic acid. If it is necessary to decompose polysilicic acid regardless of the amount of adsorption, it is ideal to control the amount of highly polymerized Si-O-Si bonds during the adsorption of silicic acid. Coexisting ions and structure of ion exchange resin was focused as a factor for controlling the polymerization during silicic acid adsorption.

According to the results of the change in the speciation of silicic acid, the more coexisting ions were present, the higher degree of polymerization of Si-O-Si bond was formed. Based on this fact, silicic acid can be intentionally and easily eluted by removing the strong acid ions, which tend to become coexisting ions, with the weakly basic anion exchange resin layer in advance. Further, it is desirable to elute the silicic acid immediately after the adsorption. Even if there is no supply of

silicic acid from the outside, the chemical state of silicic acid changes over time and turns into a highly polymerized Si-O-Si bond.

According to the result of directly observing the formation of Si-O-Si bond by changing the crosslinkage of the ion-exchange resin, the ion-exchange resin with lower cross-linking is more efficient for regeneration of the ion-exchange resin column. The high crosslinkage increases the amount of highly polymerized Si-O-Si bonds. However, this result is premised on the action of the regenerant. By comparing the ion exchange groups of the type I and type II anion exchange resins with the same degree of cross-linking, it was confirmed that regeneration of type II with a narrow space around the ion exchange group was inefficient. This effect is thought to be due to the ease of diffusion of regenerated chemicals. Summarizing these results, low cross-linking type I resin is desirable as the resin that facilitates the elution of silicic acid.

In Chapter 4, focusing on the recent problems of water treatment, it was shown that the ultra-pure water production system with low risk can be constructed from the change of the chemical state of silicic acid. The presence of fine particles in ultrapure water is a problem currently attracting attention in the semiconductor industry.In this example, the appropriate silicic acid removal method was shown to be electro-deionization (EDI).

The EDI unit has the feature that after the ions are adsorbed on the ion exchange resin, they are discharged almost without remaining. This feature allows us to address the changes in silicic acid speciation that we have discussed so far:

・Silicic acid is adsorbed on the ion exchange resin and polymerizes.
・The chemical state of silicic acid becomes complicated with time after adsorption.
・Silicic acid adsorption is an equilibrium reaction (ion exchange reaction), so there is a risk that polymerized silicic acid will be released into ultrapure water.
・Adsorption of coexisting ions other than silicic acid complicates silicic acid speciation and sometimes accelerates polymerization.

As described above, it was shown that the raw water containing silicic acid can be treated more efficiently by directly observing the change in the chemical state of silicic acid and clarifying the polymerization conditions. As a result of trial calculation, if the heating regeneration can be stopped by the regenerative ion exchange unit, as the subject of this study, the initial cost of the ion exchange unit can be reduced by about 10% and the running cost can be reduced by about 30%.

And I was able to give suggestions for solving unsolved problems.

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