Removal of Colloidal Silica from Water with Anion Exchange Resins

Wataru AGUI, Hirobumi SHIMOYAMADA,*
Masahiko ABE,^{*,**} and Keizo OGINO,^{*,**}

Rohm and Haas, Japan Research Center, 2763, Happo, Washinomiya-machi,
Kita-Katsushika-Gun, Saitama 340-02

*Faculty of Science and Technology, Science University of Tokyo
2641 Yamazaki, Noda-shi, Chiba 278

**Institute of Colloid and Interface Science, Science University of Tokyo
1-3, Kagurazaka, Shinjuku-ku, Tokyo 16

(Accepted October 5, 1993)

Summary

This study describes the dissolved state of colloidal silica in water and its adsorption properties on anion exchange resins (AERs). A colloidal silica solution of 3 % was prepared by ion exchange resin method from a sodium silicate solution. The colloidal silica in water formed about 10 nm particles in diameter. When leaving the colloidal silica solution at less than pH=7, the gelation was occurred. The gelation rate became the fastest at pH=5.2. The adsorption properties of colloidal silica on various AERs were investigated in batch adsorption. When added strong base anion exchange resins (SBAERs) to the colloidal silica solutions of about 560 $\mu\text{g/mL}$ as SiO_2 , the colloidal silica concentration in water decreased rapidly, at the same time, ionic silica was newly generated on the resin surface. The total amounts of silica removed by SBAERs became larger than the stoichiometrically removable amount of ionic silica by them. According to the scanning electron microscopic observation, colloidal silica adsorbed on the surface of SBAERs became to dissolve to the resin inside with the elapse of time. These results suggest that colloidal silica adsorbed on SBAERs should exist in concentrated state inside of the resins and in ionic silica at the ion exchange sites.

1 Introduction

In the production of highly purified water used for the advanced and sophisticated industries, such as atomic power and semiconductor industries, removal of silica from water is a key concern. Power plants seek to minimize deposition of colloidal silica on the

inside wall of equipment. Meanwhile, colloidal silica destroys the electric performance of wafers if deposited on the wafer's surface^{1),2)}. Ion exchange resins are indispensable for demineralization of water. Ionic silica in water is effectively removed by SBAERs. However, colloidal silica present in raw water is

difficult to remove from water with them. There are few papers on the removal of colloidal silica^{3,4)}. In addition, it is reported that under certain conditions silica can polymerize in ion exchange beds to form colloidal silica⁵⁾.The mechanism has not been elucidated. The objective of this study is to investigate the adsorption properties of colloidal silica on various AERs and to make clear the removal mechanism by them.

2 Experimental

1. Preparation of colloidal silica

Five grams of reagent grade of sodium silicate (Wako Pure Chemicals Industries,Ltd., Osaka, Japan) was dissolved in 100 mL of silica free pure water (total silica concentration is less than 1ppb). 2 mL of H-form SACER (Amberlite IR-120B) was added into the solution at intervals of every 15 min with stirring at 25 °C . Addition of the SACER was repeated until the pH and conductivity values of the solution became constant. Then the solution was filtered by a 0.22 μm membrane filter (MF). The colloidal silica concentration was adjusted to 3 % by diluted with pure water.

2. Determination of colloidal silica

Inductively coupled plasma atomic emission spectrometry (ICP-AES, SPS-7000, Seiko Instruments Inc., Tokyo, Japan) was used to determine the total

silica concentration in water. The ionic silica concentration in water was measured by the molybdate method⁶⁾. Then, the colloidal silica concentration was calculated as the difference of both concentrations.

3. Particle size measurement of colloidal silica in water

The particle size of colloidal silica was measured by dynamic light scattering using 4700 Submicron Particle Analyzer (Light source; Ar laser, Wave length; 488 nm, Temperature; 25 °C , Malvern Co., Ltd., Worcestershire, England).

4. Preparation of AERs

All ion exchange resins used here are products of Rohm and Hass company (Philadelphia, USA). AERs used in adsorption experiments have different functional groups and skeletal structures as shown in Table 1. These resins were regenerated by the ordinary regeneration methods and dehydrated for 48 h at 25 °C under reduced pressure.

5. Adsorption isotherms of colloidal silica

A suitable amount of each AER was weighed out each in a 100 mL Erlenmeyer flask. 25 mL of colloidal silica solutions of various concentrations were added into the flasks and the mixtures were stirred for 24 h at 25 °C during which equilibrium was confirmed. Then, the mixtures were filtered with a

Table 1 Characteristics of AERs.

AER	Structure	Type	Matrix
IRA-402BL	Gel	I	Hydrophobic
410	Gel	II	Hydrophobic
900	MR	I	Hydrophobic
938	MR	I	Hydrophobic
910	MR	II	Hydrophobic
93	MR	W	Hydrophobic

MR: Macroreticular

I : -N⁺(CH₃)₃
II : -N⁺(CH₃)₂C₂H₄OH
(Basicity : I>II)
W: -N⁺(CH₃)₂

0.22 μm MF and the total silica concentrations in the filtrates were measured by ICP. The adsorption amount of colloidal silica on each AER was determined by the difference of the total silica concentration before and after adsorption.

6. SEM observation of SBAER surface after adsorption of colloidal silica

Commercially available colloidal silica (Carplex FPS-5, Shionogi pharmaceutical Co., Japan) was used. The assay of SiO_2 is 92.0-98.0 %. The colloidal silica of 2.5 mg was put in 100 mL of silica free pure water in a 300 mL Erlenmeyer flask. IRA-402BL of OH form of 200 mg was placed in the flask. The mixture was stirred gently at 25 °C and filtered by a 0.45 μm MF at definite time intervals. The SBAER on the MF was dried at 60 °C for 30 min and the resin surface was observed by scanning electron microscope (SEM, JSM-5400LV, JEOL, Japan).

3 Results and discussion

1. Dissolved state of colloidal silica prepared

The ion exchange method in batch used in this work seemed to bring about the formation of more uniform colloidal silica than the column method⁷⁾. The profile of the formation of colloidal silica is shown in Fig. 1 in the relation of the conductivity and

Fig.1 Relationship between formation of colloidal silica and pH and conductivity by addition of IR-120B (H-form) at 25 °C.

pH of the sodium silicate solution and the added amount of SACER. Sodium ions were gradually exchanged with H^+ ions on the resin. As a result, colloidal silica was slowly formed. At the addition of SACER of 20 mL, the pH of the solution indicated 5.2 and the conductivity became minimum. This means the completion of the colloidal silica formation. Then, the conductivity and pH of the solution became constant at $1.1 \times 10^3 \mu\text{S/cm}$ and 2.6, respectively. The particle size distribution of colloidal silica prepared was pretty narrow in 6~13 nm. The average particle size was about 10 nm in diameter. When the colloidal silica solutions were allowed to stand in various pH, the particle of silica colloid grew gradually as described in Fig.2. Finally, gelation of colloidal silica was occurred. The gelation rate became the fastest at pH 5.2. However, the colloidal silica solution was stabilized in the weak alkali by adjusting pH with NaOH. In our adsorption experiments of colloidal silica, tests were carried out immediately after preparing the colloidal silica solution excluding NaOH.

2. Adsorption isotherms of colloidal silica on AERs

Fig.3 shows the adsorption isotherms of colloidal silica on SBAERs with trimethylamine functional

Fig.2 Change of particle size of colloidal silica with the elapse of time at 25 °C.

Fig. 3 Adsorption isotherms of colloidal silica on SBAERs at 25 °C .

group (type I) and with dimethylethanolamine functional group (type II), varying the skeletal structure of resins. As clearly found, SBAERs of type I, which has higher basicity, adsorbed colloidal silica more than those of type II . MR type resins especially having pores seemed to give larger adsorbed amounts of colloidal silica than GEL type resins. The pore sizes of IRA-900 and IRA-938 range predominantly in about 140-220 nm and 2.5~23 μm in diameter^{8, 9)}. This indicates that GEL type SBAERs substantially without pore should adsorb colloidal silica on the resin surface and MR type resins with pores adsorb it not only on the surface but also in the pores.

It was also found that weak base anion resins were not effective to remove colloidal silica from water, as given in Fig. 4.

3. Adsorption mechanism of colloidal silica on SBAERs

3.1 Effect of SBAERs on colloidal silica in water

The effect of SBAERs on colloidal silica dissolved in water was investigated. A SBAER of 100 mg was added to the colloidal silica solution (560 $\mu\text{g/mL}$ as SiO_2) of 25 mL. As shown in Fig. 5, the total silica concentration rapidly decreased to 10 $\mu\text{g SiO}_2/\text{mL}$. Ionic silica was newly generated and its concentration gradually increased to 50 $\mu\text{g/mL}$ as SiO_2 in 1 h. These results show that colloidal silica dissociates to

Fig. 4 Adsorption isotherms of colloidal silica on SBAERs at 25 °C .

Fig. 5 Change of silica concentration by addition of IRA-402BL.

form ionic silica on the surface of OH form resins with strong alkali. The pH of the solution changed from 5.3 to 6.8. The total amount (4.5 meq/g-R) of silica removed on the resin became larger than that (3.7 meq/g-R) of ion exchange capacity. On the other hand, SBAERs of salt form (Cl-form) did not show any effect on the behavior of colloidal silica in water. As shown in Fig. 6, the amount of ionic silica generated by adding type II SBAER was larger than

that by adding type I resin. This suggests that the rate of ion exchange reaction between OH group on the ion exchange site and ionic silica should be faster in type I than in type II.

In order to confirm the above statement, the reduction rate of ionic silica concentration was investigated by adding various SBAERs. As shown in Fig.7, the ionic silica concentration decreased faster in the solution to which type I resin with trimethy-

lamine functional group was added. In case of the addition of WBAERs, the decreasing rate of the colloidal silica concentration and the generating rate of the ionic silica concentration were much slower. Because they have lower basicity than others.

3.2 Effect of particle size of colloidal silica

The effect of the particle size of colloidal silica on the adsorption rate on SBAERs was checked. Colloidal silica solutions containing 10 nm and 100 nm particles in diameter were tested. The adsorption rate of the colloidal silica with larger particle size became slower on SBAERs. The result is shown in

Fig. 6 Change of silica concentration by addition of IRA-410.

Fig. 7 Change of ionic silica concentration by addition of SBAERs.

Fig. 8 Effect of particle size of colloidal silica on adsorption on SBAERs.

Fig.8. The generation rate of ionic silica on the resin surface also became slower in the larger particle size of colloidal silica. In addition, the decreasing rate of the total silica concentration was faster in MR SBAERs than in GEL ones. This indicates that MR resins with pores work effectively in removing colloidal silica.

3.3 SEM observation of SBAER surface adsorbed colloidal silica

The surface of SBAER (IRA-402BL, OH-form) adsorbed the colloidal silica (Carplex) was observed by SEM (**Fig.9**). The original surface of the resin was smooth and clean. When the resin was put in the colloidal silica solution, the resin surface was completely covered with colloidal silica coagulated with 20~30 nm particles. As time passed, the colloidal silica adsorbed on the surface seemed to move to the resin inside and finally to dissolve further inside of the resin. However, a small amount of colloidal silica still remained on the surface. Therefore, the total amounts of silica removed on the resin became larger than the ion exchange capacity. This phenomenon is similar to that of dissociation of crud on the surface of strong acid cation exchange resins¹⁰. The dissolved forms of silica in SBAERs will be investigated in future, using electron spectroscopy for chemical analysis (ESCA), X-ray analyzer and other advanced analytical instruments.

4 Conclusions

On the basis of the above results, the following conclusions were drawn.

1. Colloidal silica made by ion exchange method formed about 10 nm particles.
2. When leaving the colloidal silica in acidic conditions, the gelation was occurred.
3. MR resins with pores had larger adsorbed amounts of colloidal silica.
4. Colloidal silica was adsorbed well on the surface of SBAERs and at the same time dissociated to ionic silica to some extent.
5. Colloidal silica adsorbed on SBAERs became to dissolve to the resin inside.

(a)

(b)

(c)

Fig.9 SEM micrographs on the surface of SBAER: (a)Original surface of IRA-402BL, (b)Just after adsorption of colloidal silica and (c) 12h later.

6. SBAERs removed silica more than the ion exchange capacities at the equilibrium state in batch.

We thank Dr. J. H. Barrett, Director of Rohm and Haas Japan research Center, for his permission to submit this paper and also would like to thank Dr. H.

Kuyama, Senior Technical Adviser of the above research center, for his helpful discussions.

Reference

- 1) M. Henley, *Ultrapure Water* December, (1992) p.13.
- 2) K. Pate and L. Hollister, *Ultrapure Water Expo'93*, (1993) p.1.
- 3) T. Kataoka and A. Muto, *ICIE'91, Proceedings* (1991) p.329.
- 4) E. Zaganniaris, S. Duolut and L. Morino, *Reactive Polymer*, **17**, 15 (1992).
- 5) B. J. Hoffman and M. J. Gavaghan, *4th Semiconductor Pure Water Conference, Transcripts* (1985) p.3.
- 6) *JIS K0555*, (1990).
- 7) K. Ogino and I. Kuronuma, *J. Colloid and Interface Science*, **56**, 629 (1976).
- 8) H. Kuyama, "Chelate Resin and Ion Exchange Resin", ed. by N. Hojo, Kodan-sha Scientific (1981) p.150.
- 9) Amberlite Catalog, issued by Organo, June (1987).
- 10) N. Higosaki, T. Yagihashi and T. Kagawa, Patent, Japan Kokai, Hei 5-15876.

水中に溶存するコロイド状シリカの 各種陰イオン交換樹脂による除去

安居院 渡, 下山田 博文*,
阿部 正彦**,荻野 圭三**,

ローム・アンド・ハース日本リサーチセンター イオン交換樹脂研究部
〒340-02 埼玉県北葛飾郡鷺宮町八甫 2763

*東京理科大学 理工学部
〒278 千葉県野田市山崎 2641

**東京理科大学 界面化学研究所
〒162 東京都新宿区神楽坂 1-3

(1993年10月5日受理)

要 旨

純水製造において、水中に溶存するシリカの除去は重要な課題である。本報では、ケイ酸ナトリウム溶液からイオン交換法により調製したコロイド状シリカを用い、コロイド状シリカの水中での溶存状態および各種陰イオン交換樹脂に対する吸着特性並びに吸着機構をバッチ法により検討した。生成したコロイド状シリカの粒径は直径約10 nmであった。コロイド状シリカは強塩基性陰イオン交換樹脂の表面および孔内部に吸着され、その際コロイド状シリカの一部はイオン状シリカに解離することが分かった。強塩基性イオン交換樹脂により除去された全シリカ量は、吸着平衡状態において樹脂のイオン交換容量以上であった。電子顕微鏡を用いた観察により、樹脂表面に吸着されたコロイド状シリカは、時間の経過に伴って樹脂内部に溶解していくことが分かった。