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

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論文題名　：　Study on behavior of silicic acid in ion exchange resin and efficient treatment of water resources (イオン交換樹脂中のケイ酸の挙動と水資源の効率的処理についての研究)

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論　文　内　容　の　要　旨

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 existing state of silicic acid, in order to make the treatment of raw water containing silicic acid more efficient. In previous studies, as silicic acid polymerization has been suggested based on indirect observation, water treatment proposals had difficulty at this point. In addition, ion exchange units are often operated empirically based on the suggestion of indirect silicic acid polymerization. There is a possibility that cost reduction can be achieved by improving the processing appropriately. Therefore, it is essential to have direct confirmation of the chemical state of silicic acid, and improvement of water treatment appropriately based on direct observation.

Chapter 1 describes the general introduction and problem statement of the research. Chemical engineering analysis results are shown as an example of indirect suggestion of the polymerization of silicic acid. In addition, as an example of previous study of NMR was introduced for a direct observing method to confirm the chemical state of silicic acid. ^{29}Si MAS NMR spectra reveal silicic acid in natural water is present as monosilicic acid even unsaturated as to amorphous silica.

In Chapter 2, ^{29}Si MAS NMR spectra showing the only peak of monosilicic acid present in water, changes the various Si-O-Si bonds after being adsorbed on OH^- type anion exchange resin. This is the first example of direct confirmation that silicic acid is polymerized in the ion exchange resin and to be studied in this dissertation. The elution of silicic acid from the ion exchange resin is discussed from the viewpoint of the change in the chemical state of silicic acid, and the reason why heating is necessary for the regeneration process of the ion exchange resin column is explained. According to the elution experiment of silicic acid based on the selectivity of the ion exchange reaction, not all the eluted silicic acid adsorbed on the ion exchange resin was derived from the ion exchange reaction. Considering the change in the chemical state of silicic acid adsorbed on the ion exchange resin before and after the interaction with NaOH, the monomer ($Si(OH)_3O^-$) is desorbed by the ion exchange reaction with OH^- ion. However, desorption of polysilicate ions does not suggest the ion exchange reaction but the decomposition of the siloxane bond (≡Si-O-Si≡). 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. 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.

In Chapter 3, the methods for efficient elution of silicic acid are described to suppress the formation of highly polymerized Si-O-Si bonds. Even under unsaturated 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. According to the results of the change in the chemical state of silicic acid, by changing the amount and type of coexisting ions during the silicic acid adsorption, 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.

In addition, according to the experimental results in controlling the formation of Si-O-Si bond by changing the structure of the ion exchange resin, the formation of polysilicic acid in a fixed shape was promoted as the space around the ion exchange group becomes narrower and the proportion of Si-O-Si bonds with high degree of polymerization increases. Therefore, although the chemical state of polysilicic acid becomes complicated, the ion exchange resin having a low degree of cross-linking is more efficient for regeneration of the ion exchange resin column. Furthermore, a comparison between type I and type II ion-exchange groups showed that type I can regenerate the ion-exchange resin column more efficiently than type II, which has a bulky ion-exchange group. This effect is considered to be due to the ease of diffusion of the regenerated chemical. Summarizing these results, low cross-linking type I resin is desirable as the resin that facilitates the elution of silicic acid. The results of the elution test using the ion-exchange resin column also support this fact. 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.

In Chapter 4, based on the results of the whole research, the prospects and a summary are presented by focusing on the recent challenges in ultrapure water industry. The presence of fine particles in ultrapure water is currently a subject of great interest in the semiconductor industry. From the following facts revealed by this research, the risk of particulate generation can be suppressed by assuming that silicic acid is the source of particulates.

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

By direct observation of the changes in the chemical state of silicic acid and clarifying the conditions under which the chemical state changes, the raw water containing silicic acid can be treated more efficiently. As a result of trial calculation, if the heating regeneration can be stopped by the regenerative water purifier, as the subject of this study, the initial cost of the ion exchange water purifier can be reduced by about 10% and the running cost can be reduced by about 30%. It can be concluded that not only solving water quality and operational troubles, but also to improve efficiency including reducing the ion removal costs, are possible by the understanding of a chemical environment where polysilicic acid is difficult to elute.