초저이온 농도에서 혼합층 이온교환칼럼의 실리카 제거능

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Parametric Studies on the Performance of Mixed-bed Ion Exchange for Silica Removal at Ultralow Concentrations

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Introduction

Ion exchange is the reversible stoichiometric exchange of ions between a resin particle and a liquid, without substantial change in the solid structure. Ion exchange has been used frequently as an economical and convenient separation method for producing high purity water. Stimulated by the appearance of high-capacity and durable ion exchange resins, ion exchange has been used commercially in widely divergent fields where high purity water is needed.

A typical mixed-bed ion exchange(MBIE) unit used to produce ultrapure water, of which conductance is less than 0.055 μS/cm at 25°C, is prepared by intimate mixing of strong-acid cation resin in the hydrogen form and strong-base anion resin the hydroxide form. These ions exchange cations and anions in the liquid phase, respectively, and the exchanged hydrogen and hydroxide ions produce water by neutralization reaction. Presently, use of MBIE for the treatment of low level solids water requires realistic estimates of MBIE performance.

Haub and Foutch[1,2] developed a MBIE model appropriate for hydrogen cycle operation at ultralow concentrations. Their model considers the dissociation of water, cation resin ratio, exchange rates, resin capacities, resin particle sizes, reversibility of exchange, and bulk/film neutralization. Divekar et al.[3] added temperature effects to Haub and Foutchs model. Zecchini[4] extended the model for the multi-ionic system with univalent ions. Bulusu[5] developed the model further to handle the multi-component system of the ions with arbitrary valences. These mathematical models still have room to improve the accuracy through experimental data obtained under various industrial conditions.

To evaluate and improve the accuracies of the developed models, much experimental works have been performed. Yoon et al.[6,7] studied the effects of the resin ratio of cation to anion resins and temperature on the performance of MBIE at ultralow concentrations. Noh et al.[8,9] obtained experimental data to evaluate the MBIE performance for the variable feed concentrations and for the multicomponent system. De Luca et al.[10] studied the cation exchange equilibria between Amberlite IR-120 resin and aqueous solution of calcium, magnesium, potassium, sodium chloride and hydrochloric acid. They reported the experimental data for ion exchange equilibria of the ternary and quaternary systems. Even though those experimental studies have contributed to trim the models, they have been restricted to NaCl feed solution or to relatively high concentrations.

It has been required to enlarge the range of the theoretical analysis and application of MBIE by evaluating the performance of MBIE unit under the various conditions at ultralow ionic concentrations. Thus, the objective of the present study is to obtain and analyze the equilibrium and breakthrough data of silica under the various conditions. The results of the present study will be used to develop and simulate the model, which has an ability to predict the performance of MBIE for silica removal at ultralow concentrations and thus, becomes the useful tool for the reasonable design and operation of the unit in industries.

Experimental

The experiments for the present study were performed using both batch and continuous systems. The batch system was used for the equilibrium data, and the continuous system for the breakthrough data of silica. The batch system simply consists of an 1-liter batch reactor, a circulator, a stirrer, and accessories for heating and measuring the experimental parameters such as temperature and pH. The reactor is equipped with several baffles inside to improve the degree of mixing. A constant-temperature reservoir and a water circulator were used to maintain a constant temperature.

The feed solution was prepared by diluting the concentrated solution with pure water, and the concentrated solution was obtained by dissolving the calculated weights of SiO_2 powder in a 100ml flask with pure water. This dissolving procedure was usually continued for 4 days to ensure the equilibrium state of dissolution. The volume of the solution taken periodically as samples was recorded exactly so that the change of the total volume of the solution could be calculated. To avoid any leaching from the bottle itself, the samples were analyzed within at most 6 hours using off-line UV and ion chromatography(IC).

The continuous column system is composed mainly of an experimental column, its accessories for feeding, heating, and measuring the experimental parameters such as flow rate, temperature and pH, and IC(and/or UV) for measuring effluent concentration. The experimental column was made from transparent Pyrex glass to see the resins loaded inside the column. Glass wool with stainless steel screens was used to support the mixed-bed resins and to ensure uniform flow distribution.

To evaluate the effect of temperature on the MBIE performance for silica removal, the specified concentration of SiO_2 solution was introduced into the experimental column at different temperatures. The sample was taken periodically and analyzed by UV and IC. Because the feed concentrations for the experiments were very low, special attention was given to prevent water contamination.

Dowex Monosphere resins provided by the Dow Chemical Company was used for the study. The resins were rinsed with pure water and stored in plastic containers. For the experiments, the specified volumes of the cation and anion resins were taken from the containers and mixed. Then, the resins were placed in the column carefully followed by being checked to ensure complete mixing and uniform packing throughout the column cross section. After the system was assembled and stabilized at the experimental conditions, the feed solution was flowed into the column.

Results and Discussion

3.1 Batch system

In order to measure the selectivity coefficient of the anion resin for silica over hydroxide ion, the batch system was used with 1.0×10^{-4}M SiO_2 solution as feed solution. The results of the sample analysis were described as the concentration ratio(C/Co) vs. run time. Co is the initial concentration of the feed solution. Another set of experiments was performed with 1.0×10^{-4}M $NaCl/SiO_2$ solution to analyze the fate of silica compared to that of chloride ion. In the present paper, the results of a selected experimental run are given.

Fig.1 shows the silica concentration profiles with three different temperatures. As shown in the figure, the concentrations decrease rapidly at the early stage of the reaction and start to increase until the equilibrium state, regardless of temperature. From this, it can be said that silica is removed by physical adsorption as well as ion exchange at the beginning of the process and then, a part of the adsorbed silica desorbes from the resin. The figure also shows that the concentration of silica is lower at higher temperature until 8 hours after the start, but the equilibrium concentration is higher. This means that as temperature increases, the ion exchange reaction becomes faster and the selectivity coefficient of the resin becomes lower. Using the equilibrium concentrations of silica, the selectivity coefficients of the resin for silica over hydroxide ion were obtained and expressed as a function of temperature as follows:

$$K = 0.345 - 1.032\log(T/20) + 0.124(1 - 20/T) \qquad (1)$$

Fig. 2 shows the comparison of the silica breakthrough curve to that of chloride. The curves of two ions show a different trend from each other. The concentration of silica decreases during the first 2 - 3 hours and then goes back to the initial value. However, concentration of chloride decreases very rapidly for the first 1 hour and continue to decrease until the equilibrium state. This is because of the re-exchange process of silica on the resin with chloride in solution, resulting from the big difference between the selectivity coefficients of the resin for chloride and for silica. The selectivity coefficient for chloride is about 22, much bigger than that for silica.

3.2 Continuous column system

The selective results of the continuous experiments are given in Figs. 3 and 4, from which one can see that different level of initial leakage of silica appears in the effluent of the exchange process. These leakages might be due to the insufficient contact time between the solution and the resins, which results from the high flow rate and the relatively short bed depth. These conditions were selected for the reasonable duration of the experimental runs. Fig. 3 shows that as temperature increases, the slope of the curve becomes sharper and the initial leakage decreases, which means that the ion exchange rate increases with temperature. It is especially observed in the figure that the breakthrough curves increase to more than C/Co=1.0 and then drop to the equilibrium state. This is also considered to be because silica adsorbed physically on the resin surface desorbes into solution as seen in the results of the batch experiment. Fig. 4 gives the effect of the ratio of cation resin to anion resin on the silica breakthrough curve at 30°C. With a decrease in the ratio(with more amount of anion resin), the initial leakage of silica becomes low and the breakthrough time increases. However, the slope of the curve seems not to change, which means that the ion exchange rate is independent on the amount of resin.

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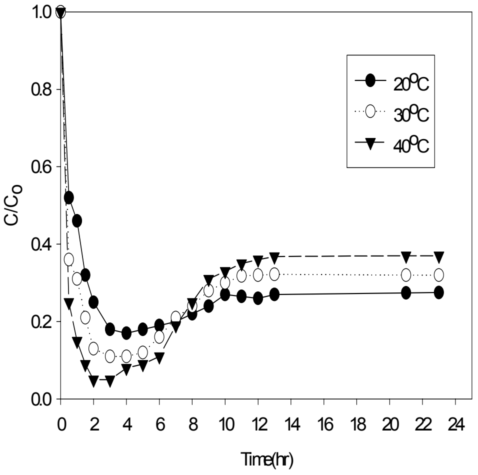

Fig. 1. Concentration profiles of silica at different temperatures.

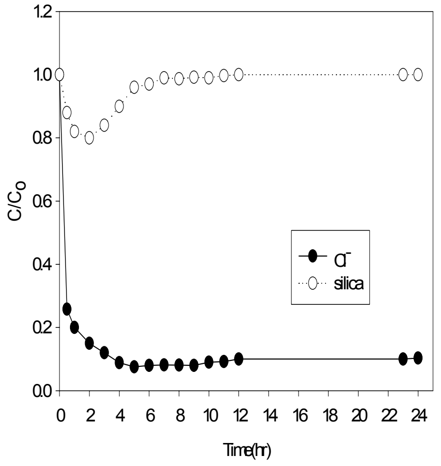

Fig. 2. Concentration profiles of silica and Cl^- at 30°C.

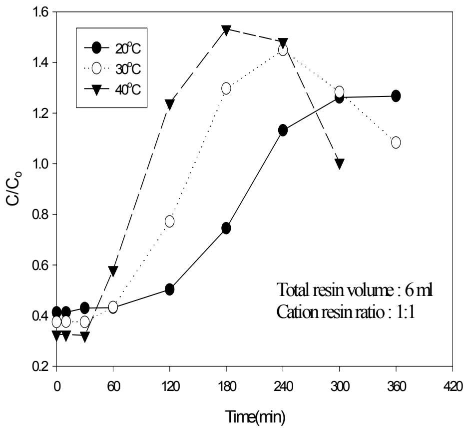

Fig. 3. Effect of temperature on silica breakthrough curves.

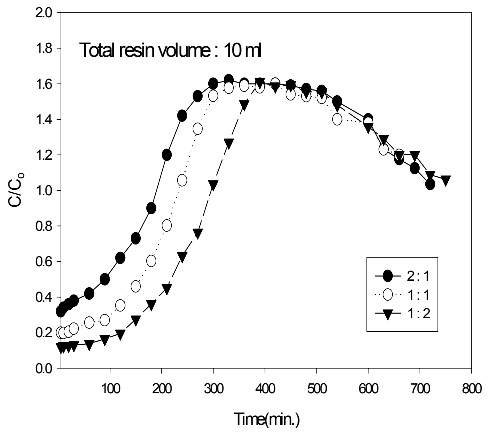

Fig. 4. Effect of cation resin ratio on silica breakthrough curves at 30°C.