Korean J. of Chem. Eng., **13**(2), 150-158 (1996)

THE MIXED-BED ION EXCHANGE PERFORMANCE AT ULTRALOW CONCENTRATIONS
1. VARIABLE FEED CONCENTRATION AND INCOMPLETE MIXING OF RESINS

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(Received 26 August 1995 • accepted 14 November 1995)

Abstract—Experimental data were obtained to evaluate the performance of mixed-bed ion exchange for the cases of variable feed concentration and incomplete mixing of anion and cation resins observed in large scale industrial units. For variable feed concentration, step changes in feed concentration were arbitrarily introduced into a test column. For incomplete mixing, only anion resin was loaded in the upper 20% of the column and more cation resin in the lower portion. Feed concentrations of 5.0×10^{-5}-2.0×10^{-4} M NaCl were used for the experiments, with flow rates of 0.665-7.0 ml/sec. The effluent from the column was collected periodically and analyzed using on-line/off-line ion chromatography. The step changes in feed concentration affect the breakthrough times of sodium and chloride. Sodium breakthrough curve is more sensitive to the step changes than chloride breakthrough curve. With the same volumes of cation and anion resins, incomplete mixing of resins increases the cation exchange rate slightly and decreases the anion exchange rate slightly. As the cation resin volume increases, the effect of the incomplete mixing of resins decreases. The breakthrough curves of both ions, plotted as the ratio of effluent to the influent concentration versus run time in hour, give some detailed results about the effects of the conditions.

Key words: *(Mixed-Bed) Ion Exchange, Ultrapure Water, Ultralow Concentrations, Resin, Breakthrough*

INTRODUCTION

Ion exchange is defined as a reversible exchange of like-charged ions between a liquid and a water-insoluble solid without substantial changes in the structure of the solid. It was first recognized as a physical-chemical phenomena in the middle of nineteenth century. The utilization of the ion exchange process on a commercial scale started at the turn of the twentieth century, stemmed from the application of both natural and synthetic silicates to water softening [Dowex, 1958]. The recent appearance of high-capacity and durable ion exchangers has stimulated much interest in ion exchange, resulting in a number of applications in widely divergent fields.

A typical mixed-bed unit used to produce ultrapure water, of which conductance is less than 0.055 μS/cm at 25 ℃ [Grammont et al., 1986], consists of a strong-acid cation resin in the hydrogen form and a strong-base anion resin in the hydroxide form [Helfferich, 1965]. A cation in the ionic solution is exchanged for a hydrogen ion on the cation resin and an anion is exchanged for a hydroxide ion on the anion resin at the same time. The exchanged hydrogen ion then reacts with the hydroxide ion to produce pure water. This neutralization reaction makes the exchange process fast and irreversible [Kunin and McGarvey, 1951].

Mixed-bed ion exchange (MBIE) provides a convenient and economical method to produce ultrapure water, and is thus applicable to many significant industries which need ultrapure water. Nuclear and coal-fired electrical power plants are the major industrial user of ultrapure water and utilize MBIE to avoid erosion and corrosion problems in the steam cycle. Electronic and instrument industries require ion exchange to make pure water for process rinsing. The pulp, paper, and petroleum industries also need pure water for the operation of high pressure boilers. Presently, use of MBIE for the above applications, and, in particular, for the treatment of low level solids water requires realistic estimates of mixed-bed performance. However, the fundamental theories and detailed modeling of the ion exchange process are far behind the current technical applications. Thus, mathematical models and laboratory work are imperative to develop an understanding of the process.

Haub and Foutch [1986a, b] have developed a theoretical hydrogen cycle model to describe MBIE at ultralow ionic concentrations. Their model considers the dissociation of water, cation-resin fraction, exchange rates, resin capacities, resin paricle sizes, reversibility of exchange, and bulk/film neutralization. Divekar et al. [1987] have developed Haub and Foutch's model further to include the effect of temperature on the performance of MBIE. Zecchini [1990] has extended the model to address amine form operation. However, these mathematical models still have spaces to improve through experimental data obtained under various conditions.

King [1991] experimentally studied the effect of temperature on the performance of MBIE column for ultralow concentrations of sodium and chloride. He showed that the sodium breakthrough curve depends slightly on temperature while the dependency of the chloride breakthrough curve on temperature is substantial. This result may be due to the relatively high selectivity coefficient for chloride compared to sodium. King [1991] believed that the selectivity coefficient for chloride is much more sensitive in tem-

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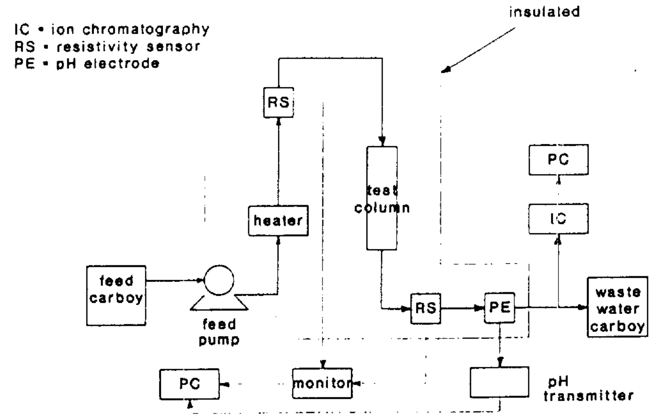

Fig. 1. Flow diagram for MBIE experimental system.

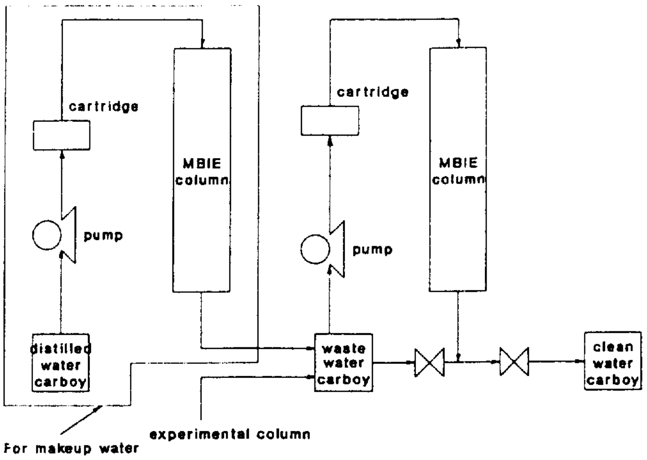

Fig. 2. Flow diagram for water purification system.

perature. Recently, Yoon et al. [1995] investigated the effect of cation and anion resin ratio on MBIE performance at ultralow concentration. They reported that the anion resin affects the sodium breakthrough curve and the cation resin affects the chloride breakthrough curve. The large amount of oppositely-charged resin gives a sharper breakthrough while the small amount gives a wide breakthrough curve. This is due to the difference of mass transfer coefficient of ions in alkaline and acidic solutions.

Feed concentration in industrial MBIE units is not always constant, but fluctuates in a certain range, or involves upsurges beyond the range for a short time. When the exchange resins are exhausted after a period of service, they are required to be reconditioned. Separation of cation and anion resins, followed by the regeneration of each resin, is mechanically accomplished using density difference between cation and anion resins. This density difference causes incomplete mixing of resins when they are remixed after regeneration. Thus, variable feed concentration and incomplete mixing of resins make it difficult to estimate the performance of MBIE correctly, and as a result, the operating schedule of the units becomes ineffective. The major objective of the present study is to experimentally evaluate the effects of variable feed concentration and incomplete mixing of resins on the performance of MBIE. The data obtained in this study will provide a valuable data base for understanding the performance of MBIE operating under various conditions such as major cooling water leakage and incompletely mixed beds observed in full-scale industrial units.

EXPERIMENTAL

Fig. 1 shows the schematic diagram of MBIE experimental system. The system is composed mainly of an experimental column, its accessories for feeding, heating, and measuring experimental parameters such as temperature, resistivity and pH, and an ion chromatography (IC) for measuring effluent concentration. A Dionex IC was used for this work. There are two different flow paths in the system; one is to feed a solution of the specific concentration to the experimental column, and the other is to provide high purity water for chemical and feed preparation. Fig. 2 presents this supporting flow system with water purification columns.

The experimental column used for this work was made from the Pyrex glass and transparent to see the loaded resins. A fritted disk, made from foam packing material with a stainless steel screen, was used to support the mixed-bed resins and to ensure unifrom flow distribution. For the incompletely mixed beds experiments, another disk was placed between the unmixed and the mixed portions to prevent the resins from being mixed during the expermental runs.

Because the feed concentrations for these experiments were very low, special attention was paid to remove the sources of water contamination. Ultrapure water was prepared by passing either new water from the distillation column, or the effluent of the experimental column through high capacity MBIE columns in series (see Fig. 2). Resistivity greater than 18.2 Meg-ohm-cm at room temperature was checked to make sure water quality.

Water produced by the purification column was collected in a carboy and used to prepare either the feed solution or the chemicals for the IC. A leaching problem from the carboy became significant after about 48 hours. Water stored in the carboy more than 12 hours was fed into the purification columns again to ensure water quality.

The feed solution was prepared by diluting a concentrated solution with pure water. The concentrated solution was obtained by dissolving the calculated amount of salt in a 1000 ml flask with pure water. After pippetting 10 ml of the concentrated solution to a 10 liter carboy and adding pure water, vigorous agitation was used, and complete mixing was checked by conductivity measurement. Then, the solution was added to carboys for the feed solution. Only a specified carboy was used for a certain duty. If necessary, the makeup feed water was made and added to the feed carboys.

Dowex resins provided by the Dow Chemical Company were used for this study. The physical properties of the resins are shown in Table 1. These resins were rinsed with pure water from the purification columns and stored in plastic containers. For the experiments, specific wet volumes of cation and anion resins were taken from the resin containers and mixed. Then, the resins were placed in the experimental column carefully and checked to ensure complete mixing and uniform packing throughout the column cross-section. The column was filled with pure water fully, while being tipped to remove any air bubbles between the resin particles and promote uniform packing. After assembling the system, pure water was fed into the column until the column was brought to the desired experimental conditions.

To maintain a constant temperature, the experimental line from

Table 1. Physical properties of Dowex resins*

Parameter	Cation	Anion
Name	HGR-W2-H	SBR-P-C-OH
Capacity (meq/ml)	2.18 (Na^+ form)	1.1 (Cl^- form)
Selectivity coefficient	Na-H 1.13	Cl-OH 22.0
Void fraction	0.335-0.34	0.335-0.34
Water retention capacity (%)	48.2	54.3
Density (lb/ft^3)	50.0	41.0
Diameter (cm)	0.08	0.06
Appearance	light yellow to amber solid (bead)	white to dark amber solid (bead)

*From the vendor

Table 2. Experimental conditions* for variable feed concentration experiments

Run no.	Flow rate (ml/sec)	Cation resin fraction	Column depth (cm)	Feed conc. (eq/l)	Comments
R1	0.667	0.372	13.4	2.0E-4	·Duplicate of R2
R2	0.667	0.374	13.2	2.0E-4	·Constant feed conc.
R3	0.667	0.375	13.2	2.0E-4	·Feed conc. changed to 1.0E-3 for 4 hrs.
R4	0.665	0.377	14.0	1.0E-4	·Constant feed conc.
R5	0.665	0.379	13.9	1.0E-4	·Feed conc. changed to 1.0E-3 for 5 hrs & 0.5E-3 for 4 hrs

*All experiments were conducted under the same conditions of
·Temperature = 25 ℃
·Column inside diameter = 2.54 cm

the feed pump to the pH transmitter was insulated using heating tapes. Two temperature sensors were used to read the entrance and the exit temperatures of the column. After the system was stabilized at the experimental conditions, the feed solution was introduced into the system and flowed from the top of the column to the bottom. When the feed solution reached the top portion of the column, the resistivity of the entrance portion would decrease. This point was considered as the starting point of the run. Flow rate was measured periodically at the end of the flow path using a graduated cylinder and a stop watch.

Periodically, on-line resistivity and pH data were collected during the run and recorded on computer output files by Labtech software. Water samples were collected periodically and analyzed using on-line or off-line procedure. For both on-line and off-line procedures, the samples were injected through the sampling pump which was controlled by the AI-450 software. The post-run processing of the chromatography data was performed by using utilities in the AI-450 program and a spreadsheet. The following is a detailed description of the specific procedures for the variable feed concentration and the incomplete mixing of resins experiments.

1. Variable Feed Concentration

For the experiments, step changes in feed concentration were arbitrarily introduced into the experimental column for several hours during the runs. The normal feed concentration was 2.0×10^{-4} M for early experiments. Later, the lower concentration of 1.0×10^{-4} M was used. The concentrations of the peaks were five to ten times higher than the normal feed concentrations. To introduce a peak in feed concentration into the column, the valve for the normal feed solutions was switched to the concentrated solution. Then, the resistivity at the entrance of the column was checked. The starting point of the peak was determined when the resistivity started to decrease. To return to the normal feed concentrations, the valve was switched to the normal feed concentration. The point that the resistivity increased was the ending point of the peak.

For the variable feed solution experiments, an on-line procedure was utilized because of the long period of the experimental run, resulting from a deep bed and low flow rate. This procedure could remove a possible source of contamination from a sample bottle. The IC was connected directly to the flow system and automatically collected and analyzed the effluent samples every hour and recorded the results on computer files.

2. Incomplete Mixing of Resins

The incompletely mixed bed experiments were initially performed with relatively high flow rate of about 12.0 ml/sec, which had a superficial velocity much closer to the industrial conditions of 2.5 cm/sec. Through some preliminary runs under the high flow rate, it was decided to reduce the total length of the flow path as much as possible to decrease the pressure drop. The flow line from the IC to the system was also removed, and the sample analysis was completed with an off-line procedure. In addition, this flow rate introduced a number of air bubbles into the column. The air bubbles might be the source of carbonate or bicarbonate, which affect the breakthrough curve of chloride strongly. After several preliminary runs, the experimental column was replaced by a smaller column of 1.85 cm inside diameter. The new column made it possible to decrease the flow rate significantly, while maintaining the same superficial velocity.

To make an incompletely mixed bed, about half of the measured anion resin was mixed with the measured cation resin and placed in the bottom of the column. The rest of the anion resin was charged in the upper portion of the column. Samples were collected periodically using sample* bottles. The bottles were rinsed at least three times using ultrapure water before sampling and filled fully to remove air in the bottles. To avoid the leaching from the bottle itself, the samples were analyzed within at most 6 hours.

RESULTS AND DISCUSSION

The results obtained from analyzing the samples were given in terms of peak area and peak height. Either peak area or the peak height from the chromatograms can be used to determine ionic concentration through calibration curves. However, the peak area was selected in the present study because of its smaller standard deviation than that of the peak height.

In general, the experimental data were plotted and presented in terms of concentration as a function of run time in hours. When plotted, the data showed smooth breakthrough curves, even though they tended to scatter at the early stage of each run, especially for the variable feed concentration experiments.

1. Variable Feed Concentration

Eight experimental runs including three preliminary runs were conducted to investigate the effects of variable feed concentration on the performance of MBIE. Table 2 shows the experimental conditions of five runs selected for data analysis. All experiments

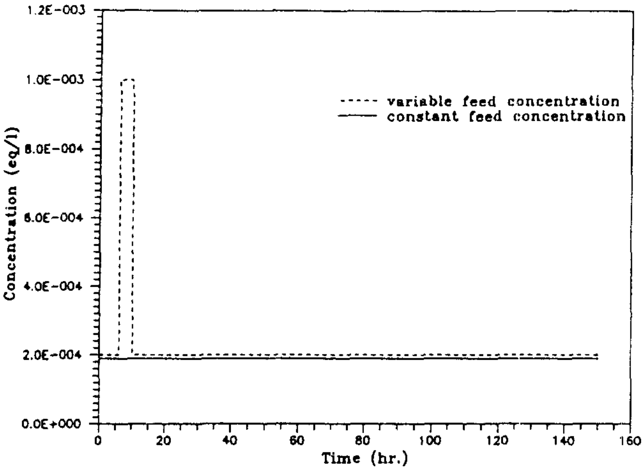

Fig. 3. Feed concentration profiles for constant and variable feed concentration experiments with one peak.

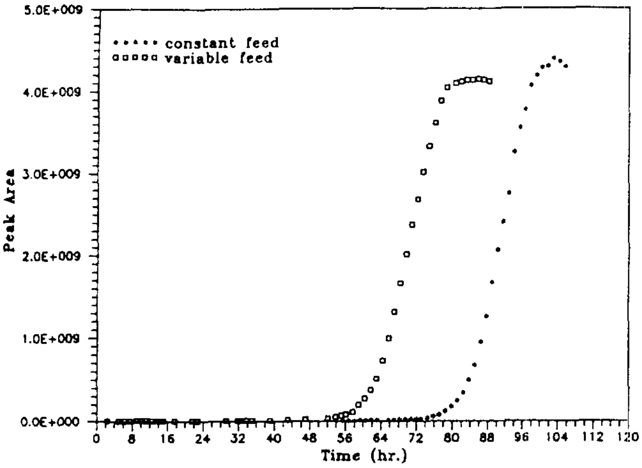

Fig. 4. The effect of one peak in feed concentration on chloride breakthrough curve.

were carried out under similar flow rates and temperatures. Usually, a much longer time was required to reach the equilibrium concentration for sodium than chloride, provided the same amount of each resin was used. This is due to higher selectivity coefficients for the anion resin than the cation resin. For this study, less cation resin was used so that both ions reached equilibrium at nearly the same time, although these low cation-to-anion resin ratios are rarely used in industry. Based on the desired flow rates, appropriate column depth and feed concentration were determined to give reasonable experimental periods. The maximum period of a run was about 250 hours. The results of Run R2 and its duplicated run, Run R1, were compared to evaluate the reproducibility of the experimental system. The agreement between these two runs was entirely satisfactory, with the maximum difference of less than 2.0%.

For the experiments, step changes in feed concentration were arbitrarily introduced into the experimental column during the runs. Fig. 3 shows the feed concentration profiles for Runs R2 and R3. Run R2 had constant feed concentration and Run R3 had one peak in the feed concentration profile. The peak was introduced into the column 6 hours after starting the run and maintained for 4 hours. The feed concentration was then dropped to the initial concentration and kept constant for the rest of the run. The effluent concentrations of both runs were plotted as the relative concentration versus run time. The relative concentration is peak area obtained from the chromatograms. Figs. 4 to 7 show the comparison of either chloride or sodium breakthrough curves from the constant and the variable feed concentration experiments.

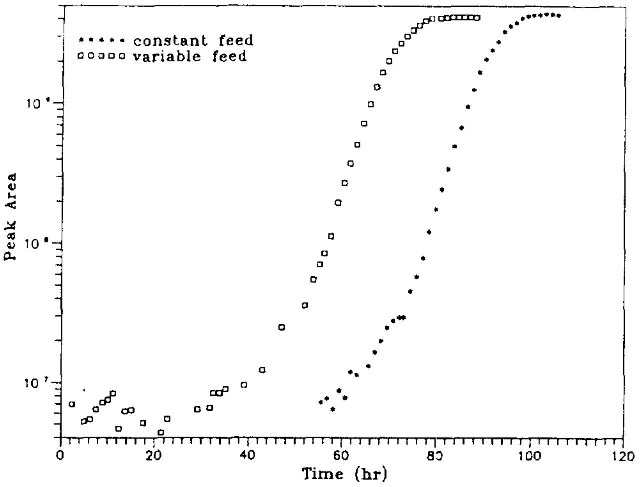

Fig. 5. Semilog plot of experimental data for the effect of one peak in feed solution on chloride curve.

In Fig. 4, the profile indicates that the chloride curve starts to rise after 70-80 hours for Run R2 and for Run R3 after 50-60 hours. Thus, introducing a peak in feed concentration results in faster breakthrough time, as we expect. It appears that the peak does not affect the shape of breakthrough curves. It may be interesting to calculate the total amounts of chloride removed through Runs R2 and R3 before the breakthrough time. For both runs, the flow rate was about 2.4 liter/hour (0.667 ml/sec) and the normal feed concentration was 7.11 ppm chloride. Assuming that there is no chloride leakage in the effluent until the breakthrough curves start to rise, a total amount of 1.195-1.36 g chloride was removed in 70-80 hours for Run R2. For Run R3, the normal concentration was changed to 35.5 ppm chloride and maintained for 4 hours. Totally, 1.194-1.365 g chloride was removed in 50-60 hours, which is close to that for Run R2. This fact may mean that if peak concentration and its duration are known, the chloride breakthrough time can be predicted.

Fig. 5 contains the same data as Fig. 4, plotted as log concentration versus run time. This semilog plot makes it possible to amplify and investigate the curves at the early run times. As shown in this figure, there is a low level of leakage after the peak is introduced. This might result from insufficient contact time between the solution and the resins. When the feed returns to the normal concentration, the leakage seems to disappear.

Figs. 6 and 7 show the effluent concentration profiles of sodium for Runs R2 and R3. The curves appear to have similar slopes to each other after breakthrough. The slopes are relatively broad compared to those for chloride. This is because the anion resin has a higher selectivity coefficient than the cation resin. Closer inspection of the curves in Fig. 6 indicates that the curve for Run R3 begins to rise between 30-40 hours. For Run R2, the breakthrough time is about 50-60 hours. The normal feed concen-

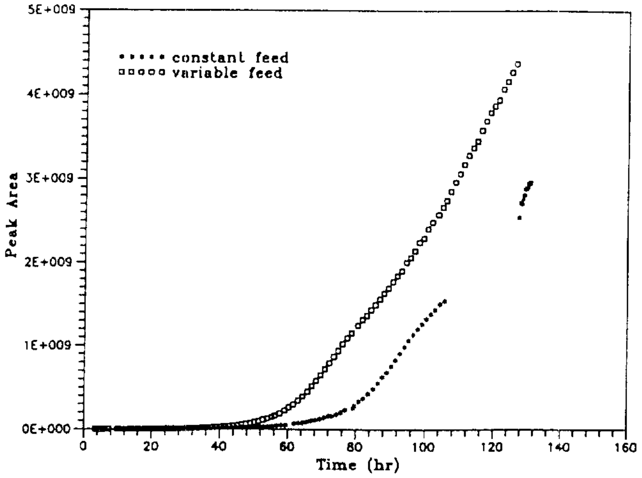

Fig. 6. The effect of one peak in feed concentration on sodium breakthrough curve.

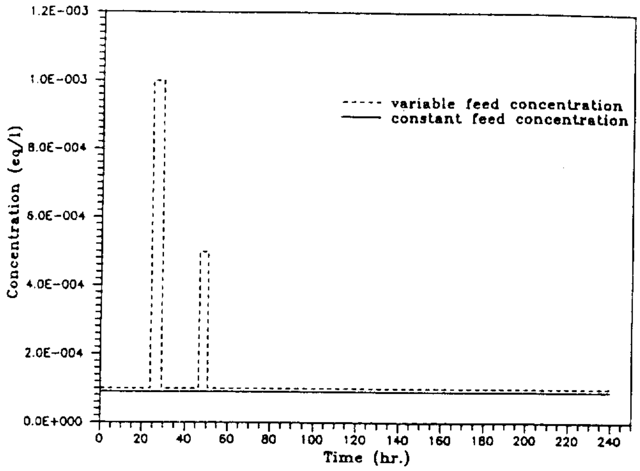

Fig. 8. Feed concentration profiles for constant and variable feed concentration experiments with two peaks.

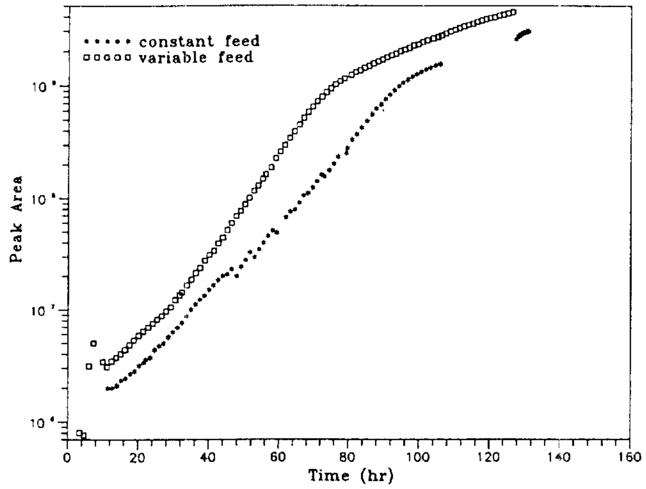

Fig. 7. Semilog plot of experimental data for the effect of one peak in feed solution on sodium curve.

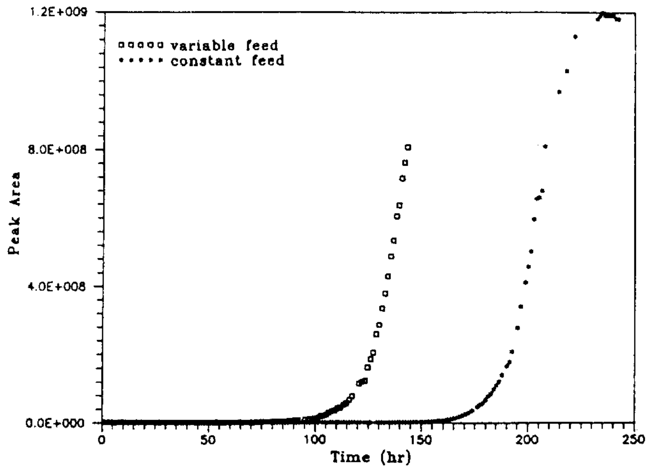

Fig. 9. The effect of two peaks in feed concentration on chloride breakthrough curve.

tration was 4.61 ppm sodium and the flow rate was 2.4 liter/hour. With the assumption of sodium free effluent until breakthrough, slightly less sodium is removed by introducing a peak into a constant feed concentration (0.553-0.664 g for Run R2 and 0.509-0.619 for Run R3). Fig. 7 shows that the effluent of Run R3 starts to have higher concentrations than that of Run R2 after the peak is introduced. This is not found in chloride breakthrough curves (see Fig. 5). This is probably due to the much lower selectivity coefficient of the cation resin.

Similarly, Runs R4 and R5 have a constant feed concentration and two peaks in feed concentration, respectively. The feed solution for these runs was less concentrated (1.0×10^{-4} eq/*l*) than that for Runs R2 and R3 (2.0×10^{-4} eq/*l*). Fig. 8 shows the feed concentration profiles of the runs. For Run R5, feed concentration was maintained constant for the first 24 hours and increased rapidly to 1.0×10^{-3} eq/*l*. Five hours after the increase, feed concentration dropped to the initial concentration and remained constant for 18 hours. Then, the feed introduced a second peak of 5.0×10^{-4} eq/*l* for 4 hours.

Fig. 9 shows the effects of the peaks in feed concentration on chloride breakthrough curves. As expected, the breakthrough time is shorter for Run R5 than for Run R4. At first inspection, the two curves are further apart than those in the experiments with one peak in feed concentration. The figure indicates chloride breakthrough between 140-160 hours for Run R4 and between 80-100 hours for Run R5. Based on the experimental conditions, the total amount of chloride removed until breakthrough is 1.217-1.431 g for Run R4 and 1.203-1.411 g for Run R5. Like the results of the one-peak experiments, a close amount of chloride appears to be removed by introducing two peaks in feed concentration.

Fig. 10 is a semilog plot of the data in Fig. 9. The data in Fig. 10 show an instability at the early stage of the runs. The actual concentrations in this period are considered to be below one part per billion (ppb). Thus, the detection level of the IC is illustrated in this figure. There is no significant difference in the effluent concentrations of Runs R4 and R5 until breakthrough.

Figs. 11 and 12 show the comparisons of the effluent sodium concentrations of Runs R4 and R5 in a linear and a semilog plot, respectively. In Fig. 11, two small peaks in the curve of Run R5 are detected where two peaks in feed concentration are introduced. These peaks result from the insufficient contact time be-

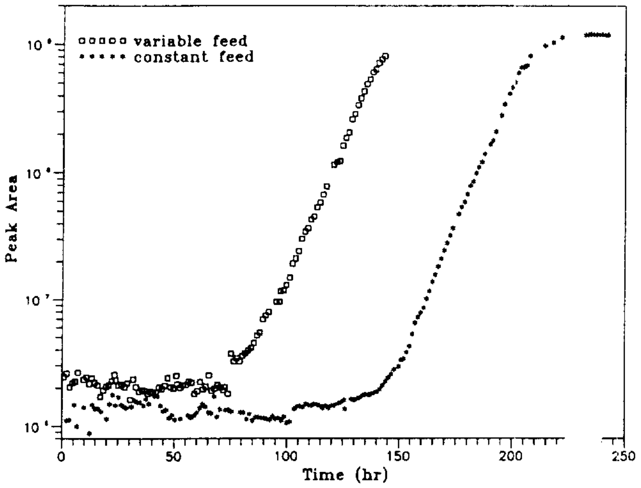

Fig. 10. Semilog plot of experimental data for the effect of two peaks in feed solution on chloride curve.

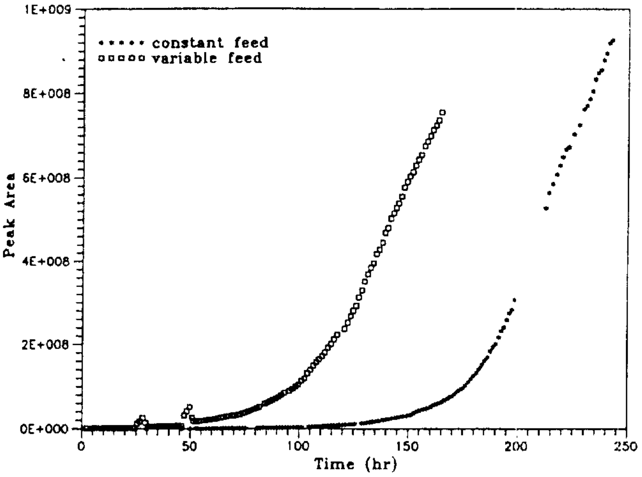

Fig. 11. The effect of two peaks in feed concentration on sodium breakthrough curve.

tween the solution and the cation resin. The breakthrough time of Run R5 appears to be after introduction of the first peak into the column. This fact can be confirmed through Fig. 12. It is, therefore, expected that much less sodium is removed until breakthrough when the two peaks are introduced in feed concentrtaion than when feed concentration is constant.

2. Incompletely Mixed Bed

Ten experimental runs were performed to characterize general trends of breakthrough curves with incompletely mixed beds. Table 3 shows the experimental conditions of the selected runs. All the experiments were conducted under the same conditions except for the ratio of the cation resin to the anion resin. Off-line samples were collected every 30 minutes and analyzed by the IC. The results of the analysis were expressed in terms of C/Co, the ratio of the measured effluent concentration to the influent concentration, as a function of run time in hours. The feed concentration, Co, was held constant for the experiments. On-line pH and resistivity data were collected every 30 minutes. The results of Runs R6 and R8 were compared to verify the general reproducibility of the experimental data.

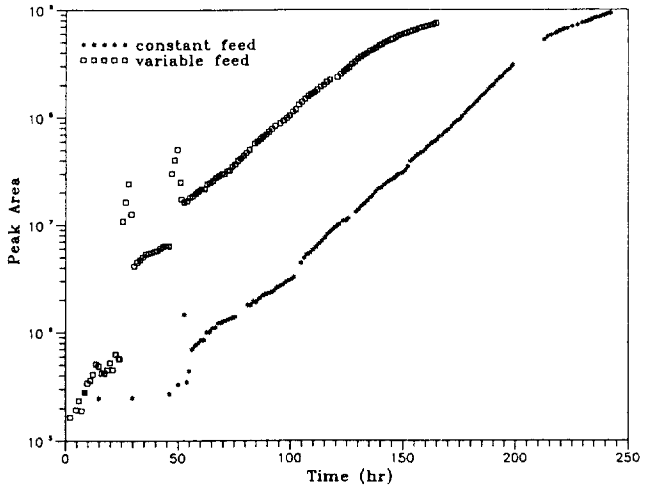

Fig. 12. Semilog plot of experimental data for the effect of two peaks in feed solution on sodium curve.

Table 3. Experimental conditions* for incompletely mixed bed experiments

Run no.	Flow rate (ml/sec)	Bed depth (cm)	Cation resin fraction	Comments
R6	6.92	4.1	0.505	·Complete mixing
R7	6.90	4.2	0.505	·Incomplete mixing ·Unmixed top 21.4% ·0.638 FCR** in mixed portion
R8	6.93	4.1	0.506	·Duplicate of R6
R9	7.00	4.2	0.610	·Complete mixing
R10	6.94	4.0	0.600	·Incomplete mixing ·Unmixed top 20.0% ·0.732 FCR in mixed portion

*All Experiments were conducted under the same conditions of
·Feed concentration = 5.0×10^{-5} eq/*l*
·Column inside diameter = 1.849 cm
·Temperature = 21 ℃
**FCR = Fraction of Cation Resin

For Run R7, an incompletely mixed bed experiment, approximately 5 ml of each resin was taken and about half of the measured anion resin volume was mixed with the cation resin and placed in the lower portion of the column. The rest of the anion resin was placed in the upper portion of the column. This incompletely mixed portion was 21.4% of the total bed depth. This would be considered as a realistic experimental condition because the anion resin is likely to be rich in the top portion of industrial beds after regeneration procedure due to its lower density than the cation resin. The effluent profile of this run was then compared with that of Run R6, a completely mixed bed experiment. The comparison of the results of these experiments is given in Figs. 13 and 14.

Figs. 13 and 14 indicate the effects of incomplete mixing of the resins on chloride and sodium breakthrough curves, respectively. In these figures, it can be seen that different levels of initial leakages of sodium and chloride appear in the effluent of the exchange process. These leakage might result from the high flow rate and the short bed depth. Compared to the chloride ef-

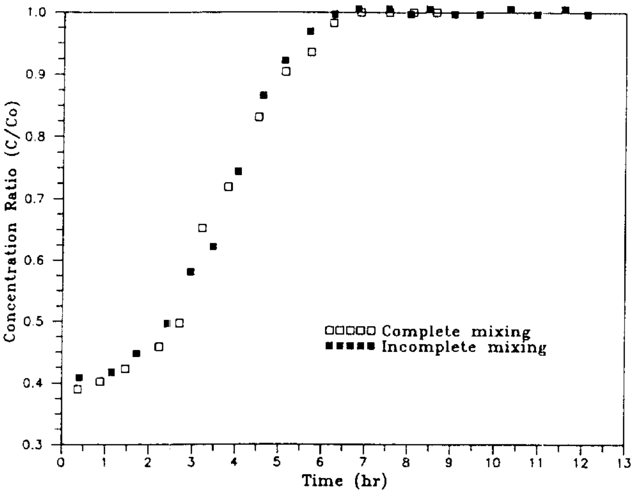

Fig. 13. The effect of incomplete mixing of resins on chloride breakthrough curve with FCR=0.5.

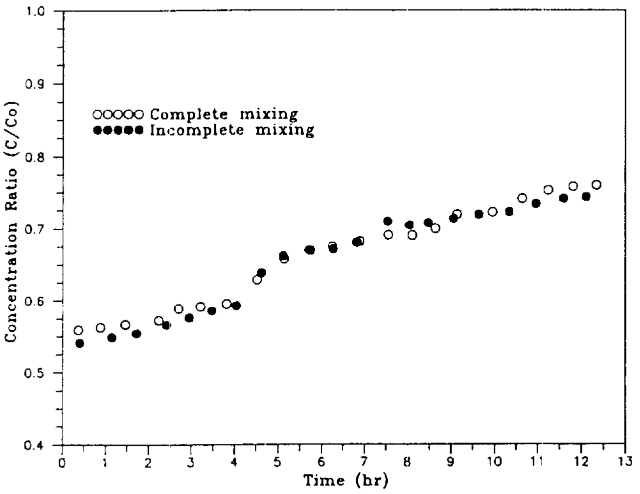

Fig. 14. The effect of incomplete mixing of resins on sodium breakthrough curve with FCR=0.5.

fluent concentration, the sodium effluent concentration shows higher level of leakage and more gradual breakthrough curves. These would be due to the lower selectivity coefficient of the cation resin than the anion resin. It has been said that as the selectivity coefficient is higher, the breakthrough curve is steeper and the equilibrium is more favorable [Helfferich, 1962a, b].

As shown in Figs. 13 and 14, the comparison does not give as much difference between complete and incomplete mixing of the resins as expected. An interesting point is, however, that incomplete mixing has an effect on breakthrough curves of both ions only in the first 3-4 hours. A close investigation of those figures shows that incomplete mixing of the resins increases the sodium exchange rate slightly and decreases slightly the chloride exchange rate during the first 3-4 hours. These experimental results agree well with previous studies of Harries [1988] and Yoon et al. [1995]. Harries [1988] showed that the cation exchange was more favorable in an alkaline medium than a neutral or acidic medium because the mass transfer coefficient of sodium is higher in high pH, while that of chloride is higher in low pH. In addition,

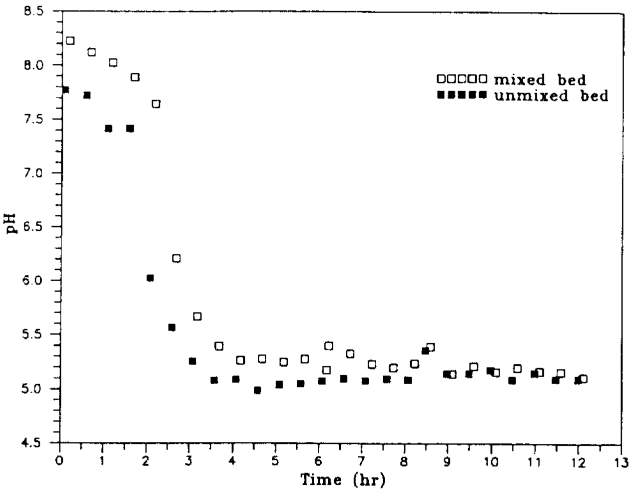

Fig. 15. Comparison of pH in incompletely and completely mixed bed with FCR=0.5.

Yoon et al. [1995] evaluated the effect of cation resin ratio on the performance of MBIE and found that the cation or anion exchange with a lower oppositely-charged resin ratio was affected adversely. They claimed that a change of the cation resin fraction would change the pH of the aqueous phase within the bed, resulting in the change of the exchange rate of both ions. The experiment for the present work was performed with only anion resin in the upper portion and more cation resin in the lower portion of the column. Because the experiments utilized downflow, incomplete mixing of the resins will make the exchanges of both ions start in a more alkaline solution. This affects the mass transfer coefficients of sodium and chloride by the way Harries [1988] claimed and, eventually, results in an increased exchange rate of sodium and a decreased exchange rate of chloride. Fig. 14 indicates that this pH effect on the cation exchange rate disappears after the first 4-6 hours. This is because the mixed bed acts like a cation single bed as active sites on the anion resin are exhausted and, therefore, neutralization reaction is only affected by the addition of new hydroxide ions.

Fig. 15 gives pH profiles of Runs R6 and R7. In this figure, it is known that incomplete mixing causes lower pH in the effluent than complete mixing. A possible interpretation of these pH profiles is that pH increases through the unmixed upper portion and begins to decrease through the mixed lower portion and finally becomes lower at the bottom of the bed than for complete mixing. As pH decreases in the mixed portion, the cation exchange rate decreases and the anion exchange rate increases along with the bed depth. This might result in compensating effects on each exchange rate and thus slight differences in breakthrough curves of both ions.

Runs R9 and R10 were done with relatively large amount of the cation resin in the column; the cation resin fraction was about 0.6 for both runs. The results of these experiments are presented in Figs. 16 and 17. Harries [1988] found that the effect of pH is more substantial on the anion exchange than on the cation exchange. Thus, the slope change of the anion breakthrough curve is greater than that of the cation breakthrough curve when the resin fraction is changed. Fig. 16 indicates slightly sharper slopes of chloride breakthrough curves compared with that in Fig. 13. Figs. 16 and 17 show that the change in the anion leakage seems

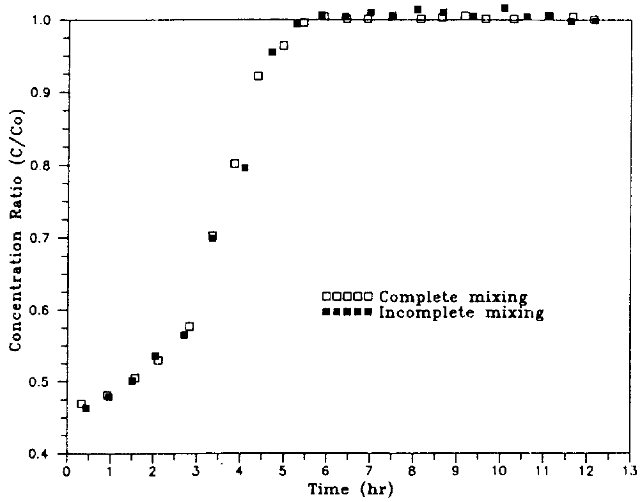

Fig. 16. The effect of incomplete mixing of resins on chloride breakthrough curve with FCR=0.6.

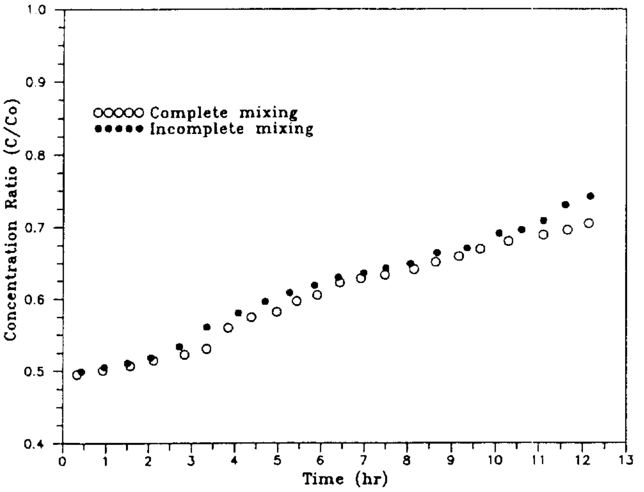

Fig. 17. The effect of incomplete mixing of resins on sodium breakthrough curve with FCR=0.6.

to be slightly greater than that of the cation leakage; the initial leakage in Run R6 was 0.39 chloride and 0.56 sodium and in Run R9, 0.47 chloride and 0.50 sodium. Therefore, it is worthwhile to mention that the level of anion leakage is slightly more sensitive to the change of the cation resin fraction than that of cation leakage.

In Figs. 16 and 17, it is also found that incomplete mixing of the resins has less effect on the breakthrough curves of chloride and sodium with more cation resin. Comparison of breakthrough curves in these figures with those in Figs. 13 and 14 shows inconsistency in the pattern of the effect of incomplete mixing on breakthrough curves of both ions at the early stage of the exchange processes. Figs. 13 and 14 indicate an increased cation exchange rate and a decreased anion exchange rate. Figs. 16 and 17 show negligible differences in breakthrough curves of both ions. Therefore, it can be concluded firmly that the effect of incomplete mixing of resins on the cation and anion exchange rates decreases as the cation resin ratio increases.

Fig. 18 shows the comparison of pH profiles obtained from Runs R9 and R10. Compared with Fig. 15, the highest value of pH at the beginning of the process decreases with more cation resin. Also, it indicates more acidic effluent with incomplete mixing in the first 2-3 run hours. This pH profile would mean a slower cation exchange rate and a faster anion exchange rate at the bottom portion of the bed, which are shown in Figs. 16 and 17. If the runs were continued after the present experimental period, pH will be expected to increase by the same rate as the cation exchange rate decreases.

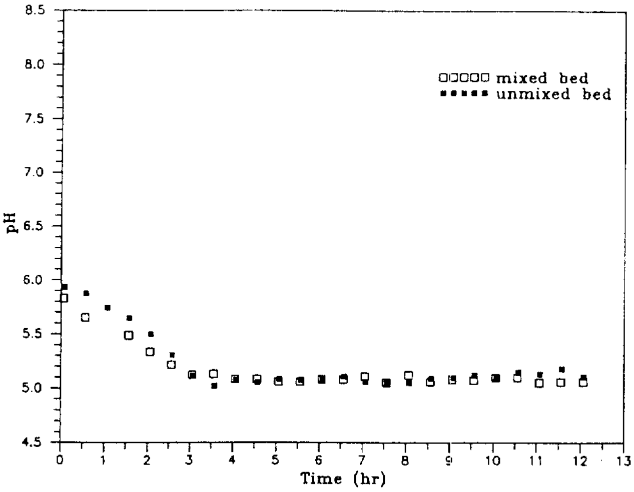

Fig. 18. Comparison of pH in incompletely and completely mixed bed with FCR=0.6.

CONCLUSIONS

The effects of variable feed concentration and incomplete mixing of resins on the performance of MBIE at ultralow ionic concentration were experimentally evaluated. For the variable feed concentration experiments, step changes in feed concentration were arbitrarily introduced into the experimental column. For the incompletely mixed bed experiments, only anion resin was loaded in the upper 20% of the column and more cation resin in the lower portion. From both experiments, the following conclusions are drawn;

1. Introducing step changes in feed concentration affects the breakthrough times of chloride and sodium, but not the slopes of curves. After the peaks are introduced, there is a low level of leakage of both ions due to insufficient contact time between the solution and the resins. When the feed returns to the normal concentration, the leakage of chloride disappears. But, the sodium effluent starts to have higher concentrations after the peaks are introduced. Therefore, the amount of sodium removed until breakthrough is more sensitive to the step changes in feed concentration than the amount of chloride. This would be due to the much lower selectivity coefficient of sodium than that of chloride.

2. Incomplete mixing of resins with the same amounts of cation and anion resins increases the sodium exchange rate slightly and decreases the chloride exchange rate slightly at the early stage of the exchange processes. This is due to the difference of the mass transfer coefficients of sodium and chloride in an alkaline and an acidic solution. The effect of incomplete mixing of the resins on the sodium breakthrough curve diminishes as active sites on the anion resin are exhausted. As the cation resin fraction

increases, the effect of incomplete mixing of resins decreases.

ACKNOWLEDGEMENTS

This research was funded by Korea Science and Engineering Foundation.

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