THE MIXED-BED ION EXCHANGE PERFORMANCE AT ULTRALOW CONCENTRATIONS

1. VARIABLE FEED CONCENTRATION AND INCOMPLETE MIXING OF RESINS

Byeong Il Noh, Tae Kyung Yoon* and Byung Hyun Moon**

 Dept. of Chem. Eng., Dongseo Univ., Pusan 617-010, Korea
*Dept. of Chem. Eng., Dongeui Univ., Pusan 614-714, Korea
**Dept. of Environ. Eng., Changwun Natl. Univ., Kyungnam 641-773, Korea

(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 0.065-7.0 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, stemming 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 °C [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 [Hefflerich, 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 users of ultrapure water and utilize MBIE to avoid 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 Fouch [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 particle sizes, reversibility of exchange, and bulk/film neutralization. Divekar et al. [1987] have developed Haub and Fouch'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 space 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-
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 re-mixed 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 uniform 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 experimental 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 pipetting 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