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The Effect of a Synthetic Flocculant on Ion-Exchange Resin

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Abstract

Experiments were conducted to determine if a synthetic flocculant would foul ion-exchange resin used in deionization plants. It was found that unreacted flocculant fouled the surface of cation-exchange resin, restricting mass transfer, but that total capacity was not significantly affected. Several samples of used resin from a deionization plant did not show evidence of surface fouling, but did have less capacity than new resin. This indicated that unreacted flocculant had not been present in the plant feed water.

INTRODUCTION

In the Texas Division of Dow Chemical U.S.A. there are two deionization plants that provide water for the boilers at four power plants. The river water fed to the deionization plants is clarified using a synthetic organic flocculant. The flocculant, Nacolyte 8102 (trademark of Nalco Chemical Co.), is a cationic polyamine and has a molecular weight of about 40,000. There was some concern that this polyelectrolyte might be fouling the cation-exchange resin, the first resin to be contacted by the river water. The study reported here was undertaken to determine the effect of the free or unreacted polyelectrolyte on Dowex HCR-W (trademark of Dow Chemical Co.), a strong acid cation exchange resin used in the deionization plants.

THEORY

Each molecule of the flocculant contains many positively charged groups when in solution, and thus behaves similarly to a large collection

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of partially immobilized cations. In the process of flocculation, these positive sites associate themselves with negative sites commonly found on the colloids and particles in natural waters (*1*). However, if there is an excess of polyelectrolyte in the water, some of it may remain unreacted or in a free state. This free polyelectrolyte, it was reasoned, could react with exchange resin beads and become reversibly or irreversibly bonded.

If the polyelectrolyte molecules penetrate into the pores and irreversibly bond to internal sites, the capacity of the resin will decrease. If these molecules are unable to enter into the beads, but bind to the bead surfaces, the mass transfer rate into the beads would be expected to decrease due to pore blockage. Either of these conditions is detectable by monitoring breakthrough curves of successive cycles for a column initially containing new resin. The capacity of the exchanger can be calculated from a breakthrough curve by integrating the area behind the curve. An increase in mass transfer resistance can be detected by a change in the slope of the breakthrough curve.

To detect either of these effects, experiments were conducted to obtain a series of breakthrough curves, starting with fresh, unused resin. Several cycles were run using a synthetic river water as the feed, and then several more cycles were run using the same feed water to which polymer was added. Breakthrough curves were also obtained for used resin samples.

EXPERIMENTAL METHODS

Two glass columns were arranged in the laboratory to simulate the primary trains found in the deionization plants of the Texas Division. The columns were 7/8-in. i.d. and 18-in. long. Glass frets from small Buchner funnels were welded to the columns to retain the resin. Three-way stopcocks were attached to the top and bottom. A peristalic pump was used to meter the liquid through the columns, which were arranged in series. The first column contained cation-exchange resin and the second anion-exchange resin. The pH and electrical conductivity of the anion-exchange column effluent were monitored. The feed flow rate was maintained at 75 mL/min, or 4.75 gpm/ft^2. The plant vessels are operated at about 5 gpm/ft^2. Residence in the laboratory beds was about 1 min, while in the plant it is 30 min or more.

The cation exchange column was filled with 130 mL (tapped) or 11 in. of Dowex HCR-W resin in the sodium or exhausted form. The anion column was filled with an excess of Dowex WGR-2 so that the cation resin would completely exhaust before the anion. The WGR-2 is a weak base resin and will not split salts. It was found that this resin, when new, will exchange bicarbonate ion, but then, as the cycle progresses, this ion is displaced by the strong acid anions.

The laboratory regeneration procedure for each column was as follows:

(1) Thoroughly backwash with deionized water
(2) Regenerate at 17 mL/min with 500 mL 10% HCl or 5% NaOH
(3) Rinse with 500 mL of deionized water at 17 mL/min
(4) Fast rinse with deionized water to effluent conductivity of 5 μmhos/cm
(5) Begin run

The quantity of acid or base used was sufficient to completely regenerate the resins.

The feed water used for the experiments was a synthetic river water with the composition shown in Table 1. Because of the analytical difficulties encountered in measuring the individual ion concentration for many samples, the effluent ionic solutes were treated as one species and measured as conductivity. Total ionic concentration and conductivity for Brazos River water at Freeport, Texas were found to be related as follows:

$$c = 0.02\kappa \pm 5\%$$

in which c is the concentration of ions (meq/L), and κ is the conductivity (μmhos/cm).

RESULTS

Shown in Figs. 1–4 are normalized breakthough curves for several experiments. The abscissa are in units of normalized time. The value of the total capacity used was 2.0 equiv/L and the void fraction was 0.4, as given in the product literature. The experimental value for the total capacity of new resin was found to be 1.96 equiv/L. The ordinates are

TABLE 1

Composition of Synthetic River Water[a]

	mg/L	meq/L
$MgSO_4$	131	2.18
$CaCl_2 \cdot 2H_2O$	160	2.88
$NaHCO_3$	367	4.37
Na_2SO_4	151	2.13

[a]Total ionic concentration: 23.1 meq/L. Conductivity: 970 μmhos/cm.

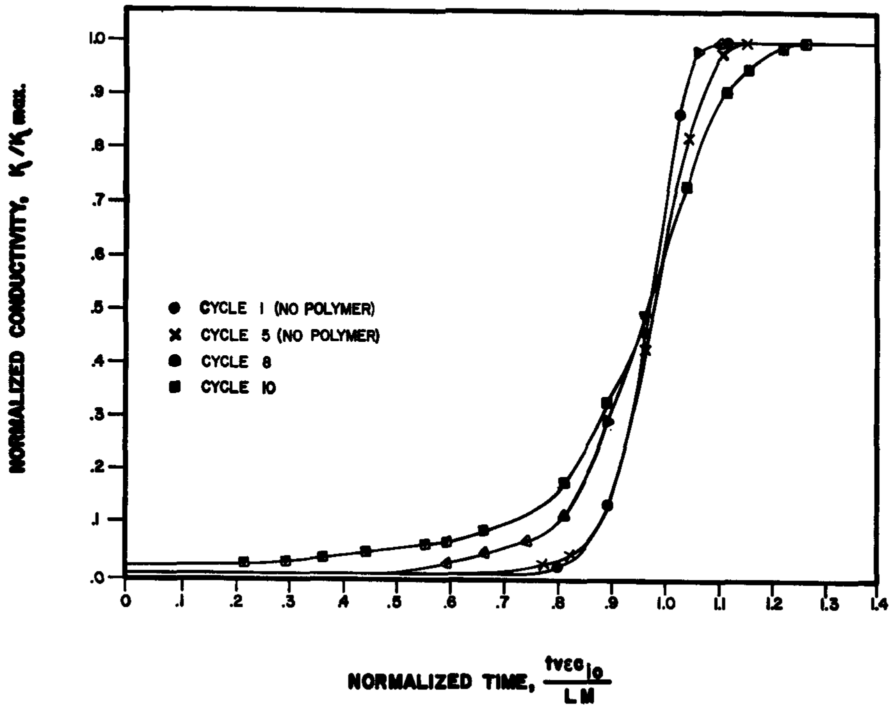

FIG. 1. Effect of Nacolyte 8102 flocculant on the breakthrough curve for Dowex HCR-W cation exchange resin. Feed water conductivity = 970 μmhos/cm.

in units of normalized conductivity, which closely approximates the normalized total ionic concentration. Notice that the denominator is the maximum value of conductivity for the run rather than the feed value. This was used because the release of bicarbonate ion caused the maximum value to exceed the feed value.

In Fig. 1 the effect that dissolved but unreacted Nacolyte 8102 has on cation-exchange resin is shown. For Runs 1–6, no polyelectrolyte was added to the synthetic river water, while for Runs 7–11, 5 mg/L of the synthetic flocculant was metered into the feed. Commencing with Run 7, and becoming more pronounced as the cycle number increased, leakage was premature and breakthrough occurred more gradually. This is the effect expected if the mass transfer resistance increased with each successive run. The total capacity of the resin did not change greatly; a decrease was experienced of about 3% for Cycle 10 and 2% for Cycle 8. The results, then, indicate that exchange sites are not being irreversibly

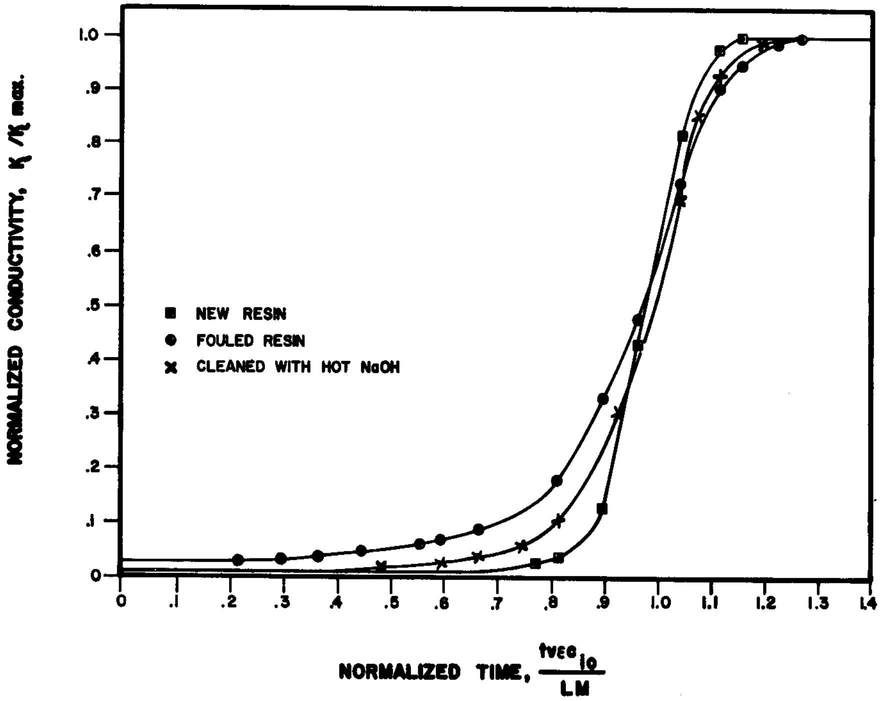

FIG. 2. Effect of cleaning flocculant-fouled Dowex HCR-W cation exchange resin with sodium hydroxide. Breakthrough curves are shown. Feed water conductivity = 970 μmhos/cm.

consumed by the flocculant, but that the pore openings are being restricted.

An attempt to clean the resin was made first by washing it with 500 mL of 5% NaOH, and then by circulating 5% NaOH at 140°F through the column for 2 hr. The resin was regenerated as normal after the first cleaning, and with 1 L of 10% HCl after the second cleaning. The first attempt did not improve the performance of the resin, but more than 50% of the operating capacity was restored with the second cleaning, as shown in Fig. 2. The operating capacity is determined by considering the resin exhausted when the product water reaches a predetermined conductivity, which is normally 50 μmhos/cm.

An additional experiment was conducted to determine if a sand bed preceding the ion-exchange beds would remove or adsorb the polyelectrolyte. Four cycles were run with synthetic river water to which 3 mg/L of flocculant was added. A column of sand with average diameter of 1 mm was then installed prior to the cation-exchange column. This sand bed had the same dimensions as the cation-exchange bed. Four more

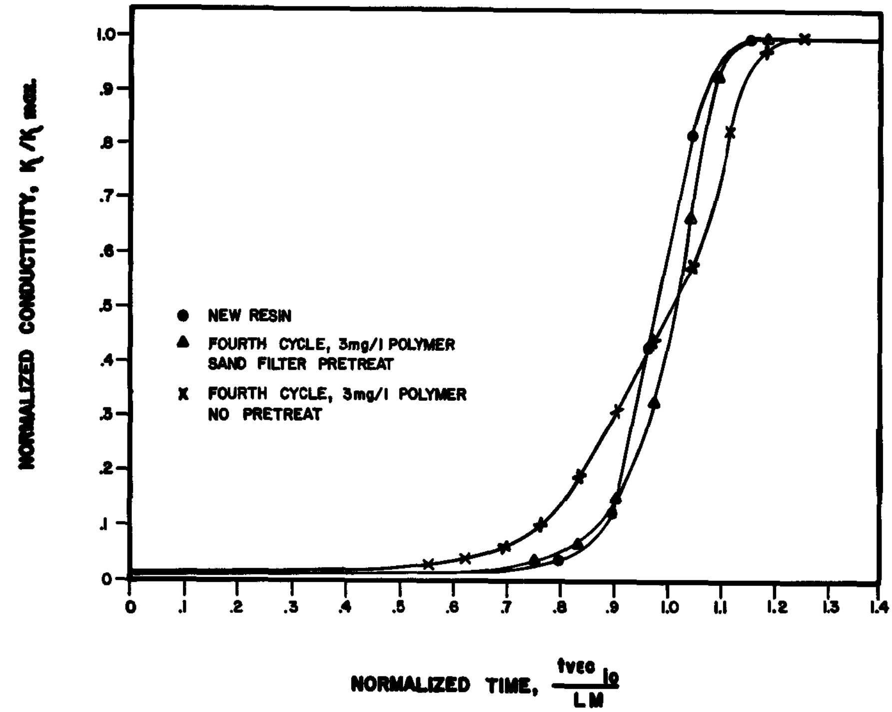

FIG. 3. Effect of Nacolyte 8102 flocculant on Dowex HCR-W cation exchange resin breakthrough curve with and without sand filter pretreatment. Feed water conductivity = 910 μmhos/cm.

cycles were then run as at first. The breakthrough curve of the fourth cycle of each set is compared with that for new resin in Fig. 3. The sand appears to have been effective in removing the polyelectrolyte. Besides protecting resin beds and boilers from suspended solids, then, sand filters can also protect against synthetic flocculant fouling.

In Fig. 4 the breakthrough curves are compared for new resin, a used resin removed from a deionization plant in the Texas Division, and a reclaimed resin. The reclaimed resin had been in service for many years and was cleaned by thorough washing to remove broken beads and dirt. Note that there is no evidence of flocculant fouling. The capacity of the used in-service resin is about 6% less than the new, and the reclaimed resin is about 10% less. Since both resins had been used to deionize water treated with Nacolyte 8102, free or unreacted flocculant must never have been present in significant amounts. It is known that flocculant feed rates have exceeded that required for optimum clarification by as much

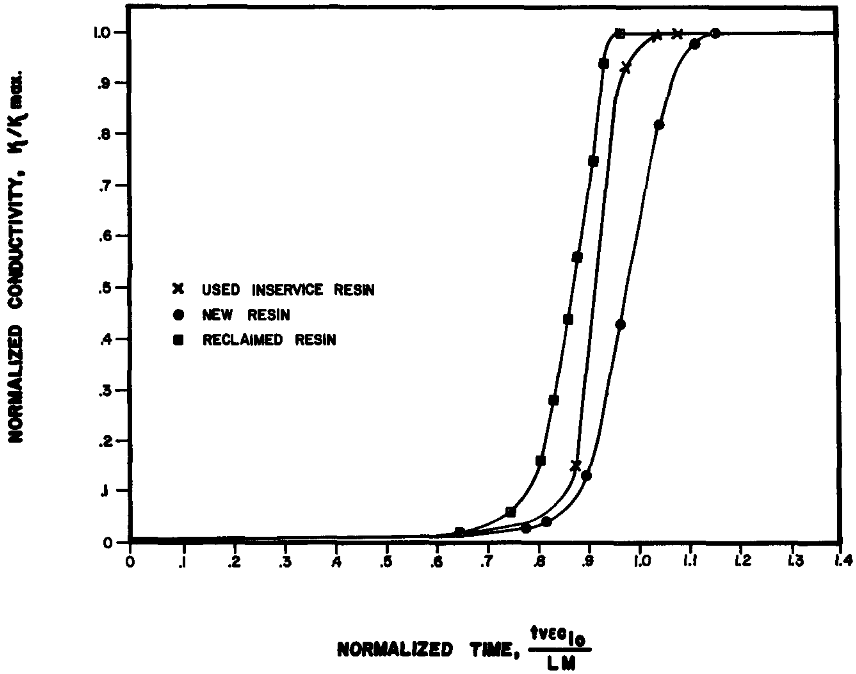

FIG. 4. Comparison of breakthrough curves for new and used samples of Dowex HCR-W cation exchange resin. Feed water conductivity = 970 μmhos/cm for the new resin, 910 μmhos/cm for the in-service resin, and 900 μmhos/cm for the reclaimed resin.

as 100% at times, therefore a natural water system must have capacity to react with considerably more of the flocculant than is needed for proper treatment.

CLOSING COMMENTS

The method used in this work to examine the condition of an ion-exchange resin has proven to be very useful for determining total capacity and operating capacity. It can be used with either cation- or anion-exchange resins and any aqueous feed in which the concentration of the constituents of interest can be measured. By plotting breakthrough curves in terms of the normalized variables, data from experiments with various size resin beds and resin types can be directly compared.

SYMBOLS

c_{io} concentration of cations in feed, equiv/L
L resin bed depth, cm
M total capacity of resin, equiv/L
t time, min
v average liquid velocity in resin bed, cm/min
ε void fraction of resin bed
κ conductivity of effluent, μmhos/cm

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