

The pounds of carbon exhausted per day if the COD removed is assumed to be 98 percent.
The on-line time for each of the columns.

tertiary treatment plant treats a municipal secondary effluent and is to employ fixed-bed carbon adsorption columns. Parallel treatment using two rows of two columns in series (in other words, a total of four columns) will be used. The flowsheet consists of lime coagulation, settling, ammonia stripping, recarbonation, settling, multimedia filtration, carbon adsorption, and chlorination. From batch-type slurry tests it has been found that 0.42 g COD/g carbon is adsorbed when $C_e = C_0$. Pertinent data are: flow = 5700 m³/d, COD in feed to carbon columns = 20 mg/l, contact time function based on an empty carbon bed = 30 min, and unit liquid flow rate = 4.4 l/s-m². Each column is kept on-line until the entire mass of carbon in the column is completely exhausted. Determine:
The volume of each column, m³.
The diameter and height of each column, m.
The mass of carbon in each column if the packed density is 400 kg/m³.

The kilograms of carbon exhausted per day if the COD removed is assumed to be 98 percent.
The on-line time for each of the columns.

ION EXCHANGE

The ion exchange process consists of a chemical reaction between ions in a liquid phase and ions in a solid phase. Certain ions in the solution are preferentially sorbed by the ion exchanger solid and, because electroneutrality must be maintained, the exchanger solid releases replacement ions back into the solution. For instance, in the softening of water by the ion exchange process, the calcium and magnesium ions are removed from the solution and the exchanger solid releases sodium ions to replace the removed calcium and magnesium ions. The reactions are stoichiometric and reversible and obey the law of mass action.

The first commercially used ion exchange materials were naturally occurring porous sands that were commonly called zeolites. These minerals have a deficit of positive atoms within their crystalline structure and, as a result, they have a net negative charge which is balanced by exchangeable cations held within the pore capillaries. Zeolites were the first ion exchangers used to soften waters; however, they have been almost completely replaced in recent years by synthetic organic exchange resins which have a much higher ion exchange capacity. Synthetic cation exchange resins are polymeric materials that have reactive groups, such as the sulfonic, phenolic, and carboxylic, that are ionizable, and may be charged with exchangeable cations. Also, synthetic anion exchange resins are available that have ionizable groups, such as the quaternary ammonium or amine groups, which may be charged with exchangeable anions. Thus, synthetic resins are available that have both cation and anion exchange capabilities. Certain minerals, such as montmorillonite clays, have appreciable cation ex-

change capacity and are used for special ion exchange applications.

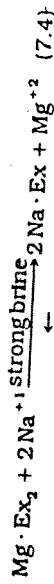
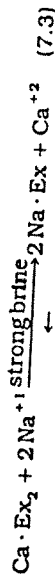
Ion exchange is used extensively in both water and wastewater treatment. Some of the common applications are water softening, demineralization, desalting, ammonia removal, treatment of heavy metal wastewaters, and treatment of some radioactive wastes. (1) One of the largest uses of ion exchange in environmental engineering is the softening of water by the exchange of sodium ions for calcium and magnesium ions. Since removal of all of the hardness is undesirable for a domestic water supply, a portion of the flow may bypass the exchangers to give a blended water of the desired hardness. This process is termed split-flow softening. (2) Ion exchange is used for the removal of all cations and anions from a water. In total demineralization, the cationic resins are charged with the hydrogen ion and the anionic resins are charged with the hydroxyl ion. The cationic resins exchange hydrogen ions for cations and the anionic resins exchange hydroxyl ions for anions. Thus the treated water has only hydrogen and hydroxyl ions, which makes it essentially pure water. Industries using high pressure boilers require demineralized water as boiler water. In addition, there are other industries that require demineralized water. (3) Ion exchange may be used for partial demineralization of wastewaters in tertiary treatment and of brackish waters for water supplies. Several ion exchange techniques may be employed, one of which is split-flow demineralization. (4) The natural zeolite, clinoptilolite, may be used to remove ammonia in advanced waste treatment plants in lieu of or in addition to other methods of ammonia removal. (5) Ion exchangers may be used to remove heavy metallic ions from certain wastewaters. The heavy metallic ions are thus concentrated in the spent regenerate. An example is the treatment of wastewaters from a metal plating industry that contains zinc, cadmium, copper, nickel, and chromium. (6) Clays and other minerals possessing ion exchange capacities are used to treat low- or moderate-level radioactive wastes to preferentially remove heavy metallic radionuclides such as Cs¹³⁷.

A number of texts and references are available on the theory and application of the ion exchange process and laboratory evaluation procedures (Betz, 1962; Dorfner, K., 1971; Dow, 1964; Helfferich, F., 1962; Kitchener, J. A., 1961; Kunin, R., 1960).

The softening of a hard water by an exchanger solid, either a zeolite or a synthetic resin, may be represented by the following reactions:

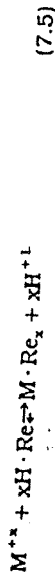


where Ex represents the exchanger solid. As shown by the reactions, a hard water may be softened by exchanging Na⁺¹ from the exchanger solid for the Ca⁺² and Mg⁺² in the solution. After the solid is saturated with the Ca⁺² and Mg⁺², it may be regenerated by a strong salt solution since the reactions are reversible. The regeneration reactions are

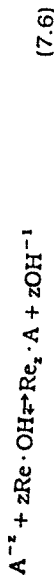


After regeneration, the exchanger solid is washed to remove the remaining brine and then is placed back on-line to soften more water.

In the demineralization of water, the water is first passed through cation exchange resins charged with the hydrogen ion. The cation removal may be represented by the reaction



where M⁺ represents the cationic species present and x is the valence number. After passing through the cation exchange resins, the water then passes through anion exchange resins charged with the hydroxyl ion. The anion removal may be represented by the reaction



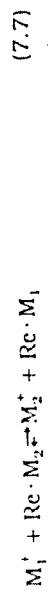
where A⁻ represents the anion species present and z is the valence number. After the resins become exhausted, the cation exchange resins are regenerated using a strong mineral acid such as sulfuric or hydrochloric acid. In a similar manner, the anion exchange resins are regenerated using a strong base such as sodium hydroxide.

Exchange resins are usually bead- or granular-shaped, having a size of about 0.1 to 1.0 mm. The ion exchange ability of resins may be classified as "strong" or "weak" according to the characteristics of the exchange capability (Dorfner, K., 1971). The strong acid cation resins have strong reactive sites such as the sulfonic group (-SO₃H), and the resins readily remove all cations. Conversely, the weak acid cation exchange resins have weak reactive sites

such as the carboxylic group (-COOH), and these resins readily remove cations from the weaker bases such as Ca⁺² and Mg⁺² but have limited ability to remove cations from strong bases such as Na⁺¹ and K⁺¹. The strong base anion exchange resins have reactive sites such as the quaternary ammonium group, and these resins readily remove all anions. The weak base anion exchange resins have reactive sites such as the amine group, and these resins remove mainly anions from strong acids such as SO₄⁻², Cl⁻¹, and NO₃⁻¹, with limited removal for HCO₃⁻¹, CO₃⁻², or SiO₄⁻⁴.

Ion exchange resins or zeolites have a limited number of exchange sites available, and the total solid-phase concentration, q₀, is termed the ion exchange capacity. For cation exchange resins it is usually between 200 to 500 meq per 100 gms. Since a cation exchanger must remain electrically neutral during the exchange reaction, all of the exchange sites must be occupied by sufficient cations to balance the negative charge of the exchanger. Thus, for a system involving Ca⁺², Mg⁺², and Na⁺¹, the sum of the solid-phase concentrations of these ions must, at any time, be equal to the cation exchange capacity, q₀. Electron neutrality applies to anion exchangers as well as cation exchangers.

Since ion exchange is a chemical reaction, the law of mass action may be applied. The generalized equation for cation exchange by a resin may be represented by



where M₁⁺, M₂⁺ are cations of different species and Re is the resin. The mass action constant is as follows:

$$K \frac{M_1^+}{M_2^+} = \frac{[Re \cdot M_1][M_2^+]}{[Re \cdot M_2][M_1^+]} \tag{7.8}$$

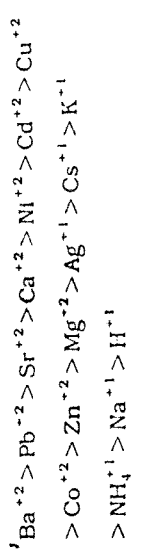
$$= \left[\frac{M_1}{M_2} \right]_{\text{solid}} \times \left[\frac{M_2}{M_1} \right]_{\text{solution}} \tag{7.9}$$

where
 $K \frac{M_1^+}{M_2^+}$ = mass action constant or selectivity coefficient.

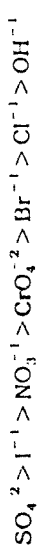
In Eqs. (7.8) and (7.9) the bracketed terms represent equilibrium concentrations expressed in an appropriate concentration unit. The magnitude of K represents the relative preference for ion exchange. Thus, it is the relative pref-

erence of the resin to sorb cation M₁⁺ as compared to cation M₂⁺.

The greater the selectivity coefficient, K, the greater is the preference for the ion by the exchanger. An ion exchanger tends to prefer: (1) ions of higher valence, (2) ions with a small solvated volume, (3) ions with greater ability to polarize, (4) ions that react strongly with the ion exchange sites of the exchanger solid, and (5) ions that participate least with other ions to form complexes. For the usual cation exchangers, the preference series for the most common cations is as follows (Heffertich, F., 1962):



This series is for strong acid resins—that is, those having strong reactive sites such as the sulfonic group (-SO₃H). Weak acid resins—that is, those having weak reactive sites such as the carboxylic group (-COOH)—will have the H⁺¹ position to the left of that shown above depending upon the strength of the reactive site. For very weak sites, the H⁺¹ may fall to the left as far as Ag⁺¹. For the usual anion exchangers, the preference series for the most common anions is as follows (Heffertich, F., 1962):



This series is for strong base resins—that is, those having strong reactive sites such as the quaternary ammonium group. For weak base resins—those having weak reactive sites such as the secondary or tertiary amine group—the OH⁻¹ will fall farther to the left depending upon the strength of the reactive group. It should be understood that the previous series are to be used as a guides and that exceptions occur. Since equilibria are involved, the most suitable method to determine the uptake by a certain exchanger solid for a particular ion in a solution is to perform sorption tests. These may be done by (1) using a column to obtain the breakthrough curve for the particular ion of interest or (2) using batch-type slurry tests to obtain the uptake of the particular ion.

The rate of ion exchange depends upon the rates of the various transport mechanisms involved and the rate of the exchange reaction itself. These are as follows: (1) movement of the ions from the bulk solution to the film or boundary layer surrounding the exchanger solid, (2) diffusion of the

ions through the film to the solid surface. (3) diffusion of the ions inward through the pores of the solid to the exchange sites, (4) exchange of ions by the reaction, (5) diffusion of the exchanged ions outward through the pores to the solid surface, (6) diffusion of the exchanged ions through the liquid film or boundary layer surrounding the solid, and (7) movement of the exchanged ions into the bulk solution. Weber (1972) has shown that in a stirred batch process or in a continuous-flow process operated at the velocities used in water and waste treatment systems, the rate of exchange is usually controlled by step 2 or, in some cases, by step 3. Step 2, the diffusion of ions through the film or boundary layer, is frequently referred to as *film diffusion*, and step 3, the diffusion of ions through the pores, is termed *pore diffusion*.

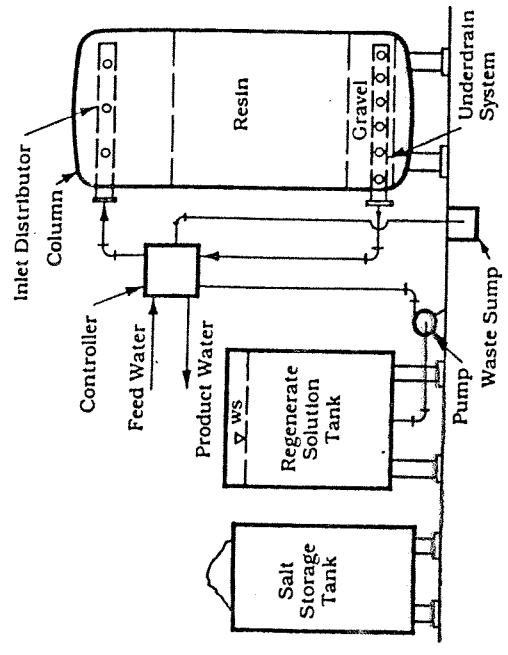
Contacting Techniques and Equipment

All of the operating techniques ordinarily used for adsorption are also used for ion exchange. Thus, there are batch, column, or fluidized-bed processes. Column processes may consist of fixed-bed columns in which the beds are stationary or moving-bed columns in which both the liquid and the ion exchanger solid move countercurrently. Also, fluidized beds may be operated countercurrently. Of all the contacting systems, the fixed-bed columns are the most common and the second most popular are the countercurrent moving-bed columns. The popularity of these two contacting techniques is due mainly to their reduced labor costs. Frequently in ion exchange applications, there may be several columns or stages in series.

Figure 7.1 shows a schematic drawing of typical equipment required for a fixed-bed column used for water softening with a sodium-charged exchange resin. The equipment consists of the exchange column, a salt storage tank, a regeneration solution tank, and all required appurtenances. The exchange column is usually a steel cylindrical tank with an inlet distribution system and an underdrain collection system. The resins inside the vessel are supported on a graded gravel layer. The controller controls the flow to and from the column and contains the necessary valves to change the system from the softening cycle to the regeneration cycle and vice versa.

During the softening cycle, the water enters the top of the bed and flows downward at a constant flow rate of about 1 to 8 gpm/ft². Once the allowable breakthrough of hardness occurs in the effluent, the controller is activated so that backwashing is accomplished to remove any suspended material that may have accumulated by filtering action

Figure 7.1. Typical Fixed-Bed Column Equipment for Softening Using Sodium-Charged Resin

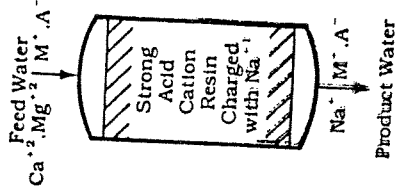


during the softening cycle. After backwashing, the salt solution, which is usually 5 to 10 percent salt, is passed through the exchanger bed at a controlled rate to regenerate the resins. Once regeneration is completed, a slow rinse flow is passed through the bed to displace the remaining regenerate solution to waste. This is followed by a fast, short rinse to remove the last traces of the regenerate solution from the bed. Once the fast rinse is completed, the column is placed back on-line to continue the softening process.

The breakthrough curves for an ion exchange column and an adsorption column are similar, and the contacting techniques are almost identical. Consequently, the same procedures for the design of adsorption columns may be used for ion exchange columns. The scale-up approach by Fornwalt and Hutchins (1966) and the kinetic approach by Thomas (1948) also may be applied to the design of ion exchange columns by the same procedures presented in Chapter 6. A laboratory- or pilot-scale breakthrough curve is required for both procedures. The breakthrough curve for a column shows the solute or ion concentration in the

Design Procedure

Figure 7.2.
Ion Exchange Softening



effluent on the y -axis versus V represents the amount of solute or ions taken up by the column and is $\int (C_0 - C) dV$ from $V = 0$ to $V = V_B$ = the allowable breakthrough volume under consideration. At the allowable breakthrough volume, V_B , the area above the breakthrough curve is equal to the amount of ions removed by the column. At complete exhaustion, $C = C_0$ and the area above the breakthrough curve is equal to the maximum amount of ions removed by the column. At complete exhaustion, the entire exchange column is in equilibrium with the influent and effluent flows. Also, the ion concentration in the influent is equal to the ion concentration in the effluent.

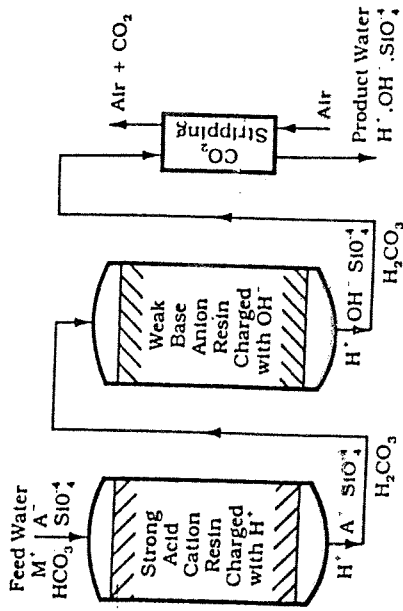
Another design approach is to determine the meq or equivalent weights of the ions removed by a test column using the breakthrough curve. The throughput volume under consideration should be the allowable breakthrough volume, V_B , at the allowable breakthrough concentration, C_a . The ratio of the amount of ions removed per unit mass of exchanger is computed. Then, using this ratio, the mass of exchanger required is calculated from the allowable breakthrough volume for the design column and the concentration of the polyvalent metallic ions to be removed from the liquid flow. For this method to be valid, the flow rate used for the test column in terms of bed volumes per hour must be similar to the flow rate of the design column. A design procedure based on mass transfer fundamentals and the unit transfer concept is also available (Michaels, A. S., 1952).

Softening and Demineralization

Softening may be achieved by using a strong acid cation exchanger on the sodium cycle (that is, charged with Na^{+1}), as depicted in Figure 7.2. The Ca^{+2} , Mg^{+2} , and other divalent or polyvalent metallic ions are sorbed by the exchanger solid, and Na^{+1} ions are released into the solution. Since electroneutrality must be maintained, one meq of divalent or polyvalent cations removed causes one meq of sodium ions to be released. Once breakthrough occurs the bed is regenerated using a strong brine (NaCl) solution.

Demineralization where silica reduction is not required may be accomplished by the flowsheet shown in Figure 7.3. This consists of a strong acid cation exchanger on the hydrogen cycle, a weak base anion exchanger on the hydroxyl cycle, and a carbon dioxide stripper or degasifier-cation unit. Once the water passes through the cation exchanger,

Figure 7.3. Ion Exchange Demineralization



changer the cations have been removed and exchanged for hydrogen ions, resulting in an acidic water. The bicarbonates and carbonates present are converted to carbonic acid due to the low pH. The water then passes through a weak base anion exchanger and the anions, with the exception of silicates, are removed. The water then passes through a carbon dioxide stripper (degasifier), where excess carbon dioxide is removed. The product water will contain some silicate ions since weak base anion exchangers have limited removal for these. If the carbon dioxide content is not objectionable or the feed water has a low alkalinity, carbon dioxide stripping is not required. Regeneration is achieved using a solution of a strong mineral acid, such as sulfuric or hydrochloric, for the cation exchanger, and a sodium hydroxide solution for the anion exchanger.

Demineralization where silica removal is required may be accomplished by the flowsheet shown in Figure 7.4. This consists of a strong acid cation exchanger on the hydrogen cycle, a carbon dioxide stripper or degasifier, and a strong base anion exchanger on the hydroxyl cycle. Once the water passes through the cation exchanger, it goes through the carbon dioxide stripper where excess carbon dioxide is removed. The water then goes through the strong base anion exchanger, which removes all anions, including silicates. If the feed water has a low alkalinity the carbon dioxide stripper may be omitted. The product water will be essentially pure since the cations and anions have been removed, leaving only the hydrogen and hydroxyl ions, which form water.

Figure 7.4. Ion Exchange Demineralization

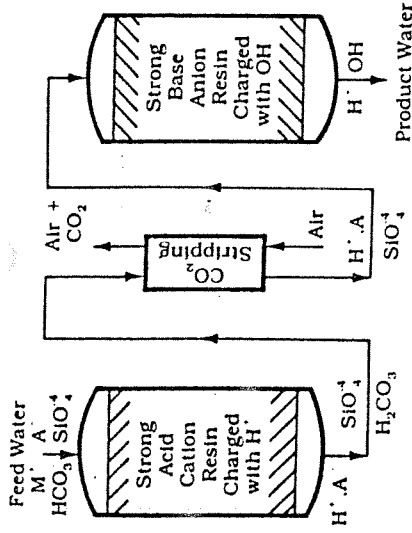
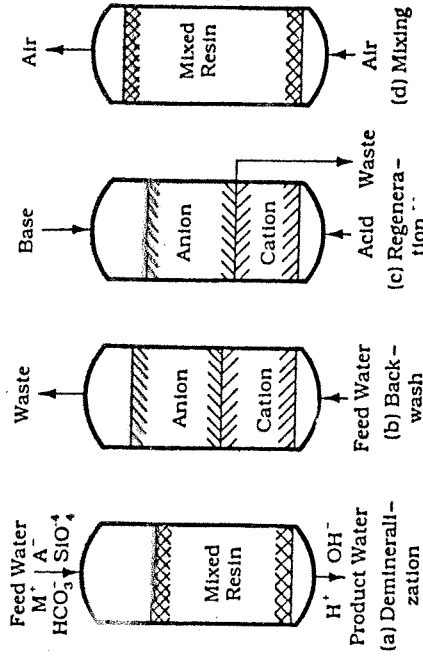


Figure 7.5. Mixed-Resin Demineralization



Demineralization may also be accomplished by a mixed-resin bed consisting of both strong acid cation exchange resins mixed with strong base anion exchange resins, as depicted in Figure 7.5 (a). The flowsheets shown in Figures 7.3 and 7.4 give up to 99 percent dissolved solids removal; however, a mixed-resin bed will give greater removal. Once breakthrough occurs in the mixed bed, it is backwashed to separate the resins. Since the anion resins are less dense than the cation resins, they will move to the top of the bed, as shown in Figure 7.5 (b). Regeneration is accomplished using a strong mineral acid solution and a strong base so-

lution, as illustrated in Figure 7.5 (c). After regeneration, air is introduced into the bottom of the bed to remix the resins, as shown in Figure 7.5 (d). Frequently mixed-resin beds are used to polish waters demineralized by the flowsheets shown in Figures 7.3 and 7.4.

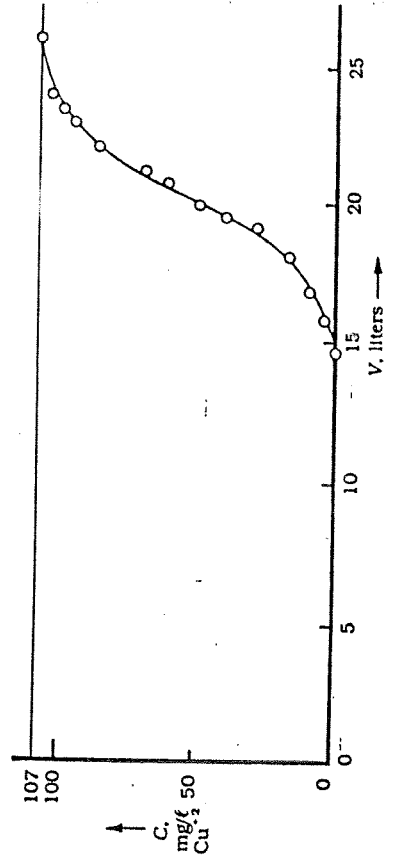
Other demineralization flowsheets employing more than two exchange columns may be used and are reported in the literature (Betz, 1962; Dorfner, K., 1971; Helfferich, F., 1962; Klitchener, J. A., 1961; Kunin, R., 1960; Nordell, E., 1961; Perry, R. H., & Chilton, C. H., 1973; Weber, W. J., 1972).

Example Problem 7
Ion Exchange in Wc
Treatment

An industrial wastewater with 107 mg/l of Cu^{+2} (3.37 meq/l) is to be treated by an exchange column. The allowable effluent concentration, C_a , is 5 percent C_o . A breakthrough curve, shown in Figure 7.6, has been obtained from an experimental laboratory column on the sodium cycle. Data concerning the column are: inside diameter = 0.5 in., length = 18 in., mass of resin = 41.50 gm on a moist basis (23.24 gm on a dry basis), moisture = 44 percent, bulk density of resin = 44.69 lb/ft³ on moist basis, and liquid flow rate = 1.0428 l/day. The design column will have a flow rate of 100,000 gal/day, the allowable breakthrough time is seven days of flow, and the resin depth is approximately two times the column diameter. Using the kinetic approach to column design determine:

1. The pounds of resin required.

Figure 7.6. Breakthrough Curve for Example Problem 7.1



- The diameter and depth.
- The height of the sorptic zone.

Solution

In this problem, the design equation to be used is Eq. (6.12). The data for the breakthrough test are given in columns (1) and (2) of Table 7.1.

Table 7.1. Reduced Data from Breakthrough Test

(1) V (liters)	(2) C (mg/l)	(3) C (meq/l)	(4) C/C ₀	(5) C ₀ /C	(6) C ₀ /C-1
15.9	4.45	0.14	0.041	24.29	23.29
16.9	9.85	0.31	0.091	10.97	9.97
18.1	17.16	0.54	0.159	6.30	5.30
19.1	27.56	0.88	0.259	3.86	2.86
19.5	40.03	1.26	0.371	2.70	1.70
20.0	49.56	1.56	0.459	2.18	1.18
20.7	62.90	1.98	0.582	1.72	0.72
21.2	68.89	2.20	0.647	1.55	0.55
22.0	86.41	2.72	0.800	1.25	0.25
22.9	94.03	2.96	0.871	1.15	0.15
23.4	98.17	3.09	0.917	1.09	0.09
24.0	102.93	3.24	0.961	1.05	0.05
26.0	107.00	3.37	1.000	1.01	0.01

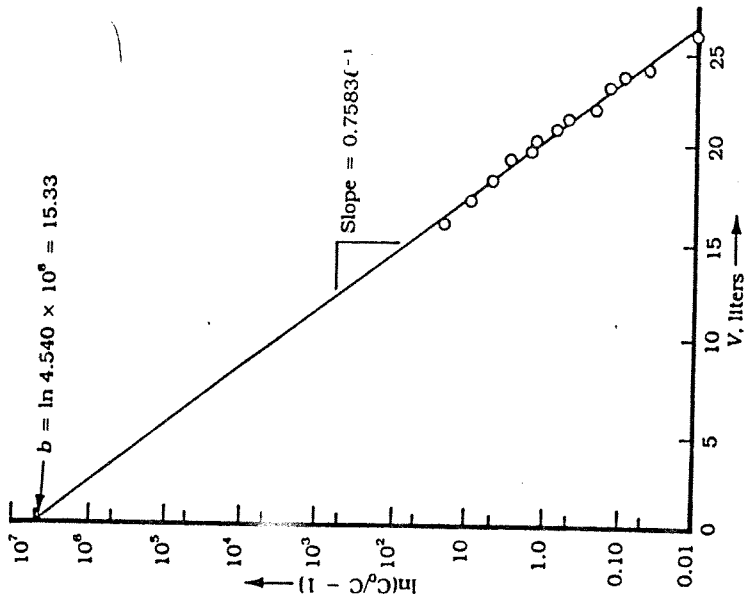
The plot of $\ln(C_0/C - 1)$ versus V is shown in Figure 7.7. The slope is $k_1 C_0 / Q$ or $0.7583 \ell^{-1}$. The value of $k_1 = (\text{slope})(Q/C_0)$ or $k_1 = (0.7583 \ell)(1.0428 \ell/\text{day}) / (3.37 \text{ meq})(1000 \text{ meq}/\text{eq})(\text{gal}/3.785 \ell) = 61.994 \text{ gal}/\text{day}\text{-eq}$. The y-axis intercept, b , equals $\ln 4.540 \times 10^8$ or 15.33. Since $b = k_1 q_0 M / Q$, rearranging gives $q_0 = bQ / k_1 M = (15.33)(1.0428 \ell/\text{day})(61.994 \text{ gal}/\ell)(23.24 \text{ gm})(454 \text{ gm}/\text{lb})(\text{gal}/3.785 \ell) = 1.3309 \text{ eq}/\text{lb}$. The mass of resin may be computed from

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_1 q_0 M - k_1 C_0 V}{Q}$$

or

$$\begin{aligned} \ln\left(\frac{C_0}{0.05 C_0} - 1\right) &= \frac{61.994 \text{ gal}}{\text{day}} \left| \frac{1.3309 \text{ eq}}{\text{day}\text{-eq}} \right| \frac{\text{lb}}{\text{lb}} \\ &\times \frac{\text{day}}{100,000 \text{ gal}} \left| \frac{M}{61.994 \text{ gal}} \right| \frac{3.37 \text{ meq}}{\text{day}\text{-eq}} \left| \frac{\ell}{\ell} \right| \\ &\times \frac{\text{eq}}{1000 \text{ meq}} \left| \frac{3.785 \ell}{\text{gal}} \right| \frac{\text{day}}{\text{day}} \left| \frac{700,000 \text{ gal}}{100,000 \text{ gal}} \right| \end{aligned}$$

Figure 7.7. Plot for Example Problem 7.1



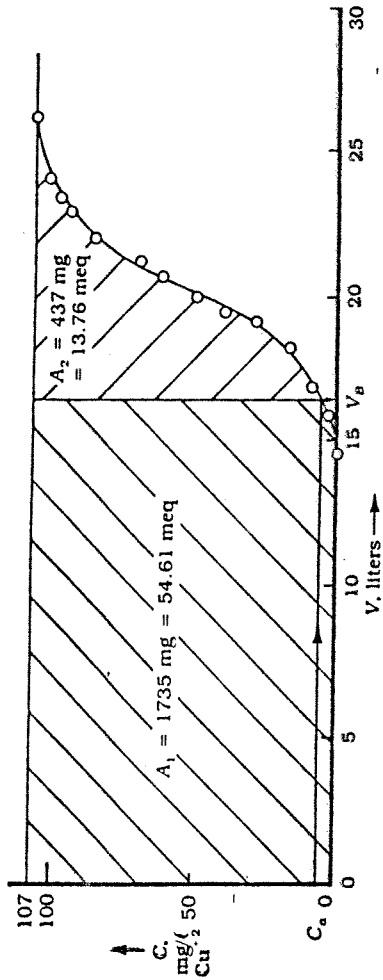
From which $M = 10,278 \text{ lb dry weight}$. $Ft^3 = (10,278 \text{ lb})(10.56)(\text{ft}^3/44.69 \text{ lb}) = 410.7 \text{ ft}^3$. Since $(\pi/4)(D^2)(2D) = 410.7 \text{ ft}^3$, $D = 6.39 \text{ ft}$. Use $D = 6.50 \text{ ft}$ and $Z = (410.7 \text{ ft}^3)(4/\pi)(1/6.50 \text{ ft})^2 = 12.38 \text{ ft}$. At 5 percent C_0 breakthrough, the breakthrough volume = 700,000 gal. Using 95 percent C_0 and the previous equation gives a throughput volume of 1,444,760 gal. Thus $V_T = 1,444,760 \text{ gal}$, $V_B = 700,000 \text{ gal}$, and $V_Z = 1,444,760 - 700,000 = 744,760 \text{ gal}$. Substituting into the equation $Z_s = Z[V_Z/(V_T - 0.5 V_Z)]$ gives

$$\begin{aligned} Z_s &= 12.38 \text{ ft} \left[\frac{744,760}{1,444,760 - 0.5(744,760)} \right] \\ &= 8.60 \text{ ft} \end{aligned}$$

For the test column and breakthrough curve given in Example Problem 7.1, determine the mass of C_0 in

removed per 100 gm resin on a dry weight basis at the allowable breakthrough volume, V_B , for $C_a = 0.05 C_0$. Also, determine the meq of Cu^{+2} ion removed per 100 gm resin on a dry weight basis at complete exhaustion. The dry weight of resin used was 23.24 gm.

Figure 7.8. Breakthrough Curve for Example Problem 7.2



Solution

The meq weight of Cu^{+2} is 63.54/2 or 31.77 mg. The area above the breakthrough curve from V equal to zero to V equal to the volume under consideration is equal to the ion content removed by the exchanger. Figure 7.8 shows the breakthrough curve and the area above the breakthrough curve out to V_B , the allowable breakthrough volume for $C_a = 0.05 C_0$. The area, A_1 , is 1735 mg or 1735/31.77, which is equal to 54.61 meq. From the allowable breakthrough volume, V_B , to the volume at exhaustion, the area, A_2 , is 437 mg or 437/31.77, which is equal to 13.76 meq. At exhaustion, the total area is 54.61 + 13.76 or 68.37 meq. The copper removed at $C_a = 0.05 C_0$ is 54.61 meq/23.24 gm or 235.0 meq/100 gm dry weight. The copper removed at exhaustion is 68.37 meq/23.24 gm or 294.2 meq/100 gm dry weight.

Example Problem 7.3 Ion Exchange Softening

A well water is to be softened by split-flow ion exchange with the exchanger on the sodium cycle. The flow is 50 gpm, the hardness = 225 mg/l as CaCO_3 , the desired hardness is 50 mg/l as CaCO_3 , and the moisture content

of the resin is _____ percent. A test column has been used in the laboratory to obtain a breakthrough curve. The computed hardness removed by the resin at the allowable breakthrough concentration $C_a = 0.05 C_0$ was 282 meq/100 gm resin on a dry weight basis. Determine the pounds of resin required if the allowable breakthrough is seven days.

Solution

A materials balance on the flow downstream from the exchanger is $Q_e(0) + (Q_b)(225) = (Q_e + Q_b)50$, where Q_e = flow through the exchanger and Q_b = flow bypassing the exchanger. From the balance, $Q_b = 0.2857 Q_e$. Since $Q_b + Q_e = 50$ gpm, $0.2857 Q_e + Q_e = 50$ gpm or $Q_e = 38.89$ gpm. The hardness of the well water in meq/l is (225 mg/l)/(meq/50 mg) or 4.50 meq/l. The hardness removed in seven days is (38.89 gal/min)(1440 min/day)(7 day/week)(3.785 l/gal)(4.50 meq/l) = 6,676,930 meq. Thus, the amount of resin = (6,676,930 meq)/(100 gm/282 meq)(lb/454 gm) = 5215 lb[(1 - 0.45)] = 9482 lb moist weight.

Example Problem 7 Ion Exchange Softening

A well water is to be softened by split-flow ion exchange with the exchanger on the sodium cycle. The flow is 3.2 l/s, the hardness is 225 mg/l as CaCO_3 , the desired hardness is 50 mg/l as CaCO_3 , and the moisture content of the resin is 45 percent. A test column has been used in the laboratory to obtain a breakthrough curve. The computed hardness removed by the resin at the allowable breakthrough concentration $C_a = 0.05 C_0$ was 282 meq/100 g resin on a dry weight basis. Determine the kilograms of resin required if the allowable breakthrough is seven days.

Solution

A materials balance on the flow downstream from the exchanger is $Q_e(0) + Q_b(225) = (Q_e + Q_b)50$, where Q_e = flow through the exchanger and Q_b = flow bypassing the exchanger. From the balance, $Q_b = 0.2857 Q_e$. Since $Q_b + Q_e = 3.2$ l/s, $0.2857 Q_e + Q_e = 3.2$ l/s or $Q_e = 2.49$ l/s. The hardness of the well water in meq/l is (225 mg/l)/(meq/50 mg) or 4.50 meq/l. The hardness removed in seven days is (2.49 l/s)(60 s/min)(1440 min/

$$\frac{d(\text{d/wk})}{4.50 \text{ meq/l}} = \frac{C_0(1-b)/b}{4} \text{ meq/l} \text{ min, the}$$

$$\text{amount of resin} = (6,776.78) \times (100 \text{ g}/282 \text{ meq/kg})$$

$$1000 \text{ g}) = 2403 \text{ kg dry weight. On a moist basis, this}$$

$$\text{is } (2403 \text{ kg}) / (1 - 0.45) = 4369 \text{ kg moist weight.}$$

Design Considerations

Zeolite or resin beds used for softening usually have an exchanger bed of 2.0 to 8.5 ft in depth and operate at 1 to 8 gpm/ft². Since ion exchangers are regenerated without removing the exchanger solid from the vessel, the height to diameter ratio is not as critical as for carbon adsorption columns. Usually, the height of resin to diameter ratio is from 1.5:1 to 3:1. The column height should be sufficient to allow for expansion of the bed during the backwash. On backwashing, zeolites expand to about 25 percent of the bed depth, whereas synthetic resins expand to about 75 to 100 percent of the bed depth. The maximum column height is usually 12 ft. If a column height greater than 12 ft is required, two columns in series can be used. Prefabricated steel cylinders may be obtained in diameters up to 12 ft in 3-in. intervals; however, 6-in. intervals are more common and diameters range from 2 ft-6 in. to 12 ft. At an allowable breakthrough of 5 percent C_0 , usually 65 to 85 percent of the ion exchange capacity will be used for removing hardness. Synthetic cation exchange resins with strong acid exchange sites have ion exchange capacities from about 350 to 520 meq/100 gm dry resin. Moist densities are from 43.0 lb/ft³ (689 gm/l) to 54.0 lb/ft³ (865 gm/l), and the moisture content may be from 40 to 60 percent. Dry resins may swell up to 55 percent of their original volume upon becoming moist. The ion exchange capacity, density, and moisture content depend upon the particular resin under consideration. Regeneration of synthetic resins on the softening cycle is done with a 5 to 25 percent brine solution. Usually a 5 to 10 percent solution is used. In regeneration, the brine solution is passed through the bed in either a downward or upward direction. The unit liquid flow rate is 1 to 2 gpm/ft². After regeneration, a slow rinse flow is passed through the bed in the direction of the softening flow to rinse the brine from the bed. After the slow rinse, a short, fast rinse is used to flush any remaining brine from the bed. Usually 30 to 150 gal of rinse water are required per ft³ resin. Salt requirements are from 5 to 20 lb salt per ft³ resin bed, with 5 to 10 lb per ft³ being typical.

Strong acid cation exchangers on the hydrogen cycle are regenerated using a H₂SO₄ or HCl solution. If H₂SO₄ is used, a 2 percent solution should first be passed through

the exchanger followed by a 10 percent solution. The lower concentration is first used to avoid precipitation of CaSO₄ in the exchanger bed. The H₂SO₄ required is from 6 to 12 lb per ft³ resin. If HCl is used, a 15 percent solution should be employed and the HCl required is from 5 to 10 lb per ft³ resin. Strong base exchangers on the hydroxyl cycle are regenerated with a 2 to 10 percent NaOH solution. Regeneration requires from 3 to 6 lb NaOH per ft³ resin.

Test columns should be regenerated in the same manner as a design column in order for the breakthrough curve to be representative. That is, the resin should be regenerated with the regenerate ion, then a test performed to complete exhaustion. Next, the resin should be regenerated, then the test should be rerun to obtain the design breakthrough curve.

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