16

Ion Exchange

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Terminology for Ion Exchange

Term	Definition
Counterion	Ion in solution that can exchange with an ion attached to a stationary functional group.
Empty-bed contact time	Volume of the resin in the bed including pore volume divided by the volumetric flow rate to the fixed bed.
Film diffusion	Effective rate at which ions migrate across the stagnant film surrounding the resin particles in the fixed bed.
Gel-type resin	Translucent polymeric resin with low degree of crosslinking and a high water content with an open matrix.
Helfferich number	Ratio of the rate of mass transfer by film diffusion to the rate of mass transfer by intraparticle diffusion.
Intraparticle diffusion	Effective rate at which ions migrate inside the resin particles.
Ion exchange	Process in which ions attached to a stationary functional group exchange for ions in a solution. Ions are exchanged on an equivalence basis.
Macroreticular resin	Opaque polymeric resin having a high degree of crosslinking and low water content with a closed matrix.
Presaturant ion	Ion that comes attached to the virgin resin or is exchanged onto the resin during the regeneration process.
Regeneration curves	Breakthrough curves obtained from a fixed-bed ion exchange operation during the regeneration cycle.
Resin swelling	Enlarging of an ion exchange resin due to the exchange of a larger preferred ion over a smaller less preferred ion.
Saturation loading curves	Breakthrough curves obtained from a fixed-bed ion exchange operation during the loading cycle.

Term	Definition
Selectivity	Preference of one ion over another for exchange onto an ion exchange site on a resin.
Separation factor	Quantitative description of the preference of one ion over another for a given ion exchange resin.
Service flow rate	Volumetric flow rate to the ion exchange column divided by the volume of the resin in the bed including pore volume.
Strong acid cation resin	Ion exchange resin that will readily give up a proton over a wide pH range.
Strong base anion resin	Ion exchange resin that will readily give up a hydroxide ion if the pH is less 13.
Synthetic resins	Spherical beads that contain a network of crosslinked polymers containing functional groups.
Total ion exchange capacity	Total amount of chemical equivalents available for exchange per unit weight or unit volume of resin.

Ion exchange is a process used to remove dissolved ionic constituents that can cause aesthetic and health issues. The ion exchange process for water treatment is considered to be a nonconventional process because it is not widely used in large-scale plants. The types of ion exchange materials used in water treatment, basic mechanisms involved in the ion exchange process, process design considerations, and example problems that apply ion exchange fundamentals to system design and operation are discussed in this chapter.

16-1 Evolution of Ion Exchange Technology

In drinking water treatment applications, ion exchange is primarily used for water softening and demineralization (e.g., removal of Ca^{2+}, Mg^{2+}, Na^+, Cl^-, $SO_4{}^{2-}$, $NO_3{}^-$). The vast majority of ion exchange installations in the United States are small, point-of-use devices at individual households. The application of ion exchange to municipal systems has been limited. Applications include the removal of hardness (softening), nitrate, barium, radium, arsenic, perchlorate, and chromate. There have been several full-scale systems designed for industrial applications, such as the demineralization of water for prevention of scale formation in power plant boilers, removal of calcium and magnesium in car-washing facilities, and production of ultrapure water for making pharmaceuticals and semiconductor materials.

With increased concern for the health effects of other contaminant ions such as barium, radium, fluoride, nitrate, arsenate, perchlorate, and

uranium, the use of ion exchange and inorganic adsorbents for full-scale applications in water treatment has increased. While much attention has been placed on the use of conventional synthetic ion exchange resins, research is ongoing to develop specialty resins that are selective for some contaminant ions. Natural and synthetic inorganic materials (e.g., zeolites) that have adsorption properties and exhibit favorable capacities for contaminant ions are also being developed and evaluated.

Natural Exchange Materials

In water treatment applications, ion exchange involves the exchange of an ion in the aqueous phase for an ion in the solid phase. The solid phase or ion exchanger is insoluble and can be of natural origin such as kaolinite and montmorillonite minerals or a synthetic material such as a polymeric resin. These exchangers have fixed charged functional groups located on their external and/or internal surface, and associated with these groups are ions of opposite charge called ''counterions'' (see Fig. 16-1a). These mobile counterions are associated by electrostatic attraction to each of the charged functional groups to satisfy the criterion that electroneutrality is maintained at all times within the exchange material as well as in the bulk aqueous solution. Depending on the charge of the functional group on the exchanger, the counterion can either be a cation if the functional group is negative or an anion if the functional group is positive and can exchange with another counterion in the aqueous phase.

The application of natural ion exchange materials for water treatment may have been used as far back as biblical times when Moses sweetened the waters of Mariah (Exodus 15:23–25). In approximately 320 BC, Aristotle
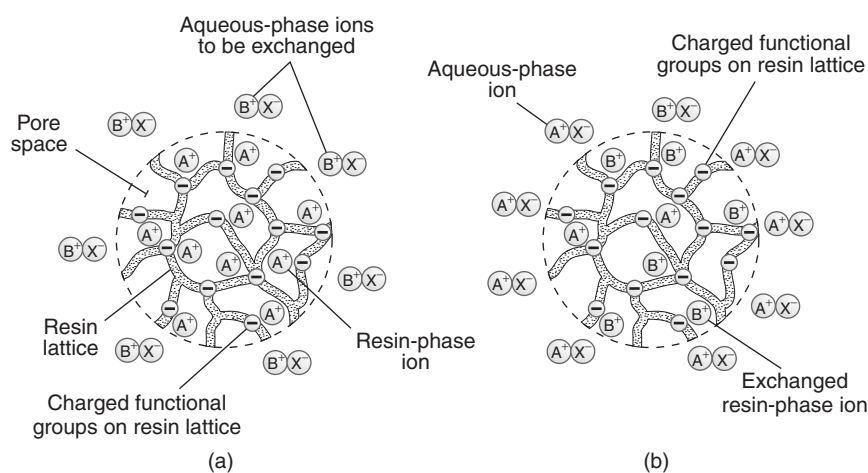
Figure 16-1
Schematic framework of functional cation exchange resin: (a) resin initially immersed in an aqueous solution containing B^+ cations and X^- anions and (b) cation exchange resin in equilibrium with aqueous solution of B^+ cations and X^- anions.

used 20 earthen containers containing a material with ion exchange properties to produce freshwater from seawater (Wachinski and Etzel, 1997). It was not until 1854 that the first reported systematic study of the ion exchange phenomenon was reported by Thompson and Way (Kunin and Myers, 1950). They observed ammonium ions adsorbing onto soils, releasing calcium ions in equivalent amounts, and the aluminum silicates present in the soils were responsible for the exchange. In 1876, Lemberg observed that the mineral leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$) could be transformed into analcite ($Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$) by leaching the mineral with a solution of sodium chloride (Kunin and Myers, 1950).

In the early twentieth century, many contributions were made in the understanding of the ion exchange phenomenon in clays, peat, charred bone, soils, and other silicates. In fact, one of the first known synthetic mineral ion exchange materials was developed and composed of processed natural greensand, which is referred to as a natural zeolite material. Although these zeolite materials exhibited low capacities and poor abrasion characteristics, they were the first exchangers used in large quantities for water treatment application.

Synthetic Exchange Materials

In 1935, development of sulfonated coal exchangers by Leibknecht in Germany and synthetic phenol–formaldehyde exchangers by Adams and Holmes in England led to the discovery of the first synthetic resin materials that were stable and had high anion exchange capacities (Kunin and Meyers, 1950). Unlike aluminosilicate zeolites, these materials were highly resistant to regenerant solutions of mineral acids. The discoveries of these researchers led D'Alelio to develop and patent sulfonated, crosslinked polystyrene resins in 1945 (Kunin and Meyers, 1950). The work of Leibknecht, Adams, Holmes, and D'Alelio forms the basis of modern-day synthetic organic ion exchangers. The first large domestic ion exchange facility was a softening plant (756 ML/d or 20 mgd) built by the Metropolitan Water District of Southern California (Streicher et al., 1947). The plant was first built in 1946 using silica-based synthetic media but was later converted to modern polystyrene divinyl benzene resin. It was operated until the early 1970s.

Exchange Mechanisms for Synthetic Resins

For most ion exchange applications in water treatment, synthetic organic resins are utilized because of their relatively large available exchange capacities and ease of regeneration. The schematic framework of a synthetic organic cation ion exchange resin initially immersed in an aqueous solution containing cation B^+ with its coion X^- is illustrated on Fig. 16-1a. The resins are spherical beads consisting of a network of crosslinked polymers containing functional groups with fixed coions, which are negative ($-$) charges located on each functional group along the polymer matrix. Associated with these fixed coions are A^+ cations, which are mobile and free to move in the pores of the polymer matrix. Cation A^+ is referred to as the presaturant ion.

When the cation exchange resin (saturated with A^+) is immersed in solution, there is a tendency for A^+ to diffuse into the bulk solution and X^- into the resin because of the concentration differences between the solution and resin phases. If these ions carried no charge, then their concentration differences would equalize by diffusion, and equilibrium would be obtained. However, because the ions are charged and electroneutrality is maintained, initially there is a small migration of A^+ into the bulk solution and X^- into the resin, causing a net positive charge in the bulk solution and a net negative charge in the ion exchanger. The first few A^+ ions diffusing into the bulk solution and X^- ion diffusing into the resin establish an electric potential difference between the bulk solution and the resin phase. This potential difference, called the *Donnan potential*, causes a small shortage of anions in the bulk solution and cations within the resin phase, which acts to maintain electroneutrality. The Donnan theory was developed to explain the equilibrium behavior of ion distributions across membranes (Helfferich, 1995; Weber, 1972). Consequently, counterion B^+ can diffuse into the negatively charged resin phase and replace A^+ stochiometrically while X^- anions are repelled back into the positively charged bulk solution due to this Donnan exclusion potential. As shown on Fig. 16-1b, equilibrium is established eventually where the concentration differences of the ions are balanced by the electric field. In other words, the electrical potentials are equal in both phases because the voltage difference is balanced by the concentration difference. At equilibrium, the resin phase will still contain a higher concentration of counterions A^+ and B^+ than in the bulk solution, and electroneutrality will be maintained between the bulk solution and the resin phase. A similar explanation can be made for a strong-base anion exchange resin with the exception being the charges are reversed.

16-2 Synthetic Ion Exchange Media

Synthetic ion exchange resins are almost always used in water treatment practices. Synthetic polymeric resins are very durable and their properties can be modified to selectively remove both anions and cations. The resins can be regenerated using various salt or acid solutions depending upon the particular application. A discussion of the structure, manufacturing process, and various types of synthetic resins is presented below.

Resin Structure   Ion exchange polymeric resin is composed of a three-dimensional, crosslinked polymer matrix that contains covalently bonded functional groups with fixed ionic charges. Vinyl polymers (typically, polystyrene and polyacrylic) are used for the resin matrix backbone. Divinylbenzene (DVB) is used to crosslink the polymer backbone. The overall steps involved in making both polyacrylic and polystyrene cation exchange resins are displayed on Fig. 16-2.

Figure 16-2
Major steps involved in synthesis of cation ion exchange resin by polymerization of (a) methacrylic acid with divinylbenzene crosslinking and (b) styrene with divinylbenzene crosslinking followed by sulfonation. (Adapted from Weber, 1972)

An important distinction for resins, with respect to their polymeric backbone, is whether the resin is a microreticular (gel) or macroreticular resin, which depends upon the degree of crosslinking within the resin's polymer backbone. Gel-type resins have about 4 to 10 percent DVB crosslinking with a typical value of 8 percent. The pore structure of a gel-type resin is determined by the distances between the polymer chains and crosslinking member that vary with (1) the exchanging ions, (2) ionic strength, (3) temperature, (4) the number of fixed ionic charges, and (5) the degree of crosslinking. Gel-type resins are translucent with high water content and can exhibit a significant amount of swelling or shrinking depending on the presaturant ion. Because gel-type resins lose their pore structure upon drying, they have very low Brunauer–Emmett–Teller (BET) nitrogen surface areas (see Chap. 15 for discussion of BET surface area), typically less than 2 m^2/g. The ion exchange rate is very fast for a gel-type resin due to its rather open matrix (Kunin, 1979; Rohm and Haas, 1975).
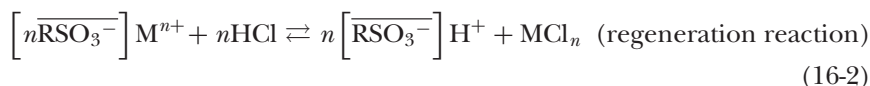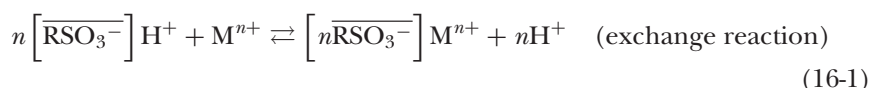
Macroreticular resins have approximately 20 to 25 percent DVB crosslinking and are opaque. Macroreticular resins are made up of microspheres linked together to form a resin bead (Kunin, 1979; Rohm and Haas, 1975). Macroreticular resins retain their structural integrity when dried, and as a result, they have BET surface areas of about 7 to 600 m²/g and particle porosities of 20 to 60 percent. In addition, macroreticular resins do not swell or shrink significantly due to ion exchange reactions.

Classification of Resins by Functional Groups

Based on the functional groups bonded to the resin backbone, the four general types of exchange resins are (1) strong-acid cation (SAC), (2) weak-acid cation (WAC), (3) strong-base anion (SBA), and (4) weak-base anion (WBA). The distinctions are based on the pK values of the functional groups as summarized in Table 16-1. These resin types are discussed in more detail in the following sections.

STRONG-ACID EXCHANGERS

In SAC exchange resins, a charged sulfonate group typically acts as the exchange site. The term ''strong'' in SAC has nothing to do with the physical strength of the resin but is derived from Arrhenius theory of electrolyte strength in which the functional group on the resin is dissociated completely in its ionic form at any pH. In other words, the resin's low pK_a (<0) implies SAC exchangers will readily give up a proton over a wide pH range (1 to 14). The general exchange and regeneration reactions for the hydrogen form can be written as

$$n\left[\overline{\mathrm{RSO_3^-}}\right]\mathrm{H^+} + \mathrm{M}^{n+} \rightleftarrows \left[n\overline{\mathrm{RSO_3^-}}\right]\mathrm{M}^{n+} + n\mathrm{H^+} \quad \text{(exchange reaction)}$$

$$\text{(16-1)}$$

$$\left[n\overline{\mathrm{RSO_3^-}}\right]\mathrm{M}^{n+} + n\mathrm{HCl} \rightleftarrows n\left[\overline{\mathrm{RSO_3^-}}\right]\mathrm{H^+} + \mathrm{MCl}_n \quad \text{(regeneration reaction)}$$

$$\text{(16-2)}$$

In Eq. 16-1, the overbar refers to the immobile resin phase, $\mathrm{H^+}$ is the presaturant ion associated with the resin before exchange, M^{n+} is the counterion in solution being exchanged out of solution, and n is the charge on the counterion in solution. For the reaction shown in Eq. 16-1, based on the pK_a of SAC resins and the large hydrated radius of hydrogen, SAC resins have little affinity for hydrogen ion and will readily exchange it for another cation. Because the hydrated radius of the $\mathrm{H^+}$ ion in a SAC exchanger is much larger than other cations, the resin will typically shrink upon exchange (≈ 7 percent for a gel-type resin, 3 to 5 percent for macroreticular type resin). The sodium form of a SAC will also behave in a similar manner, although the shrinkage will be less than observed for the hydrogen form. Equation 16-2 represents the regeneration expression for a strong-acid cation exchange resin using HCl as the regenerant solution.

Table 16-1
Characteristics of ion exchange resins used in water treatment processes

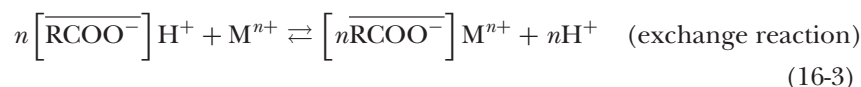| Resin Type	Acronym	Fundamental Reaction[a]	Regenerant Ions (X)	pK	Exchange Capacity, meq/mL	Constituents Removed
Strong-acid cation	SAC	$n[RSO_3^-]X^+ + M^{n+}$ $\rightleftharpoons [nRSO_3^-]M^{n+} + nX^+$	H^+ or Na^+	<0	1.7–2.1	H^+ form: any cation; Na^+ form: divalent cations
Weak-acid cation	WAC	$n[RCOO^-]X^+ + M^{n+}$ $\rightleftharpoons [nRCOO^-]M^{n+} + nX^+$	H^+	4–5	4–4.5	Divalent cations first, then monovalent cations until alkalinity is consumed
Strong-base anion (type 1)	SBA-1[b]	$n[R(CH_3)_3 N^+]X^- + A^{n-}$ $\rightleftharpoons [nR(CH_3)_3 N^+]A^{n-} + nX^-$	OH^- or Cl^-	>13	1–1.4	OH^- form: any anion; Cl^- form: sulfate, nitrate, perchlorate, etc.
Stong-base anion (type 2)	SBA-2[c]	$n[R(CH_3)_2(CH_3CH_2OH)N^+]X^- + A^{n-}$ $\rightleftharpoons [nR(CH_3)_2(CH_3CH_2OH)N^+]A^{n-} + nX^-$	OH^- or Cl^-	>13	2–2.5	OH^- form: any anion; Cl^- form: sulfate, nitrate, perchlorate, etc.
Weak-base anion	WBA	$[R(CH_3)_2N]HX + HA$ $\rightleftharpoons [R(CH_3)_2N]HA + HX$	OH^-	5.7–7.3	2–3	Divalent anions first, then monovalent anions until strong acid is consumed

[a]Term within brackets represents the solid phase of the resin.
[b]Greater regeneration efficiency and capacity than SBA-2.
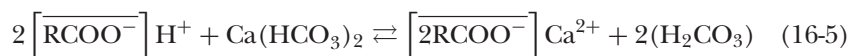[c]Greater chemical stability than SBA-1.

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WEAK-ACID EXCHANGERS

In WAC exchange resins the functional group on the resin is usually a carboxylate and the exchange reaction can be written as

$$n\left[\overline{\mathrm{RCOO^-}}\right]\mathrm{H^+} + \mathrm{M}^{n+} \rightleftarrows \left[n\overline{\mathrm{RCOO^-}}\right]\mathrm{M}^{n+} + n\mathrm{H^+} \quad \text{(exchange reaction)}$$

$$(16\text{-}3)$$

$$\left[n\overline{\mathrm{RCOO^-}}\right]\mathrm{M}^{n+} + n\mathrm{HCl} \rightleftarrows n\left[\overline{\mathrm{RCOO^-}}\right]\mathrm{H^+} + \mathrm{MCl}_n$$

$$\text{(regeneration reaction)} \quad (16\text{-}4)$$

Weak-acid cation resins have $\mathrm{p}K_a$ values in the range of 4 to 5 and thus will not readily give up a proton unless the pH is greater than 6. At a pH less than 6, WAC resins have a great affinity for hydrogen and will not exchange it for another cation; therefore, the apparent cation exchange capacity of a WAC exchanger is a function of pH. As the pH increases, the apparent capacity increases to a maximum total capacity between pH values of 10 and 11.

Weak-acid exchangers usually require alkaline species in the water to react with the more tightly bound hydrogen ions. Consider the following reaction between a weak-acid exchanger and alkalinity:
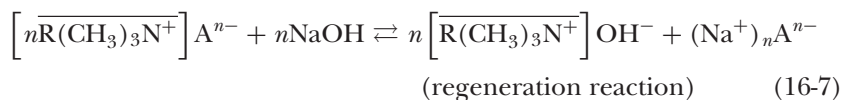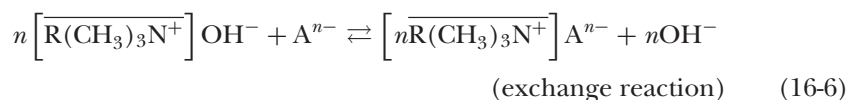
$$2\left[\overline{\mathrm{RCOO^-}}\right]\mathrm{H^+} + \mathrm{Ca(HCO_3)_2} \rightleftarrows \left[\overline{2\mathrm{RCOO^-}}\right]\mathrm{Ca}^{2+} + 2(\mathrm{H_2CO_3}) \quad (16\text{-}5)$$

The exchange is essentially neutralization with bicarbonate alkalinity neutralizing the $\mathrm{H^+}$ on the resin. Weak acids will dissociate alkaline salts such as $\mathrm{NaHCO_3}$ but not nonalkaline salts like NaCl or $\mathrm{NaSO_4}$. Because weak-acid exchangers exhibit a higher affinity for $\mathrm{H^+}$ than strong-acid exchangers do, they exhibit higher regeneration efficiencies. Weak-acid resins do not require as high a concentration of regenerant as required for regenerating strong-acid resins to the hydrogen form. The carboxylic functional groups will utilize up to 90 percent of the acid (HCl or $\mathrm{H_2SO_4}$) regenerant, even with low acid concentrations. By comparison, strong-acid resin regeneration requires a large excess of regenerant solution to provide the driving force for exchange to take place.

Weak-acid exchangers have been used in water treatment to remove cations in high-alkaline (e.g., high $\mathrm{CO_3}^{2-}$, $\mathrm{OH^-}$, and $\mathrm{HCO_3}^-$ concentrations) waters with low dissolved carbon dioxide and sodium. Simultaneous softening and dealkalization can be accomplished with weak-acid exchangers. It has also been reported that sometimes WBA resins are used in conjunction with strong-acid exchangers to reduce regenerant requirements and produce treated water with the same quality as just using strong-acid exchangers alone.
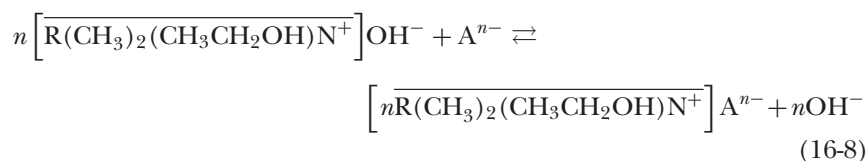
STRONG-BASE EXCHANGERS

Strong-base anion exchange resins typically have a quaternary amine group as the fixed positive charge. For a type 1 quaternary group, the exchange

reaction for a resin in the hydroxide form can be written as

$$n\left[\overline{R(CH_3)_3N^+}\right]OH^- + A^{n-} \rightleftarrows \left[n\overline{R(CH_3)_3N^+}\right]A^{n-} + nOH^-$$

(exchange reaction)   (16-6)

$$\left[n\overline{R(CH_3)_3N^+}\right]A^{n-} + nNaOH \rightleftarrows n\left[\overline{R(CH_3)_3N^+}\right]OH^- + (Na^+)_n A^{n-}$$

(regeneration reaction)   (16-7)

For a type 2 quaternary group, the exchange reaction for a resin in the hydroxide form can be written as

$$n\left[\overline{R(CH_3)_2(CH_3CH_2OH)N^+}\right]OH^- + A^{n-} \rightleftarrows$$

$$\left[n\overline{R(CH_3)_2(CH_3CH_2OH)N^+}\right]A^{n-} + nOH^-$$

(16-8)

As shown in Eqs. 16-6 and 16-8, the main difference between type 1 and type 2 resins is the ethanol group in the type 2 quaternary amine. The purpose of the ethanol group is to reduce the resin's affinity for hydroxide ions. Strong-base anion resins have pK_b values of 0 to 1, implying that they will readily give up a hydroxide ion if the pH value is less than 13. The operational pH of SBA resins (pH < 13) makes the apparent anionic exchange capacity independent of pH. Strong-base anion exchangers in the hydroxide form will shrink upon exchange due to other anions typically having hydrated radii smaller than hydroxide. Type 1 has a slightly greater chemical stability, while type 2 has a slightly greater regeneration efficiency and capacity.
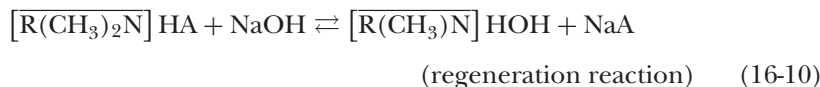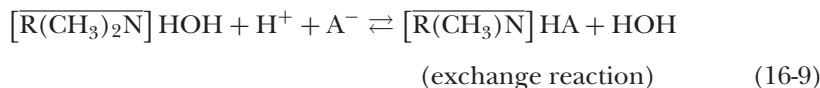
Strong-base anion resins are less stable than strong-acid resins and are characterized by the fishy odor of amines even at room temperature. Strong-base anion exchange resins will degrade to release both the tertiary amine and methanol at $60°C$ (Bolto and Pawlowski, 1987).

Strong-base exchangers traditionally have been used for many years to demineralize water. However, more recently SBA exchangers are increasingly being used to treat waters contaminated with nitrate, arsenic, and perchlorate ions and are usually operated in the chloride cycle, where the resin is regenerated with NaCl (Clifford and Weber, 1978; Clifford et al., 1987; Ghurye et al., 1999; Najm et al., 1999).

WEAK-BASE EXCHANGERS

In WBA exchange resins the exchange site is a tertiary amine group, which does not have a permanent fixed positive charge. Weak-base anion exchange resins are available in either chloride or freebase forms. The freebase designation indicates that the tertiary amine group is not ionized but has a water molecule (HOH) associated with it. The tertiary amine groups will adsorb ions without the exchange of an ion (Helfferich, 1995).

The exchange reaction for a WBA resin in the freebase form can be written as

$$\left[\overline{R(CH_3)_2N}\right] HOH + H^+ + A^- \rightleftarrows \left[\overline{R(CH_3)N}\right] HA + HOH$$

$$\text{(exchange reaction)} \qquad (16\text{-}9)$$

$$\left[\overline{R(CH_3)_2N}\right] HA + NaOH \rightleftarrows \left[\overline{R(CH_3)N}\right] HOH + NaA$$

$$\text{(regeneration reaction)} \qquad (16\text{-}10)$$

The reaction in Eq. 16-9 can be viewed as the ionization of the resin by hydrogen and the consequent uptake of the anion.

Weak-base anion resin behavior can also be described as the adsorption of a weak acid with the tertiary amine group acting as a Lewis base and the release of HOH as shown:

$$\left[\overline{R(CH_3)_2N}\right] HOH + HA \rightleftarrows \left[\overline{R(CH_3)_2N}\right] HA + HOH \qquad (16\text{-}11)$$

The weak-base designation is derived from the WBA resin's pK_b values of 5.7 to 7.3. Weak-base anion resins will not readily give up hydroxide ion unless the pOH is greater than the pK_b of the resin (pH values less than 8.3 to 6.7 at $25°C$). In many respects, the weak-base exchangers behave much like weak-acid exchangers. The weak-base resins remove free mineral acidity such as HCl or H_2SO_4 but will not remove weakly ionized acids such as silicic and carbonic, which is why these resins are sometimes called ''acid adsorbers.''

Weak-base resins can be regenerated using NaOH, NH_4OH, or Na_2CO_3. The regeneration efficiencies of these resins are much greater than for strong-base resins. Weak-base exchangers are used in conjunction with strong-base exchangers in demineralizing systems to reduce regenerant costs and to attract organics that might otherwise foul the strong-base resins. Where silica removal is not critical, weak-base resins may be used alone or in conjunction with an air stripper to remove CO_2.

16-3 Properties of Ion Exchange Media

Two types of properties are important for ion exchange: (1) engineering properties and (2) physical properties. The engineering properties consist of the exchange capacity and selectivity of the resin. Engineers use exchange capacity and selectivity relationships to determine the performance of the resin under specific operating conditions. The physical properties consist of particle size, stability, swelling, moisture, and density of the resin. Physical properties are important in the selection of resins for specific water treatment applications. For example, the resin particle size must be large enough to minimize column pressure drop while in operation but small enough to enable fast mass transfer of the ions for exchange. The

resins must also be durable enough to undergo swelling and shrinking of the resin during regeneration and loading. All the properties described above and the forces that impact them are discussed below.

The exchange capacity and selectivity are two important engineering parameters when considering the column design and operation of the column. The exchange capacity allows the engineer to determine how much the ionic constituent can be retained by the resin for a given resin volume. The selectivity provides the engineer with information on which ionic constituents in the water are preferred by the resin.

<div style="float:right">**Engineering Properties of Resins**</div>

EXCHANGE CAPACITY

An important property of an ion exchange resin is the quantity of counterions that can be exchanged onto the resin. This exchange capacity can be expressed in terms of total (theoretical) capacity or effective capacity. The effective capacity is that part of the total capacity that can be utilized in a column operation, which is dependent on operating conditions such as service flow rate (SFR), regeneration level, regeneration flow rate, and water quality. Because the effective capacity is site specific, the total capacity is discussed here.

Total exchange capacity

The total capacity is dependent upon the quantity of functional groups in the copolymer bead. For SAC exchange resins, one sulfonate group, on average, can be attached to each benzene ring in the matrix. Hence, the dry-weight capacity of the resin can be determined and is usually expressed in terms of milliequivalents per gram of dry resin (meq/g). For example, if a gel-type SAC in the hydrogen form has a functional monomer with an empirical formula of $C_8H_7 \cdot SO_3^-H$ (molecular weight 184) and 1 eq of exchangeable hydrogen ion, the theoretical capacity would be 1 eq per 184 g of dry resin or 5.4 meq/g dry resin (Harland and Prud'homme, 1992). Reported values are actually lower than the calculated values because some of the benzene rings are occupied by the DVB crosslinking and the materials are not homogeneous. Measurement of dry-weight capacities can be determined from direct titration of a known volume of resin. For sulfonated styrene–DVB resins, the reported dry-weight capacity is typically 5.0 ± 0.1 meq/g (Anderson, 1979). For SBA exchange resins, more or less than one functional group can be attached to the benzene ring. Consequently, the dry-weight capacity is more variable than with strong-acid resins and can range from 2 to 5 meq/g.

Expressions for exchange capacity

In most ion exchange literature, the capacity is expressed in terms of a wet-volume capacity. The wet-volume capacity depends upon the moisture

Table 16-2

Properties of styrene–divinylbenzyl, gel-type strong-acid cation and strong-base anion resins

Parameter	Unit	Strong-Acid Cation Resin	Type I, Strong-Base Anion Resin
Screen size, U.S. mesh	—	16×50	16×50
Shipping weight	kg/m^3	850	700
	(lb/ft^3)	(53)	(44)
Moisture content	%	45–48	43–49
pH range	—	0–14	0–14
Maximum operating Temperature	°C	140	OH$^-$ form 60, Cl$^-$ form 100
Turbidity tolerance	NTU	5	5
Iron tolerance	mg/L as Fe	5	0.1
Chlorine tolerance	mg/L Cl$_2$	1.0	0.1
Backwash rate	M/h	12–20	4.9–7.4
	(gal/min · ft^2)	(5–8)	(2–3)
Backwash period	min	5–15	5–20
Expansion volume	%	50	50–75
Regenerant and concentration[a]	%	NaCl, 3.0–14	NaCl, 1.5–14
Regenerant dose	kg NaCl/m^3 resin	80–320	80–320
	(lb/ft^3)	(5–20)	(5–20)
Regenerant rate	BV/min	0.067	0.067
	(gal/min ft^3)	(0.5)	(0.5)
Rinse volume	BV	2–5	2–10
	(gal/ft^3)	(15–35)	(15–75)
Exchange capacity	meq/mL as CaCO$_3$,	1.8–2.0	1–1.3
	(kgr/ft^3 as CaCO$_3$)[b]	(39–41)	(22–28)
Operating capacity[c]	meq/mL as CaCO$_3$,	0.9–1.4	0.4–0.8
	(kgr/ft^3 as CaCO$_3$)[b]	(20–30)	(12–16)
Service flow rate	BV/h	8–40	8–40
	(gal/min · ft^3)	(1–5)	(1–5)

[a]Other regenerants such as H$_2$SO$_4$, HCl, and CaCl$_2$ can also be used for SAC resins while NaOH, KOH, and CaCl$_2$ can be used for SBA regeneration.
[b]Kilograins CaCO$_3$/ft^3 are the units commonly reported in resin manufacturer literature. To convert kgr CaCO$_3$/ft^3 to meq/mL, multiply by 0.0458.
[c]Operating capacity is based on Amberlite IR-120 SAC resin. Operating capacities depend on method of regeneration and amount of regenerant applied. Manufacturers should provide regeneration data in conjunction with operating capacities for their resins.
Source: Adapted from Clifford et al., (2011).

content of the resin, which is dependent upon the functional form of the resin and will vary for a given type of resin. The wet-volume capacity is commonly expressed in milliequivalents per milliliter of resin (meq/mL), although it may also be expressed in terms of kilograins as $CaCO_3$ per cubic foot (kgr/ft^3) of resin. There are 21.8 meq/mL in 1 kgr/ft^3. As shown in Table 16-2, typical SAC exchange capacities are 1.8 to 2.0 meq/mL in the sodium form and SBA exchange capacities are 1.0 to 1.3 meq/mL in the chloride form. Weak-acid cation exchange capacities are about 4.0 meq/mL in the H$^+$ form and WBA exchange capacities are around 1.0 to 1.8 meq/mL in the freebase form, although WAC and WBA resin capacities are variable due to their partially ionized conditions and because exchange capacity is also a function of pH.

Given two different ion forms of the same resin, the capacity on a volume basis will be different due to differences in water content. The same is true for the same resin but with different degrees of crosslinking. The volume capacity is inversely proportional to the swelling of the resin. The resin volume is determined in a column in the presence of excess water after tapping the column to settle the resin. This resin volume includes the volume of the water within the interstices between resin particles. In a backwashed and settled bed, this void volume is usually 35 to 40 percent of the total bed volume.

SELECTIVITY

Ion exchange resins have a certain affinity or preference for ions in aqueous solution. This affinity or preference for a given resin is called selectivity. The direction, forward or reverse, of the ion exchange reactions shown in Eqs. 16-1 to 16-11 will depend upon the resin selectivity for a particular ion system. Take, for example, the exchange reaction shown in Eq. 16-6 for an SBA. If a dilute aqueous solution containing NO_3^- and Cl^- ions are being treated with a type I SBA resin in the OH^- form, both NO_3^- and Cl^- ions will be exchanged over the presaturant ion OH^- because they are preferred by the resin. In this case the reaction proceeds in the forward direction. Type I SBA resins also have a higher selectivity for NO_3^- ions over Cl^- ions so NO_3^- will occupy more exchange sites in a dilute solution.

Basis for selectivity

Resin selectivity depends upon the physical and chemical characteristics of the exchanging ion and resins. Chemical properties of the ions that impact selectivity are the magnitude of the valence and the atomic number of the ion. The physical properties of the resins that influence selectivity include pore size distribution and the type of functional groups on the polymer chains. The following discussion provides insight into these properties.

Example 16-1 Estimate resin requirements

A small public water system is considering removing nitrate from its water using ion exchange. The major ions contained in the well water are listed in the following table. The average daily flow rate is about 2000 m^3/d. If an SBA exchange resin is used, estimate the minimum daily volume of resin that would be required assuming that nitrate is removed completely and is the only anion exchanging on the resin. Use the information provided in Table 16-2.

| Cation	meq/L	Anion	meq/L
Ca^{2+}	1.8	Cl^-	3.5
Mg^{2+}	1.0	NO_3^-	0.5
Na^+	2.0		
Total	4.8	Total	4.8

Solution

1. Determine the minimum volume of resin required per day.
   a. From Table 16-2 the typical exchange capacity for a type I SBA resin is about 1.2 meq/mL resin (1 to 1.3 meq/mL).
   b. The required volume is

$$\left\{ \begin{array}{c} \text{Minimum} \\ \text{resin volume} \end{array} \right\} = (0.5 \text{ meq NO}_3 - \text{N/L})(2.0 \times 10^6 \text{ L/d})$$

$$(\text{mL resin}/1.2 \text{ meq})$$

$$= 8.32 \times 10^5 \text{ mL/d} = 0.832 \text{ m}^3/\text{d}$$

Comment

This type of "back-of-the-envelope" calculation is valuable when a first estimate of the resin requirements is needed for a preliminary calculation. In most cases, the resin requirement will be higher due to the presence of other anions in the water (e.g., sulfate) that will compete with nitrate ions for exchange sites, as discussed in the section on ion exchange equilibrium.

For dilute aqueous-phase concentrations at temperatures encountered in water treatment, ion exchange resins prefer the counterion of higher valence, as shown below:

Cations: $Th^{4+} > Al^{3+} > Ca^{2+} > Na^+$

Anions: $PO_4^{3-} > SO_4^{2-} > Cl^-$
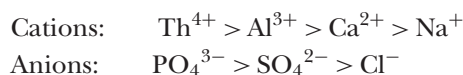
In the preference shown above, it is assumed that the spacing of the functional groups allow for the exchange of multivalent ions. Counterion preference increases with dilution of solution and is strongest with ion exchangers of high internal molality (Helfferich, 1995). Although empirical, this rule of thumb can be explained using the Donnan potential theory. As explained earlier for a cation exchanger, when a resin comes in contact with a dilute aqueous solution, large concentration gradients exist between the ions in the aqueous phase and the resin phase. The tendency is for the aqueous cations and anions to migrate into the resin phase and cations in the resin phase to migrate into the aqueous phase. However, the initial migration of ions establishes the Donnan potential, which repels any further anions from entering the resin that would cause any significant deviation from electroneutrality.

The potential attracts aqueous-phase cations into the resin to balance the diffusion of the resin-phase cations entering the aqueous solution and approaches zero when equilibrium is established. The force exerted by the Donnan potential on an ion is proportional to the ionic charge of the ion (Helfferich, 1995). A counterion with a higher charge is attracted more strongly and is preferred by the resin phase. The Donnan potential increases as the aqueous-phase concentration becomes more dilute and the molality of the fixed ionogenic groups on the resin increases. For large aqueous-phase ion concentrations, the exchange potentials of ions of different charge become negligible and ions of lower valence can sometimes be preferred over ions of higher valence.

There are some exceptions to the above general rule. For example, divalent CrO_4^{2-} has a lower preference than monovalent I^- and NO_3^- ions, as shown in the following series:

$$SO_4^{2-} > I^- > NO_3^- > CrO_4^{2-} > Br^-$$
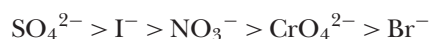
Effect of physical properties on selectivity
Resin selectivity can also be influenced by the degree of swelling or pressure within the resin bead. In an aqueous solution, both resin-phase ions and ions in aqueous solution have water molecules that surround them. The group of water molecules surrounding each ion is called the radius of hydration and is different for different ions. Typically, the radius of hydration becomes larger as the size of the ion decreases (see Table 16-3). When these ions diffuse in solution, the water molecules associated with them move as well. The crosslinking bonds that hold the resin matrix together oppose the osmotic forces exerted by these exchanged ions. These opposing forces cause the swelling pressure. In a dilute aqueous phase containing ion exchange resins, the ions with a smaller hydrated radius are preferred because they reduce the swelling pressure of the resin and are more tightly bound to the resin. As shown in Table 16-3 for a series of ions of equal charge, the hydrated radius is inversely proportional to the unhydrated

Table 16-3

Comparison of ionic, hydrated radii, molecular weight, and atomic number for a number of cations

| Ion	Ionic Radii,[a] Å	Hydrated Radii,[b] Å	Molecular Weight	Atomic Number
Li^+	0.60	10.0	6.941	3
Na^+	0.95	7.9	22.98977	11
K^+	1.33	5.3	39.0983	19
Rb^+	1.48	5.09	85.4678	37
Cs^+	1.69	5.05	132.9054	55
Mg^{2+}	0.65	10.8	24.305	12
Ca^{2+}	0.99	9.6	40.08	20
Sr^{2+}	1.13	9.6	87.62	38
Ba^{2+}	1.35	8.8	137.33	56

[a]From Mortimer (1975).
[b]From Kunin and Myers (1950).

ionic radius (Weber, 1972). For some alkali metals the order of preference for exchange is

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$

For alkaline earth metals the preference for exchange is

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Be^{2+}$$
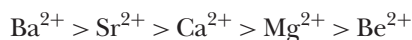
For a given series, anion exchange follows the same selectivity relationship with respect to ionic and hydrated radii as cations:

$$ClO_4^- > I^- > NO_3^- > Br^- > Cl^- > HCO_3^- > OH^-$$
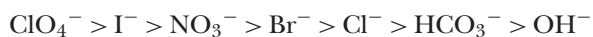
Consequently, for a given series of ions, the resin selectivity for ions increases with increasing atomic number, increasing ionic radius, and decreasing hydrated radius.

With the exception of specialty resins, WAC resins with carboxylic functional groups behave similar in preference to SAC resins with the exception that hydrogen is the most preferred ion. In a similar manner, the preference of anions for WBA resins is the same as for SBA resins with the exception that the hydroxide ion is the most preferred ion.

The above general rules for order of selectivity apply to ions in waters that have total dissolved solids (TDS) values less than approximately 1000 mg/L. The preference for divalent ions over monovalent ions diminishes as the ionic strength of a solution increases. For example, consider a sulfonic cation exchange resin operating on the sodium cycle. In dilute concentrations, calcium ion is much preferred over sodium; hence calcium will replace sodium on the resin structure. However, at high salt concentrations ($\approx$100,000 mg/L TDS), the preference reverses and this enhances
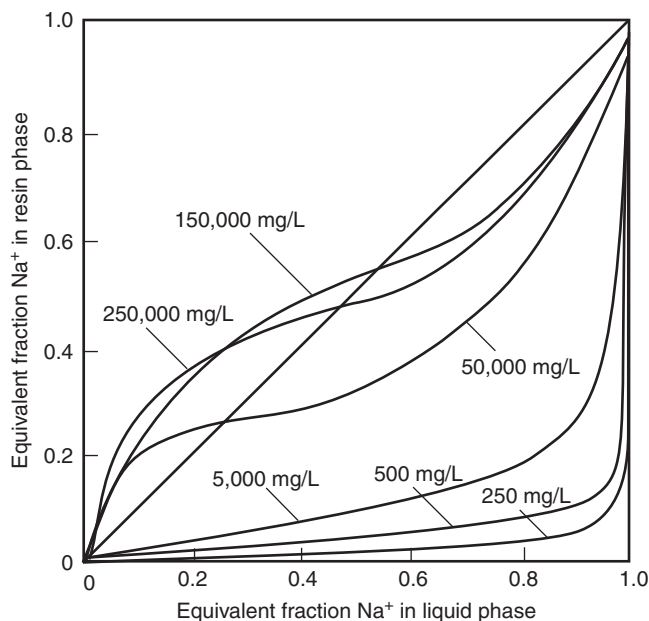
Figure 16-3
The Na^+–Ca^{2+} equilibria for sulfonic acid cation exchange resin. (Courtesy of Rohm and Haas.)

regeneration efficiency. Equilibrium isotherms for Na^+–Ca^{2+} exchange are shown on Fig. 16-3. As the TDS concentration increases, a higher concentration of sodium can be found in the resin phase. This is because as the salt concentration increases, the sodium concentration increases, and the activity coefficient for calcium decreases such that sodium is preferred over calcium.

Another important factor to consider in determining selectivity is the size of organic ions or inorganic complexes. A resin will exclude some of these ions by screening or sieving. Resins that exhibit this phenomenon are called molecular sieves. Ions too large to penetrate the resin matrix can be specifically excluded by proper selection of the resin properties. Increasing the crosslinking in the resin will produce a greater screening effect.

Most synthetic ion exchange resin materials have physical properties that make them ideal for water treatment applications such as softening, demineralization, and removal of potentially toxic ionic contaminants. For example, polystyrene and polyacrylic resins are highly stable, are very durable, and retain their predictable capacities over many years of operation. In fact, some of these resins have been in use for over 15 years. Physical properties such as mechanical, chemical, and thermal stability, water content or swelling potential, total and apparent capacities, ion exchange equilibrium, and kinetics are influenced by the resin polymeric structure.

Physical Properties of Resins

SWELLING, MOISTURE CONTENT, AND DENSITY

When resins exchange ions, the volume of the resin beads can change to reflect the differing magnitude of resin–counterion interactions, degree of resin crosslinking, and hydration. The swelling, moisture content, and density for several SAC, WAC, SBA, and WBA resins are summarized in Table 16-4. For all the resin types, the percentage of swelling decreases as the degree of crosslinking increases. Swelling of a resin due to exchange of ions can be reversible or irreversible. Reversible swelling is when the resin beads undergo a reversible volume change between one ionic form and another. The internal osmotic pressure of the resin bead increases when the resin swells and decreases when the beads shrink. Over time, the osmotic pressure swings can cause the beads to fracture, which is more likely to occur on macroporous resins than on gels. Swelling should be considered in the design of the ion exchange columns.

Table 16-4
Physical properties of several ion exchange resins

Resin	Bulk Wet Density, kg/m³	Moisture Content Drained, % by Weight	Swelling Due to Exchange, %
SAC resins—sulfonated polystyrene			
2% crosslinked	720	72–82	12–15
5–6% crosslinked	769–849	58–65	5–10
12% crosslinked	753–929	37–49	4–9
Sulfonated phenolic	640–961	44–68	7
WAC resins—acrylic or methacrylic			
Weakly crosslinked	800	51–75	60–90
Medium crosslinked	721–800	46–62	10–90
Macroporous	688–800	56	5–10
SBA resins—polystyrene matrix, trimethyl benzyl ammonium			
2% crosslinked	705	70–78	20
4% crosslinked	673	60	14
8% crosslinked	720	34–56	15–20
WBA resins			
Aminopolystyrene	640–720	25–45	5–30
Aminated acrylic polymers	240–304	1–5	3
Epoxy-polyamine	689	50–62	6–25

Source: Adapted from Perry and Chilton (1973).

Irreversible swelling is observed with acrylic SBA resins where during the first few regeneration cycles the resins can irreversibly swell 7 to 10 percent over and above the reversible volume changes (Harland, 1994).

Because the water content of a resin can vary, the resin densities of different forms of the resin can also vary. The density will depend upon the quantity of water and the ionic form of the resin. The specific gravity of wet SAC resins will vary from 1.10 to 1.35, while the wet specific gravity of SBA resins vary from 1.05 to 1.15. The bulk or shipping weight of most wet strong-acid and strong-base resins vary from 675 to 900 kg/m^3 (42 to 56 lb/ft^3). Several physical properties of both strong-acid and strong-base resins are shown in Table 16-2.

PARTICLE SIZE

Ion exchange resin beads are spherical in shape and are commercially available in particle diameter sizes of 0.04 to 1.0 mm. In the United States, the particle sizes are listed according to standard screen sizes, or "mesh" values. A comparison of metric mesh sizes is given in Table 16-5. The most common size ranges used in large-scale applications are 16 to 50 and 50 to 100 mesh size.

Manufacturers usually provide three parameters related to particle size: (1) particle size range, (2) effective size (ES), and (3) uniformity coefficient (UC). The size range provides the minimum and maximum particle sizes for a given manufactured lot of resin beads. The ES is the mesh size in millimeters that passes 10 percent of a sieved sample, d_{10}. The UC is defined as the ratio of the d_{60} to the d_{10} resin sizes. For ion exchange resins UC values are usually in the range of 1.4 to 1.6; however, it is possible to obtain resins with smaller UCs required by kinetic or hydraulic restrictions. The ES and UC of resins can be obtained from the resin manufacturer.

Particle size has two major influences on ion exchange applications. First, the rate of ion exchange decreases with increasing particle size. An increase in resin particle size for the same mass of resin will decrease the film diffusion rate and increase the intraparticle diffusion path length. Second, the head loss through the bed increases with decreasing particle

Table 16-5
Particle size in U.S. mesh and millimeters

U.S. Standard Screen Size	Particle Diameter, mm	Geometric Mean Size, mm
16–20	1.2–0.85	1.01[a]
20–50	0.85–0.30	0.50
50–100	0.30–0.15	0.21
100–200	0.15–0.08	0.11
200–400	0.08–0.04	0.056

[a]Calculated as $\sqrt{0.85 \times 1.2} = 1.01$ mm.

size, subjecting the beads to situations that could cause breakage. In many ion exchange applications, the design is based on hydraulic requirements of the resin beads and the vessel rather than on ion exchange kinetics.

STABILITY

The stability of an ion exchange resin can be an important process design consideration under certain physical, chemical, and/or radioactive conditions. Chemical reactions between the resin matrix and dissolved constituents in water, physical impairment of resin performance due to fouling by organic and inorganic constituents, and some process operating conditions can significantly affect the resin performance and cost. Consequently, it is important to understand these interactions and take steps in the design stages to identify and prevent conditions that would negatively alter the resin's performance and the possible release of material from the resin to the finished water.

Effect of physical factors

As stated above, the stability of the resin may be impacted by either chemical or physical means. Physical stresses such as excessive swelling and shrinking, mechanical compression due to large hydraulic pressure drops across the resin bed, and abrasion due to excessive backwashing can significantly reduce the structural integrity of the resin bead and thereby shorten the resin operating life. With respect to swelling and shrinking, the acrylic resin is particularly durable due to its more elastic properties compared to the more rigid polystyrene matrix. However, in column operations with high operating pressures, the elasticity of acrylic resins can cause the beads to compress and result in inadequate liquid distribution and reduced flow.

Effect of chemical factors

Strong-acid cation exchange resins, especially the sulfonated polystyrene–DVB type, can be susceptible to oxidation. For example, oxidation can occur from free-chlorine attack of the DVB crosslinking, causing increased moisture retention of the resin, weakening the resin structurally, leading to compression of the beads, and affecting the service cycle. In addition, the resin can also lose capacity and must eventually be replaced. If an oxidant in the process water is unavoidable, it may be beneficial to use a resin with higher DVB crosslinking. Strong-acid cations with higher crosslinking (10 to 15 percent) will last longer than a typical SAC with 8 percent crosslinking. Chloride-regenerated SBA (type II) resins used to treat groundwater have lasted for more than 8 years and have still maintained over 90 percent of their capacity. Strong-base anions resins are also susceptible to releasing amines, which can lead to the formation of N-nitrosodimethylamine (NDMA), which can be a health concern (Kimoto et al., 1979; Najm and Trussell, 2001).

Precipitates such as calcium sulfate and ferric hydroxide can foul SACs. If the resin contains a large quantity of exchanged calcium and is regenerated with sulfuric acid, calcium sulfate precipitate will form inside the resin particles and reduce its capacity. In addition, excessive quantities of iron and manganese, if oxidized, can form precipitates and foul the resin. Weak-acid cation exchange resins can be fouled by calcium sulfate, but are not as susceptible to oxidation as SACs.

Effect of fouling
Two major types of fouling can occur with SBA resins, silica fouling and organic fouling. When used in the hydroxide form in a demineralization process, silicic acid is concentrated at the exchange front within the bed. Silicic acid will polymerize into an inorganic solid that will not behave as an exchangable anion. The silica can accumulate in the SBA resin until silica-free water cannot be produced.

Natural organic matter composed of humic and fulvic acids is negatively charged and can irreversibly exchange/adsorb onto SBA resins. Consequently, it usually requires large volumes of regenerant and rinses to bring the fouled resin back to its original capacity.

Weak-base resins are also subject to oxidation and fouling, depending on the type of resin. Special care should be taken with these resins prior to their use to ensure their stability will not be adversely affected. Manufacturers will normally provide a user guide to proper selection and use of these types of resins to prevent degradation.

16-4 Ion Exchange Equilibrium

As shown in Eqs. 16-1 through 16-11, the general equilibrium expressions for ion exchange are most often reversible. The reversibility implies that equilibrium is independent of the direction from which the equilibrium state is approached. Based on the previous discussion of selectivity (i.e., the inherent preference of a resin for one ion over another), the ratios of concentrations of various ions in solution will be different from the concentration ratios in the resin phase at equilibrium. In this section, methods for calculating ion exchange performance based on equilibrium expressions is presented for single (or binary) and multiple ions present in water.

Two methods have been used to develop ion exchange equilibrium expressions. One method treats ion exchange as a chemical reaction and applies the laws of mass action to obtain an equilibrium description. In the second method, the same equilibrium description can also be developed using the principles of Donnan exclusion theory. As mentioned above, the Donnan theory is used to describe the behavior of ions based on the unequal distribution of ions across a membrane when an electrolyte solution on one

side of the membrane contains ionic species that cannot diffuse through the membrane. The Donnan theory provides a more rigorous thermodynamic basis for ion exchange equilibrium description, which the mass action laws do not include. A more rigorous thermodynamic approach may be found in Helfferich (1995). Because both methods result in the same equilibrium expression, the equilibrium description based on the mass action laws will be used to develop an expression for the apparent equilibrium constant.

Ion Exchange Selectivity

If it is assumed that ion exchange is a simple stochiometric reaction, then the mass action laws can be applied to obtain an equilibrium expression. For simplification, a generalized form of the stochiometric reaction for Eqs. 16-1 through 16-10 can be written as

$$n\left[\overline{R^{\pm}}\right]A^{\pm} + B^{n\pm} \rightleftarrows \left[n\overline{R^{\pm}}\right]B^{n\pm} + nA^{\pm} \qquad (16\text{-}12)$$

where $\overline{R^{\pm}}$ is the ionic group attached to an ion exchange resin, A and B are exchanging ions, and n is the valence of the exchanging ion. In water treatment, ion exchange applications most often involve dilute ionic solutions where the ions behave independently of one another and are treated as ideal solutions (i.e., activity coefficients are assumed to be unity). In the resin phase, the ion concentrations can be much larger (5 to 6 M, 10 percent DVB SAC; Weber, 1972) and the activity is not unity and will be a function of ionic strength. With respect to Eq.16-12, all binary exchange reactions can be expressed as

$$K_A^B = \frac{\left[A^{\pm}\right]^n \left\{\overline{R^{\pm}B^{n\pm}}\right\}}{\left\{\overline{R^{\pm}A^{\pm}}\right\}^n \left[B^{n\pm}\right]} \qquad (16\text{-}13)$$

where

$K_A^B =$ selectivity coefficient or apparent equilibrium constant for A exchanging with ion B onto resin

$[A^{\pm}] =$ aqueous-phase concentration of presaturant ion, mol/L

$[B^{\pm}] =$ aqueous-phase concentration of counterion, mol/L

$\left\{\overline{R^{\pm}A^{\pm}}\right\}, \left\{\overline{R^{\pm}B^{n\pm}}\right\} =$ activities of resin-phase presaturant ion and counterion, respectively

Because concentrations are measured more easily than activities, the resin phase can be expressed in terms of concentrations, and Eq. 16-12 can be written in general terms as

$$K_j^i = \frac{C_j^n q_i}{q_j^n C_i} \qquad (16\text{-}14)$$

where C_j = aqueous-phase concentration of presaturant ion, mol/L
q_i = resin-phase concentration of counterion, mol/L
q_j = resin-phase concentration of presaturant ion, mol/L
C_i = aqueous-phase concentration of counterion, mol/L

Ion exchange resin manufacturers provide equilibrium data as selectivity coefficients. The selectivity coefficient can depend on the valence, the type of resin and its saturation, and the nature and concentration of the ion in the raw water.

Selectivity coefficients for SAC and SBA resins are presented in Table 16-6. For both SAC and SBA resins, the ion preference for the resin increases as the value of the selectivity coefficient increases. Generally, selectivity increases with increasing valence of both SAC and SBA resins.

Example 16-2 Determination of selectivity expression

Write a selectivity expression for the exchange of calcium onto a SAC resin in the sodium form and for the exchange of nitrate onto an SBA resin in the chloride form.

Solution to Part A

1. For the exchange of calcium, Ca^{2+}, onto an SAC resin in the sodium, Na^+, form, the following stochiometric expression can be written:
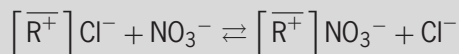
$$2\left[\overline{R^-}\right]Na^+ + Ca^{2+} \rightleftarrows \left[2\overline{R^-}\right]Ca^{2+} + 2Na^+$$
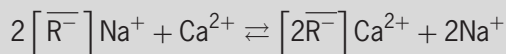
2. Using the general form of Eq. 16-14, the following selectivity expression can be written:

$$K_{Na^+}^{Ca^{2+}} = \frac{q_{Ca^{2+}}C_{Na^+}^2}{C_{Ca^{2+}}q_{Na^+}^2}$$

Solution to Part B

1. For the exchange of nitrate, NO_3^-, onto an SBA resin in the chloride, Cl^-, form, the following stochiometric expression can be written:

$$\left[\overline{R^+}\right]Cl^- + NO_3^- \rightleftarrows \left[\overline{R^+}\right]NO_3^- + Cl^-$$

2. Using the general form of Eq. 16-14, the following selectivity expression can be written:

$$K_{Cl^-}^{NO_3^-} = \frac{q_{NO_3^-}C_{Cl^-}}{C_{NO_3^-}q_{Cl^-}}$$

Table 16-6
Selectivity coefficients for SAC and SBA resins

Cation	Selectivity, $K^i_{Li^+}$	Anion	Selectivity, $K^i_{Cl^-}$
Li^+	1.0	HPO_4^{2-}	0.01
H^+	1.3	CO_3^{2-}	0.03
Na^+	2.0	OH^- (type I)	0.06
UO_2^{2+}	2.5	F^-	0.1
NH_4^+	2.6	SO_4^{2-}	0.15
K^+	2.9	CH_3COO^-	0.2
Rb^+	3.2	HCO_3^-	0.4
Cs^+	3.3	OH^- (type II)	0.65
Mg^{2+}	3.3	BrO_3^-	1.0
Zn^{2+}	3.5	Cl^-	1.0
Co^{2+}	3.7	CN^-	1.3
Cu^{2+}	3.8	NO^-	1.3
Cd^{2+}	3.9	HSO_4^-	1.6
Ni^{2+}	3.9	Br^-	3
Mn^{2+}	4.1	NO_3^-	4
Pb^{2+}	5.0	I^-	8
Ca^{2+}	5.2	SeO_4^{2-}	17
Sr^{2+}	6.5	CrO_4^{2-}	100
Ag^{2+}	8.5		
Ba^{2+}	11.5		
Ra^{2+}	13.0		

Source: Adapted, in part, from Weber (1972).

Ion exchange reactions with inorganic ions have a relatively constant free-energy change; thus equilibrium constants do not vary significantly with solution conditions. However, it has been reported that the equilibrium constants for organic ions do change with resin loading (Semmens, 1975). The concept of selectivity coefficients or apparent equilibrium constants is used primarily in the theoretical treatment of ion exchange equilibrium and in qualitatively assessing the ion exchange preference. For quantitative analysis or process design evaluation, separation factors are used more commonly than selectivity coefficients.

Separation Factors

Equilibrium can be expressed in terms of equivalent fractions instead of concentration because equivalent charges are exchanged. The binary separation factor α^i_j is a measure of the preference for one ion over another during ion exchange and can be expressed as

$$\alpha^i_j = \frac{Y_i X_j}{X_i Y_j} \tag{16-15}$$

where $X_j =$ equivalent fraction or mole fraction of presaturant ion in aqueous phase

$X_i =$ equivalent fraction or mole fraction of counterion in aqueous phase

$Y_j =$ resin-phase equivalent fraction or mole fraction of presaturant ion

$Y_i =$ resin-phase equivalent fraction or mole fraction of counterions

The equivalent fraction in the aqueous phase is calculated from the following:

$$X_i = \frac{C_i}{C_T} \quad X_j = \frac{C_j}{C_T} \tag{16-16}$$

where $C_T =$ total aqueous ion concentration, eq/L

$C_i =$ aqueous-phase concentration of counterion, eq/L

$C_j =$ aqueous-phase concentration of presaturant ion, eq/L

The equivalent fraction in the resin phase is expressed as

$$Y_i = \frac{q_i}{q_T} \quad Y_j = \frac{q_j}{q_T} \tag{16-17}$$

where $q_T =$ total exchange capacity of resin, eq/L

For process design calculations, binary separation factors are primarily used in ion exchange calculations because they are experimentally determined and account for the solution concentration and the total ion exchange capacity.

Substituting Eqs. 16-16 and 16-17 into Eq. 16-15 yields

$$\alpha_j^i = \frac{q_i C_j}{C_i q_j} \tag{16-18}$$

where $\alpha_j^i =$ separation factor of ion i with respect to ion j, unitless (concentrations are in eq/L)

For the special case of monovalent ion exchange with a monovalent presaturant ion (all ions are 1 eq/mol), the separation factor is constant and equal to the selectivity coefficient. For multivalent ion (i) exchange with a resin having a monovalent presaturant ion (j), the separation factor and selectivity coefficient are related by the ratio of presaturatant ion concentrations in the liquid and resin phases (Harland, 1994):

$$K_j^i = \alpha_j^i \left(\frac{C_j}{q_j} \right)^{|\pm Z|-1} \tag{16-19}$$

where $Z =$ charge on ion, unitless (concentrations are in mol/L)

As shown in Eq. 16-19, for low multivalent ion concentrations the separation factor for multivalent/monovalent exchange is inversely proportional to the equivalent aqueous-phase concentration of ion j raised to the power $|\pm Z| - 1$. It is common to have sodium or chloride as the presaturant ion

for cationic or anionic resins, respectively. The separation factor is inversely proportional to the aqueous-phase sodium or chloride concentration for low concentrations of exchanging multivalent ions because the amount of resin in the sodium or chloride forms will not change significantly for small cation or anion concentrations. Accordingly, ion exchange resins are very efficient for scavenging low concentrations of multivalent cations and anions.

It is important to note that the separation factor may not be a constant but rather is influenced by various factors: exchangeable ions (size and charge), properties of the resins, including particle size, degree of crosslinking, capacity, and type of functional groups occupying the exchange sites; water matrix, which includes total concentration, type, and quantity of organic compounds present in solution; reaction period; and temperature. Because separation factors can be influenced by several factors, they are usually determined by performing an equilibrium experiment called a binary isotherm. A binary isotherm involves performing a batch equilibrium experiment for a binary system. Both binary component systems and isotherms are discussed in the following sections.

Binary Component Systems

A binary component system involves the exchange of a presaturant ion with only one other component ion present in solution. For the binary system, the total aqueous-phase equivalent concentration can be expressed as

$$C_T = C_i + C_j \qquad (16\text{-}20)$$

where C_T = total aqueous ion concentration, eq/L
      C_i = counterion concentration, eq/L
      C_j = presaturant ion concentration, eq/L

Total resin-phase equivalent concentration can be expressed as

$$q_T = q_i + q_j \qquad (16\text{-}21)$$

where q_T = total resin-phase ion concentration, eq/L resin
      q_i = counterion concentration, eq/L resin
      q_j = presaturant ion concentration, eq/L resin

Consequently, substitution of the expression for q_T into Eq. 16-18 yields the following expression for calculating the resin-phase concentration of the counterion of interest:

$$q_i = \frac{C_i q_T}{C_i + C_j \alpha_i^j} \qquad (16\text{-}22)$$

Note that $\alpha_i^j = 1/\alpha_j^i$ in the above expression. For a given counterion concentration, Eq. 16-22 can be used to estimate the resin-phase concentration provided the binary separation factor and the total resin capacity are known. Similarly, the following equation can be used to calculate the aqueous-phase concentration of the counterion given the total aqueous-phase

concentration, binary separation factor, and the resin-phase concentrations of the counterion and presaturant ion:

$$C_i = \frac{q_i C_T}{q_i + \alpha_j^i q_j} \tag{16-23}$$

Separation factors for commercially available SAC and SBA exchange resins are given in Table 16-7. Based on the definition of Eq. 16-15, a separation factor greater than 1 means that ion i is preferred over ion j. For example, if $\alpha_{Cl^-}^{NO_3^-} = 2.3$, expressed in equivalents, at equal aqueous-phase concentrations, NO_3^- is preferred over chloride by 2.3 to 1.0. The magnitude of the separation factors is different for WAC and WBA resins from those shown in Table 16-7 for SAC and SBA resins. When separation factors for a given resin are unknown, they may be determined experimentally using binary isotherms. Clifford (1999) provides a detailed experimental procedure and example for determining separation factors.

Table 16-7
Separation factors for several commercially available cation and anion exchange resins[a]

Strong-Acid Cation Resins[b]		Strong-base Anion Resins[c]	
Cation	$\alpha_{Na^+}^i$	**Anion**	$\alpha_{Cl^-}^i$
Ra^{2+}	13.0	$UO_2(CO_3)_3^{4-}$	3200
Ba^{2+}	5.8	ClO_4^{-d}	150
Pb^{2+}	5.0	CrO_4^{2-}	100
Sr^{2+}	4.8	SeO_4^{2-}	17
Cu^{2+}	2.6	SO_4^{2-}	9.1
Ca^{2+}	1.9	$HAsO_4^{2-}$	4.5
Zn^{2+}	1.8	HSO_4^-	4.1
Fe^{2+}	1.7	NO_3^-	3.2
Mg^{2+}	1.7	Br^-	2.3
K^+	1.7	SeO_3^{2-}	1.3
Mn^{2+}	1.6	HSO_3^-	1.2
NH_4^+	1.3	NO_2^-	1.1
Na^+	1.0	Cl^-	1.0
H^+	0.67	BrO_3^-	0.9
		HCO_3^-	0.27
		CH_3COO^-	0.14
		F^-	0.07

[a]Values are approximate separation factors for 0.005–0.010 N solutions (TDS = 250–500 mg/L as $CaCO_3$).
[b]SAC resin is polystyrene divinylbenzene matrix with sulfonate functional groups.
[c]SBA resin is polystyrene divinylbenzene matrix with $-N^+(CH_3)_3$ functional groups (i.e., a type 1 resin).
[d]ClO_4^-/Cl^- separation factor is for polystyrene SBA resins; on polyacrylic SBA resins, the ClO_4^-/Cl^- separation factor is approximately 5.0.
Source: Adapted From Clifford et al. (2011).

Example 16-3 Binary exchange calculation

Nitrate is to be removed from water containing high chloride concentration. The chemical composition of the water is given below. The water contains some bicarbonate and sulfate, but for this calculation it is assumed they are negligible. Using an SBA resin with a total capacity of 1.4 eq/L, estimate the maximum volume of water that can be treated per liter of resin.

Cation	meq/L	Anion	meq/L
Ca^{2+}	0.9	Cl^-	2.5
Mg^{2+}	0.8	SO_4^{2-}	0.0
Na^+	2.6	HCO_3^-	0.0
		NO_3^-	1.8
Total	4.3	Total	4.3

Solution

1. Estimate the maximum useful capacity of nitrate on the SBA resin in the chloride form using Eq. 16-22.

   a. The separation factor for nitrate over chloride can be obtained from Table 16-7:

   $$\alpha_j^i = \alpha_{Cl^-}^{NO_3^-} = 3.2$$

   $$\alpha_i^j = \alpha_{NO_3^-}^{Cl^-} = \frac{1}{\alpha_j^i} = \frac{1}{\alpha_{Cl^-}^{NO_3^-}} = \frac{1}{3.2} = 0.3125$$

   b. The maximum useful capacity of the resin for nitrate using Eq. 16-22 is

   $$q_{NO_3^-} = \frac{C_{NO_3^-}q_T}{C_{NO_3^-} + C_{Cl^-}\alpha_{NO_3^-}^{Cl^-}}$$

   $$= \frac{(1.8 \text{ meq } NO_3^-/L \text{ H}_2O)(1.4 \text{ eq/L resin})(1000 \text{ meq/eq})}{(1.8 \text{ meq } NO_3^-/L \text{ H}_2O) + (2.5 \text{ meq } Cl^-/L \text{ H}_2O)(0.3125)}$$

   $$= 976 \text{ meq } NO_3^-/L \text{ resin}$$

2. The volume of water that can be treated per volume of resin per cycle is calculated by dividing the nitrate capacity by the influent nitrate concentration:

   $$V = \frac{q_{NO_3^-}}{C_{NO_3^-}} = \frac{976 \text{ meq } NO_3^-/L \text{ resin}}{1.8 \text{ meq } NO_3^-/LH_2O} = 542 \text{ L H}_2O/L \text{ resin}$$

In water treatment, the application of ion exchange involves treatment of groundwaters containing multiple cations and anions (e.g., Na^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, SO_4^{2-}). Some waters may also contain ions of more significant health threat, such as Ba^{2+}, Ra^{2+}, Pb^{2+}, Cu^{2+}, NO_3^-, $HAsO_4^-$, F^-, and ClO_4^-. Consequently, a multicomponent expression is needed to describe the competitive interactions between the ions for the resin site at equilibrium. In a multicomponent system, the total capacity of the resin and the total concentration of exchanging ions in solution can be expressed as

$$q_T = q_i + q_j + \cdots + q_n \tag{16-24}$$

$$C_T = C_i + C_j + \cdots + C_n \tag{16-25}$$

where q_T = total resin-phase ion concentration, eq/L resin
  q_i = resin-phase concentration of counterion i, eq/L resin
  q_j = resin-phase concentration of presaturant j, eq/L resin
  q_n = resin-phase concentration of counterion n, eq/L resin
  C_T = total aqueous-phase ion concentration, eq/L
  C_i = aqueous-phase concentration of counterion i, eq/L
  C_j = aqueous-phase concentration of presaturant j, eq/L
  C_n = aqueous-phase concentration of counterion n, eq/L

Applying Eq. 16-24 to Eq. 16-22 yields the following expression for q_i in terms of n exchanging ions:

$$q_i = \frac{q_T C_i}{\sum_{k=1}^n \alpha_i^k C_k} \tag{16-26}$$

where C_k = aqueous-phase concentration for ion k (presaturant ion when $k = j$), eq/L resin
  α_i^k = separation factor for counterion i with respect to ion k

Note that α_i^k assumes the separation factors are known with respect to the ion concentrations being sought on the resin phase for ion i. Since the separation factors are reported in terms of the presaturant ion, Eq. 16-26 would be easier to use if the separation factors were with respect to the presaturant instead of the resin phase ion. If the subscript j is set equal to p where p is equal to the presaturant ion, the following expression for the separation factor in Eq. 16-26 can be obtained:

$$\alpha_i^k = \alpha_i^p \alpha_p^k = \frac{\alpha_p^k}{\alpha_p^i} \tag{16-27}$$

Substitution of Eq. 16-27 into Eq. 16-26 yields the following expression:

$$q_i = \frac{q_T C_i}{\sum_{k=1}^N \left(\frac{\alpha_p^k}{\alpha_p^i} C_k \right)} = \frac{q_T C_i}{\frac{1}{\alpha_p^i} \sum_{k=1}^N \left(\alpha_p^k C_k \right)} = \frac{q_T \alpha_p^i C_i}{\sum_{k=1}^N \left(\alpha_p^k C_k \right)} \tag{16-28}$$

If all the liquid-phase ion concentrations and the total resin capacity are known, the resin-phase concentrations can be calculated using the separation factors referenced to the presaturant ion as reported in Table 16-7. Similarly, Eq. 16-28 can be solved for C_i in terms of n exchanging ions:

$$C_i = \frac{C_T q_i}{\alpha_p^i \sum_{k=1}^n q_k \big/ \alpha_p^k} \tag{16-29}$$

where q_k = resin-phase concentration of ion k (presaturant ion when $k = j$), eq/L resin

α_k^i = separation factor for ion i with respect to ion k

α_p^k = separation factor for ion k with respect to presaturant ion p

Example 16-4 Multicomponent equilibrium calculation

Consider the removal of nitrate from well water using an SBA exchange resin in the chloride form. The major ions contained in the well water are given below. Assuming nitrate is removed completely from solution, calculate the maximum volume of water that can be treated per liter of resin assuming equilibrium conditions. Assume total resin capacity of the SBA is 1.4 eq/L.

Cation	meq/L	Anion	meq/L
Ca^{2+}	0.9	Cl^-	1.0
Mg^{2+}	0.8	SO_4^{2-}	1.5
Na^+	2.6	NO_3^-	1.8
Total	4.3	Total	4.3

Solution

1. Applying Eq. 16-28 with the use of the separation factors provided in Table 16-7, the summation term in the denominator can be calculated.

$$\sum_{k=1}^N \left(\alpha_p^k C_k \right) = (1.0)\,(1 \text{ meq/L}) + (9.1)\,(1.5 \text{ meq/L})$$

$$+ (3.2)\,(1.8 \text{ meq/L}) = 20.41 \text{ meq/L}$$

2. Calculate q_i for each ion.

$$q_{Cl} = \frac{(1.4 \text{ eq/L})\,(1.0)\,(1 \text{ meq/L})}{20.41 \text{ meq/L}} = 0.069 \text{ eq/L}$$

$$q_{SO_4^{2-}} = \frac{(1.4 \text{ eq/L})\,(9.1)\,(1.5 \text{ meq/L})}{20.41 \text{ meq/L}} = 0.936 \text{ eq/L}$$

$$q_{NO_3^{-}} = \frac{(1.4 \text{ eq/L})\,(3.2)\,(1.8 \text{ meq/L})}{20.41 \text{ meq/L}} = 0.395 \text{ eq/L}$$

Check : $0.069 + 0.936 + 0.395 = 1.4$ eq/L total capacity.

Note that because the sulfate concentration is more preferred over nitrate ($9.1 \gg 3.2$), the equilibrium capacity of nitrate is low. In other words, nitrate will occupy only about 28 percent (0.395/1.4) of the exchange sites on the resin.

3. Calculate the maximum quantity of water that can be treated per cycle before nitrate breakthrough occurs.

$$\text{Maximum volume treated} = \frac{(0.395 \text{ eq/L resin})\,(10^3 \text{ meq/eq})}{1.8 \text{ meq/L water}} = 219 \text{ L water/L resin}$$

Comment

When comparing the maximum bed volumes treated in Examples 16-3 and 16-4, with sulfate present, the capacity of nitrate is reduced by 60 percent. The impact of divalent anions on exchange capacity is significant. Note that this example applies to equilibrium applied in a batch reactor. In a column system, only the portion of the resin that is exhausted will be in equilibrium with the feed water. In the mass transfer zone, the resin will be in local equilibrium with the concentrations in the water in that region of the bed.

16-5 Ion Exchange Kinetics

The transport mechanisms for fixed-bed ion exchange processes are similar to those for fixed-bed adsorbers as discussed in Chap. 15 where the combined effects of liquid- and solid-phase transport is coupled with equilibrium thermodynamics. In the ion exchange process, these effects may include diffusion and convection coupled with the process exchange rate, electrochemical effects, and sometimes chemical reaction. Since ions diffuse at different rates, charge separation can arise inducing an electric field causing ionic migration to satisfy electroneutrality within the resin particle as discussed in Sec. 16-1. For example, as cation A diffuses into the resin particle, it is transferring charge to the resin, and this charge must be

offset by an equivalent charge by another ion (e.g., presaturant ion) or ions diffusing out of the resin particle into solution to satisfy the local electrical balance. As explained by Helfferich and Hwang (1991) if the ions diffusing out of the resin particle carried a weaker charge, a larger flux of the faster ion would result. For the charged ions, a net transfer of electric charge would result and violate the requirement of electrical neutrality. A small deviation from electrical neutrality causes an electric field that produces a force that enables all the charged ions in the electric field to move with a certain velocity (e.g., electrophoresis) called drift velocity. The direction of the drift of ions is that of diffusion of the slower ion. Consequently, drift velocity of the ion increases the flux of the slow diffusing ion and decreases the flux of the faster one, equalizing the net fluxes and so preventing any further buildup of the net charge.

For ion exchange processes, the ion flux (J_i) contains both the diffusive and electrical flux terms as given by the Nernst–Plank (NP) equation and can be written for both the aqueous phase ($J_{l,i}$) and resin phase ($J_{s,i}$) as

$$J_{l,i} = -D_{l,i}\left[\frac{\partial C_i(z,t)}{\partial r} + \frac{Z_i F C_i(z,t)}{RT}\frac{\partial \phi(z,t)}{\partial r}\right] \qquad (16\text{-}30)$$

$$J_{s,i} = -D_{s,i}\left[\frac{\partial C_{p,i}(r,z,t)}{\partial r} + \frac{Z_i F C_{p,i}(r,z,t)}{RT}\frac{\partial \phi(r,z,t)}{\partial r}\right] \qquad (16\text{-}31)$$

where $J_{l,i}$ = flux of ion i into the resin particles, eq/m$^2 \cdot$ s
$J_{s,i}$ = flux of ion i inside the resin particles, eq/m$^2 \cdot$ s
$D_{l,i}$ = aqueous-phase diffusion coefficient of ion i, m^2/s
$D_{s,i}$ = solid- or resin-phase diffusion coefficient of ion i, m^2/s
C_i = aqueous-phase concentration of diffusing ion i, eq/L
$C_{p,i}$ = aqueous-phase concentration of diffusing ion i in the resin pores, eq/L
ϕ = electrical potential caused by migration of ion in solution, mV
F = Faraday constant 96,484 C/mol
R = universal gas constant, 0.08205 L $\cdot$ atm/mol $\cdot$ K
T = temperature, K
Z_i = charge of the diffusing ion, ($-$)
r = dependant parameter in radial direction of the particle, m
z = dependent parameter in axial direction of fixed bed, m
t = dependent parameter of time of operation, d

For most ion exchange problems encountered in water treatment, the flux terms in Eqs. 16-30 and 16-31 can be simplified by assuming electroneutrality exists within aqueous film surrounding the resin phase and within the resin phase, and the flux of the nonexchanging coion across the resin–liquid

interface is negligible (Hokanson, 2004).

$$\sum C_i\,(z,\,t) = 0 \quad \text{(aqueous phase)} \tag{16-32}$$

$$\sum C_{p,\,i}\,(r,\,z,\,t) = 0 \quad \text{(resin phase)} \tag{16-33}$$

$$J_i = (\text{nonexchanging coion}) = 0 \tag{16-34}$$

Based on these assumptions the following condition of no net current flow can be derived:

$$\sum J_i = 0 \quad \text{(no net current flow)} \tag{16-35}$$

Equations 16-30 and 16-31 reduce to a form similar to Fick's law, and the flux is equal to the product of an ''effective'' diffusion coefficient and a concentration gradient. The effective diffusion coefficient includes electrical effects and is not constant and depends upon concentrations, diffusion coefficients, and charges of all the individual exchanging ions. Equation 16-30 and 16-31 can be rewritten in terms of an effective diffusion or mass transfer coefficient as

$$J_{l,i} = k_{f,i} \left[C_{b,i}\,(z,\,t) - C_{s,i}\,(z,\,t) \right] \quad \text{(aqueous phase)} \tag{16-36}$$

$$J_{s,i} = -\frac{D_{l,i}\varepsilon_p}{\tau_p}\frac{\partial C_{p,i}\,(r,\,z,\,t)}{\partial r} \quad \text{(resin phase)} \tag{16-37}$$

where $k_{f,i}$ = film diffusion or mass transfer coefficient, m/s
$C_{b,i}$ = bulk aqueous-phase concentration of ion i, g/m^3
$C_{s,i}$ = aqueous-phase concentration of ion i at the external surface of the resin particle, g/m^3
ε_p = void fraction of the resin particle, dimensionless
τ_p = resin particle tortuosity, dimensionless

Equations 16-36 and 16-37 are incorporated into fixed-bed and intraparticle mass balances, respectively; to provide a set of equations or model that can describe the fixed-bed ion exchange process (Hokanson, 2004; Wagner and Dranoff, 1967; Graham and Dranoff, 1972, Wildhagen et al., 1985; Haub and Foutch, 1986). The model mechanisms consist of advective transport of exchanging ions through the fixed-bed exchanger, diffusion of exchanging ions through the film surrounding the resin particles, and intraparticle diffusion of the exchanging ions within the resin particles. It is typically assumed that the rate of ion exchange on the resin is fast as compared to the mass transfer rates in the fluid and solid phases.

Rate-Controlling Step in Fixed-Bed Ion Exchange Process

Most ion exchange applications in water treatment involve two rate controlling steps in-series, liquid-phase (film), and effective intraparticle mass transfer. Determination of the rate-controlling step must consider the mass flux. According to Eqs. 16-36 and 16-37, the flux terms contain the product of the mass transfer rate and the driving force for mass transfer. The slower

flux will determine the rate-controlling step. Intuitively, one may think that since the stagnant film thickness surrounding the resin particles is small as compared to the diffusion path length (surface of the resin particle to the center of the resin particle) within the resin particle, that the intraparticle mass transfer rate controls the overall rate of mass transfer. Film transfer coefficients are typically on the order of 10^{-5} to 10^{-6} m/s versus intraparticle diffusion coefficients on the order of 10^{-9} to 10^{-10} m^2/s. However, the driving force for each phase must also be considered. For Eq. 16-36 the driving force between the bulk solution and the surface of the resin particle cannot be greater than the bulk solution concentration. For Eq. 16-37, the driving force can be as high as the concentration of the fixed charges on the resin particle, which can be very large. As a result, the rate-controlling step can be difficult to determine.

As pointed out by Helfferich and Hwang (1991), liquid-phase mass transfer rate usually controls the ion exchange process when: (1) liquid-phase concentration is low, causing a small driving force in the liquid phase; (2) the resin exchange capacity is high, causing a large driving force in the resin phase; (3) the resin particle size is small, causing a small mass transfer length in the resin; (4) there is a low degree of crosslinking in the resin particle, causing an open resin matrix; and (5) the advective flow in the fixed bed is slow, causing the thickness of the stagnant film surrounding the resin particles to be large. In addition, the selectivity of the resin may also play a small role in impacting the driving force. The following expression was developed for predicting which phase would control the mass transfer rate (Helfferich, 1995):

$$\text{He} \equiv \frac{q_T D_p \delta}{\text{C}D_l r_0}\left(5 + 2\alpha_j^i\right) \tag{16-38}$$

where   He = Helfferich number, dimensionless

   δ = stagnant film thickness between the bulk solution and the resin particle external surface, m

   r_0 = resin particle radius, m

When He $\ll$ 1, intraparticle diffusion will control the rate of mass transfer for the ion exchange process, and when He $\gg$ 1 liquid-phase diffusion will control the mass transfer rate in the ion exchange process. For He values near unity both rates will contribute in some degree to the control of the mass transfer rate.

A number of variables can influence the mass transfer rate and include particle size, flow rate, resin particle pore structure, and solution concentration. The resin particle size has a significant impact on process kinetics. As the resin particle size decreases, mass transfer rates increase in both the liquid and resin phases. The liquid-phase mass transfer rate is inversely proportional to resin particle size and as the particle size decreases the mass transfer rate increases. Similarly, the intraparticle mass transfer rate increases as the inverse of particle size raised to a higher power. There is a

trade-off between process kinetics and head loss in the bed. As the particle size decreases, the process kinetics increase, which will provide for a smaller mass transfer zone and higher capacity utilization in a given fixed bed, but at the expense of a higher head loss in the bed. The benefits of increased exchange rates with smaller resin particles must be weighed against the increased head loss within the fixed bed.

Flow rate can influence both the length of the mass transfer zone and fixed bed. If the film diffusion is controlling the rate of mass transfer, increasing the flow rate may decrease the film thickness for diffusion, decrease the length of the mass transfer zone and increase the capacity of the fixed bed. This will occur as long as the length of the mass transfer zone is shorter than the length of the fixed bed. If intraparticle diffusion is controlling the rate of mass transfer, and the flow rate is increased, the mass transfer zone will not be impacted, but the empty-be contact time (EBCT) will be less and the bed usage rate will be lower. If the flow rate was decreased, the mass transfer zone length could increase; depending upon the magnitude of the He number, and the EBCT would increase causing the usage rate to increase as long as the mass transfer zone length is less than the bed length.

As discussed above, for gel-type resins with an open matrix (e.g., microreticular resin), film transfer is usually controlling the overall rate of mass transfer in the fixed bed. However, if the degree of resin crosslinking is high for a given resin (e.g., macroreticular resin), the resin matrix becomes very tortuous and intraparticle diffusion may control the rate of ion exchange in the fixed bed.

With respect to initial ion concentration, film diffusion is likely to be controlling for low initial concentrations. At high initial ion concentrations, intraparticle diffusion is more likely to control the rate of mass transfer. This usually occurs during regeneration when using high concentrations of regenerate solutions.

16-6 Ion Exchange Process Configurations

The ion exchange process is conducted in a fixed bed of resin with the water passing through the resin until a certain treatment objective is reached. The resin is then taken offline and regenerated, while another column is used to supply continuous treatment (if needed). A typical full-scale ion exchange plant operating in the down-flow mode is shown on Fig. 16-4.

Regeneration Methods

The regeneration steps of an ion exchange resin are important to the overall efficiency of the process. There are two methods for regenerating an ion exchange resin: (1) co-current, where the regenerant is passed through the resin in the same flow direction as the solution being treated, and (2) countercurrent, where the regenerant is passed through the resin

Figure 16-4
Full-scale ion exchange plant operating in downward mode.

in the opposite direction as the solution being treated. Co-current and countercurrent regenerations are considered in the following discussion.

CO-CURRENT OPERATION

Co-current operation consists of the regeneration step being conducted in the same flow direction as the solution being treated. The direction of both flows is usually downward. When small concentrations of the unwanted ion(s) can be tolerated in the effluent (referred to as leakage) and the exchange in the regeneration step is favorable, co-current operation is chosen. However, in recent studies it has been found that co-current operation can reduce leakage of some unwanted ions more effectively than countercurrent systems (Clifford et al., 1987; Ghurye et al., 1999). For nitrate and arsenate ions it was found that the co-current process produced less leakage than the countercurrent process because the exchanged mass of these ions is located near the outlet of the resin bed. Consequently, flushing these ions back through the column with the countercurrent process produces more leakage. The location of these ions within the bed will depend upon the ions in the water matrix and their separation factors for a given resin. For example, for many SBA resins, sulfate has a higher affinity than either nitrate or arsenate. Consequently, the sulfate will push most of the exchanged arsenate and nitrate toward the end of the column. Upon regeneration, the preference for sulfate over chloride is reversed at high chloride concentrations and sulfate is easily removed from the resin.

COUNTERCURRENT OPERATION

In most cases, countercurrent operation will result in lower leakage levels and higher chemical efficiencies than co-current operation. In situations where (1) high-purity water is necessary, (2) chemical consumption must be reduced to a minimum, or (3) the least waste volume is produced, the countercurrent method of operation is used.

Countercurrent operation with the service flow operated in the upward direction will only be effective if the resin can be prevented from fluidizing. Any resin movement during the upflow cycle will destroy the ionic interface (exchange front) that ensures good exchange. A number of methods have been devised to prevent resin particle movement during upflow operation. Some of the more commonly used methods are presented in Table 16-8.

Advances in the use of fixed beds make certain processes more economical or provide better product purity. Two types of advances in fixed-bed design are the use of mixed beds of strong-acid and strong-base resins and the use of layered beds of a weakly ionized resin above a strong ionized resin, as discussed below.

MIXED BEDS

For the production of deionized water, a column containing intimately mixed strong-acid (in the H^+ form) and strong-base resins (in the OH^- form) provides better water quality than the individual resins segregated in series. With mixed resins, the effluent from the contactor will be deionized water. The reactions from salt to base to water or from salt

Table 16-8

Methods for preventing particle movement during upflow operation

Type of Method	Description
Completely filled column	The ion exchange column is completely filled with resin and service and regeneration steps are run counterflow. A reservoir tank above the column provides space for occasional backwashing.
Use of inert granules to fill headspace	Compressible inert granules are used to fill the column's headspace during the service cycle, and they prevent the upward movement of the particles during upflow regeneration. A small reservoir is used periodically to withdraw the inert granules to backwash the resin.
Use of air or water blocking	Air or water can be introduced at the top of the column during upflow regeneration to block movement of particles. Blocking will result in increased waste volumes and has been virtually abandoned. However, only moderate air pressure is required and has been used successfully in some designs.

to acid to water will occur so rapidly that there are virtually no back reactions. Unfortunately, mixed beds cannot be regenerated in place and regeneration will require the separation of the two resin types into layers. Properly selecting the densities and particle sizes of the resins is the best method. Strong-base anion resins are normally lighter than SAC resins; hence backwashing prior to regeneration will place the SBA resin above the SAC resin. During regeneration, the regenerant solution is introduced at the top (e.g., NaOH) and bottom (e.g., HCl) of the respective beds and is simultaneously withdrawn at the interface. After regeneration, resins must be well mixed by an air-scouring operation. Probably the most important factor in achieving good product water is how well the resins are mixed, especially close to the exit of the bed.

FIXED-BED OPERATION

In the production of deionized water, the use of fixed beds has been the traditional approach to ion exchange. There are many important design features that must be addressed when considering ion exchange columns. Proper distribution and collection of flow is critical to good operation. For traditional downflow systems, the influent can be distributed with either a water hold-down system, where the entire vessel is kept completely filled with liquid at all times, or an air hold-down system, where the liquid level is kept several millimeters above the resin level when liquid is being introduced into the column. A water hold-down design is easier to install, operate, and control and is used most often in normal applications.

A schematic of an air or water hold-down system is provided on Fig. 16-5. In hold-down systems relatively large volumes of air or water are needed to maintain the packed resin bed in place during upflow regeneration. Although hold-down systems provide good water quality and regeneration
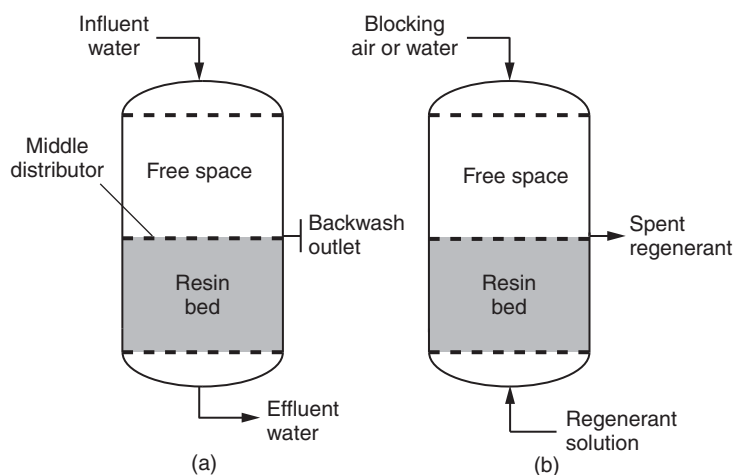
Figure 16-5
Air and water ion exchange hold-down system: (a) loading cycle and (b) regeneration cycle.

efficiency, they are equipment intensive. The issues associated with hold-down systems include the following: (1) the middle distributor can undergo mechanical damage due to resin swelling and shrinking, (2) there is high water and air consumption, (3) the regeneration process is time consuming, (4) the process is labor intensive, and (5) large vessels are required.

Recently, new design applications have made it possible to operate an ion exchange system continuously with ion removal and regeneration occurring simultaneously in different portions of a moving resin bed. Three ion exchange continuous operation systems that utilize the Dow UPCORE, the Bayer-Lewatit, and the Calgon ISEP systems discussed in this section. In addition, the MIEX process, which operates in a completely mixed reactor, was recently developed for removing dissolved organic carbon is also discussed.

Types of Ion Exchange Processes

UPCORE SYSTEM
The UPCORE system, a countercurrent system in which the service flow is in the downward direction and the regeneration flow is in the upward direction, is illustrated on Fig. 16-6. If needed, the system can be converted to a co-current process. The top collector/distributor is surrounded by a small layer of floating inert material that enables the service water, spent regenerant, rinse water, and fine particles to pass while retaining the resin particles. The process is insensitive to fluctuations in service flow rates. During upflow regeneration, the resin bed is lifted in the compacted form moving up against the inert material at the top of the bed to maintain the packed state. During regeneration, fine particles (dirt, fine resin particles, etc.), which are trapped during the service cycle, are washed out with the regenerant and rinse waters. Usually such systems are used on groundwaters or similar supplies where backwashing is rarely required. To provide backwashing, a separate backwashing vessel is normally
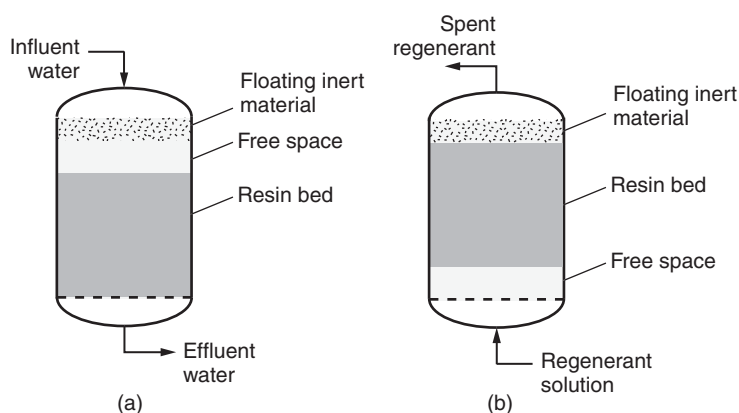

Figure 16-6
UPCORE countercurrent ion exchange systems: (a) loading cycle and (b) regeneration cycle.

provided and the media is moved hydraulically from its normal vessel to the backwashing vessel, washed, and then moved back. Obviously, this arrangement is not attractive unless backwashing is rarely required.

BAYER–LEWATIT UPFLOW FLUIDIZED SYSTEM

The Bayer–Lewatit upflow fluidized system, a countercurrent system in which the service flow is in the upward direction and the regeneration flow is in the downward direction, is shown on Fig. 16-7. Nozzle plate distributors are located at the top and bottom of the resin bed to ensure the resin is evenly distributed and held in place. A fine polishing resin layer is placed in the upper layer and is the first resin to be regenerated to reduce leakage. A small amount of inert floatable material is placed between the resin and the upper nozzle plate. The purpose of the floatable material is to prevent small beads or particles of resin from clogging the upper nozzle plate, and it also provides a more even flow distribution of the regenerant through the resin bed. Enough freeboard is provided to allow for expansion of the resin. The use of the upflow fluidized process is supposed to minimize the formation of clumps of resin and mechanical stress on the resins, causing swelling breakdown and attrition. The downflow rinse step minimizes the quantity of rinse water because the density of the rinse water is lower than the regenerant solution.

CALGON ISEP SYSTEM

The Calgon ISEP process, a countercurrent process, is illustrated schematically on Fig. 16-8 and photographically on Fig. 16-9. The process consists of about 20 to 30 small ion exchanger columns on a rotating platform. As the platform rotates at any given time, most of the columns are in the treatment mode while the others are in various phases of the regeneration cycle. The configuration provides for a flexible operation. A large valve is
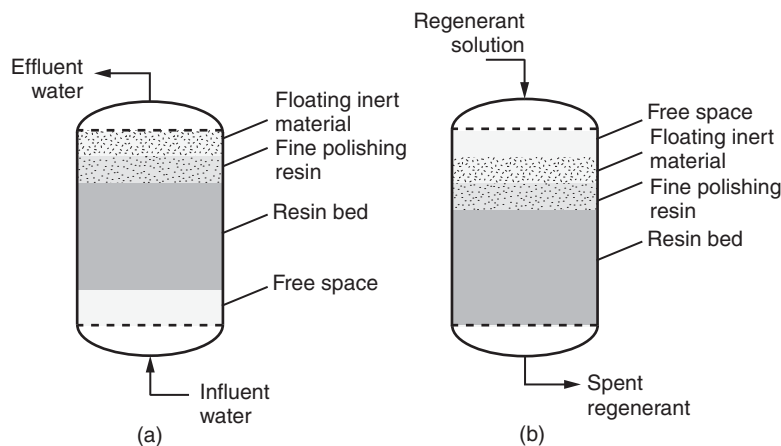

Figure 16-7
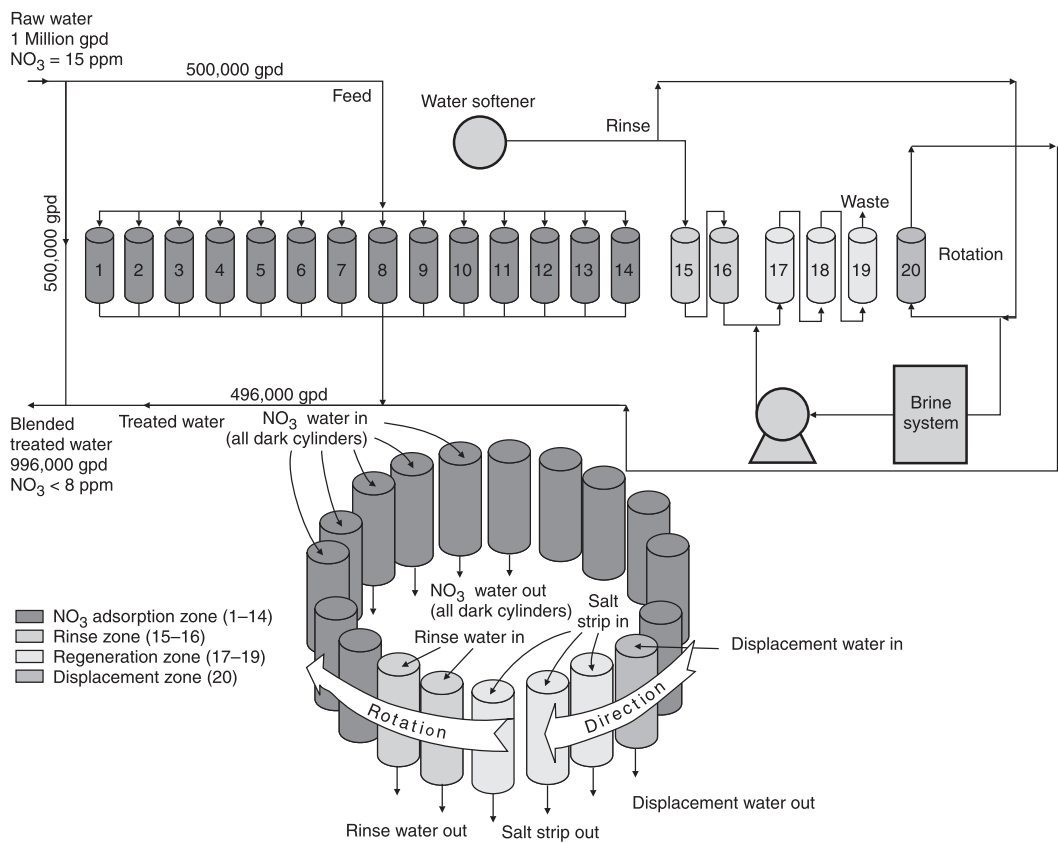Bayer–Lewatit upflow fluidized ion exchange system: (a) loading cycle and (b) regeneration cycle.

Figure 16-8
Schematic of Calgon ISEP ion exchange process.

Figure 16-9
Photograph of ion exchange cannisters on rotating platform in Calgon ISEP ion exchange process (see Fig. 16-8).

used to control the various types of flows (service, regenerant, and rinse) to the columns. The process provides continuous treatment and is fully automated. The service cycles are short as compared to other conventional ion exchange processes, which enable ISEP to have a relatively low resin inventory. The ISEP process typically produces less brine waste as compared to a conventional system and produces low leakage by providing better control over the mass transfer zone.

MIEX MAGNETIC ION EXCHANGE RESIN

The Orica Limited Company of Australia developed the MIEX process for removal of dissolved organic carbon (DOC) from drinking water supplies. The process consists of a SBA exchange resin, usually in the chloride form, with a magnetic component built into it. The resin beads, which are smaller than the conventional resin beads (i.e., diameter $\approx 180\ \mu m$), are contacted with the water in a completely mixed reactor. A typical process flow diagram employing the MIEX resin is shown on Fig. 16-10. The negatively charged DOC molecules exchange with presaturant chloride ion on the resin and are removed from the water. The resin and water are then separated in an upflow settler as the resin beads will agglomerate due to their magnetic properties and rapidly settle out of the water. The settling rate can be as
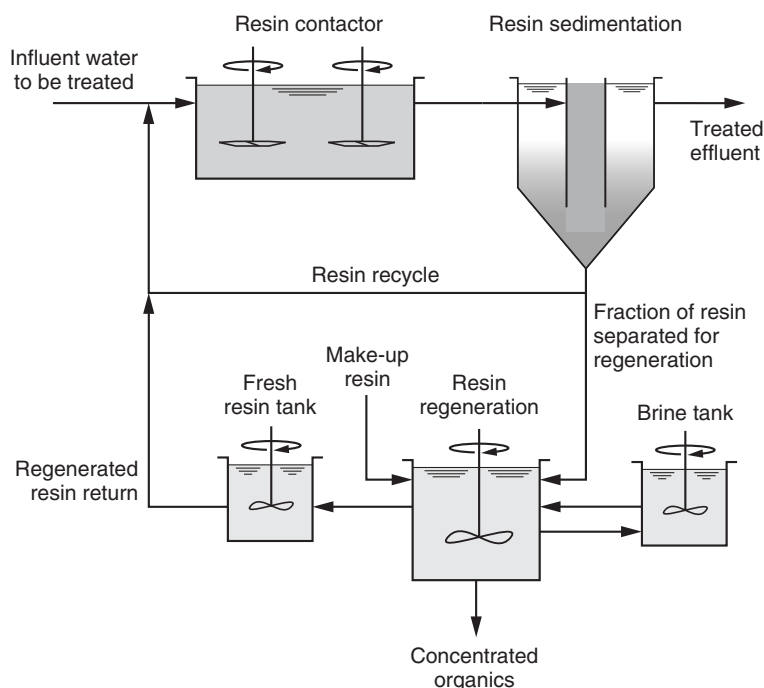

Figure 16-10
Schematic process flow diagram for use of MIEX ion exchange resin for pretreatment of surface water to reduce concentration of natural organic matter (NOM) before addition of coagulating chemical.

high as 15 m/h. The treated water goes on to further treatment. The settled resins are recovered and recycled to the front of the process. A portion of the recovered resin beads (5 to 10 percent) is removed for regeneration. The resin is regenerated with about 10 percent by weight NaCl for 30 min. The regenerated resin beads are stored and reintroduced into the process as needed. An important advantage of the MIEX DOC resin, compared to other ion exchange resins, is its apparent abrasion-resistant properties.

Because the DOC removal remains consistent in the contactor, the DOC leakage is controlled at a predetermined level. Also, because the resin has a high selectivity for DOC, the only inorganic anion that is exchanged is SO_4^{2-}.

Based on preliminary test results, it appears that the removal of DOC on the resin is a surface phenomenon. While other ion exchange resins may be suitable, the time it takes for the DOC to diffuse into the resin may limit their applicability. The performance of MIEX depends on the resin dose, the concentration and nature of the DOC, and the contact time. Reported DOC removal values have been as high as 80 percent, but site-specific testing is required. A pilot study for the City of West Palm Beach, Florida, achieved 67 percent TOC removal with MIEX, compared to 57 percent TOC removal with enhanced coagulation (MWH, 2010). Use of MIEX also reduced coagulant use and sludge production by about 80 percent compared to enhanced coagulation alone.

MIEX is a relatively new technology; as of the end of 2010, about 15 MIEX systems had been installed at treatment plants greater than 3785 m^3/d (1 mgd) in North America.

16-7 Engineering Considerations in Ion Exchange Process Design

Important engineering considerations in developing an ion exchange treatment process include (1) problem definition, (2) establishment of treatment goals, (3) preliminary process analysis, (4) bench- and pilot-scale studies, and (5) development of process design criteria. These considerations are summarized in Table 16-9, discussed below briefly, and illustrated in a case study in the following section.

Problem Definition

Initial consideration of an ion exchange process requires definition of the problem. Defining the problem will require characterization of the composition of the water to be treated (see Table 16-9). The presence of oxidants or reductants in the stream should also be evaluated. Depending upon the specific conditions, the most likely location to apply treatment should be determined so that possible design constraints such as process size, geography, and utility services (sewers, brine waste lines) can be considered in the initial phases of the design.

Table 16-9
Summary of engineering considerations for analysis of ion exchange process

Item	Key Elements/Objectives
Problem definition	1. Characterize water to be treated, including (a) quantitative analysis of the ionic and nonionic constituents and their concentrations, (b) water temperature, (c) pH, (d) turbidity, and (d) density. 2. Evaluate the presence of oxidants and/or reductants in the process stream. 3. Determine the location of the treatment process that minimizes the impact of brine disposal and provides utility services (i.e., sewers, brine waste lines, roadways for salt transport).
Define treatment goals/ design criteria and constraints	1. Required purity of the water. 2. Maximum allowable waste volume. 3. Design constraints (availability of chemicals, space requirements, regulatory permitting, and cost considerations).
Preliminary process analysis	1. Literature survey of previous studies to determine process capabilities and limitations. 2. Select several resins for preliminary assessment and followup bench and pilot plant studies. 3. Using published and manufacturers' data for the resins selected, conduct equilibrium and/or mass transfer model calculations to evaluate process capabilities and limitations.
Bench-scale studies	1. Assess performance of ion exchange resin types. 2. Develop preliminary operating parameters and characteristics. Operating parameters may include (a) saturation and elution curves to assess ion exchange performance, (b) hydraulic considerations (flow rate, head loss, backwashing rate), (c) regeneration requirements (i.e., salt requirements, backwash cycle time, rinse requirements, column requirements), and (d) scaleup requirements.
Pilot plant studies	1. Pilot-scale tests to validate bench-scale test results. 2. Develop long-term operational information, including information on fouling.
Develop design critera for full-scale plant	1. Based on the results of the bench-scale and pilot plant studies, develop design criteria for full-scale design, including (a) scaleup considerations; (b) column design details, including volume of resin, surface area of columns, number of columns, sidewall height, pressure drop, and inlet and outlet arrangements; (c) overall cycle time; and (d) regeneration requirements, including volume, salt quantity and concentration, rinse water, and regeneration cycle time.

The next step is outlining the actual goals of the process such as required purity of the treated water and maximum waste volumes allowable (see Table 16-9). This step should include identifying possible design constraints such as the availability of chemicals, space requirements, regulatory permitting requirements and/or guidelines, and cost limitations.

Treatment Goals and Objectives

Preliminary studies start with selection of promising ion exchange resins for bench-scale testing. Ions that can be removed by each type of ion exchange resin and the regenerant typically used for water treatment applications are summarized in Table 16-10. Preliminary calculations and a literature review combined with resin manufacturer's performance specifications can be used to assess and choose promising resins for bench-scale testing. When choosing a resin, the capacity, selectivity, and ease of regeneration need to be considered. Typical operating conditions for SBA and SAC resins in removing a number of common contaminants are summarized in Table 16-2. Ion exchange modeling software that includes column equilibrium and mass transfer models has been developed to describe the ion exchange process (Clifford and Majano, 1993; Guter, 1998; Hokanson et al., 1995; Liang et al., 1999; Snoeyink et al., 1987).

Preliminary Process Analysis

Bench-scale studies are used to identify ion exchange resins and operating parameters that will provide the best possible performance and cost effectiveness over the design life period. For a specific application, the main criteria to be developed in a bench-scale study are length of removal run, service flow rate, regenerant dose, backwash flow rate, and regenerant concentration. Other variables such as resin stability under cyclic operation must be monitored over long periods of time and will require pilot-scale

Bench- and Pilot-Scale Studies

Table 16-10

Types and characteristics of ion exchange resins

Resin Type	Functional Group	Ions Removed	Regenerant	Operating pH Range
Strong-acid cationic (SAC) resin	Sulfonate, SO_3^-	Ca^{2+}, Mg^{2+}, Ra^{2+}, Ba^{2+}, Pb^{2+}	HCl or NaCl	1–14
Weak-acid cationic (WAC) resin	Carboxylate, $RCOO^-$	Ca^{2+}, Mg^{2+}, Ra^{2+}, Ba^{2+}, Pb^{2+}	HCl	>7
Strong-base anionic (SBA) resin	Quaternary amine, $RN(CH_3)_3^+$	NO_3^-, SO_4^{2-}, ClO_4^-, $HAsO_3^{2-}$, SeO_3^{2-}	NaOH or NaCl	1–13
Weak-base anionic (WBA) resin	Tertiary amine, $RN(CH_3)_2H^+$	NO_3^-, SO_4^{2-}, ClO_4^-, $HAsO_3^{2-}$, SeO_3^{2-}	NaOH or $Ca(OH)_2$	<6

Source: Adapted from Najm and Trussell (1999).

testing. Before considering these variables, it will be useful to discuss the use of small laboratory columns.

USE OF SMALL-DIAMETER COLUMNS

Small-diameter columns can be used to develop meaningful process data if operated properly. Column studies are used primarily to evaluate and compare resin performance in terms of capacity and ease of regeneration. For example, an automated small-column system used to perform laboratory studies for the removal of perchlorate from a groundwater is shown on Fig. 16-11 and schematically on Fig. 16-12. Operational parameters that correspond to full-scale values are summarized in Table 16-2 for SBA resins. Because the main issues of concern are mass transfer and operating exchange capacity, small (1.0- to 5.0-cm-inside-diameter) columns can be scaled directly to full-scale design if the loading rate and empty-bed contact time are the same. Because resin particles are small and the ratio of column diameter to particle diameter is large (>25), the error due to channeling of the water down the walls of the column is minimized.

The hydraulics of full-scale operation cannot be modeled completely by small-scale columns because deviations in flow patterns can exist and should be evaluated at the pilot scale (see Fig. 16-13). However, if full-scale depth is not possible to match in the preliminary studies, a minimum packed-bed depth of 0.6 to 0.9 m (2 to 3 ft) should be adequate to properly design a
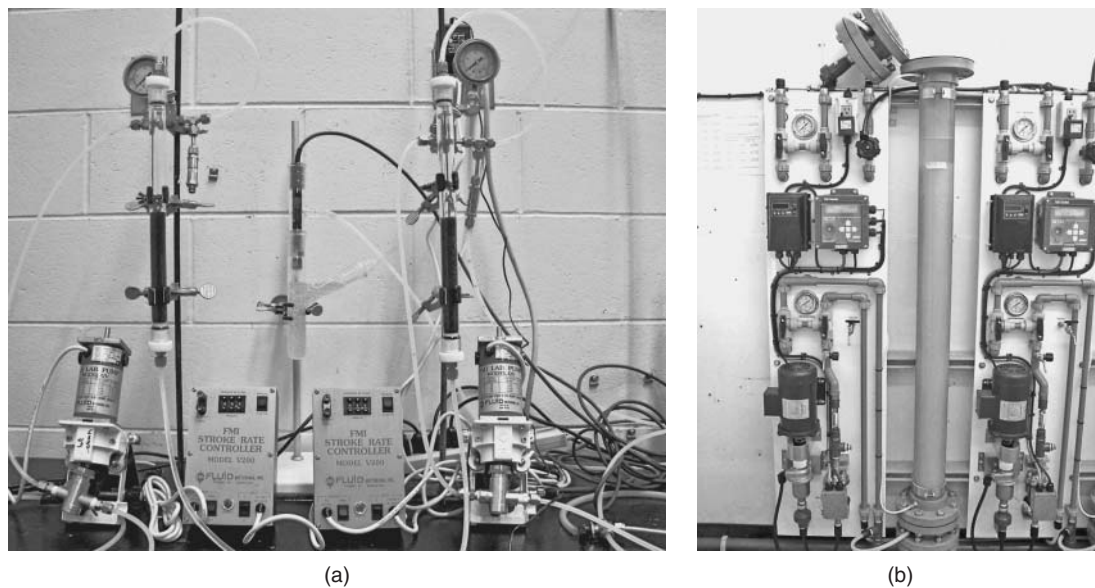
(a)   (b)

Figure 16-11
Ion exchange system, used to perform preliminary experiments: (a) small-scale laboratory columns and (b) larger laboratory-type ion exchange column.
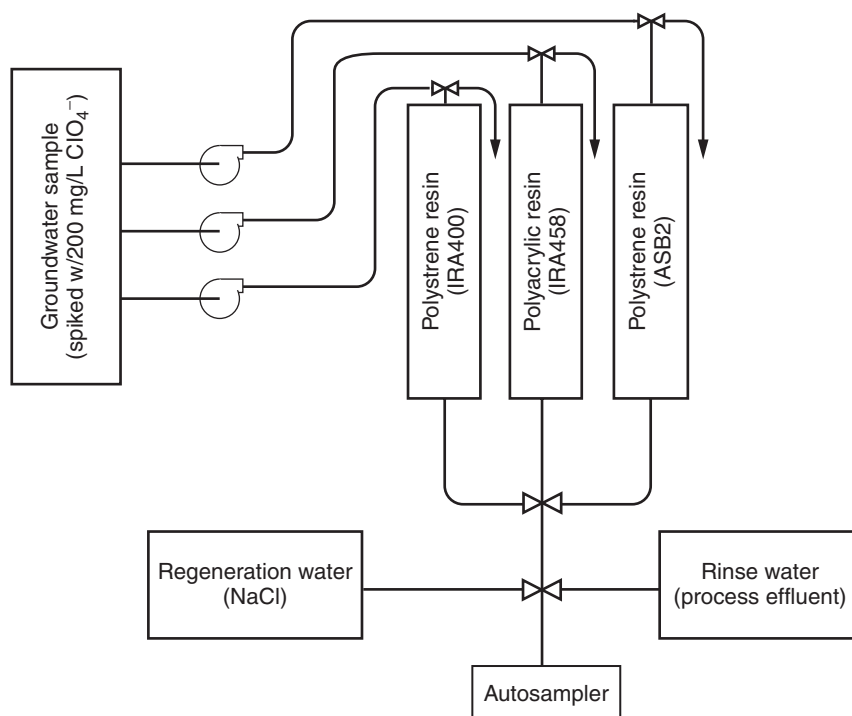
Figure 16-12
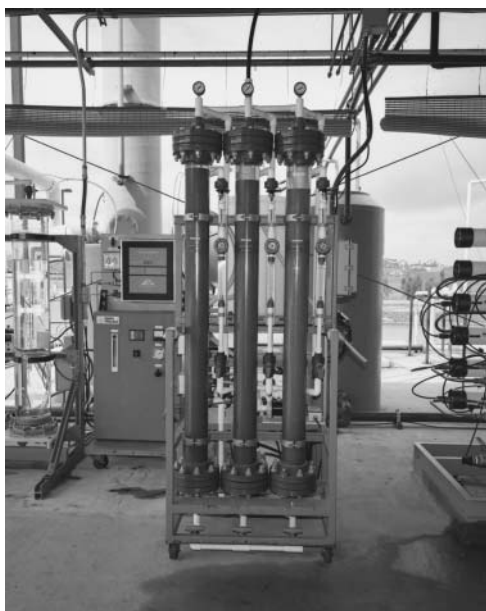Schematic of small-scale laboratory ion exchange system shown in Fig. 16-11.

Figure 16-13
Pilot-scale ion exchange column used to verify bench-scale column tests and obtain data on fouling.
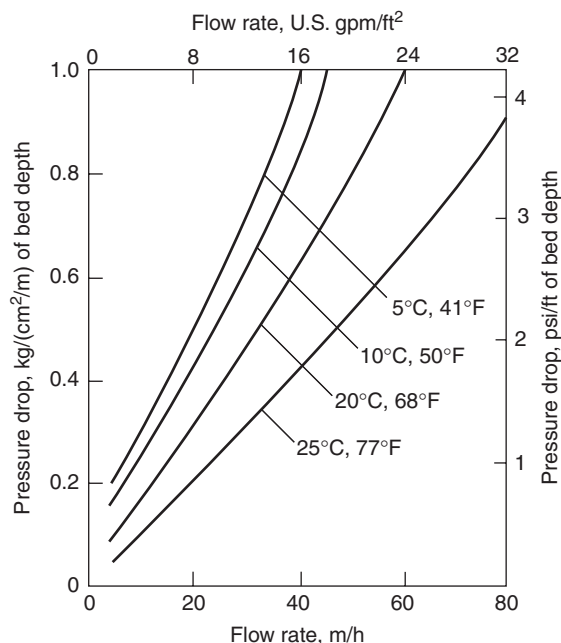
Figure 16-14
Pressure drop curves at various water temperature as function of filtration flow rate for strong-base type I acrylic anion exchange resin (A-850, Purolite).

laboratory or pilot exchange column. For most commercially available resins pressure drop curves versus flow rate and temperature and bed expansion (for backwash) versus flow rate and temperature can be obtained from the manufacturer. For example, performance curves for both the pressure drop and bed expansion as a function of flow rate are given on Figs. 16-14 and 16-15, respectively. During operation, the maximum pressure drop in an ion exchange column should not exceed 172 kPa (25 psi).

SATURATION LOADING AND ELUTION CURVES
The two main types of data collected from small-scale column testing are saturation loading curves and elution curves. Data developed from these curves form the basis for the pilot plant studies and for the development of full-scale designs.
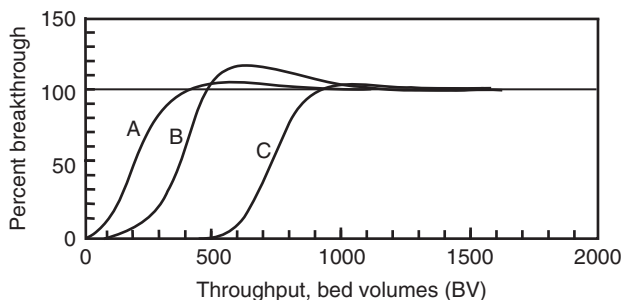
Saturation loading curves
The saturation loading curve is obtained by passing the process stream or a simulated stream of the same chemical composition through a fully regenerated column of resin. A sample of the actual process stream should be fed through the column for a couple of runs. During the runs, samples of the effluent are collected and analyzed until the effluent concentration of the contaminant of interest equals the influent concentration. The effluent concentration is plotted in terms of percent breakthrough, equivalents per liter, or normality as a function of the number of bed volumes of process
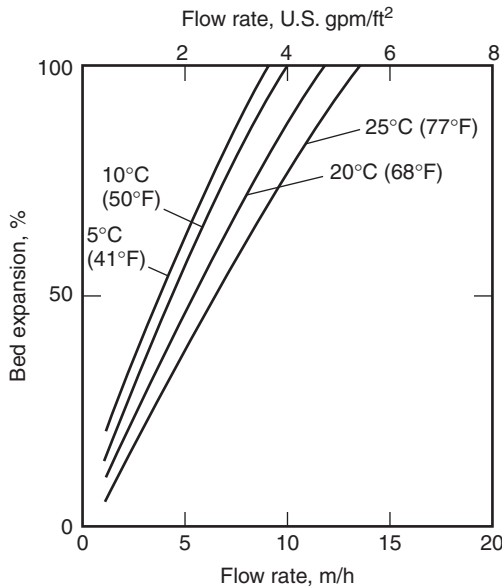
Figure 16-15
Filter bed expansion as function of backwash flow rate at various water temperatures for strong-base type I acrylic anion exchange resin (A-850, Purolite).

stream treated to develop a saturation loading curve. Bed volumes are defined as the average flow rate through the ion exchange column divided by the volume of the resin in the column, including the void fraction.

Generalized saturation loading curves for water containing three ions (A, B, and C) that were treated through an exchange column are presented on Fig. 16-16. As shown on Fig. 16-16, each anion has an effluent profile with the less preferred ions (i.e., A and B) appearing first in the effluent followed by the preferred anion (i.e., C). The observed chromatographic effect shown on Fig. 16-16 depends upon the equilibrium and mass transfer conditions within the column. Percentage concentrations greater than 100 are possible because of the competitive effects among the competing ions, which force previously exchanged ions off the resin. For example, the highest observed effluent concentration for ion B is about 120 percent, or

Figure 16-16
Generalized saturation loading curves for compounds A, B, and C.

1.2 times its average influent concentration. In the previous sections, both binary and multicomponent equilibria were discussed and mathematical descriptions were developed. The chromatographic effect within a column can be described when these equilibrium descriptions are incorporated into mass balance expressions. Saturation loading curves similar to the ones shown on Fig. 16-16 but over several loading and regeneration cycles provide the performance data necessary for design engineers to size the columns and determine the operational aspects of the column design.

Regeneration curves

After completing each saturation loading curve, the resin must be eluted with an excess of regenerant to fully convert it back to its presaturant form. A regeneration curve is obtained, similar to a breakthrough curve, by collecting sample volumes of regenerant after it has passed through the bed and determining the concentrations of the ions of interest in each sample volume. The bed volumes of regenerant used can be converted in terms of a salt loading rate by multiplying it by the salt concentration used and dividing by the volume of the resin bed. These data can be used to choose a regeneration level that will be optimum with respect to operating capacity (resin conversion) and regenerant efficiency.

Generalized regeneration curves for ions A, B, and C for the regeneration of a resin are presented on Fig. 16-17. Notice that with a salt loading of about 240 kg/m^3 all of ion A elutes rapidly and is replaced by chloride ions if the resin is an SBA form and sodium if the resin is an SAC form. Ion B requires a little longer to be removed and requires about 350 kg/m^3. Ion C requires about 850 kg/m^3 to ensure that a significant fraction is removed. From equilibrium theory it is known that divalent ions (i.e., ion
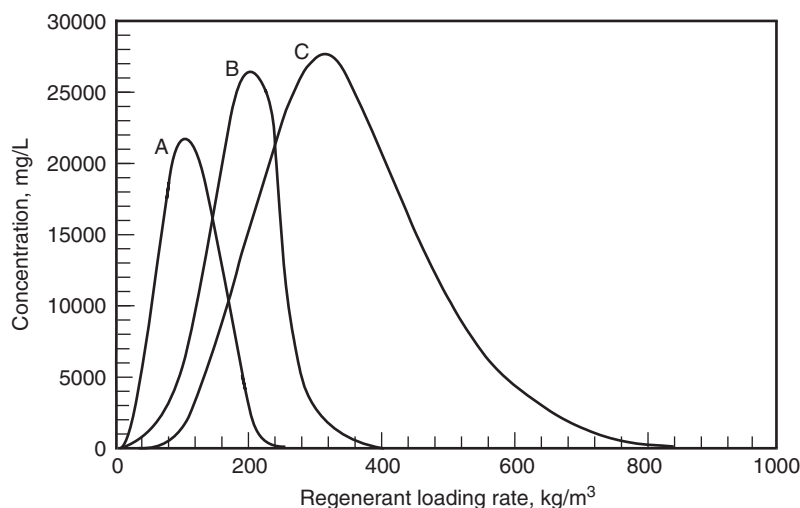

Figure 16-17
Generalized regeneration curves for regeneration of a resin loaded with compounds A, B, and C.

A on Fig. 16-17) will not be preferred in concentrated solutions and hence are easily replaced by sodium or chloride ions.

SERVICE FLOW RATE (SFR) ASSESSMENT

There are two types of flow rates of interest in ion exchange applications: (1) the volumetric flow rate and (2) the surface area loading rate. The volumetric flow rate, usually expressed in $L/L \cdot h$ (gpm/ft^3) or bed volumes per hour (BV/h), is inversely related to the contact time between the solution and the resin and thus the kinetics of exchange. The surface area loading rate, expressed in m/h (gpm/ft^2), is a measure of the superficial flow velocity through the resin bed. The superficial flow velocity must be considered in the scaleup to ensure that excessive flow rates that could damage the resin do not occur.

To determine the optimum SFR, the rate must be varied during the saturation loading tests over a range of choices to see if any noticeable maximum in breakthrough capacity is achieved at a specific flow rate. Typically, the volumetric flow rate is the criterion used because it is directly related to the film mass transfer rate. The main goal in determining the optimum SFR is to reduce the capital cost of equipment. The optimum SFR will minimize the impact of the film mass transfer resistance and consequently shorten the length of the mass transfer zone. The higher the acceptable flow rate, the smaller the contactor can be for a given treatment flow because the mass transfer zone length can be contained in a smaller column. Typical service flow rates range from 8 to 40 BV/h (1 to 5 gpm/ft^3).

Example 16-5 Calculation of BV/h

An ion exchange column has a column loading time of 56 h at a service flow of 6.0 ML/d. The column has a diameter of 3.66 m and a resin depth of 1.1 m. Calculate the service flow in BV/h.

Solution

1. Calculate the volume of the bed occupied by the resin:

$$BV = area \times depth = \tfrac{1}{4}\pi(3.66 \text{ m})^2 \times 1.1 \text{ m} = 11.67 \text{ m}^3$$

2. Calculate the service flow rate in BV/h:

$$BV/h = Q \times (1 \text{ BV}/11.67 \text{ m}^3)$$

$$= (6.0 \times 10^6 \text{ L/d})(d/24 \text{ h})(m^3/1000 \text{ L})(1 \text{ BV}/11.67 \text{ m}^3)$$

$$= 21.6 \text{ BV/h}$$

REGENERATION REQUIREMENTS

The three variables of concern during regeneration are (1) concentration of the regenerant, (2) regenerant flow rate, and (3) regenerant dosage.

Concentration and flow rate

A typical scheme to determine optimum conditions would be to choose a fairly slow (2 to 5 BV/h or less) rate and an excess of regenerant, then vary the concentration of regenerant and develop elution curves for each concentration. An optimum concentration would be one that elutes the resin as rapidly as possible. Next, the optimum rate can be determined by keeping the optimum concentration and excess regenerant dose constant while varying the flow rate. Normally, a slower flow rate will allow for a more complete attainment of equilibria conditions but may not be as important a factor when the separation factor favors the ion already on the resin. In many ion exchange applications the only way to fully convert a resin is to use an excess of regenerant.

Regenerant dose

Using the experimentally determined values of concentration and flow rate, the optimum dose of regenerant can be determined. The dose is usually expressed in grams of regenerant per liter of resin (pounds of regenerant per cubic foot of resin). An elution curve should be developed for the optimum set of conditions. Using this curve, it is possible to determine regeneration efficiency and column utilization curves as a function of regenerant dosage.

During regeneration, if $\alpha < 1$, an excess of regenerant must be used to convert the resin to 100 percent regenerant form. Instead of converting the resin completely to this form, the amount of regenerant is chosen so that the column will be converted to a degree that will give the required quality of effluent for a reasonable run length. A plot of regeneration efficiency and column utilization versus regeneration level for a strong-acid exchanger being used for softening is given on Fig. 16-18.

Regeneration efficiency is the actual hardness (or other species of interest) removed by the given amount of salt (or other regenerant) divided by the theoretical hardness that could be removed by that amount of salt assuming 100 percent conversion. Column utilization represents the actual hardness removed by the regenerant divided by the total available exchange capacity of the resin in the column. The product of the two percentages for a given dosage is plotted on Fig. 16-18. The curve peaks roughly where the two curves intersect, and this peak usually indicates the optimum conditions.

OPERATION TO BREAKTHROUGH

Once the above parameters have been established, it is necessary to operate the column to an allowable breakthrough point and leakage level for
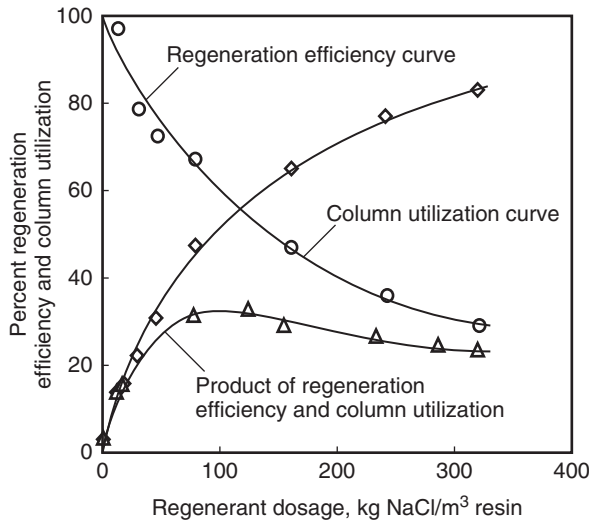
Figure 16-18
Efficiency and column utilization as function of regeneration level for strong-acid resin used for softening. Conditions: influent hardness, 500 mg/L as CaCO$_3$; service flow rate, 267 L/min · m^3; regeneration rate, 67 L/min · m^3; 10% NaCl.

a number of cycles (3 to 5) to stabilize the system. The break point is defined as the point where the target ions first appear in the column effluent. Leakage is defined as the appearance of a low concentration of undesired influent ions in the column effluent during the initial part of the exhaustion. Leakage is caused by residual ions in the resin at the bottom of the column due to incomplete regeneration that are displaced by other ionic species coming down the column. A cycle can then be run to get a good indication of what can be expected in the full-scale column.

Once the results of the bench-scale studies are available, the findings are used to develop design criteria for the full-scale installation. Scale-up considerations, the selection of service flow rates, regeneration requirements, and inlet and outlet considerations are considered below.

Development of Column Design Criteria

SCALEUP CONSIDERATIONS
Data derived from small-column experiments can be scaled up directly to any diameter column should the height of the bed remain constant. If the small-column experiments were done at a reasonable height (0.6 to 1 m), then increasing the height in a full-scale design usually will not change the shape of the breakthrough curve when plotted as concentration versus time, but will extend service time. In exchanges where the separation factor is greater than 1 for the ion to be removed, the mass transfer zone length or exchange zone will be relatively small with respect to the column height. Increasing the column depth for the same flow rate will not increase the breakthrough capacity with respect to bed volumes.

COLUMN DESIGN DETAILS

Maintaining the same volumetric flow rate as determined in the small-scale experiments will produce similar cycle times and effluent concentration profiles. If the height of the column is kept constant, then the superficial velocity will also remain equal. If the column is deepened and the volumetric flow rate is kept the same, the superficial velocity will be increased by the proportion that the height has increased. The increased flow should not be a problem, unless a critical range of flow velocities is reached. Typical superficial velocities are in the range of 10 to 36 m/h (4 to 15 gpm/ft^2). Excessive velocities will increase the pressure drop through the column and could adversely affect the stability of the resin beads. Once the optimum service flow rate is known, the design details of the full-scale columns, including volume of resin, surface area of columns, number of columns, side wall height, and pressure drop, can be determined. For example, the amount of resin volume needed to treat a given flow of water will be

$$\text{Required resin volume, m}^3 = \frac{\text{treated-water flow rate (L/min)}}{\text{service flow rate (L/min} \cdot \text{m}^3)} = \frac{Q}{\text{SFR}}$$

$$\text{(16-39)}$$

Based on this volume and the desired depth of the resin, the diameter of a single column can be determined. Should the required diameter be much larger than 4 m (12 ft), two or more columns should be used. Typical bed depths used in the industry range from 0.75 to 3 m (2.5 to 10 ft). Determination of the column design details is illustrated in the following section.

One of the major reasons for poor ion exchange performance is the poor design of the feed distribution and outlet effluent collection facilities in contactors. The feed must be distributed uniformly over the resin surface and collected uniformly from the bottom of the column to prevent channeling, maldistribution of flow, and density currents. If the ion exchange columns are not properly designed, premature breakthrough and excessive leakage can result.

REGENERATION REQUIREMENTS

Unless the treated-water flow demand is intermittent, to prevent interruption of the service cycle for regeneration, two or more columns or a treated-water storage reservoir are required. If the exhaustion cycle is long (16 to 24 h), a reservoir can provide sufficient water during regeneration time, normally 1 to 2 h. Based on manufacturer's design data or laboratory studies, the regeneration requirements can be calculated. For most ion exchange applications, a typical regeneration cycle is as follows:

1. End of service run
2. Backwash
3. Regeneration

4. Slow displacement rinse

5. Fast rinse

6. Stand-by [optional if extra column(s) in service and the regeneration time is breakthrough volume/(number of columns −1)]

7. Beginning of service cycle

Backwashing

Backwashing is typically done to reclassify the resin so that there will be a gradual increase in particle size from top to bottom and to help prevent channeling. Ion exchange media will act as good filter media; hence backwashing will remove trapped particulate matter from the resin. Fifty to 75 percent bed expansion is normal, and proper freeboard should be allowed for in-column design. Backwashing will typically last 5 to 15 min. Every ion exchange system should be designed so it can be backwashed, but backwashing is often only necessary at infrequent intervals. This is particularly true when treating groundwater, which is relatively free of particles.

Backwashing can have important impacts on leakage. When regeneration is in the co-current mode and leakage is an issue, backwashing after each regeneration cycle is performed to thoroughly mix the resin and dramatically reduce leakage. When regeneration is in the countercurrent mode, backwashing is best avoided altogether, but if required, it should be done before regeneration so leakage is minimized.

Regenerant consumption

Regenerant consumption per cycle based on design criteria must be determined. The rinses following regeneration are normally operated in the co-current mode: the slow rinse for one to two bed volumes at the regeneration flow rate to displace most of the regenerant from the bed and the fast rinse at the rate of service flow rate for 10 to 30 min. The rinse can be monitored using an online conductivity meter at the effluent of the column to determine when the cycle is complete. An inventory of used brine and rinse volumes must be calculated to adequately prepare for disposal. The disposal of brine is typically a costly part of operation and maintenance cost along with regenerant chemical costs. The disposal of concentration brines may be the critical factor in many potential applications.

16-8 Ion Exchange Process Design Case Study

The purpose of the case study presented in this section is to illustrate the steps required in developing design criteria for an ion exchange plant. Although the approach is developed for the removal of perchlorate ions from a groundwater, the same steps would be required for other ionic

constituents. The laboratory and pilot plant information for this design approach case study was taken from Najm et al. (1999).

Problem Definition

A groundwater that is being considered for use as a municipal drinking water source was found to have a perchlorate concentration of 90 μg/L. At the time of this discovery, the regulatory agency was considering a maximum contaminant level of 4 μg/L. The municipality is proposing to pump and treat about 0.16 m³/s (2500 gpm) using an ion exchange process. Water quality parameters for the groundwater are presented in Table 16-11.

Treatment Goals/Design Criteria and Constraints

A full-scale ion exchange system including a regeneration facility to treat the groundwater to the above regulatory requirement is to be designed so that an assessment of the cost of treatment can be made. The design criteria that need to be determined are

1. Column requirements (number of columns, column dimensions)
2. Maximum SFR and head loss requirements
3. Cycle times (regeneration time, rinse time)
4. Regeneration and rinse requirements (quantities)
5. Type of resin

Preliminary Process Analysis

To determine the important design and operational parameters required for effective treatment of perchlorate from this groundwater, laboratory and pilot plant studies are needed. Based on a review of the literature and past experience, three SBA ion exchange resins (two polystyrene and one polyacrylic resin) were selected for bench and pilot plant studies.

Laboratory and Pilot Plant Studies

The design sequence begins with performing laboratory and pilot plant studies to determine the most efficient resin in terms of operational or

Table 16-11
Water quality parameters for groundwater for ion exchange process design case study

Parameter	Unit	Value
Alkalinity	mg/L as $CaCO_3$	122
Hardness	mg/L	163
pH	Unitless	7.8
Nitrate	mg/L as N	6.6
Sulfate	mg/L	53
Perchlorate	μg/L	90
TOC	mg/L	0.9
Temperature	°C	15

working capacity, regeneration requirements including regenerant salt concentration and loading, rate and regeneration, and rinse volume requirements. Once these parameters are established, pilot plant testing is performed to evaluate long-term performance of the most promising resin(s). The results of the pilot plant studies are used to establish the full-scale design criteria listed above.

LABORATORY STUDIES

It should be noted that all of the laboratory and pilot plant data developed in this case study are not presented. Only the information pertinent to determining the most efficient and least cost design is presented (see Najm et al., 1999). Laboratory studies were performed on the groundwater to evaluate the three ion exchange resins selected for study, characterize the perchlorate breakthrough, evaluate the regeneration efficiency, and identify the conditions for pilot testing. Column breakthrough was defined as exceeding the perchlorate minimum reporting limit of 4 μg/L so as to minimize perchlorate leakage. Typical saturation and elution curves for an SBA resin are shown on Fig. 16-19.

Countercurrent regeneration was employed using salt loading rates of 240, 480, and 720 kg NaCl/m^3 (15, 30, and 45 lb NaCl/ft^3). Rinse volumes were determined when the conductivity of the effluent rinse decreased to less than 700 S/cm. From the results of the laboratory study it was found that SBA resins are effective for the removal of perchlorate from groundwater, but the process requires optimization. Polystyrene resins had a higher affinity for perchlorate but are difficult to regenerate, whereas the polyacrylic resins have a moderate affinity for perchlorate and can be regenerated effectively. Perchlorate leakage occurred at a salt loading of 240 kg NaCl/m^3 (15 lb NaCl/ft^3), and further testing is necessary to identify long-term working capacity and a salt loading of 480 kg NaCl/m^3 (30 lb NaCl/ft^3) or greater for effective regeneration to eliminate perchlorate leakage.

PILOT PLANT STUDIES

Based on laboratory studies, pilot plant studies were conducted to demonstrate the performance of the three resins operated under full-scale operating conditions for several regeneration cycles and to validate the laboratory results. The pilot plant design and operational parameters presented in Table 16-12 were based on the typical design values summarized in Table 16-2 for SBA resins. The important parameters of the pilot plant study are displayed below.

Based on the results of the pilot study, the polyacrylic resin was found to provide the best working capacity while minimizing the salt quantity requirements. A pilot plant result for the most promising SBA resin operated for 31 loading cycles is displayed on Fig. 16-20. The resin was regenerated using 16 BV of 480 kg/m^3 (30 lb/ft^3) salt regeneration, salt strength of
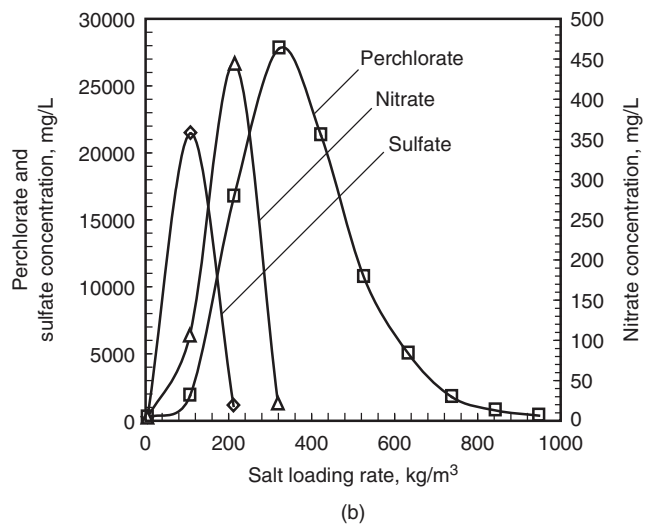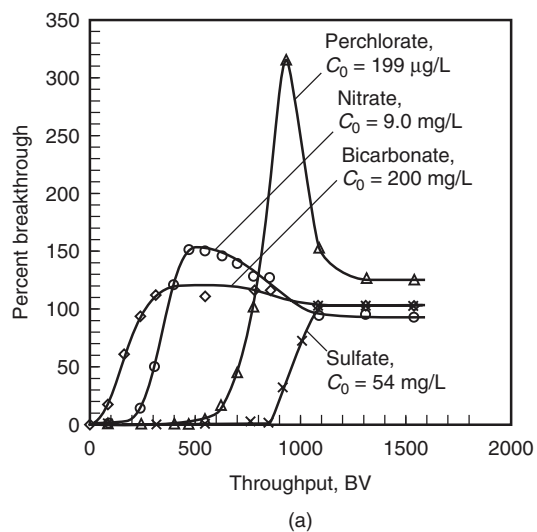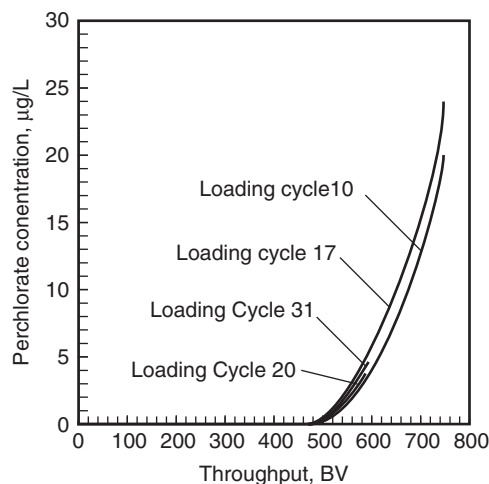
Figure 16-19
Typical saturation and regeneration curves: (a) saturation loading curves for perchlorate contaminated groundwater on SBA resin and (b) regeneration curves for regeneration of strong-base resin loaded with perchlorate, sulfate, and nitrate (Adapted from Najm and Trussell, 2001).

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Table 16-12

Operational parameters utilized for pilot plant studies to assess resin performance

Parameter	SI Units	Value	U.S. Customary Units	Value
Operational mode	—	Countercurrent	—	Countercurrent
EBCT	min	1.5	min	1.5
Column diameter	m	0.0509	ft	0.167
Resin depth	m	0.862	ft	2.83
Service flow rate	BV/h	40	gpm/ft^3	5.0
Flow rate per column	m^3/h	0.0681	gpm	0.3
Column resin volume	m^3	0.00176	ft^3	0.062
Regenerant type	—	NaCl	—	NaCl
Regenerant strength	%	3	%	3
	mg/L	30,000	—	—
Salt loading rate	kg^3/m^3	480	lb/ft^3	30
Regeneration and rinse flow rate	m^3/h	0.0363	gpm	0.16
Regeneration volume	BV	16	BV	16
Rinse volume	BV	2–6[a]	BV	2–6[a]
Backwash rate	m/h	6.0	gpm/ft^2	2.5

[a]Column rinsed until effluent conductivity decreased to less than 700 S/cm.

Figure 16-20
Pilot plant effluent profiles for perchlorate on SBA resin operated for total of 31 cycles at 480 kg/m^3 (30 lb/ft^3) salt regeneration rate (Adapted from Najm and Trussell, 2001).

10 percent (specific gravity 1.07), and between 2 and 6 BV of rinse water. The initial breakthrough occurred at 560 BV and consistently produced regenerated column runs with a design leakage of less than 4 μg/L. Consequently, the columns could be loaded up to 560 BV prior to regeneration without exceeding the allowable design leakage point. Because perchlorate

breakthrough (at 4 µg/L) consistently occurred at 560 BV for 31 cycles, full regeneration of the resin was accomplished.

Development of Full-Scale Design Criteria

Design criteria for a full-scale ion exchange treatment plant were developed based on the results of the bench-scale and pilot plant study. The plant is sized for a maximum finished water capacity of $0.160 \text{ m}^3/\text{s}$ (2500 gpm). The plant is sized such that one column is in the regeneration mode on standby while the others are in the operational mode. The service flow rate used in the pilot plant study was 40 BV/h, which is on the high end of service flow rates. The high rate was used to decrease the time required to perform the pilot studies. Consequently, a lower SFR of 28 BV/h (3.5 gpm/ft^3) was used for the full-scale design (see summary design criteria in Table 16-13).

ION EXCHANGE COLUMN DESIGN
Design of the ion exchange columns involves the determination of the volume of resin, the surface area of resin required, the number of columns, the sidewall height, and the pressure drop.

Volume of resin
The number of columns can be found by first calculating the total volume of resin required assuming a typical SFR of 28 BV/h (3.5 gpm/ft^3):

$$\text{Total required resin volume} = \frac{Q}{\text{SFR}} = \frac{0.160 \text{ m}^3/\text{s}}{(28 \text{ BV/h})(1 \text{ h}/3600 \text{ s})}$$

$$= 20.6 \text{ m}^3 (727 \text{ ft}^3)$$

Surface area of resin required
As discussed above, the EBCT of the pilot plant should be about the same as the EBCT used in the full-scale design. Because a resin depth of 0.863 m (2.83 ft) was used in the pilot plant study, a similar full-scale design with a depth of 1.0 m (3 ft) will be used. Consequently, the total ion exchange surface area required is determined to be

$$\text{Total required surface area} = \frac{\text{resin volume}}{\text{resin depth}} = \frac{20.6 \text{ m}^3}{1.0 \text{ m}} = 20.6 \text{ m}^2 (223 \text{ ft}^2)$$

Ion exchange columns come in standard sizes from the manufacturer. Typically, they may have column diameters of 1.0 m (4 ft), 2.0 m (6 ft), 3.0 m (10 ft), 4.0 m (13 ft), and 5.0 m (16 ft). If a 3-m column diameter is chosen for the design, the column would provide 7.1 m² (76.4 ft²) of service area and the volume occupied by the resin would be 7.1 m³.

Table 16-13
Summary of design criteria for perchlorate removal case study

Parameter	SI Units	Value	U.S. Customary Units	Value
Design product water capacity	m^3/s	0.160	gpm	2,536
Minimum water temperature	°C	15	°F	59
Resin type	—	SBA, polyacrylic, type I	—	SBA, polyacrylic, type I
Effective resin size	mm	0.6	in.	0.024
SFR	BV/h	28	gpm/ft^3	3.6
EBCT	min	2.14	min	2.14
Resin depth	m	1.0	ft	3.0
Total minimum sidewall depth	m	3.15	ft	10.3
Required resin volume	m^3	20.6	ft^3	728
Column diameter	m	3.0	ft	10
Number of columns	—	4	—	4
BVs to perchlorate breakthrough (single column)	BV	560	BV	560
Salt loading rate (NaCl)	kg/m^3	480	lb/ft^3	30
Salt strength	%	10	%	10
Rinse volume	BV	6	BV	6
Clean-water head loss rate	kPa/m	60.8	psi/ft	2.7
Clean-water head loss	kPa	60.8	psi	8.8
Regeneration volume per column	BV	4.5	BV	4.5
Number of regenerations for each column per year	—	438	—	438
Spent regeneration solution volume per column	m^3	32	gal	8,454
Annual regeneration solution volume per column	m^3/yr	14,016	Mgal/yr	3.7
Salt quantity required per column	kg	3,408	lb	7,513
Annual salt quantity required per column	kg/yr	1.5×10^6	lb/yr	3.3×10^6
Rinse volume required per column	m^3	43	gal	11,360
Annual rinse volume per column	m^3/yr	18,834	Mgal/yr	5.0
Total annual salt requirements	kg/yr	4.50×10^6	lb/yr	9.9×10^6
Total annual regeneration solution volume	m^3/yr	42,048	Mgal/yr	11.1
Total annual rinse requirements	m^3/yr	56,502	Mgal/yr	15.0
Total regeneration cycle time	min	32.4	min	32.4

Number of columns
If the total column area is divided by the area of one column, the number
of columns required can be calculated as

$$\text{Required number of columns} = \frac{\text{total column area}}{\text{area of one column}} \frac{20.6 \text{ m}^2}{7.1 \text{ m}^2} = 2.9 \approx 3$$

With one column in the regeneration or standby mode a total of four 3.0-m-
(10-ft) diameter columns are required.

Sidewall height

The total sidewall height of the column must include the depth of the resin, height for inlet distributor, height for resin support, and height for backwashing. As discussed above, the depth of the resin was chosen as 1.0 m. The heights for the inlet distributor and resin support underdrain can be obtained from the manufacturer, which in this case were 1.0 and 0.5 m, respectively. The sidewall height of the ion exchange columns must include room for bed expansion due to backwashing. Bed expansion can be calculated using manufacturer's performance curves such as those shown on Fig. 16-15.

If the backwash superficial velocity from the pilot study is 6.0 m/h (2.43 gpm/ft^2) and the water temperature is 15°C, the percent bed expansion required during backwashing and extra height required for backwashing can be determined. From Fig. 16-14, the percent expansion required is about 65 percent. The expanded height required for backwash is

$$\text{Expanded bed height} = 0.65 \times 1.0 \text{ m} = 0.65 \text{ m}$$

The total sidewall height should be a minimum of 3.15 m (1.0 + 0.65 + 1.0 + 0.5) (10.33 ft).

Pressure drop

Before continuing the design calculations, the column pressure drop needs to be checked. As noted previously, the maximum pressure drop for the ion exchange resin bed should not exceed 172 kPa (25 psi). Manufacturers provide pressure drop curves for commercially available resins such as shown previously on Fig. 16-14. The superficial velocity for this system is 28 m/h, the initial pressure drop through the resin is 0.62 kg/cm^2/m of bed depth, as shown on Fig. 16-14. For 1.0 m of resin depth, the clean-water pressure drop is 0.62 kg/cm^2, or 60.8 kPa (8.8 lb/in.^{2}). In this case, the clean-water pressure drop column design is well below the maximum allowable pressure drop (60.8 kPa $\ll$ 172 kPa). If these curves are not available, the column head loss can be calculated (see Chap. 11, Eq. 11-13). Typically, the pressure drop can be determined in the pilot plant studies if the loading rate and EBCT used in the pilot columns are the same as those in the full-scale design.

OVERALL CYCLE TIME

As discussed above, perchlorate breakthrough in the pilot plant study consistently occurred at 560 BV for 31 cycles, at which time full regeneration of the resin was accomplished. The time for each column loading cycle can be calculated by dividing 560 BV by the SFR as shown:

$$\frac{\text{Time}}{\text{Loading cycle}} = \frac{\text{bed volumes/loading cycle}}{\text{SFR}} = \frac{560 \text{ BV}}{28 \text{ BV/h}} = 20 \text{ h}$$

If the columns are staggered or started at different times, then each column will be regenerated every 20 h and the blended effluent will not exceed 4 µg/L perchlorate concentration.

REGENERATION REQUIREMENTS

Based on the results of the pilot plant studies, it was found that the perchlorate-loaded columns could be regenerated fully using 480 kg $NaCl/m^3$ (30 lb $NaCl/ft^3$) of resin with a salt strength of 10 percent. For the full-scale design, 480 kg $NaCl/m^3$ (30 lb/ft^3) salt loading rate with a 10 percent salt strength (specific gravity 1.07) will be used. The salt solution can be calculated from the specific gravity of the salt and the salt strength as

$$10\% \text{ salt solution} = (0.1 \text{ kg NaCl/kg soln}) \ (1070 \text{ kg soln/m}^3 \text{ soln})$$

$$= 107 \text{ kg NaCl/m}^3 \text{ soln}$$

Regeneration volume

The regeneration volume can be calculated by dividing the salt requirements per volume of resin by the salt solution concentration:

$$\text{Required regeneration volume per bed volume} = \frac{480 \text{ kg NaCl/m}^3 \text{ resin}}{107 \text{ kg NaCl/m}^3 \text{ soln}}$$

$$= 4.5 \text{ L m}^3 \text{ soln/m}^3 \text{ resin}$$

Salt quantity

The total quantity of salt required on an annual basis can be calculated by multiplying the number of regenerations in a year by the quantity of salt required per regeneration. The number of regenerations can be calculated by dividing the number of hours in a year by the loading cycle time per column:

$$\text{Number of regenerations for each column per year} = \frac{(365 \text{ d/yr}) \ (24 \text{ h/d})}{20 \text{ h/regen}}$$

$$= 438/\text{yr}$$

The quantity of salt per regeneration per column is calculated as

$$\text{Salt quantity per column regeneration}$$

$$= (7.1 \text{ m}^3 \text{ resin/regen}) \ (480 \text{ kg NaCl/m}^3 \text{ resin})$$

$$= 3408 \text{ kg NaCl (7531 lb)}$$

The annual salt consumption requirement per column is given as

$$\text{Annual salt quantity required per column}$$

$$= (438 \text{ regen/yr}) \ (3408 \text{ kg NaCl/regen})$$

$$= (1.5 \times 10^6 \text{ kg NaCl/yr}) \ (3.3 \times 10^6 \text{ lb/yr})$$

The volume of spent regeneration solution per column regeneration is given as

$$\text{Spent regeneration solution per column}$$

$$= (7.1 \text{ m}^3 \text{ resin/BV}) \times 4.5 \text{ BV}$$

$$= 32 \text{ m}^3/\text{column} \quad \text{or} \quad 1130 \text{ gal/column}$$

The total annual volume of spent regeneration solution per column is calculated as

$$\text{Total annual spent regeneration solution per column}$$
$$= (32 \text{ m}^3/\text{column}) \, (438 \text{ columns/yr})$$
$$= 14{,}016 \text{ m}^3/\text{yr} \quad \text{or} \quad 3.7 \text{ Mgal/yr}$$

The total annual quantity of salt required and regeneration solution generated for the whole plant will be three times the above quantities because within every 20-h period each of the three columns in service will be regenerated. The total plant quantity values are shown in Table 16-11.

Rinse water requirement
The quantity of rinse water can be determined based on the rinse quantity used in the pilot plant study. In the pilot plant study, 2 to 6 BV were used to reduce the conductivity of the rinse water below 700 S/cm. To be conservative, 6 BV will be used for the full-scale design. The quantity of rinse volume per regeneration is calculated as

$$\text{Rinse volume per column} = (7.1 \text{ m}^3 \text{ resin/BV}) \, (6 \text{ BV})$$
$$= 43 \text{ m}^3/\text{column} \quad \text{or} \quad 11{,}360 \text{ gal/column}$$

The total annual rinse volume is given as

$$\text{Annual rinse volume per column} = (43 \text{ m}^3/\text{column}) \, (438 \text{ columns/yr})$$
$$= 18{,}834 \text{ m}^3/\text{yr} \quad \text{or} \quad 5.0 \text{ Mgal/yr}$$

Regeneration cycle time
The cycle time for the salt regeneration is calculated by multiplying the EBCT by the number of bed volumes of regeneration solution per column. The EBCT is first calculated by dividing the resin depth in the column by the superficial velocity as shown:

$$\text{EBCT} = \frac{1 \text{ m}}{28 \text{ m/h}} (60 \text{ min/h}) = 2.14 \text{ min}$$

$$\text{Regeneration time per column} = \text{EBCT} \left(\frac{\text{BV}}{\text{regen}} \right)$$
$$= (2.14 \text{ min/BV}) \, (4.5 \text{ BV}) = 9.6 \text{ min}$$

Similarly, the cycle time for the rinse step is calculated as

$$\text{Rinse time per column} = \text{EBCT} \left(\frac{\text{BV}}{\text{regen}} \right) = (2.14 \text{ min/BV}) \, (6 \text{ BV})$$
$$= 12.8 \text{ min}$$

Typical backwash times range from 5 to 20 min, so choosing a backwash time of 10 min, the total time a column will be out of service for the

regeneration cycle, can be estimated to be

Total regeneration cycle time per column
= regeneration time per column + rinse time per column
   +backwash time per column   (16-40)
= 9.6 min + 12.8 min + 10 min
= 32.4 min

The design parameters developed for the full-scale process design for perchlorate removal are summarized in Table 16-13.

**Case Study
Design Summary**

Problems and Discussion Topics

16-1   A SAC exchanger is employed to remove calcium hardness from water. The capacity of the resin is 2.0 meq/mL in the sodium form. If calcium concentrations in the influent and effluent are 44 and 0.44 mg/L, determine the maximum volume of water that can be treated per cycle given the following:

Cations	meq/L	Anions	meq/L
Ca^{2+}	2.2	HCO_3^-	2.9
Mg^{2+}	1.0	Cl^-	3.1
Na^+	3.0	SO_4^{2-}	0.2
Total	6.2	Total	6.2

16-2   Consider the removal of perchlorate from well water using an SBA exchange resin. The following table lists the major anions contained in the well water. Assuming perchlorate is completely removed from solution, calculate the maximum volume of water that can be treated per liter of resin assuming equilibrium conditions. Assume total resin capacity of the SBA is 1.4 eq/L.

Parameter	Unit	Value
Alkalinity	mg/L as $CaCo_3$	200
Perchlorate	mg/L	200
Nitrate	mg/L	9.0
Sulfate	mg/L	55
pH	Unitless	8.0

16-3   A small public water system is considering removing calcium from its water using ion exchange. The average daily flow rate is about 2 ML/d and the influent calcium concentration is 200 mg/L as $CaCO_3$. If a SAC exchange resin in the sodium form is to be used, estimate the minimum daily volume of resin that would be required assuming that calcium is completely removed and is the only cation

exchanging on the resin. Assume the total resin capacity of the SAC resin is 2.0 eq/L in the chloride form.

16-4   Describe the differences between SAC exchanger resins and SBA exchanger resins.

16-5   Explain the differences between type I and type II exchanger resins.

16-6   Describe and explain the operational advantages of using co-current regeneration versus countercurrent regeneration.

16-7   A small public water system is considering removing barium from its well water using ion exchange. The average daily flow rate is about 1.5 ML/d (400,000 gpd) and the influent barium concentration is 11.3 mg/L. If an SBC exchange resin is to be used, estimate the minimum daily volume of resin that would be required assuming that barium is completely removed and is the only cation exchanging on the resin.

16-8   An SBA exchanger resin is used to remove nitrate ions from well water that contains high chloride concentration. Usually bicarbonate and sulfate are present in the water (assume they are negligible). The total resin capacity is 1.5 eq/L. Calculate the maximum volume of water that can be treated per liter of resin. The water has the following composition:

Cations	meq/L	Anions	meq/L
Ca^{2+}	1.4	SO_4^{2-}	0.0
Mg^{2+}	0.8	Cl^-	3.0
Na^+	2.6	NO_3^-	1.8
Total	4.8	Total	4.8

16-9   A small municipal water supply treats a maximum daily flow of 5.0 ML/d, maximum weekly flow of 25 ML/wk, and a maximum nitrate concentration of 18 mg/L. The plant treats 5 ML of water and operates only 7 h per day and 5 days per week, and there is sufficient storage capacity for the weekend demand. The treatment objective for the ion exchange process is 0.6 mg/L NO_3-N and will be blended with untreated water at 18 mg/L NO_3-N to produce a final product water of 8 mg/L or less NO_3-N. With a standard of 10 mg/L as NO_3-N, determine the flow rate of the ion exchanger and blending rate.

16-10   A groundwater contains the following anion concentration exchanger ($NO_3-N = 18$ mg/L, $SO_4^{2-} = 50$ mg/L, $Cl^- = 35$ mg/L, and $HCO_3^- = 85$ mg/L). Assuming nitrate is removed completely from solution, calculate the equilibrium exchange capacity for each ion, and the maximum volume of water that can be treated per liter of resin, assuming equilibrium conditions. Assume total resin capacity of the SBA is equal to 1.4 eq/L.

16-11 Given the information in Problems 16-8 and 16-9, design a 5-ML/d ion exchanger for nitrate removal. Determine the number of columns required assuming 4-m diameter columns and a minimum bed depth of 0.762 m and the regenerant requirements including salt used, brine production, total volume of brine storage tank, and regeneration cycle time for the ion exchanger. Based on pilot studies, it was found that adequate regeneration can be obtained with a salt dose of 320 kg/m^3 resin, a salt concentration of 14 percent, and the specific weight of the salt is 2.165. The capacity of the brine storage tank must be sufficient to handle 10 resin regenerations. The water temperature is 10°C. Assume the working capacity for the SBA resin is the same as the maximum volume treated determined in Problem 16-8.

16-12 Perchlorate at a concentration of 100 μg/L was discovered recently in a groundwater that is being considered for use as a drinking water source. Because the action level for perchlorate is 4 μg/L, the regulatory agency is requiring remediation of the groundwater. The municipality is proposing to pump and treat about 0.158 m^3/s (2500 gpm) using ion exchange process. To obtain information on the treatment of the water that can be used for the design of a full-scale treatment plant, pilot plant ion exchange studies have been performed. Using the information given below on the water quality and the pilot plant study parameters, design an ion exchange system including a regeneration facility to treat the groundwater to the above regulatory requirement. Determine the following full-scale design criteria: plant size (number of columns, column dimensions) maximum service loading rate, single-column service time, single-column regeneration and rinse volume requirements and regeneration time, head loss requirements, and spent-brine disposal. Assume the inlet distributor and resin support underdrain require 1.0 and 0.5 m of column height, respectively.

Water quality parameters

Parameter	Unit	Value
Alkalinity	mg/L as CaCO$_3$	150
Hardness	mg/L	140
PH	Unitless	7.8
Nitrate	mg/L as N	4.0
Sulfate	mg/L	50
Perchlorate	μg/L	85
TOC	mg/L	1.5
Temperature	°C	10

Summary of the pilot plant operational parameters

Parameter	SI Units	Value
Operational mode	—	Countercurrent
EBCT	min	1.5
Column diameter	m	0.0509
Resin depth	m	0.862
Service flow rate	BV/h	30
Flow rate per column	m^3/h	0.0681
Backwash rate	m/h	6.0
Column resin volume	m^3	0.00176
Regenerant type	—	NaCl
Regenerant strength	%	10
	mg/L	100,000
Salt loading rate	kg/m^3	480
Regeneration and rinse flow rate	m^3/h	0.0363
Regeneration volume	BV	10
Rinse volume	BV	6
Initial BV to breakthrough[a]	BV	550

[a]Full regeneration and no leakage occurred for 31 cycles.

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