

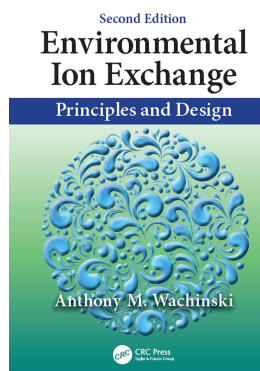
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Fundamental Principles and Concepts of Ion Exchange

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3 Fundamental Principles and Concepts of Ion Exchange

This chapter provides a basic understanding of the ion exchange process, ion exchangers, and the terminology associated with the process and its design.

A rigorous theory associated with the ion exchange process is absent. The authors recommend Helfferich's *Ion Exchange* (1962) and Weber's *Physicochemical Processes for Water Quality Control* (1972) to provide a strong theoretical background. The major manufacturers have developed models to predict performance. Readers are directed to Dow Water & Process Solutions' Computer Assisted Design for Ion Exchange (CADIX), an ion exchange software program developed to aid in the design of softener and demineralization systems. Purolite Pure Design™ ion exchange simulator program is aimed at the engineer to aid in the design of water-related exchange systems for boron removal, softening, and dealkalization. Programs are also offered by Lenntech and LanXess. This chapter provides the basic knowledge of the fundamental concepts to better enable the engineer to use the programs.

INTRODUCTION

To produce water of a determined quality or treat wastewater to a specific chemical composition is not usually feasible by using chemical precipitation or membrane technology, but low-pressure membrane technology should be considered for pre-treatment to the ion exchange process. This concept applies even if several streams treated differently from one another are blended. The only readily usable means to achieve a desired effluent composition is by using ion exchange, where the replacement of one ion for another can be accomplished in a predictable manner.

Most uses for ion exchange involve the removal or concentration of unwanted ions in the feed water to the exchanger. Because ion exchange is stable and allows the predictable exchange of unwanted for wanted ions, it can be used as either a chemical feeder or a removal process. Applications of specific ion exchange in the process industries are numerous, for example recovering ionic metals, separating wanted from unwanted ionic constituents, and feeding medications into a wound or incision after surgery. A Google search of the term *ion exchange* results in about 9.5 million "hits." These are all in addition to the normal uses, such as hardness removal, deionization as an alternative to distillation, dealkalization, and heavy metal removal from wastewaters.

BASICS

Ion exchange describes a myriad of terms, for example the ion exchange process, the ion exchange phenomenon, and the unit process of ion exchange. It is referred to as both an adsorption process and a sorption process. However, ion exchange is most often defined as the reversible exchange of ions between a solid and a liquid in which there is no substantial change in the structure of the solid. Used to soften water by exchanging calcium and magnesium ions for sodium ions, ion exchange is also widely used to remove metals from industrial effluents. Ion exchange cannot effectively remove dissolved organics such as pesticides and polychlorinated biphenyls (PCBs) because these materials do not ionize. Dissolved organics can be removed effectively by polymeric adsorbents, which resemble ion exchange resins in that they too can be regenerated and reused. Some organics, typically humates and fulvates, can foul resins, especially strong base resins. These resins are often used as scavenger resins to remove organics. Bench-scale testing must be performed (see Chapter 4) to determine the performance of the resins in removing these organics (The Purolite Company, 2006).

The basic component of any ion exchange system is the insoluble solid, usually referred to as the ion exchanger or ion exchange resin. In most water and wastewater applications, the liquid is water and the solid is any number of natural or synthetic ion exchangers. A variety of natural and synthetic ion exchangers exist and are described in detail in this chapter.

BATCH/COLUMNAR OPERATION

Ion exchange processing can be accomplished in either a batch or column mode. The batch mode involves mixing the resin and solution in a batch tank, allowing the exchange to come to equilibrium, and then separating the resin from solution. The degree to which the exchange takes place is limited by the preference the resin exhibits for the ion in solution. Consequently, the utilization of the resin's exchange capacity is limited unless the selectivity for the ion in solution is far greater than for the exchangeable ion attached to the resin. Because batchwise regeneration of the resin is chemically inefficient, batch processing by ion exchange has, in the author's opinion, limited potential application in treating water for purposes outlined in Chapter 1 and will not be discussed further.

BASIC COLUMNAR OPERATION

The primary function of most fixed-bed (columnar) ion exchange operations is the removal of an ionic species from solution in exchange for another ionic species for the purpose of concentrating a desirable material into a small volume, or removing an undesirable constituent. The latter may be accomplished by exchange with an unobjectionable ionic species, for example the softening of water using a cation exchanger in the sodium cycle. In most cases, the removal of all ions or particular ionic species must be as complete as possible, and the ion exchange resin must have the capacity to treat a large volume of liquid per unit volume of exchanger.

In Chapter 5, we will see that ion exchange resins in fixed-bed operations are primarily designed for removing soluble ionic species and, therefore, cannot be expected to adsorb macro- or colloidal-ionic species except at the surface of the particle.

Because of their ionic nature and particle size, ion exchange beds are very effective filters; however, they are not normally used for this purpose. If they are used and the filter load is heavy, one cannot expect them to function efficiently as ion exchangers. Readers are directed to Wachinski's *Ion Exchange Treatment for Drinking Water* (2004) for his thinking on the use of low-pressure membranes for pretreatment of ion exchange systems; see also Wachinski's *Membrane Processes for Water Reuse* (2013) for an in-depth treatment of membrane processes role in pretreatment.

Figure 3.1 shows a typical column operation used to soften a hard water containing calcium, magnesium, and sodium salts. Water with the indicated constituents is passed through an ion exchange column containing an ion exchanger or resin that has been regenerated such that the exchange sites are in the sodium form. The chemical constituents in the treated water are shown leaving the ion exchange column. Figure 3.2 shows typical hardware.

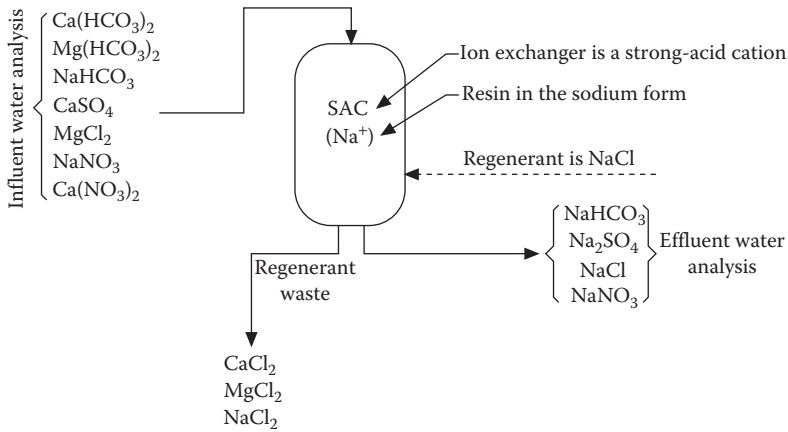


FIGURE 3.1 Typical columnar softening.

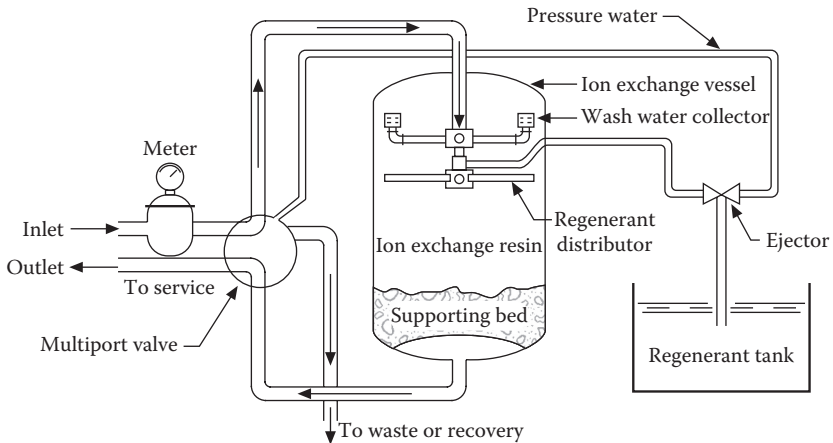


FIGURE 3.2 Typical ion exchange unit.

NATURAL ION EXCHANGERS

Many materials found in nature are able to capture certain ions and retain them in an exchangeable state. This is known as the exchange capacity of the material.

Most natural ion exchange materials are crystalline aluminosilicates with cation exchange properties (i.e., they remove positively charged cations from solution), although certain aluminosilicates can also act as anion exchangers. Cation exchangers include the zeolites, analcity, chabazite, hormotome, hevlantite, and natrolite. Apatite and hydroxylapatite are two aluminosilicates used to remove anions in full-scale operations.

Zero-valent iron is a natural ion exchange material used for arsenic, chromium VI, nitrate, bromate, chlorate, and perchlorate removal, and is discussed in Chapter 5.

Zeolites are relatively soft minerals and are not very abrasion resistant. Their frameworks are less open and more rigid than those of most other ion exchangers. They, therefore, swell very little, and the counter ions in their pores are not very mobile.

Many coals are natural ion exchangers. They contain carboxylic and possibly other weak-acid groups and can thus be used as cation exchangers. Most of these materials, however, swell excessively, are easily decomposed by an alkali, and tend to peptize. They must, therefore, be “stabilized” before use. Soft and hard lignitic coals have been stabilized by treatment with solutions of copper, chromium, or aluminum salts. Moreover, most lignitic and bituminous coals and anthracites can be converted into strong-acid cation exchangers by sulfonation with fuming sulfuric acid. Sulfonic acid groups are introduced and additional carboxylic acid groups are formed by oxidation.

A number of other natural materials exhibit ion exchange properties. Alumina, alginic acid, colloidin, and keratin are a few typical examples of this group. A still larger number of materials can be transformed into ion exchangers by chemical treatment. From many soluble substances that carry ionogenic groups, insoluble ion-exchanger gels can be obtained simply by cross-linking with agents such as formaldehyde. Pectins and carageenan are typical examples of ion-exchanger gels. Conversely, from many insoluble substances, ion exchangers can be produced by incorporation of fixed ionic groups. The most common procedures are sulfonation and phosphorylation of materials such as olive pits, nut shells, spent ground coffee, tar, wood, paper, cotton, lignins, and tannins.

Inorganic ion exchangers are used in both industrial and municipal water, and wastewater treatment applications. The first applications, such as the use of aluminosilicates for softening, have been improved by the use of synthetic resins. Greensand (glauconite) is still used today in connection with iron and manganese removal. Activated alumina is made by dehydroxylating aluminum hydroxide. It has a high surface area of about 200 m²/g. It is used to remove trace inorganics such as fluoride, arsenic, selenium, and phosphate. Clinoptilolite is used to remove ammonia from water and wastewater.

One inorganic material in particular has been shown to be an effective ion exchange medium for the removal of heavy metals. Etzel and Keramida (1979) used the clay mineral vermiculite—a layered silicate consisting of two tetrahedral sheets composed of aluminosilicates and a central trioctahedral layer—to remove copper, zinc, and nickel from synthetic and actual wastewaters.

SYNTHETIC ION EXCHANGERS

The majority of ion exchange resins are made by the copolymerization of styrene and divinylbenzene (DVB). The styrene molecules provide the basic matrix of the resin, and the DVB is used to crosslink the polymers to allow for the general insolubility and toughness of the resin. The degree of cross-linking in the resin's three-dimensional array is important because it determines the internal pore structure, which in turn affects the internal movement of exchanging ions.

Visualize the synthetic resin shown in [Figure 3.3](#) as a “whiffle ball”—a skeleton-like structure having many exchange sites. The skeleton, insoluble in water, is electrically charged, holding ions of opposite charge at the exchange sites.

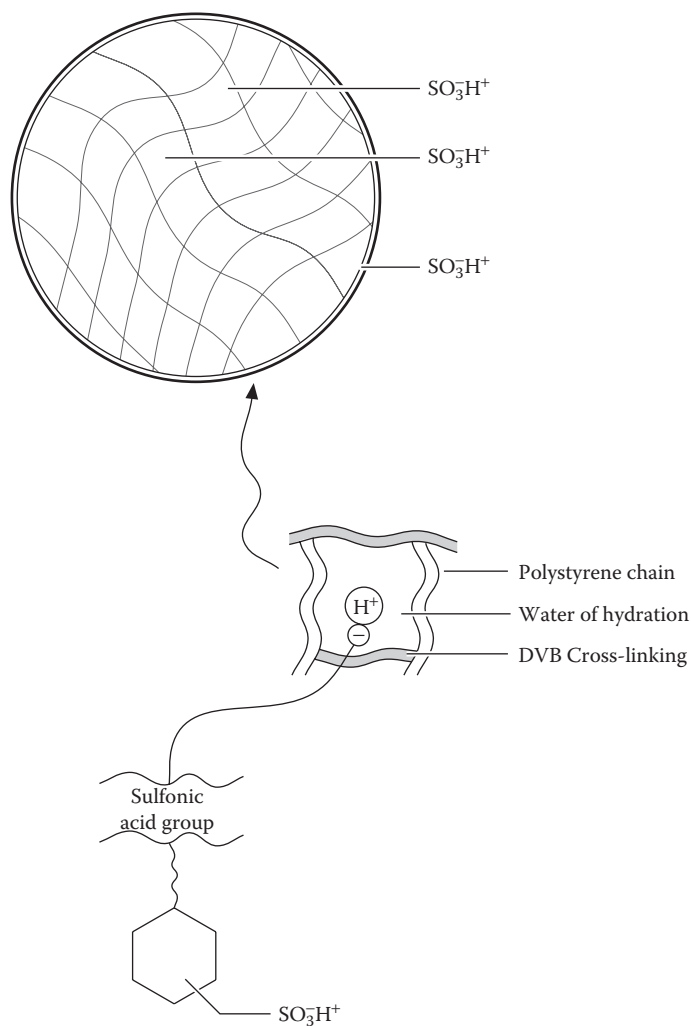


FIGURE 3.3 Cation exchange resin—strongly acidic (hydrated).

Synthetic resins are available in bead form and range in size from 20 mesh (0.84 mm in diameter) to 325 mesh (0.044 mm in diameter). Most ion exchange applications in water and wastewater are accomplished with resins in the 20–50 and 20–60 mesh size range.

Recent developments in polymer chemistry have resulted in the production of macroporous (or macroreticular) resins that have a discrete pore structure. These resins are more resistant to thermal and osmotic shocks as well as oxidation. The more porous resins are also more resistant to organic fouling than gel-type resins.

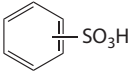
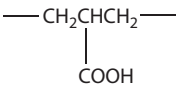
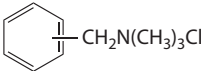
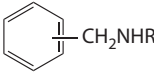
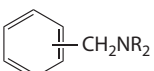
Table 3.1 shows that synthetic exchangers are generally divided into four major classifications depending on the resin's functional group (but two types of weak base). The functional group determines whether cations or anions are exchanged and whether the resin is a strong or weak electrolyte.

SYNTHETIC CATION EXCHANGERS

Cation exchangers are available with numerous fixed ionic groups exhibiting a range of different properties and acid strengths. The most common are strong-acid resins (SARs) with sulfonic groups ($-\text{SO}_3^-$) and weak-acid resins (WARs) with carboxylic acid groups and phosphonic acid groups.

In general, strong-acid cation exchangers substitute one ion for another depending on the resin's selectivity, and as such operate at all pH values. Their capacity is less

TABLE 3.1
Classification of the Major Ion Exchange Resins

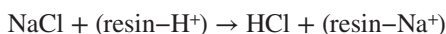
Type	Active Group	Typical Configuration
Cation Exchange Resins		
Strong acid	Sulfonic acid	
Weak acid	Carboxylic acid	
Anion Exchange Resins		
Strong base	Quaternary ammonium	
Weak base	Secondary amine	
Weak base	Tertiary amine (aromatic matrix)	

than stoichiometric, however, and they must be regenerated more frequently than WARs, which exhibit much higher capacities and regenerate almost stoichiometrically. WARs operate only over a limited pH range.

Strong-Acid Cation Exchange Resins

All major strongly acidic cation exchange resins involved in water and wastewater treatment applications have a chemical matrix consisting of styrene and DVB. The functional groups are sulfonic acid radicals. These resins differ mainly in DVB content and gelular or macroreticular structure.

SARs are so named because their chemical behavior resembles that of a strong acid. A strong-acid cation resin can convert a neutral salt into its corresponding acid if operated in the acid form. This ability is known as salt-splitting and distinguishes SARs from WARs, which cannot salt-split. The equation for salt-splitting is



Strong-acid exchangers can be operated in any form but are typically operated in the hydrogen cycle, where the resin is regenerated with a strong acid such as HCl or H₂SO₄, or in the sodium cycle where the resin is regenerated with NaCl.

Author's note: Probably the most important thing you will get from this book is that a resin (in this case a strong-acid resin) can be regenerated or put into any cycle that you wish. Ion exchangers can be operated in the K⁺ cycle, the Ca⁺⁺ cycle, and the Mg⁺⁺ cycle—any cycle that will allow the ion exchanger to work for you.

A strong-acid cation exchanger in the hydrogen cycle will remove nearly all major raw water cations and is the first step in demineralizing water. The equation for removing calcium sulfate from a raw water with an ion exchanger in the hydrogen cycle is

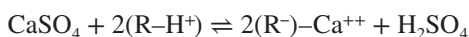


Figure 3.4 shows the same water treated by the sodium cycle exchanger in Figure 3.1, treated by a strong-acid cation resin in the hydrogen cycle. The resin in the bed is regenerated by either HCl or H₂SO₄. Regeneration will be further discussed later in this chapter. “In general, a strong acid can be regenerated using any monovalent, divalent, or trivalent acid or salt.”

The strong-acid exchangers require excess strong-acid regenerant (typical regeneration efficiency varies from 25% to 45% in concurrent regeneration), and they permit little leakage. In addition, they have rapid exchange rates, are stable, and may last 20 years or more with little loss of capacity. They exhibit less than 7% swelling going from Na⁺ to H⁺ form and are useful for softening and demineralization (removal of all cations with little leakage).

Generally, in most domestic water softening, one would use a strongly acidic cation exchange resin with an 8% DVB cross-linking. However, if a condition called oxidative decross-linking occurs, it would be best to use a resin with greater resistance to oxidative attack. Amberlite IR-122 resin, for example, with its higher DVB content is typical. In very severe decross-linking problems, a macroreticular type is recommended, where up to 20% DVB can be used as the cross-linker.

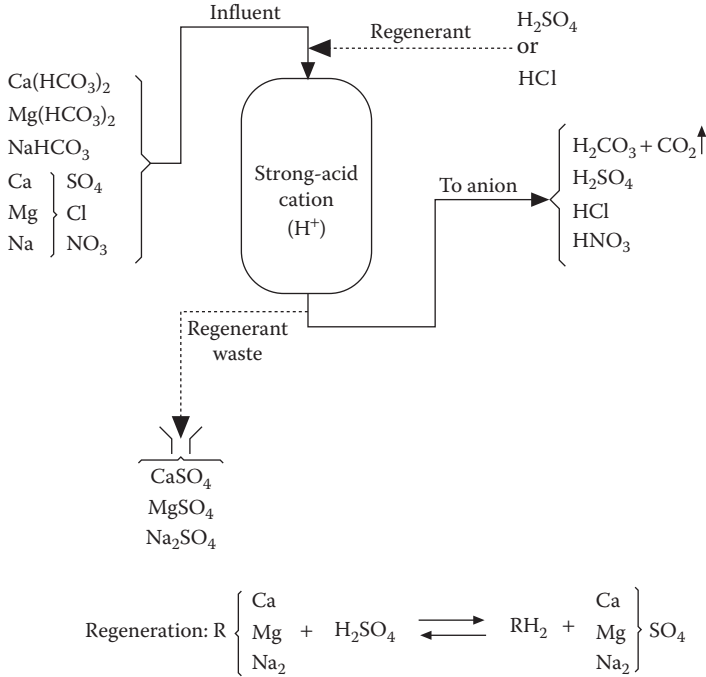


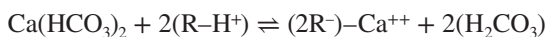
FIGURE 3.4 Hydrogen cycle strong acid cation exchange.

Weak-Acid Cation Exchange Resins

Carboxylic acid is the functional group associated with weak-acid cation exchangers (see [Table 3.1](#)). As such, weak-acid cation resins are not highly dissociated and do not exchange their H^+ as readily as strong resins. Because they exhibit a higher affinity for hydrogen ions than SARs, WARs show higher regeneration efficiencies. They are usually regenerated with strong acids such as HCl or H_2SO_4 . WARs do not require the same concentration driving force that is required to convert SARs to the hydrogen form. The carboxylic functional groups have a high affinity for H^+ and will utilize up to 90% of the acid (HCl or H_2SO_4) regenerant, even with low acid concentrations. This is in contrast to SAR regeneration, where a large excess of regenerant (of which 60%–75% goes unutilized) is required to create the concentration driving force.

On account of their high affinity for the hydrogen ion, WARs can be used only at pHs above 4 or 5, as shown in [Figure 3.5](#).

WAR exchangers differ from SARs in that WARs require the presence of some alkaline species to react with the more tightly held hydrogen ions of the resin, for example,



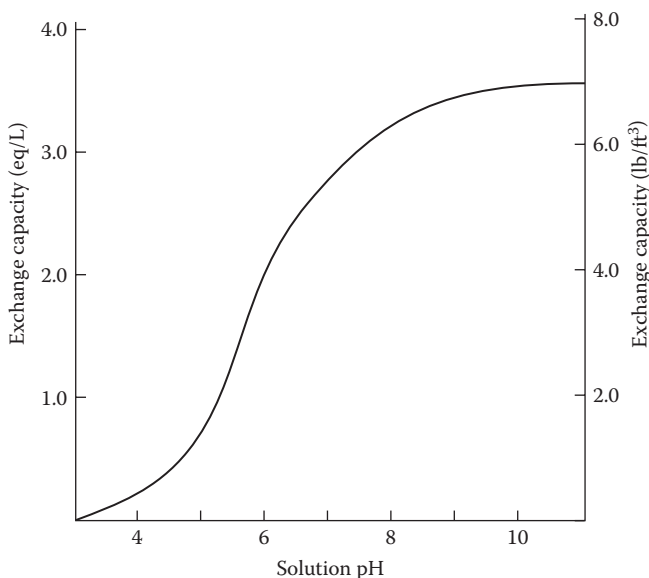


FIGURE 3.5 Capacity of weak-acid cation resin as a function of solution pH.

The exchange is, in effect, a neutralization with the alkalinity (HCO_3^-), neutralizing the H^+ of the resin. WAR will split alkaline salts but not nonalkaline salts (e.g., NaHCO_3 but not NaCl or Na_2SO_4).

Weak-acid cation resins are used to remove the cations associated with high alkalinity, that is, CO_3^{2-} , OH^- , and HCO_3^- , and low in dissolved CO_2 and sodium. WARs are used primarily for achieving simultaneous softening and dealkalization. They are sometimes used in conjunction with a strong-acid polishing resin, which allows for economic operation in terms of regenerant requirements, but also produces a treated water of quality comparable to the use of just an SAR.

SYNTHETIC ANION EXCHANGERS

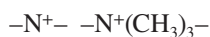
Anion exchangers were developed almost exclusively as synthetic resins; organic exchangers were among the earliest ion exchange resins produced. The first patents issued for anion exchangers were for resins having weak-base amino groups. Later, resins with strong-base quaternary ammonium groups were prepared.

Anion exchangers are available with numerous fixed ionic groups. The most common are strong-base resins (SBRs) with quaternary ammonium groups ($\text{CH}_2\text{N}(\text{CH}_3)_3\text{Cl}$) and weak-base resins (WBRs) with tertiary amines in an aromatic or aliphatic matrix.

In general, strong-base anion exchangers operate at all pH values, but their capacity is less than stoichiometric, and they must be regenerated more frequently than WBRs, which exhibit much higher capacities and regenerate almost stoichiometrically. WBRs operate only over a limited pH range.

Strong-Base Anion Exchange Resins

SBRs are available. In Type I resins, the functional groups consist of three methyl groups:



In Type II resins, an ethanol group replaces one of the methyl groups. Type I resins exhibit greater stability. Type II resins exhibit slightly greater regeneration efficiency and capacity.

Strong-base exchangers are so named because they have the ability to split strong or weak salts. This ability distinguishes them from WBRs, which cannot salt-split.

The reactions with sulfate and chloride and a strong-base anion exchanger in the hydroxyl form are

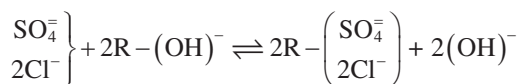


Figure 3.6 shows the same water treated by the hydrogen cycle exchanger as the one shown in Figure 3.4. The resin in this case is regenerated by sodium hydroxide.

In general, when placed in the hydroxide form, strong-base exchangers require an excess of regenerant (with typical efficiencies varying between 18% and 33%). Typically,

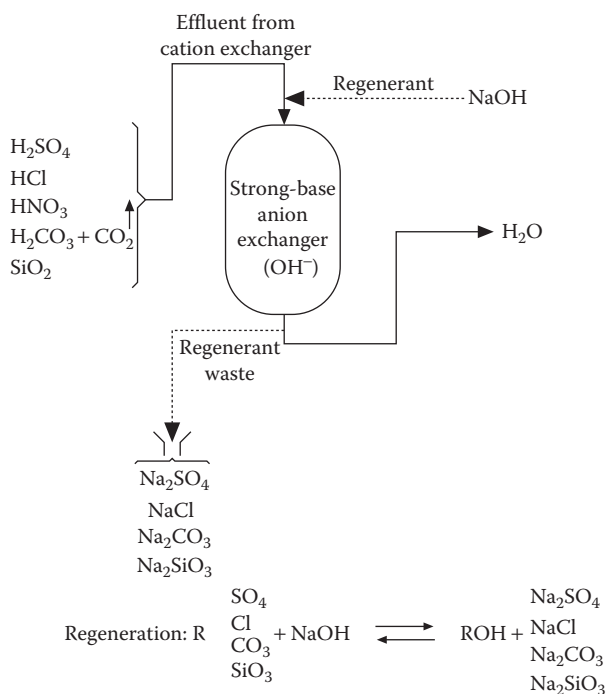


FIGURE 3.6 Strong-base ion exchange reactions.

high-quality sodium hydroxide is used as the regenerant, but again the regenerant used depends on the desired form in which the resin is to be used. A problem with SBRs is that they tend to irreversibly sorb humic acid substances, losing their capacity. Activated carbon or a weak-base organic trap is typically used to prevent fouling.

Type I exchangers are typically used for maximum silica removal. They are more difficult to regenerate and swell more (from Cl^- to OH^- form) than Type II exchangers. The principal use of Type I is to make the highest quality water. When they are loaded with silica, they must be regenerated with warm NaOH (see resin manufacturer's literature.)

Weak-Base Anion Exchangers

The functional groups associated with weak-base anion exchangers are secondary and tertiary amines and are often based on phenol-formaldehyde or epoxy matrices instead of polystyrene-DVB. They do not remove anions above a pH of 6 (see Figure 3.7). They regenerate with a nearly stoichiometric amount of base (with the regeneration efficiency possibly exceeding 90%) and are resistant to organic fouling. In addition, they swell about 12% going from the OH^- to salt form, they do not remove CO_2 or silica, and they have capacities about twice as great as that of strong-base exchangers. They are useful, following strong-acid exchangers to save cost of regenerant chemicals, as organic "traps" to protect strong-base exchangers, and to remove color.

Weak-base anion exchange resins behave much like their weak-acid counterparts and will not remove CO_2 , that is, weakly ionized acids such as carbonic and silicic acids. WBRs remove free mineral acidity (FMA) such as HCl or H_2SO_4 , that is, anions associated with the hydrogen ion and that are strong acid formers such as sulfate, chloride, or nitrate. For this reason, WBRs are often called "acid adsorbers." Any ions associated with cations other than hydrogen are not removed.

WBRs do not have a hydroxide ion form as do SBRs. Consequently, regeneration need not provide hydroxide ions, only neutralize the absorbed acid. Less expensive weakly basic reagents such as ammonia or sodium carbonate may be used, along with sodium hydroxide.

Once again, the regeneration efficiencies of these resins are much greater than those for SBRs. Weak-base exchangers are used in conjunction with SBRs in

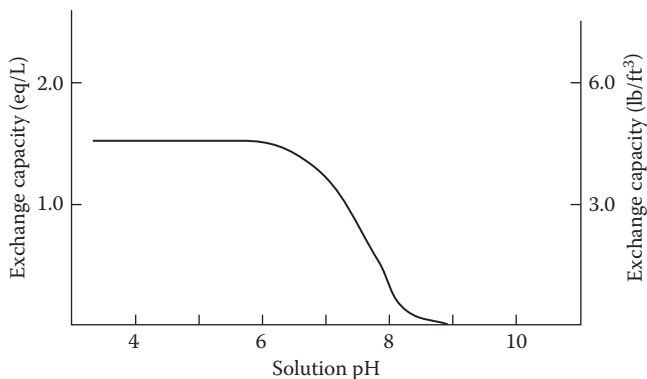


FIGURE 3.7 Capacity of weak-base anion resin as a function of solution pH.

demineralizing systems to reduce regenerant costs and to attract organics that might otherwise foul the SBRs. Where silica removal is not critical, WBRs may be used by themselves in conjunction with an air stripper to remove CO_2 (see Chapter 5).

The major advantage of weak-base anion exchange resins is that they can be regenerated with stoichiometric amounts of regenerant and are, therefore, much more efficient. They also have a much higher capacity for the removal of chlorides, sulfates, and nitrates. There are three typical weakly basic anion exchange resins: styrene-DVB, acrylic-DVB, and epoxy. Again, gel or macroreticular varieties of resins based on these raw materials are available and used. For treatment of waters that do not present organic fouling problems, the gel type of weakly basic resin is used.

For waters containing organic contaminants (humic and fulvic acids), macroreticular weakly basic anion resins are preferred. Since their development in the late 1960s, acrylic resins are beginning to be used more and are found to be more effective from an economic standpoint. [Figure 3.8](#) shows a typical weak-base ion exchange application.

SELECTIVITY

“The success of any ion exchange system is dependent on the cycle in which the resin is operated, that is, operate the ion exchange resin in the proper cycle.” Do not limit yourself to the hydrogen cycle or the sodium cycle, the chloride cycle, or the hydroxyl cycle. Make the ion exchange resin work for you.

Each ion exchange resin has its own order of exchange preference. In general, a trivalent ion is preferred over a divalent ion, which is further preferred over a monovalent ion. A bumping order based on valence exists. A bumping order based on atomic number ions of the same valence also exists.

ORDER OF SELECTIVITY (RELATIVE AFFINITY)

In general, the higher the valence of an ion, the higher its ability to be removed by a resin. For example, for a resin in the hydrogen form, if a divalent cation came along, it would be taken preferentially to the monovalent cation (H^+) on the resin. If a trivalent cation came along, it would preferentially displace the divalent cation (in nearly all circumstances).

Now imagine the ion exchange material is in the hydrogen form. If a sodium ion is introduced, the sodium ion would displace the hydrogen ion, that is, the sodium ion would stay on the resin and the hydrogen ion would be carried out. If we then introduce a calcium ion, the calcium ion would displace two sodium ions and the calcium ion would stay on the resin. If we then introduce aluminum ions, two aluminum ions would displace six calcium ions. [Table 3.2](#) shows the order of selectivity of a typical strong-acid resin. [Table 3.3](#) shows the order of selectivity of a typical strong-base resin.

In the design of ion exchange systems, one must be careful about the cycle in which one chooses to operate the resin, because this will determine whether one gets the job done.

“Changing the degree of cross-linking does not change the order of selectivity but does change relative affinities.”

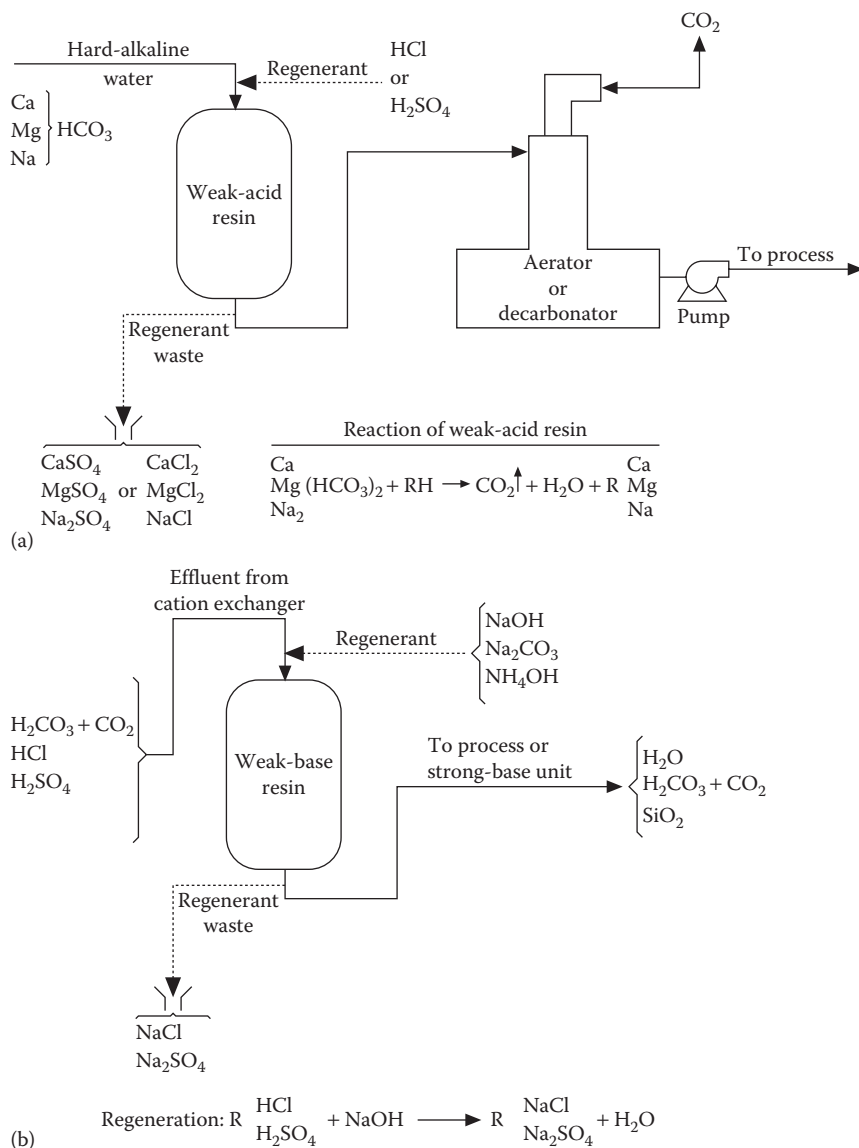


FIGURE 3.8 (a) Weak-acid and (b) weak-base ion exchange reactions.

As shown in Table 3.4, the higher the number, the easier for that ion to displace ions lower than it. For example, to remove Ag from a wastewater stream, use Dowex cation resin with 16% cross-linking. If there is any sodium in water, with a selectivity of 2.37, Ag will easily displace it and the Ag is monovalent. If you are trying to remove a specific ion, you want the highest spread you can get, and if you can get different levels of cross-linking to do that, even better. A minimum selectivity delta of two is required for most exchanges.

TABLE 3.2
Order of Selectivity—Typical Strong-Acid Resin

Ion	Valence
Barium	+2
Strontium	+2
Calcium	+2
Magnesium	+2
Beryllium	+2
Silver	+2
Thallium	+1
Cesium	+1
Rubidium	+1
Ammonia	+1
Potassium	+1
Sodium	+1
Hydrogen	+1
Lithium	+1

Source: Dr. Etzel's class notes.

Note: This order will vary with different resins, but usually the order shifts only by one or two. Trivalent replaces divalent, which in turn replaces monovalent ions.

TABLE 3.3
Order of Selectivity—Typical Strong-Base Resin

Ion	Valence
Thiocyanate	-3
Iodide	-2
Nitrate	-1
Bromide	-1
Cyanide	-1
Bisulfite	-1
Nitrite	-1
Chloride	-1
Bicarbonate	-1
Acetate	-1
Hydroxide	-1
Fluoride	-1

Source: Dr. Etzel's class notes.

TABLE 3.4
Selectivity Scale for Selected Cations on Dowex Cation Resin at 4%, 8%, and 16% DVB Cross-Linking

Ion	X4a	X8a	X16a
Monovalent			
Li	1.00	1.00	1.00
H	1.32	1.27	1.47
Na	1.58	1.98	2.37
NH ₃ OH	1.90	2.25	3.28
NH ₄	1.90	2.55	3.34
K	2.27	2.90	4.50
Rb	2.46	3.16	4.62
Cs	2.67	3.25	4.66
Ag	4.73	8.51	22.9
Tl	6.71	12.4	28.5
Divalent			
UO ₂	2.36	2.45	3.34
Mg	2.95	3.29	3.51
Zn	3.13	3.47	3.78
Co	3.23	3.74	3.81
Cu	3.29	3.85	4.46
Cd	3.37	3.88	4.95
Be	3.43	3.99	6.23
Ni	3.45	3.93	4.06
Mn	3.42	4.09	4.91
Ca	4.15	5.16	7.27
Sr	4.70	6.51	10.1
Pb	6.56	9.91	18.0
Ba	7.47	11.5	20.8
Trivalent			
Cr	6.60	7.60	10.5
Ce	7.50	10.6	17.0
La	7.60	10.7	17.0

Source: Dr. Etzel's class notes.

Note: Lithium is arbitrarily set at 1.00.

^a Cross-linking with divinylbenzene at 4%, 8%, and 16%.

This order varies with different resins (depending on the manufacturer), but usually the order is shifted by only a few elements. Trivalent replacing divalent and divalent replacing monovalent are always the same.

Table 3.4 also shows the relative affinity of selected cation resins as a function of valence and cross-linking with DVB at 4%, 8%, and 16%. Lithium is assigned a value of 1.00. Table 3.5 presents the relative selectivity of selected anions for Dowex strong

TABLE 3.5
Order of Selectivity for Dowex Strong-Base Anion Resin

Ion	Relative Selectivity
Dichlorophenate	53
Salicylate	28
Phenate	8.7
Iodide	7.3
Bisulfate	6.1
Nitrate	3.3
Bromide	2.3
Nitrite	1.3
Cyanide	1.3
Bisulfite	1.3
Bromate	1.01
Chloride	1.00
Hydroxide	0.65
Bicarbonate	0.53
Dihydrogen phosphate	0.34
Formate	0.22
Acetate	0.18
Fluoride	0.13
Aminoacetate	0.10

Note: Chloride is arbitrarily set at 1.00.

base anion resin. Chloride is assigned a value of 1.00. Contact the resin manufacturer you have chosen for the relative exchange order of a particular resin.

Use the following rules as a guide to understanding the relative selectivity patterns of exchange.

1. At low aqueous concentrations and ordinary temperatures, the extent of exchange or the exchange potential increases with increasing valence of the exchanging ion
 $\text{Na}^+ < \text{Ca}^{++} < \text{Al}^{+++}$
2. At low aqueous concentrations, ordinary temperatures, and constant valence, the exchange potential increases with increasing atomic number.
 $\text{Li} < \text{Na} < \text{K}; \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}; \text{F} < \text{Cl} < \text{Br} < \text{I}$
3. At high concentrations, the differences in exchange potentials of ions of different valence diminish and, in some cases, the ion of lower valence has the higher exchange potential.
 Na^+ vs. Ca^{++}
4. The exchange potentials of various ions may be approximated from their activity coefficient—the higher the activity coefficient the greater the potential.

5. The exchange potential of the hydrogen ion or the hydroxyl ion depends on the strength of the acid or base formed between the functional group, and the hydrogen or hydroxyl ion. The stronger the acid or the base, the lower the exchange potential.

SELECTIVITY DETERMINATION

Select the resin (see Chapter 5). Put the resin in the lithium cycle. Run sodium ions through and monitor how much sodium stays on the resin and how much runs through. Do this until sodium-in is equal to sodium-out. Analyze the resin to determine how much sodium is on the resin. Repeat the same for every ion. Compare the percentage of material retained as a percentage of lithium (e.g., retains twice as much lithium, i.e., 2.0).

Example: How to Use a Resin's Selectivity to Separate Silver from Calcium (see [Figure 3.9](#))

Column 1 removes both calcium and silver, but eventually the calcium displaces the silver. If we take column 2 off-line before any calcium breaks through column 1, we will have only silver on the resin. We have separated silver from calcium.

Remember:

We can regenerate a resin with any compound that will dissolve in water and ionize.

We can put a resin in any form we want.

RESIN STRUCTURE

Think of a synthetic ion exchange resin as a network of hydrocarbon radicals to which soluble ionic functional groups are attached, with the hydrocarbon network usually formed from the copolymerization of styrene and DVB. Overall, the insolubility and toughness are given to the resin by cross-linking between the hydrocarbon molecules, forming a three-dimensional matrix. The internal pore structure of the

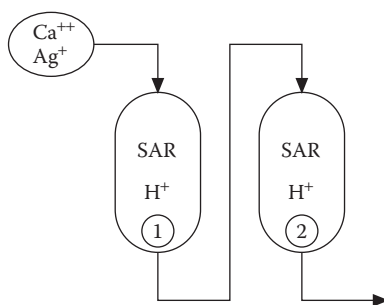


FIGURE 3.9 Silver separation diagram.

TABLE 3.6
Physical Characteristics of Amberlite® IR-120 Plus

Physical form	Hard, attrition resistant, light yellow, 16–50 mesh (U.S. Standard Screens), fully hydrated spherical particles
Shipping weight	53 lb/ft ³ (848 g/L) (sodium form) 50 lb/ft ³ (800 g/L) (hydrogen form)
Moisture content	45%
Effective size	0.50 mm
Uniformity coefficient	1.8 maximum
Density	53 lb/ft ³ (848 g/L)
Void volume	35%–40%
Sodium or hydrogen cycle	
pH	1.0–14.0
Maximum temperature	250°F (121°C)
Minimum bed depth	24 in (0.61 m)
Backwash flow rate	See detailed information in text
Service flow rate	2 gpm/ft ³ (16.0 L/L/h)

Source: Rohm and Haas, Amberlite® IR-20 Plus Specification Sheet, January 1982. With permission.

resin is determined by the extent or degree of cross-linking. Cross-linking adds stability to the styrene molecule and increases the resin's ability to resist acid or base attack. Because exchanging ions must be free to move in and out of the resin for exchange to occur, the degree of cross-linking should not be so great as to restrict this free movement of ions, although in some cases cross-linking can exclude ions larger than a given size from the resin. Table 3.6 shows the physical characteristics of Amberlite® IR-120 plus an SAR.

As you have seen and will see, resin characteristics such as selectivity and capacity are almost exclusively determined by the nature of the ionic groups attached to the framework of the resin.

CAPACITY

On a quantitative basis, the capability of a resin to exchange ions is defined as its exchange capacity, with total capacity being defined as the number of ionic sites per unit weight or volume of resin. Because it is impractical to use all available sites during exchange, the net number of sites used in a specific volume of resin in a given cycle is defined as the operating capacity. From a design point of view, resin capacity, that is, the number or quantity of counter ions (the ions in solution that we want to remove) that can be taken up by the exchanger (resin), is probably the most important property of ion exchange resin. The exchange capacity of a resin comes from the substituted functional groups in the resin matrix.

At this time, it is important to distinguish between the total capacity of a resin and its operating capacity. Total capacity is a measure of the total number of counter ions that can be exchanged. For strong-acid cation exchange resins, one sulfonate

group, on the average, can be attached to each benzene ring in the matrix. Hence, we can determine the *dry-weight capacity* of this resin, which would be expressed in milliequivalents per gram of dry resin (meq/g). The dry-weight capacity is simply a measure of the extent of functional group substitution in the exchanger and is therefore a constant for each specific resin. For sulfonated styrene-DVB resins, the dry-weight capacity is 5.0 ± 0.5 meq/g (Anderson, 1979). For strong-base anion exchangers, more or less than one functional group can be attached to each benzene ring. Hence, the dry-weight capacity is more variable than with SARs and can range from 2 to 5 meq/g.

Operating capacity is the exchange capacity of a resin operated in a columnar mode under defined operating conditions and a predetermined breakthrough level. Breakthrough occurs when a predetermined concentration of a target ion or ions (e.g., hardness) occurs in the effluent of an ion exchange system. Breakthrough is chosen arbitrarily. Figure 3.10 shows a typical breakthrough curve for an ion exchange system treating hardness.

Leakage is the result of an acid (or whatever regenerant is used) being formed during the exchange process. The regenerant formed at the top of the bed may regenerate an easily exchanged site (on the resin surface) lower down in the bed, allowing the exchanged material to escape into the effluent. A statistical probability exists of an ion entering the bed, and missing all of the exchange sites, but this is minimized by having the bed always at least 30" deep. A plot of exchange capacity versus the amount of regenerant acid used shown on the curve in Figure 3.11 is approximate. Note that on the left side (near origin), there is a large change in capacity for very little acid. This change in slope indicates that there must be some sites that are very easy to exchange and some that are very difficult to exchange.

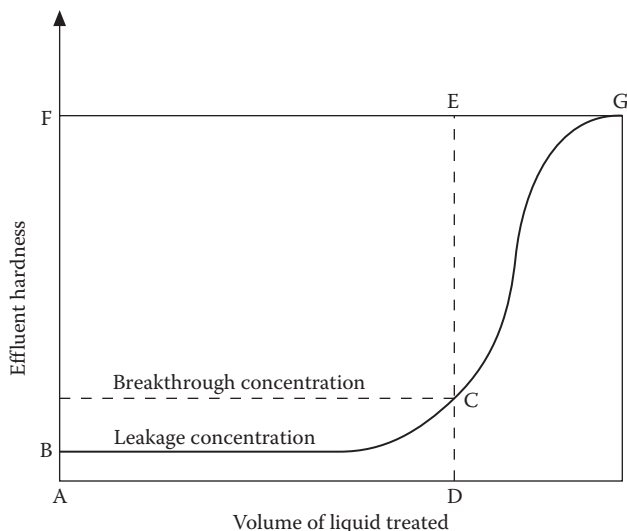


FIGURE 3.10 Typical breakthrough curve for an ion exchange process.

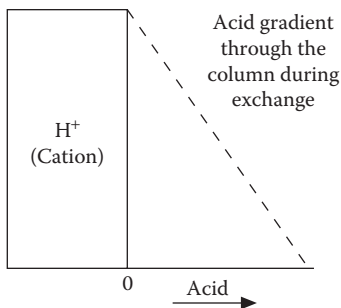


FIGURE 3.11 Acid gradient.

When the bed is exhausted, the acid gradient goes back to zero because it can no longer produce acid. The maximum acid gradient occurs in the bed just before leakage occurs. The leakage problem is most prevalent in hydrogen cycle systems because any acid can cause regeneration.

Note: When using the high-capacity part of the resin, there is a higher probability of leakage. To obtain more capacity, we must exchange more sodium onto the resin, including the less efficient sites. With more sites available for exchange, less chance exists of internal regeneration. At the low end of the resin, expect more leakage.

Leakage and breakthrough can be controlled by using two or more beds in series. When leakage begins to occur, regenerate the first bed and put it on-line after the second bed as a polishing unit (see [Figure 3.9](#)). Leakage can also be nearly eliminated by using a mixed-bed (hydrogen and hydroxyl form) unit so that the acid (regenerant) produced is destroyed as soon as it is formed.

The operating capacity of a resin is usually expressed in a weight per volume capacity, that is, meq/ml—milliequivalents of ions exchanged per milliliter of resin. Other units for expressing capacity are lb-equivalents/ft³, grams of CaCO₃ per liter, and, the most used, kilograins/ft³.

The natural exchange material greensand has a capacity of 2–5 Kgr/ft³ of sand. Zeolites (silica gels) typically exhibit capacities of 3–12 Kgr/ft³. Synthetic resin capacities range from 3 to 50 Kgr/ft³, with a usable range of 15–25 Kgr/ft³.

A few numbers to remember

$$7000 \text{ grains} = 7 \text{ kilograin (Kgr)} = 11 \text{ lb}$$

$$17.12 \text{ mg/L} = \frac{1 \text{ grain}}{\text{gallon}}$$

PARTICLE SIZE

A few words about particle size are in order. Ion exchange resins in spherical shapes are available commercially in particle diameters ranging from 0.04–1.0 mm. In the United States, the particle sizes are listed according to standard screen sizes or “mesh” values. [Table 3.7](#) shows a comparison of mesh sizes and metric sizes. The most common size ranges used in large-scale applications are 20–50, 20–60, and 50–100 mesh.

TABLE 3.7
Ion Exchange Particle Size Availability

U.S. Mesh	Diameter (mm)
16–20	1.2–0.85
20–50	0.85–0.30
50–100	0.30–0.15
100–200	0.15–0.08
200–400	0.08–0.04

Manufacturers typically provide information about three parameters related to particle size: particle size range, effective size (ES), and uniformity coefficient (UC). The size range gives the maximum and minimum sizes of particles in the batch, the ES is a screen size that passes 10% (by weight) of the total quantity, while 90% is retained, and the UC is the ratio of the mesh size (in millimeters) that passes 60% of the quantity to the ES. Typical UCs are in the range of 1.4–1.6; however, it is possible to obtain batches with smaller uniformity coefficients if required by kinetic or hydraulic restrictions. In [Figure 3.12](#), the ES is A. The UC is B/A.

Particle size has two major influences on ion exchange applications. First, the kinetics of exchange are such that the rate of exchange is proportional to either the inverse of the particle diameter or the inverse of the square of the particle diameter.

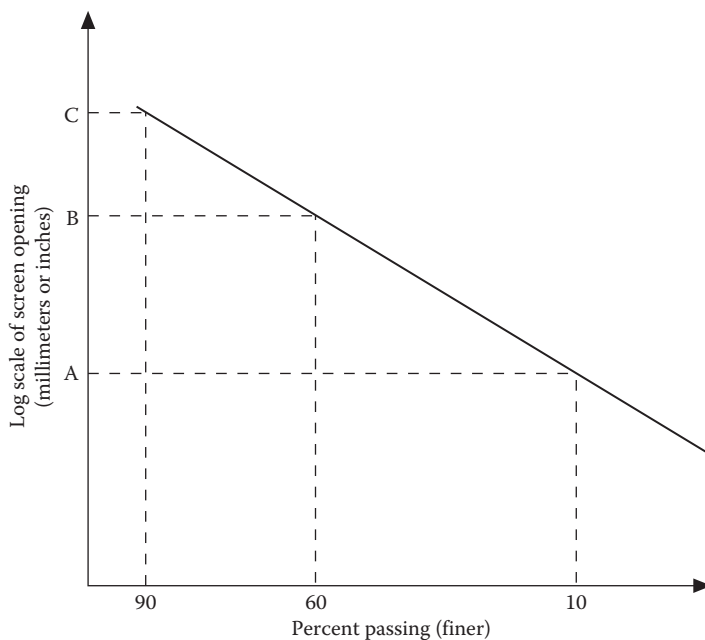


FIGURE 3.12 Resin sieve analysis.

Second, particle size has a great effect on the hydraulics of column design. Smaller particle sizes increase pressure drops through the bed, requiring a higher head to push the water through the resin beads and subjecting the beads to situations that could cause breakage. In 50% of all ion exchange applications, the design is based on hydraulic limitations of the resin beads and the vessel rather than on ion exchange chemistry.

PROCESS DESCRIPTION

The columnar ion exchange process is best illustrated by considering the basic steps of the complete cycle of an ion exchange operation. The operation of any ion exchange process involves four steps: backwash, regeneration or brining, rinse (displacement, fast, and final), and service.

BACKWASH

Backwash is carried out with a new installation and after each “run.” Water is introduced through the bottom of the ion exchange column at a rate sufficient to expand the bed by 50%–75%. The primary purpose of the backwash step is to remove any silt, dirt, iron, or other insoluble matter that has accumulated during the exchange operation. Also, any clumps of resin formed because of tight packing are dispersed, and the resin beads are reoriented. Most of the problems associated with ion exchange operation occur because of insufficient backwash.

Low-pressure membrane pretreatment to an ion exchange accomplishes many things, the most significant is the significant reduction of all particulate matter including silt, clays, insoluble iron, and microorganisms. Dissolved iron and manganese can be oxidized and removed to levels less than 0.05 mg/L. In all cases, the economics of adding low-pressure membrane pretreatment should be considered. With proper pretreatment, the purpose of backwash is now to reorient the resin and remove any resin particles, which is less because the cause of resin degradation is particulate matter abrading the softer resin. Resin life is also increased.

Figure 3.13 provides hydraulic expansion data for Amberlite® IR-120 Plus. It shows bed expansion in percent as a function of temperature and flow rate in gpm/ft². Typical flow rates are upflow at 5–7 gpm/ft² of exchanger cross-sectional area.

REGENERATION

Although the columnar ion exchange process consists of the basic steps of backwash, regeneration, rinsing, and service, the actual process is regeneration with the appropriate backwash and rinsing steps, and the service cycle. A more in-depth discussion of regeneration is in order.

Regeneration requires 5%–15% of the treated water. Typical recovery of an ion exchange process varies from a low of 75% to 90%. The reader can calculate the

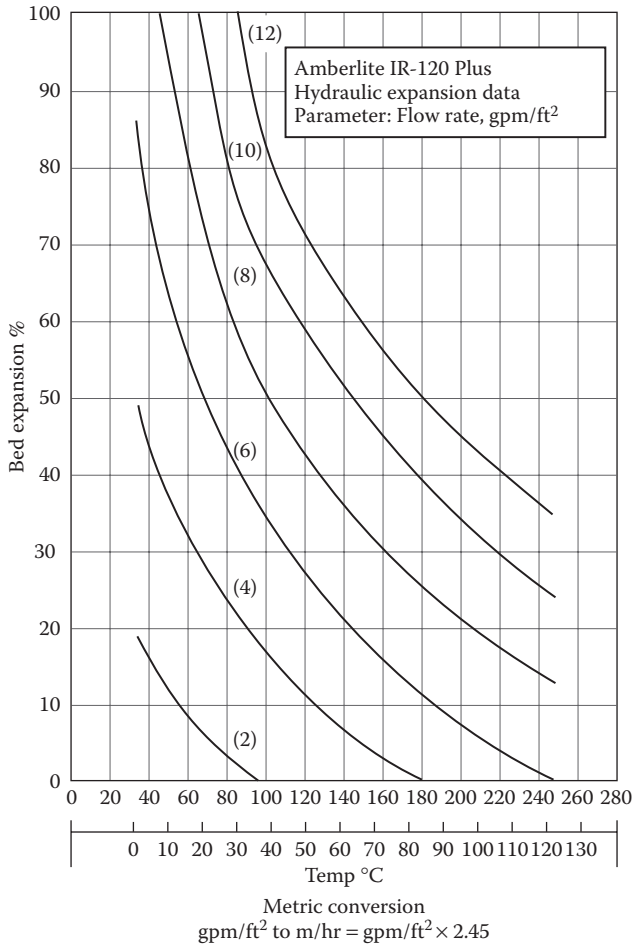


FIGURE 3.13 Hydraulic backwash data. (From Rohm and Haas, Amberlite® IR-120 Plus Specification Sheet, January 1982. With permission.)

recovery of a process using the principles described in this chapter. The regeneration process consists of three steps:

1. *Backwashing*: Wash out any dirt in bed.
2. *Regeneration*: Actual chemical addition.
3. *Rinsing*: Rinse out regeneration chemicals.

The regeneration process uses only 5% of the water treated, and thus all of the ions removed will be concentrated in about 5% of the water (20 times as concentrated).

Recall that the ion exchange resin looks very much like a whiffle ball with exchange sites on the inside and the outside. If insoluble compounds, such as calcium sulfate, are formed upon regeneration, it can block or plug the internal exchange sites.

Regeneration or brining follows backwash and is the displacement of the ions held on the resin sites. These ions were removed from the process feed water during the service cycle. If the column contains an SAR regenerated with an acid for example, hydrogen ions (H^+) are exchanged onto the resin in place of those released. This resin is now in the hydrogen form. If the column is an SBR and is regenerated with sodium hydroxide, hydroxyl ions (OH^-) are exchanged on the resin. It is then in the hydroxyl form. The regeneration step can be accomplished in either a downflow or upflow mode. When softening water, or using the column in the sodium cycle, the regeneration step is often referred to as “brining.” In most cases, concentrated sodium chloride ($NaCl$) is passed through the bed to drive the calcium and magnesium (softening), or other metals (industrial uses) off of the resin. Again, brining can be accomplished in either an upflow or downflow mode. [Table 3.8](#) provides typical regeneration data for regenerating a Rohm and Haas strong-acid ion exchange resin. All resin manufacturers provide regeneration data for their resins used in standard applications. If the reader chooses to use a resin for a nonstandard application, the regeneration requirements can be determined using software and/or the bench-scale procedures in Chapter 4.

Resin specifications show greater resin capacity when HCl is used versus H_2SO_4 . As an example, you might get 22 Kgr/ft³ using HCl and only 18 Kgr/ft³ using H_2SO_4 . Any calcium exchanged onto the resin—is eluted during regeneration as $CaSO_4$, which has a very limited solubility of only about 2200 mg/L. Thus, if there is more than 110 mg/L Ca in the raw water, there will probably be a solubility problem with H_2SO_4 regeneration. $CaCl_2$ is almost infinitely soluble, so there is no problem with HCl .

When using a sodium cycle system to soften water containing iron, resin capacity decreases over time. This is because iron is being exchanged onto internal sites and becoming oxidized to the ferric form (insoluble), thus blocking exchange sites. This effect can be minimized by more frequent regeneration, so that the iron has less time to oxidize and block the resin. Even with frequent regeneration there will still be some loss of capacity. The resin manufacturer will recommend that once or twice per year you regenerate with sodium chloride mixed with sodium bisulfite. The sodium bisulfite is such a strong reducing agent that it will reduce the insoluble ferric iron to soluble ferrous form so that you can clean up the bed. Usually 1 or 2 oz. of sodium bisulfite per ft³ of resin is sufficient. Loss of resin capacity attributed to iron fouling is all but eliminated with low-pressure membrane pretreatment that reduces iron and manganese to typically less than 0.05 mg/L.

RINSE

Rinsing follows regeneration. The purpose is to remove excess regenerant prior to putting the unit into service. This is usually conducted in a downflow mode. Softening operations involve a displacement rinse, a fast rinse, and a final rinse. After brining, the resin bed is full of brine. During the displacement rinse, the brine (concentrated $NaCl$) is slowly forced through the resin bed. The objective is to obtain optimum contact. The displacement rinse is always done at the same rate and direction as brining. Raw water is used for all rinsing, except in certain deionization operations. A high flow rate is used to remove any residual brine from the resin bed. The fast rinse is usually in the same direction as the displacement rinse (see [Table 3.8](#)).

TABLE 3.8
Resin Specifications for Amberlite® IR-120 Plus —A Strong-Acid Cation Exchanger

The recommended regeneration conditions for hydrogen cycle operation of Amberlite® IR-120 Plus are listed below:

REGENERANT CONCENTRATION^a—10% HCl or 1%–5% H₂SO₄

REGENERANT FLOW RATE—0.5–1.0 gpm/ft³ (4.0–8.0 L/L/h)

RINSE FLOW RATE—Initially same as regenerant flow rate, then can be increased to 1.5 gpm/ft³ (12.0 L/L/h)

RINSE WATER REQUIREMENTS—25–75 gal/ft³ (3.4–10.1 L/L)

REGENERATION—The tables below show the relationship between capacity and levels of sulfuric and hydrochloric acid for regeneration. Sulfuric acid concentration used after NaCl exhaustion was 10%. After CaCl₂ exhaustion, regeneration using 2% sulfuric acid was employed to avoid calcium sulfate precipitation. A 10% solution of HCl was used in both NaCl and CaCl₂ exhaustion studies.

Acid Regeneration

Exhausting Solution (ppm as CaCO ₃)	Regeneration Level (Lb of 66° Be' H ₂ SO ₄ /ft ³ of Resin)	g Acid/L Resin	Capacity
			$\left(\frac{\text{Kgr.}^{(2)} \text{CaCO}_3}{\text{ft}^3 \text{Resin}} \right)$ g CaCO ₃ /L
500 ppm	5.0	80	19.0
NaCl	10.0	160	25.0
500 ppm	5.0	80	12.5
CaCl ₂	10.0	160	17.0

Exhausting Solution (ppm as CaCO ₃)	Regeneration Level (Lb 30% HCl/ft ³ of Resin)	g acid/L Resin	Capacity
			$\left(\frac{\text{Kgr.}^{(2)} \text{CaCO}_3}{\text{ft}^3 \text{Resin}} \right)$ g CaCO ₃ /L
500 ppm	5	80	11.0
CaCl ₂	15	240	22.5
	25	400	27.5

(Continued)

TABLE 3.8 (Continued)
Resin Specifications for Amberlite® IR-120 Plus —A Strong-Acid Cation Exchanger

Amberlite® IR-120 Plus will provide excellent performance in both cold sodium cycle softeners and hot process systems. The recommended regeneration conditions for sodium cycle operation are listed below:

REGENERANT CONCENTRATION—10% NaCl

REGENERANT FLOW RATE—1 gpm/ft³ (8.0 L/L/h)

RINSE FLOW RATE—1 gpm/ft³ (8.0 L/L/h) initially, then 1.5 gpm/ft³ (12.0 L/L/h)

RINSE WATER REQUIREMENTS—25–75 gal/ft³ (3.4–10.1 L/L)

REGENERATION—The relationship between regeneration level and capacity is summarized in the table below. Data were obtained using 500 ppm (as CaCO₃) calcium chloride solution. Capacities have been adjusted downward to typify performance of material meeting “minimum” production specifications.

Regeneration Level (lbs NaCl/ft ³ Resin)	g NaCl/L Resin	Capacity (Kgr. as CaCO ₃ /ft ³ Resin)		Regeneration Efficiency (lbs NaCl/Kgr. Removed)	g NaCl/ g CaCO ₃ Removed
		CaCO ₃ /ft ³ Resin	g CaCO ₃ /L Resin		
5.0	80	17.8	40.8	0.28	1.96
15.0	240	29.3	67.1	0.51	3.57
25.0	400	34.0	77.9	0.74	5.13

Source: Rohm and Haas, Amberlite® IR-20 Plus Specification Sheet, January 1982. With permission.

Note: Acidic and basic regenerant solutions are corrosive and should be handled in a manner that will prevent eye and skin contact. In addition, the hazards of alcohol and other organic solvents should be recognized and steps to be taken to control exposure.

^a *Caution:* Nitric acid and other strong oxidizing agents can cause explosive type reactions, when mixed with organic materials, such as, ion exchange resins. Before using strong oxidizing agents in contact with ion exchange resins, consult sources knowledgeable in the handling of these materials.

Kgr.⁽²⁾ = kilograms.

SERVICE

Service is the operational mode of the system. This step follows rinsing. Process water, for example plating rinse water, is passed through the ion exchanger to remove cations or anions. The end of the service run is detected by a sharp increase in the cation or anion level of the effluent. In most industrial applications, an acceptable or predetermined level of cations or anions in the effluent is set. When this level is reached, “breakthrough” has occurred. The unit is then taken off-line and is backwashed, regenerated, and rinsed before being put back into service (see [Table 3.5](#) and [Figure 3.14](#)).

Pretreatment of process water prior to ion exchange is crucial to prevent fouling or damage to the resin. In the first edition of this book, the author recommended cartridge filtration and granular activated carbon pretreatment. “At a minimum, the water must be filtered to remove suspended solids. Cartridge filters work best because they do not require backwashing (another side stream requiring disposal). Organic substances in the process water can foul most resins and should be removed by pretreatment with activated carbon. Fouling occurs when organics in the water affix themselves to the resin by occupying the exchange sites. This phenomenon decreases the capacity of the resin. Strong oxidizing agents (e.g., chlorine) degrade most resins. These agents must be removed or destroyed by a pretreatment step.”

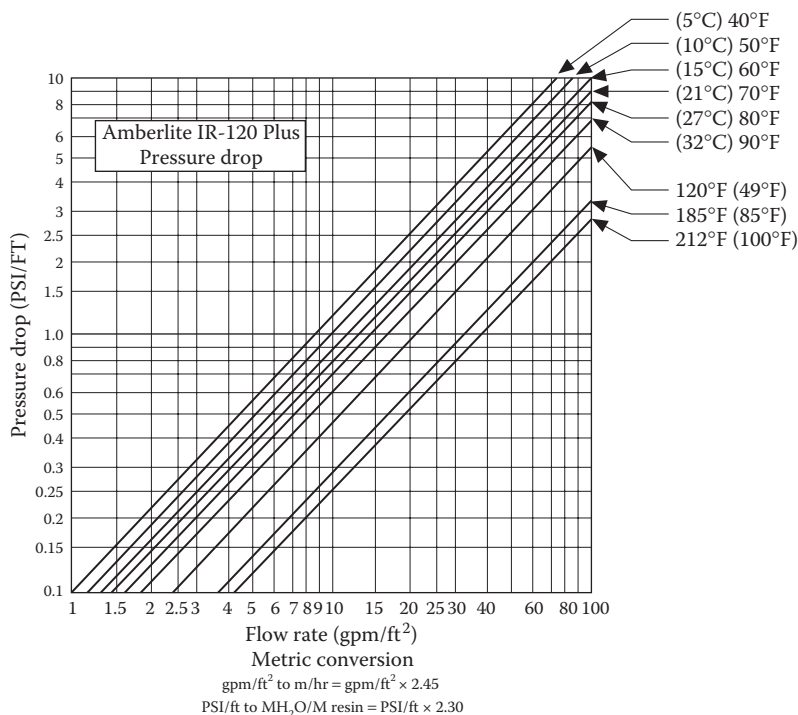


FIGURE 3.14 Pressure drop versus flow rate. (From Rohm and Haas, Amberlite® IR-20 Plus Specification Sheet, January 1982. With permission.)

The author wrote in *Ion Exchange Treatment for Drinking Water* (2004), “Today’s thinking is to not use ion exchange resins at \$50 per cubic foot and higher as filtration media, but to properly pretreat the water using, for example, hollow fiber microfiltration to remove all particulate and microorganisms, so that the exchanger does its job by exchanging dissolved ionic species, to provide particle free water to the ion exchanger and only use the exchanger to remove dissolved ionic species. Clarifiers, multimedia filters, and cartridge are often replaced with hollow fiber microfiltration systems capable of treating source water of any quality to turbidity levels less than 0.1 ntu, nonmeasurable suspended solids, iron less than 0.05 mg/L, and manganese less than 0.02 mg/L. Microfiltration removes practically all inorganic foulants, and all microorganisms are removed, reducing resin fouling and allowing for infrequent backwashing and regeneration. Low pressure membranes for particulate removal followed by granular activated carbon for organics reduction and oxidizing agent reduction or a scavenging SAR—when appropriate—should be considered. Nanofiltration or reverse osmosis can be used to further concentrate regenerant brines and in some cases to recover or reuse brines.”

EXAMPLE PROBLEMS AND SOLUTIONS

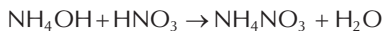
Problem 1: Real-World Regeneration

A chemical plant produces ammonium nitrate from nitric acid (HNO_3) and ammonia, both of which they make (Chapter 3). Their raw water contains only 40 mg/L of total dissolved solids (TDS) expressed as CaCO_3 . The wastewater from the plant contains 200 mg/L of $\text{NH}_3\text{-N}$ and 250 mg/L of $\text{NO}_3\text{-N}$ in addition to the original TDS. If they use 8 lb/ft³ of HNO_3 and 8 lb/ft³ of NH_4OH to get 22 and 11 Kgr/ft³ of capacity, respectively, as CaCO_3 on their resins when the regenerants have a concentration of 8% by weight, what volume of regeneration wastes do they have per day? What is the composition of the regeneration wastes in bar graph form? The cost of reusing the deionized water produced in waste treatment is too high to warrant its recovery. (Assume complete removal of all ions in the raw wastewater.)

Solution

The $\text{NH}_3\text{-N}$ was there as $\text{NH}_4\text{OH-N}$

The $\text{NO}_3\text{-N}$ was there as $\text{HNO}_3\text{-N}$



$$\frac{14}{200 \text{ mg/L}} = \frac{14}{x} = \frac{14}{y}$$

$$x = 200 \text{ mg/L HNO}_3\text{-N used to produce 200 mg/L of NH}_4\text{NO}_3\text{-N}$$

Hence 50 mg/L of $\text{HNO}_3\text{-N}$ unreacted

$$\frac{200\text{mg/L NH}_4\text{NO}_3\text{-N}}{14} = \frac{x}{50}$$

$$x = 714 \text{ mg/L NH}_4\text{NO}_3\text{-N as CaCO}_3$$

$$\frac{50\text{mg/L HNO}_3\text{-N}}{14} = \frac{y}{50}$$

$$y = 178.6 \text{ mg/L HNO}_3\text{-N as CaCO}_3$$

Cations to be removed = $40 + 714 = 754 \text{ mg/L as CaCO}_3$

$$754\text{mg/L} \div 17.12\text{mg/L/gr/gal} = 44\text{gr/gal as CaCO}_3$$

Anions to be removed = $40 + 714 + 178.6 = 932.6 \text{ mg/L as CaCO}_3$

$$932.6\text{mg/L} \div 17.12\text{mg/L/gr/gal} = 54.5\text{gr/gal as CaCO}_3$$

Volume of anion resin required

$$54.5\text{gr/gal} \times 10^5 \text{ gal} \times \frac{\text{Kgr}}{10^3\text{gr}} = 5450\text{Kgr/day as CaCO}_3$$

$$5450\text{Kgr/day} \div 11\text{Kgr/ft}^3 = 495.5\text{ft}^3 \text{ of anion resin}$$

Volume of cation resin required

$$44\text{gr/gal} \times (10^5\text{gal} + 495.5\text{ft}^3 \times 70\text{gal/ft}^3) \times \frac{\text{Kgr}}{10^3\text{gr}} = 5926\text{Kgr/day as CaCO}_3$$

$$5926\text{Kgr/day} \div 22\text{Kgr/ft}^3 = 269.4 \text{ ft}^3 \text{ of cation resin}$$

Design of cation units

Assume three units with a 24-h regeneration cycle

$$134,682\text{gal/day} \div 1440\text{min/day} = 93.5\text{gal/min}$$

With two units on-line flow rate is

$$93.5\text{gal/min} \div 2 = 46.8\text{gal/min/unit}$$

At 5 gal/min/ft²

$$46.8\text{gal/min/unit} \div 5 \text{ gal/min/ft}^2 = 9.4 \text{ ft}^2/\text{unit}$$

A 42"-diameter unit will have an area of 9.62 ft²

$$269.4\text{ft}^3 \div 3\text{units} \times 9.62\text{ft}^2/\text{unit} = 9.33\text{ft deep(ok)}$$

Design of anion units

Assume three units with a 24-h regeneration cycle

With two units on-line flow rate is

$$100,000 \text{ gal/day} \div 1440 \text{ min/day} \times 2 \text{ units} = 34.7 \text{ gal/min/unit}$$

At 2.5 gal/min/ft²

$$34.7 \text{ gal/min/unit} \div 2.5 \text{ gal/min/ft}^2 = 13.88 \text{ ft}^2$$

A 54"-diameter unit will have an area of 15.9 ft²

$$495.5 \text{ ft}^3 \div 3 \text{ units} \times 15.9 \text{ ft}^2/\text{unit} = 10.4 \text{ ft depth(ok)}$$

Regeneration needs

$$\text{Cation } 269.4 \text{ ft}^3 \times 8 \text{ lbHNO}_3/\text{ft}^3 = 2155.2 \text{ lb/dayHNO}_3$$

$$\text{Anion } 495.5 \text{ ft}^3 \times 8 \text{ lbNH}_4\text{OH}/\text{ft}^3 = 3964 \text{ lb/dayNH}_4\text{OH}$$

$$2155.2 \text{ lb/dayHNO}_3 \times \frac{50}{63} = 1710.5 \text{ lb/dayHNO}_3 \text{ as CaCO}_3$$

$$3964 \text{ lb/dayNH}_4\text{OH} \times \frac{50}{35} = 5662.9 \text{ lb/dayNH}_4\text{OH as CaCO}_3$$

$$1710.5 \text{ lb/day HNO}_3 \text{ as CaCO}_3 \times 7 \text{ Kgr/lb} = 11,973.5 \text{ Kgr/day as CaCO}_3$$

$$5662.9 \text{ lb/day NH}_4\text{OH as CaCO}_3 \times 7 \text{ Kgr/lb} = 39,640.3 \text{ Kgr/day as CaCO}_3$$

$$11,973.5 \text{ Kgr/day HNO}_3 \text{ as CaCO}_3 \text{ used}$$

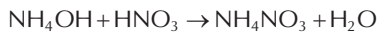
$$\underline{-5926 \text{ Kgr/day cations as CaCO}_3 \text{ exchanged}}$$

$$6047.5 \text{ Kgr/day HNO}_3 \text{ as CaCO}_3 \text{ not reacted}$$

$$39,640.3 \text{ Kgr/day NH}_4\text{OH as CaCO}_3 \text{ used}$$

$$\underline{-5450 \text{ Kgr/day anions as CaCO}_3 \text{ exchanged}}$$

$$34,190.3 \text{ Kgr/day NH}_4\text{OH as CaCO}_3 \text{ not reacted}$$



$$6047.5 \quad 6047.5 \quad 6047.5 \quad 6047.5$$

If all of the above are expressed as CaCO₃, then

$$34,190.3 - 6047.5 = 28,142.8 \text{ Kgr of NH}_4\text{OH as CaCO}_3 \text{ unreacted in regeneration waste}$$

$$40 \text{ mg/L TDS as CaCO}_3 \div 17.12 \text{ mg/L/gr/gal} = 2.34 \text{ gr/gal TDS as CaCO}_3$$

$$2.34 \text{ gr/gal} \times 134,682 \text{ gal/day} \times \frac{\text{Kgr}}{10^3 \text{ gr}} = 315 \text{ Kgr TDS as CaCO}_3/\text{day}$$

$$\text{(Cation) } 5926 - 315 = 5611 \text{ Kgr NH}_4\text{NO}_3 \text{ as CaCO}_3 \text{ in regeneration waste}$$

$$\text{(Anion) } 5450 - 315 = 5135 \text{ Kgr NH}_4\text{NO}_3 \text{ as CaCO}_3 \text{ in regeneration waste}$$

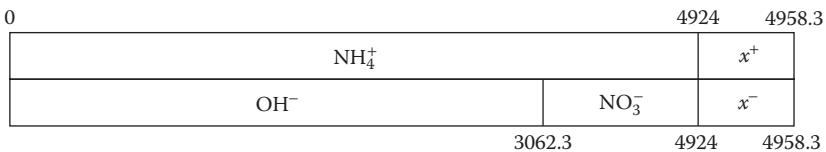
Thus

- 5611 Kgr NH_4NO_3 as CaCO_3 produced from regeneration of cation units
- 5135 Kgr NH_4NO_3 as CaCO_3 produced from regeneration of anion units
- 6047.5 Kgr NH_4NO_3 as CaCO_3 produced from reaction of excess NH_4OH as CaCO_3 and HNO_3 as CaCO_3 in regeneration waste
- 28,142.8 Kgr NH_4OH as CaCO_3 from excess NH_4OH used in regeneration
- 315 Kgr XNO_3 as CaCO_3 from regeneration of cation units
- 315 Kgr NH_4X as CaCO_3 from regeneration of anion units
- 6047.5 Kgr H_2O as CaCO_3 from reaction of NH_4OH and HNO_3 in regeneration wastes

Volume of regeneration wastes

- $2155.2 \text{ lb HNO}_3 \div 0.08 = 26,940 \text{ lb/day acid waste}$
- $3964 \text{ lb NH}_4 \text{ OH} \div 0.08 = 49,550 \text{ lb/day basic waste}$
- $6047.5 \text{ Kgr H}_2\text{O as CaCO}_3 \div 7 = 864 \times \frac{9}{50} = 155.5 \text{ lb/day H}_2\text{O produced}$
- Total = 76,645.5 lb/day regeneration waste
- $76,645.5 \text{ lb/day} \div 8.34 \text{ lb/gal} = 9190 \text{ gal/day regeneration waste}$
- $16,793.5 \text{ Kgr NH}_4\text{NO}_3 \text{ as CaCO}_3 \div 9190 \text{ gal} = 1827.4 \text{ gr / gal as CaCO}_3$
- $28,142.8 \text{ Kgr NH}_4\text{OH as CaCO}_3 \div 9190 \text{ gal} = 3062.3 \text{ gr / gal as CaCO}_3$
- $315 \text{ Kgr XNO}_3 \text{ as CaCO}_3 \div 9190 \text{ gal} = 34.3 \text{ gr / gal as CaCO}_3$
- $315 \text{ Kgr NH}_4\text{X as CaCO}_3 \div 9190 \text{ gal} = 34.3 \text{ gr / gal as CaCO}_3$

BAR CHART



Problem 2: Regeneration Waste

Calculate the concentrations of cations and anions expressed as CaCO_3 in the regeneration wastewater for a sodium softener treating 2.0 millions of gallons per day (MGD) of raw water to a residual of 1.2 gr/gal. The raw water analyses and bar graph of the raw water are shown below. Draw a bar graph of the regeneration

water. Assume the resin you have chosen is Amberlite® IR-120 Plus, with a regeneration efficiency of 0.51 lb NaCl per kilograin of hardness removed.

	240	400	430	460
Ca^{++}	Mg^{++}		Na^+	K^+
HCO_3^-		SO_4^-	Cl^-	
	265		460	

Raw Water Analyses

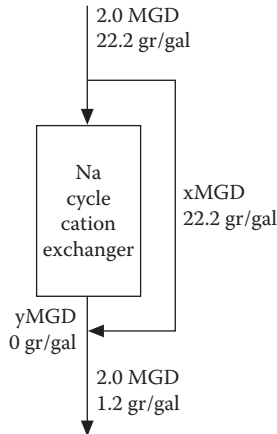
- $\text{Ca}(\text{HCO}_3)_2 = 240 \text{ mg/L as CaCO}_3$
- $\text{Mg}(\text{HCO}_3)_2 = 25 \text{ mg/L as CaCO}_3$
- $\text{MgSO}_4 = 115 \text{ mg/L as CaCO}_3$
- $\text{Na}_2\text{SO}_4 = 20 \text{ mg/L as CaCO}_3$
- $\text{NaCl} = 30 \text{ mg/L as CaCO}_3$
- $\text{KCl} = 30 \text{ mg/L as CaCO}_3$
- $\text{NO}_3 = 0 \text{ mg/L as CaCO}_3$

Design

Hardness (Ca^{++} and Mg^{++}) = 380 mg/L as CaCO_3

$$380 \text{ mg/L} \times \frac{1 \text{ gr / gal}}{17.12 \text{ mg / L}} = 22.2 \text{ gr / gal as CaCO}_3$$

Since hardness removal via softening by ion exchange is essentially an all-or-nothing process, we must design the softener with some flow-by passing the softener to obtain a finished water of 1.2 gr/gal.



Assume the resin you have chosen is Amberlite® IR-120 Plus, with a regeneration efficiency of 0.51 lb NaCl per kilograin of hardness removed:

$$\frac{(1.89 \times 10^6 \text{ gal/day})(22.2 \text{ gr/gal})(0.51 \text{ lb NaCl/Kgr})}{10^3 \text{ gr/Kgr}} = 21,398.6 \text{ lb/day}$$

NaCl required is 21,400 lb/day

Regeneration requires a volume of water equal to 6% of that produced between regenerations:

$$(0.06)(2 \times 10^6 \text{ gal}) = 120,000 \text{ gal} = 0.12 \text{ MGD of water for regeneration}$$

Calculate hardness removed each day:

$$(1.89 \text{ MGD})(380 \text{ mg/L})(8.34) = 5990 \text{ lb/day Ca and Mg as CaCO}_3 \text{ removed}$$

Calculate mg/L of hardness in regeneration wastewater:

$$5990 \text{ lb/day} = (x)(0.12 \text{ MGD})(8.34)$$

$x = 5.985 \text{ mg/L of hardness as CaCO}_3 \text{ in regeneration wastewater from unit}$

$$\begin{aligned} \text{Total Ca}^{++} + \text{Mg}^{++} \text{ in regeneration wastewater} &= 5985 \text{ mg/L} + 380 \text{ mg/L} \\ &= 6365 \text{ mg/L} \\ &\quad (380 \text{ mg/L is the water used} \\ &\quad \text{for regeneration}) \end{aligned}$$

$$\begin{aligned} \text{Ca}^{++} &= 6365 \times \frac{240}{380} = 4020 \text{ mg/L as CaCO}_3 \\ \text{Mg}^{++} &= 6365 \times \frac{140}{380} = 2345 \text{ mg/L as CaCO}_3 \end{aligned}$$

Calculate chloride in regeneration wastewater:

$$\begin{aligned} 21,398.4 \text{ lb/day NaCl} \times \frac{50}{58.45} &= 18,305 \text{ lb/day NaCl as CaCO}_3 \\ 18,305 \text{ lb/day} &= (0.12 \text{ MGD})(8.34)(x) \\ x &= 18,290 \text{ mg/L Cl}^- \text{ as CaCO}_3 \text{ in regeneration} \end{aligned}$$

Total Cl⁻ as CaCO₃ in regeneration = 18,290 + 60 = 18,350 mg/L

Calculate sodium in regeneration wastewater:

$$\begin{aligned} 21,398.6 \text{ lb/day NaCl} \times \frac{50}{58.45} &= 18,305 \text{ lb/day NaCl as CaCO}_3 \\ &\quad - 5990 \text{ lb/day exchanged on the resin} \\ &= 12,315 \text{ lb/day NaCl as CaCO}_3 \text{ not} \\ &\quad \text{exchanged on resin} \end{aligned}$$

$$12,315 = (0.12 \text{ MGD})(8.34)(x)$$

$$x = 12,305 \text{ mg/L}$$

Total $\text{Na}^+ = 12,305 + 50 = 12,355 \text{ mg/L}$ as CaCO_3 in regeneration wastewater

		4020	6365			18,711	18,751	
		Ca^{++}	Mg^{++}	Na^+		K^+		
HCO_3^-	SO_4^-	Cl^-				NO_3^-		
0	265	400					18,736	18,746

Regeneration wastewater

Problem 3

Starting with a typical midwestern groundwater, would you get more treatment capacity from a cation–anion deionization if you first treated water with sodium cycle softener, or if you did not treat it at all? Explain.

Solution

If the water is not softened, it will contain both divalent and monovalent cations, which can cause displacement of monovalent ions with divalent ions and thus leakage or premature breakthrough. Treatment with a softener would add only monovalent ions. Displacement will not take place and as such more water can be treated with the same volume of resin. So, the answer is yes.

Problem 4

Starting with water that contains the following:

- $\text{H}^+ = 100 \text{ mg/L}$ as CaCO_3
- $\text{Al}^{+++} = 60 \text{ mg/L}$ as CaCO_3
- $\text{Na}^+ = 40 \text{ mg/L}$ as CaCO_3
- $\text{K}^+ = 50 \text{ mg/L}$ as CaCO_3
- $\text{SO}_4^- = 140 \text{ mg/L}$ as CaCO_3
- $\text{Cl}^- = 110 \text{ mg/L}$ as CaCO_3

Produce 100,000 gal/day of water with a hardness of 33 mg/L as CaCO_3 , 80 mg/L of hydroxide alkalinity as CaCO_3 . No suspended solids may be present in the finished water (filtration may not be used). You have three cation and two anion exchange units available, and they can be operated in any reasonable cycle of exchange.

1. Show the set-up of the system.
2. Indicate the cycle in which each unit must operate.
3. Calculate the flow through each unit.
4. Calculate the TDS in the finished water.

Solution

0	60	100	150	250
	Al ⁺⁺⁺	Na ⁺	K ⁺	H ⁺
	SO ₄ ⁻		Cl ⁻	
0	140		250	

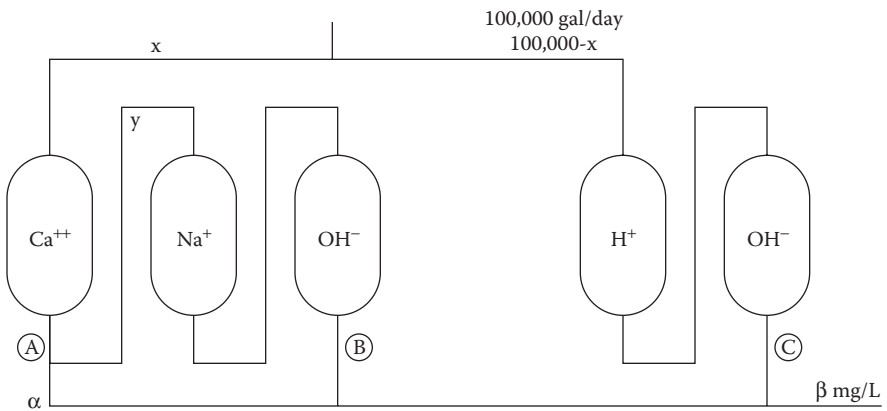
$Al_2(SO_4)_3, SO_4 = 60 \text{ mg/L as } CaCO_3$

$Na_2SO_4 = 40 \text{ mg/L as } CaCO_3$

$K_2SO_4 = 40 \text{ mg/L as } CaCO_3$

$KCl = 10 \text{ mg/L as } CaCO_3$

$HCl = 100 \text{ mg/L as } CaCO_3$



$HCl = 100 \text{ mg/L as } CaCO_3$

$CaSO_4 = 60 \text{ mg/L as } CaCO_3$

$K_2SO_4 = 40 \text{ mg/L as } CaCO_3$

$Na_2SO_4 = 40 \text{ mg/L as } CaCO_3$

$KCl = 10 \text{ mg/L as } CaCO_3$

$NaOH = 100 \text{ mg/L as } CaCO_3$

$KOH = 50 \text{ mg/L as } CaCO_3$

0 TDS

Hardness

$$60 \text{ mg/L} \times \alpha \text{ gal} = 33 \text{ mg/L} \times 100,000 \text{ gal}$$

$$\alpha = 55,000 \text{ gal}$$

Alkalinity-acidity

$$100 \text{ mg/L} \times 55,000 \text{ gal} + 150 \text{ mg/L} \times y = 100,000 \text{ gal} \times 80 \text{ mg/L}$$

$$y = 16,667 \text{ gal}$$

$$x = \alpha + y = 55,000 + 16,667 = 71,667 \text{ gal}$$

TDS

$$250 \text{ mg/L} \times 55,000 \text{ gal} + 150 \text{ mg/L} \times 16,667 \text{ gal} = \beta \times 100,000 \text{ gal}$$

$$\beta = 162.5 \text{ mg/L}$$

Problem 5: Ion Exchange

Aluminum has been linked with Alzheimer disease. Consider a drinking water containing calcium, magnesium, sodium, and potassium with a trace (2 mg/L of Al^{+++}). In what cycle could a cation exchange be run to remove only the aluminum? With what would you regenerate the resin?

Solution

CaCl_2 , chloride cycle.

Problem 6

An ion exchange unit in the sodium cycle contains 15 ft^3 of resin and requires 10 lb NaCl ft^3 for regeneration. The volume of untreated water used for regeneration is 4% of the softened water produced. The analysis of the raw water is as follows: pH 7.2; alk as CaCO_3 , 240 mg/L; Ca^{++} as Ca^{++} , 57 mg/L; Mg^{++} as Mg^{++} , 48 mg/L; Na^+ as Na^+ , 26.5 mg/L; SO_4^- as SO_4^- , 154 mg/L. The capacity of the resin is 28 Kgr/ft^3 as CaCO_3 .

1. Draw a bar graph showing the probable makeup of the chemical constituents in the raw water. Give a numerical value for each constituent.
2. Draw a bar graph showing the probable makeup of the chemical constituents in the treated water. Give a numerical value for each constituent.
3. What volume of treated water is produced per cycle?
4. Draw a bar graph showing the makeup of the probable chemical constituents in the regeneration wastes. Give a numerical value for each constituent.

Solution

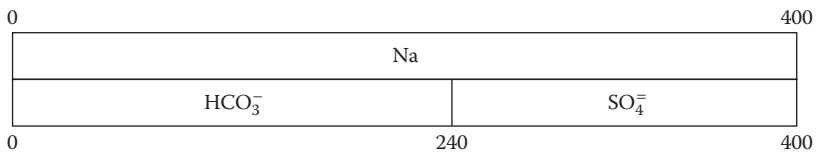
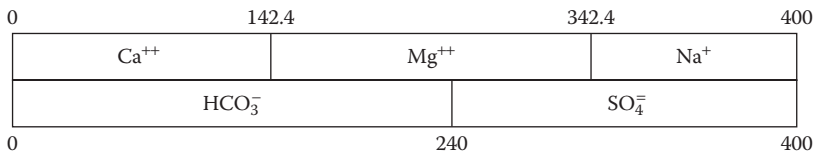
$$\text{Ca}^{++} \text{ 57 mg/L} \quad \frac{57}{20} = \frac{x}{50} \quad x = 142.4 \text{ mg/L as CaCO}_3$$

$$\text{Mg}^{++} \text{ 48 mg/L} \quad \frac{48}{12} = \frac{x}{50} \quad x = 200 \text{ mg/L as CaCO}_3$$

$$\text{Na}^+ \text{ 26.5 mg/L} \quad \frac{26.5}{23} = \frac{x}{50} \quad x = 57.6 \text{ mg/L as CaCO}_3$$

$$\text{HCO}_3^- \text{ as CaCO}_3 \quad = \quad 240 \text{ mg/L as CaCO}_3$$

$$\text{SO}_4^{--} \text{ 154} \quad \frac{154}{48} = \frac{x}{50} \quad 160 \text{ mg/L as CaCO}_3$$



$$\frac{342.4 \text{ mg/L Total Hardness (TH)}}{17.12 \text{ mg/L/gr/gal}} = 20 \text{ gr/gal T.H.}$$

$$\frac{28,000 \text{ gr/ft}^3 \times 15 \text{ ft}^3}{20 \text{ gr/gal}} = 21,000 \text{ gal treated per cycle}$$

Regeneration wastes = 840 gal

With 4% conc. factor is 25

$$\text{Ca}^{++} = 142.4 \times 25 + 142.4 = 3702.4 \text{ mg/L Ca as CaCO}_3$$

$$\text{Mg}^{++} = 200 \times 25 + 200 = 5200 \text{ mg/L Mg as CaCO}_3$$

$$\text{HCO}_3^- \text{ 240 mg/L as CaCO}_3$$

$$\text{SO}_4^{--} \text{ 160 mg/L as CaCO}_3$$

$$150 \text{ lb NaCl} \frac{150}{58.5} = \frac{x}{50} \quad x = 128 \text{ lb NaCl as CaCO}_3$$

$$128 = x \times 8.34 \times 0.00084$$

$$x = 18,271 \text{ mg/L NaCl as CaCO}_3$$

and

$$\text{Na}^+ 18,271 \text{ mg/L as CaCO}_3 - (3702.4 + 5200) = 9768.6$$

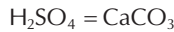
$$\text{Cl}^- = 18,271 \text{ mg/L as CaCO}_3$$

		3702.4	8502.4	18,671
Ca^{++}		Mg^{++}		$\text{Na}^+ (9768.6)$
HCO_3^-	SO_4^{--}	Cl^-		
240	400	18,671		

Problem 7

A deionization system contains 12 ft³ of cation resin and 10 ft³ of anion resin. How many pounds of H₂SO₄ and NaOH would be required to regenerate the system on a theoretical basis? The capacity of the cation resin is 18 Kgr/ft³ and the anion resin 17 Kgr/ft³, both expressed as CaCO₃.

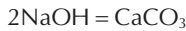
Solution



$$\frac{98}{x} = \frac{100}{18 \text{ Kgr} / \text{ft}^3 \times 12 \text{ ft}^3}$$

$$x = 211.68 \text{ Kgr H}_2\text{SO}_4$$

$$211.68 \text{ Kgr} \div 7 \text{ Kgr} / \text{lb} = 30.24 \text{ lb } 100\% \text{ H}_2\text{SO}_4$$



$$\frac{2 \times 40}{y} = \frac{100}{10 \text{ ft}^3 \times 17 \text{ Kgr} / \text{ft}^3}$$

$$y = 136 \text{ Kgr NaOH}$$

$$136 \text{ Kgr} \div 7 \text{ Kgr} / \text{lb} = 19.43 \text{ lb } 100\% \text{ NaOH}$$

Problem 8

A raw water has been analyzed and found to contain the following:

$$\text{pH} = 7.4$$

$$\text{Ca}^{++} = 30 \text{ mg/L as Ca}$$

$$\text{Mg}^{++} = 36 \text{ mg/L as Mg}$$

$$\text{Na}^+ = 46 \text{ mg/L as Na}$$

$$\text{Alk} = 270 \text{ mg/L as CaCO}_3\text{-HCO}_3^-$$

$$\text{SO}_4^{--} = 106 \text{ mg/L as SO}_4^{--}$$

$$\text{Cl}^- = 85 \text{ mg/L as Cl}^-$$

A company plans to use this raw water to produce two water sources (Source 1 and Source 2) as follows (not at the same time):

Source 1	30 mg/L total hardness as CaCO ₃ 40 mg/L alk as CaCO ₃ Rest of cations and anions are of no concern
Source 2	Zero total hardness 70 mg/L alk as CaCO ₃ 60 mg/L of SO ₄ ²⁻ as CaCO ₃

The company has a sodium cycle softener, a hydrogen cycle cation exchanger, and a hydroxyl cycle anion exchanger. The system is piped so that water can go through or around the system. Flow can also bypass the hydroxyl cycle anion exchanger. They desire 100,000 gal/day of treated water. The water is stored in open tanks.

1. Draw a flow diagram of the system.
2. Show the flows through each unit for both water sources.
3. Draw a bar diagram for each finished water source.

Solution

$$Ca^{++} = 80 \times \frac{50}{20} = 200 \text{ mg/L as CaCO}_3$$

$$Mg^{++} = 36 \times \frac{50}{12} = 150 \text{ mg/L as CaCO}_3$$

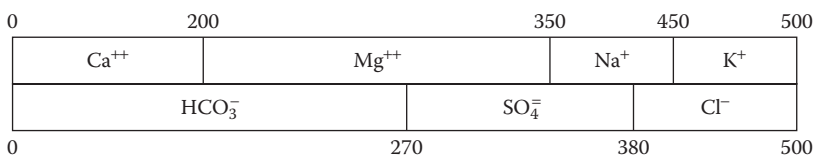
$$Na^+ = 46 \times \frac{50}{23} = 100 \text{ mg/L as CaCO}_3$$

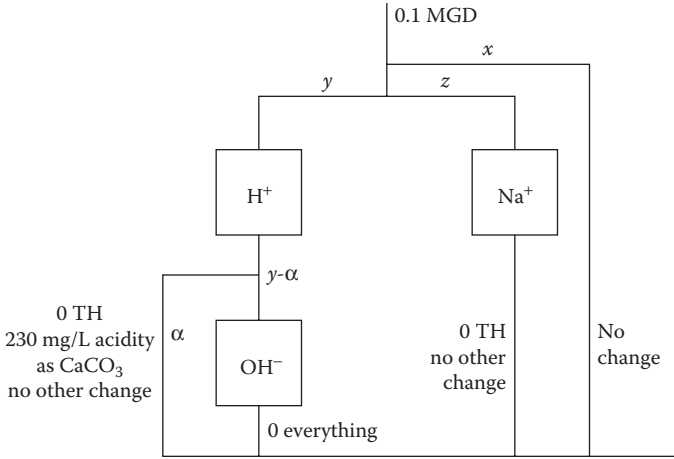
$$K^+ = 39 \times \frac{50}{39} = 50 \text{ mg/L as CaCO}_3$$

$$HCO_3^- = 270 \text{ mg/L as CaCO}_3$$

$$SO_4^{2-} = 106 \times \frac{50}{48} = 110 \text{ mg/L as CaCO}_3$$

$$Cl^- = 85 \times \frac{50}{35.5} = 120 \text{ mg/L as CaCO}_3$$





Source 1

30 mg/L = TH, 40 mg/L = alk

$$TH = (350 \text{ mg/L}) \times x = (0.1) \times (30 \text{ mg/L})$$

$$x = 0.0086 \text{ MGD}$$

$$\begin{aligned} \text{alk} &= -230 \text{ mg/L} \times \alpha + 0 + 270 \text{ mg/L} \times z + 270 \text{ mg/L} \times 0.0086 \\ &= .1 \times 40 \end{aligned}$$

$$-230 \alpha + 270z = 1.678$$

$$\begin{aligned} SO_4 &= 110 \text{ mg/L} \times \alpha + 0 + 110 \text{ mg/L} \times z + 110 \text{ mg/L} \times 0.0086 \\ &= .1 \times 110 \end{aligned}$$

$$110\alpha + 110z = 10.094$$

$$2.09 \times SO_4 = 230\alpha + 230z = 21.096$$

$$500z = 22.774$$

$$z = 0.0455 \text{ MGD}$$

$$y = 0.0459 \text{ MGD}$$

$$\alpha = 0.0459 \text{ MGD}$$

$$y - \alpha = 0$$

No treatment 0.0086

$$\text{Ca}^{++} = 200 \quad \text{Mg}^{++} = 150 \quad \text{Na}^+ = 100 \quad \text{K} = 50$$

$$\text{HCO}_3^- = 270 \quad \text{SO}_4^{--} = 110 \quad \text{Cl}^- = 120$$

Na cycle 0.0455

$$\text{Na}^+ = 450 \quad \text{K}^+ = 50$$

$$\text{HCO}_3^- = 270 \quad \text{SO}_4^{--} = 110 \quad \text{Cl}^- = 120$$

H⁺ cycle 0.0459

$$\text{H}^+ = 500$$

$$\text{HCO}_3^- = 270 \quad \text{SO}_4^{--} = 110 \quad \text{Cl}^- = 120$$

$$\begin{aligned} \text{Na}^+ &= (0.0086) \times (100) + (0.0455) \times (450) + 0 = (0.1) \times x \\ (0.86) + (20.475) &= (0.1)x \end{aligned}$$

$$x = 213 \text{ mg/L as CaCO}_3$$

$$\text{Ca}^{++} = (0.0086) \times (200) + 0 + 0 = (0.1) \times x$$

$$x = 17 \text{ mg/L as CaCO}_3$$

$$\text{Mg}^{++} = (0.0086) \times (150) + 0 + 0 = (0.1) \times x$$

$$x = 13 \text{ mg/L as CaCO}_3$$

$$\text{K}^+ = (0.0086) \times (50) + (0.0455) \times (50) + 0 = (0.1) \times x$$

$$0.43 + 2.27 = (0.1)x$$

$$x = 27 \text{ mg/L as CaCO}_3$$

$$\text{HCO}_3^- = (0.0086 \times 270) + (0.0455) \times (270 + 0.0459) \times (270) = (0.1) \times x$$

$$x = 270 \text{ mg/L as CaCO}_3$$

$$\text{H}^+ = 0 + 0 + (0.0459) \times (500) = (0.1) \times x$$

$$x = 229.5 \text{ mg/L as CaCO}_3$$

$$\text{SO}_4^- = (0.0086) \times (110 + 0.0455) \times (110) + (0.0459) \times (110) = (0.1) \times x$$

$$x = 110 \text{ mg/L as CaCO}_3$$

$$\text{Cl}^- = (0.0086) \times (120) + (0.0455) \times (120) + (0.0459) \times (120) = (0.1) \times x$$

$$x = 120 \text{ mg/L as CaCO}_3$$

0	17	30		247	274	
Ca ⁺⁺		Mg ⁺⁺	Na ⁺			K ⁺
HCO ₃ ⁻		SO ₄ ⁻			Cl ⁻	
0	40		150		270	

Source 2

TH = 0, alk = 70 mg/L as CaCO₃, SO₄⁻ = 60 mg/L as CaCO₃

$$-230\alpha + 270z = 70 \times 0.1 \text{ alk}$$

$$2.09 \times 110\alpha + 110z = 60 \times 0.1 \text{ SO}_4^-$$

$$230\alpha + 230z = 125.5 \times 0.1$$

$$500z = 195.5 \times 0.1$$

$$z = 0.0391 \text{ MGD}$$

$$110\alpha + 110 \times 0.0391 = 60 \times 0.1$$

$$110\alpha = 1.699$$

$$\alpha = 0.0154 \text{ MGD}$$

$$\alpha = 0.0154 \text{ MGD} \quad \text{H}^+ \text{ cycle}$$

$$z = 0.0391 \text{ MGD} \quad \text{Na}^+ \text{ cycle}$$

$$y - \alpha = 0.0455 \text{ MGD} \quad \text{H}^+ + \text{OH}^- \text{ cycle}$$

$$y = 0.0609 \text{ MGD}$$

$$\begin{array}{cccc} \text{H}^+ \text{ cycle} & 0.0154 & & \\ \text{H}^+ = 500 & \text{HCO}_3^- = 270 & \text{Cl}^- = 120 & \text{SO}_4^- = 110 \end{array}$$

$$\begin{aligned} \text{Na}^+ \text{ cycle} &= 0.0391 \\ \text{Na}^+ &= 450 \quad \text{K}^+ = 50 \\ \text{HCO}_3^- &= 270 \quad \text{Cl}^- = 120 \quad \text{SO}_4^{2-} = 110 \end{aligned}$$

$$\text{H}^+ + \text{OH}^- = 0$$

$$\text{Na}^+ = (0.0391) \times (450) = (0.1) \times x$$

$$x = 176 \text{ mg/L as CaCO}_3$$

$$\text{K}^+ = (0.0391) \times (50) = (0.1) \times x$$

$$x = 20 \text{ mg/L as CaCO}_3$$

$$\text{H}^+ = (0.0154) \times (500) = (0.1) \times x$$

$$x = 77 \text{ mg/L as CaCO}_3$$

$$\text{HCO}_3^- = (0.0391) \times (270) + (0.0154) \times (270) = (0.1)x$$

$$x = 147 \text{ mg/L as CaCO}_3$$

$$\text{SO}_4^{2-} = (0.0391) \times (110) + (0.0154) \times (110) = (0.1)x$$

$$x = 60 \text{ mg/L as CaCO}_3$$

$$\text{Cl}^- = (0.0391) \times (120) + (0.0154) \times (120) = (0.1)x$$

$$x = 65 \text{ mg/L as CaCO}_3$$

0	Na^+			196
	HCO_3^-	SO_4^{2-}	Cl^-	K^+
0	70	130	176	196

Alternate Solution for Source 1

$$\text{TH} = 350 \text{ mg/L} \times x = 0.1 \times 30 \text{ mg/L}$$

$$x = 0.0086 \text{ MGD}$$

$$\text{alk} = 0 \times y + 270 \text{ mg/L} \times z + 270 \text{ mg/L} \times 0.0086 = 0.1 \times 40 \text{ mg/L}$$

$$z = 0.0063 \text{ MGD}$$

$$0.1 - (0.0086 + 0.0063) = y$$

$$y = 0.0851 \text{ MGD}$$

No treatment 0.0086 MGD

$$\text{Ca}^{++} = 200 \quad \text{Mg}^{++} = 150 \quad \text{Na}^+ = 100 \quad \text{K}^+ = 50$$

$$\text{HCO}_3^- = 270 \quad \text{SO}_4^{--} = 110 \quad \text{Cl}^- = 120$$

Na cycle 0.0063 MGD

$$\text{Na}^+ = 450 \quad \text{K}^+ = 50$$

$$\text{HCO}_3^- = 270 \quad \text{SO}_4^{--} = 110 \quad \text{Cl}^- = 120$$

H⁺ + OH⁻ cycle 0.0851 MGD

zero for all elements.

$$\text{Na}^+ = (0.0086) \times (100) + (0.0063) \times (450) = (0.1) \times x$$

$$x = \frac{2.835 + .86}{0.1}$$

$$x = 37 \text{ mg/L}$$

$$\text{Ca}^{++} = (0.0086) \times (200) = (0.1)x$$

$$x = 17.2 \text{ mg/L}$$

$$\text{Mg}^{++} = (0.0086) \times (150) = (0.1)x$$

$$x = 12.9 \text{ mg/L}$$

$$\text{K}^+ = (0.0086) \times (50) + (0.0063) \times (50) = (0.1)x$$

$$x = \frac{0.43 + 0.315}{.1} = 7.5 \text{ mg/L}$$

$$\text{HCO}_3^- = (0.0086) \times (270) + (0.0063) \times (270) = (0.1) \times x$$

$$x = \frac{2.32 + 1.70}{.1} = 40 \text{ mg/L}$$

$$\text{SO}_4^{--} = (0.0086) \times (110) + (0.0063) \times (110) = (0.1) \times x$$

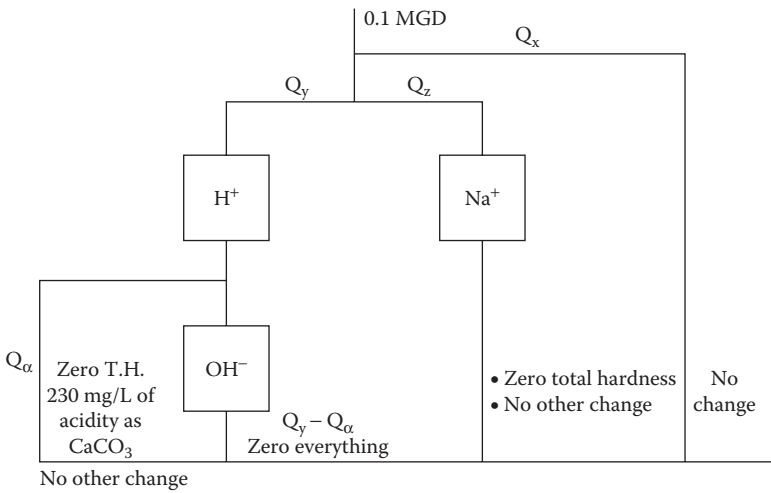
$$x = \frac{0.946 + 0.693}{0.1} = 16 \text{ mg/L}$$

$$\text{Cl}^- = (0.0086) \times (120) + (0.0063) \times (120) = (0.1) \times x$$

$$x = \frac{1.032 + 0.756}{0.1} = 18 \text{ mg/L}$$

0	17.2	30.1				67.1	74.6
Ca ⁺⁺	Mg ⁺⁺	Na ⁺			K ⁺		
HCO ₃ ⁻			SO ₄ ⁼	Cl ⁻			
0	40			56	74		

Solution



Source 1

$$\text{Total hardness} = (350 \text{ mg/L})Q_z = (0.1)(30 \text{ mg/L})$$

$$Q_z = 0.0086 \text{ MGD}$$

$$\text{Alkalinity} = (-230 \text{ mg/L})(Q_x) + 0 + (270 \text{ mg/L})$$

$$Q_z + (270 \text{ mg/L})(0.0086)$$

$$= (0.1)(40 \text{ mg/L})$$

$$(-230 \text{ mg/L})(Q_x) + (270)Q_z = 1.678$$

$$\text{SO}_4^{=} = (110 \text{ mg/L}) Q_\alpha + 0 + (110 \text{ mg/L})Q_z + (110 \text{ mg/L})(0.0086) = 0.1 \times 110$$

$$110 Q_\alpha + 110 Q_z = 10.094$$

$$Q_x = 0.0086 \text{ MGD}$$

$$Q_z = 0.0455 \text{ MGD}$$

$$Q_y = 0.0459 \text{ MGD}$$

$$Q_\alpha = 0.0459 \text{ MGD}$$

No treatment line, $Q = 0.0086 \text{ MGD}$

$$\begin{array}{cccc} \text{Ca}^{++} = 200 & \text{Na}^+ = 100 & \text{HCO}_3^- = 270 & \text{Cl}^- = 120 \\ \text{Mg}^{++} = 150 & \text{K}^+ = 50 & \text{SO}_4^{--} = 110 & \end{array}$$

Na⁺ cycle H⁺ cycle

$$Q_z = 0.0455 \text{ MGD } Q_y = 0.0459 \text{ MGD}$$

$$\text{Na}^+ = 450 \text{ mg/LH}^+ = 500 \text{ mg/L}$$

$$\text{K}^+ = 50 \text{ mg/LHCO}_3^- = 270 \text{ mg/L}$$

$$\text{HCO}_3^- = 270 \text{ mg/LSO}_4^{--} = 110 \text{ mg/L}$$

$$\text{SO}_4^{--} = 110 \text{ mg/LCl}^- = 120 \text{ mg/L}$$

$$\text{Cl}^- = 120 \text{ mg/L}$$

$$\text{Na}^+ = (0.0086)(100) + (0.0455)(450) + 0 = (0.1)x$$

$$x = 213 \text{ mg/L as CaCO}_3 = \text{Na}^+$$

$$\text{Ca}^{++} = (0.0086)(200) + 0 + 0 = (0.1)(\text{Ca}^{++})$$

$$\text{Ca}^{++} = 17 \text{ mg/L as CaCO}_3$$

$$\text{Mg}^{++} = (0.0086)(150) + 0 + 0 = (0.1)(\text{Mg}^{++})$$

$$\text{Mg}^{++} = 13 \text{ mg/L as CaCO}_3$$

$$\text{K}^+ = (0.0086)(50) + (0.0455)(50) + 0 = (0.1)(\text{K}^+)$$

$$\text{K}^+ = 27 \text{ mg/L as CaCO}_3$$

$$\text{HCO}_3^- = (0.0086)(270) + (0.0455)(270) + (0.0459)(270) = (0.1)x$$

$$\text{HCO}_3^- = x = 270 \text{ mg/L as CaCO}_3$$

$$\text{HCO}_3^- = 270 \text{ mg/L as CaCO}_3$$

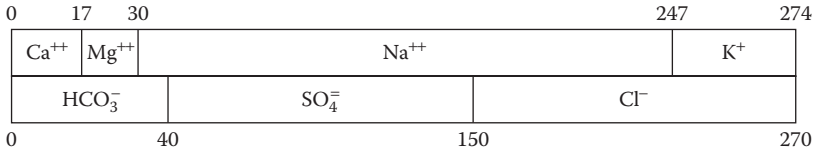
$$\text{H}^+ = 0 + (0.0459)(500) = (0.1)(\text{H}^+)$$

$$\text{H}^+ = 229.5 \text{ mg/L as CaCO}_3$$

$$\text{Cl}^- = (0.0086)(120) + (0.0455)(120) + (0.0459)(120) = (0.1)(\text{Cl}^-)$$

$$\text{Cl}^- = 120 \text{ mg/L as CaCO}_3$$

Source 1 Bar Chart



Source 2

- Zero total hardness
- Alkalinity 70 mg/L as CaCO₃
- Sulfate 60 mg/L as CaCO₃

$$(1) - 230Q_\alpha + 270Q_z = (0.1)(70) - \text{Alkalinity}$$

$$(2) 110Q_\alpha + 110Q_z = (0.1)(60)$$

Solve:

$$Q_\alpha = 0.0154 \text{ MGD, H}^+ \text{ cycle}$$

$$Q_z = 0.0391 \text{ MGD, Na}^+ \text{ cycle}$$

$$Q_y - Q_\alpha = 0.0455 \text{ MGD, H}^+ + \text{OH}^- \text{ cycle}$$

$$Q_y = 0.0609 \text{ MGD}$$

$$\text{H}^+ \text{ cycle, } Q_\alpha = 0.0154 \text{ MGD}$$

$$\text{H}^+ = 500 \quad \text{HCO}_3^- = 270 \quad \text{Cl}^- = 120 \quad \text{SO}_4^- = 110$$

$$\text{Na}^+ \text{ cycle, } Q_z = 0.0391 \text{ MGD}$$

$$\text{Na}^+ = 450 \quad \text{K}^+ = 50 \quad \text{HCO}_3^- = 270 \quad \text{Cl}^- = 120 \quad \text{SO}_4^- = 110$$

$$\text{H}^+ + \text{OH}^- = 0$$

$$\text{Na}^+ = (0.0391)(450) = (0.1)(\text{Na}^+)$$

$$\text{Na}^+ = 176 \text{ mg/L as CaCO}_3$$

$$\text{K}^+ = (0.0391)(50) = (0.1)(\text{K}^+)$$

$$\text{K}^+ = 20 \text{ mg/L as CaCO}_3$$

$$H^+ = (0.0154)(500) = (0.1)(H^+)$$

$$H^+ = 77 \text{ mg/L as CaCO}_3$$

$$HCO_3^- = (0.0391)(270) + (0.0154)(270) = (0.1)(HCO_3^-)$$

$$HCO_3^- = 147 \text{ mg/L}$$

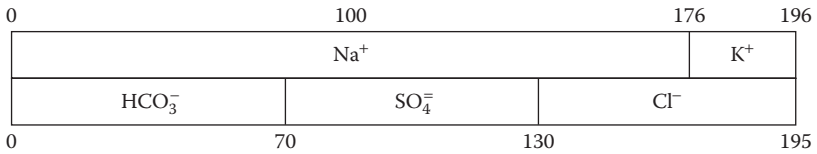
$$SO_4^{2-} = (0.0391)(110) + (0.0154)(110) = 0.1SO_4^{2-}$$

$$SO_4^{2-} = 60 \text{ mg/L as CaCO}_3$$

$$Cl^- = (0.0391)(120) + (0.0154)(120) = (0.1)(Cl^-)$$

$$Cl^- = 65 \text{ mg/L as CaCO}_3$$

Source 2 Bar Chart



Problem 9

You have been asked to check the capacity of a deionization system that is treating a water with 700 mg/L NaCl. The leakage is 2.5 mg/L NaCl. The system contains 13 ft³ of strong-acid cation resin with a capacity of 16 Kgr/ft³ and a strong-base anion resin unit containing 12 ft³ with a capacity of 14 Kgr/ft³. H₂SO₄ efficiency is 0.64 lb 56° Bé/Kgr and NaOH efficiency is 0.51 lb/Kgr. What is the capacity in gallons per cycle? How much additional capacity could you get on the cation unit by using a chemically equivalent amount of HCl? What will be the alkalinity or acidity of the equalized regeneration wastes?

Solution

Cation resin

$$13 \text{ ft}^3 \times 16 \text{ Kgr/ft}^3 = 208 \text{ Kgr as CaCO}_3$$

Anion resin

$$12 \text{ ft}^3 \times 14 \text{ Kgr/ft}^3 = 168 \text{ Kgr as CaCO}_3$$

$$\frac{700}{58.5} = \frac{x}{50}$$

$$x = 598 \text{ mg/L as CaCO}_3 \text{ or } 35 \text{ gr/gal as CaCO}_3$$

$$\frac{168,000 \text{ gr/cycle}}{35 \text{ gr/gal}} = 4800 \text{ gal/cycle}$$

$$\frac{208,000 \text{ gr/cycle}}{35 \text{ gr/gal}} = 5943 \text{ gal/cycle}$$

No increase in capacity because no calcium in raw water

Regeneration wastes = 50 to 70 gal H⁺ water/ft³ to rinse anion unit

$$\text{H}_2\text{SO}_4 60 \times 12 = 720 \text{ gal}$$

$$0.64 \times 0.98 \text{ lb/Kgr} 720 \text{ gal} \times 35 \text{ gr/gal} = 25,200 \text{ gr or } 25.2 \text{ Kgr}$$

$$(168 + 25.2) 0.64 \times 0.98 = 121.2 \text{ lb } 100\% \text{ H}_2\text{SO}_4$$

NaOH

$$0.51 \text{ lb/Kgr} \times 168 \text{ Kgr} = 85.7 \text{ lb } 100\% \text{ NaOH}$$

$$121.2 \times \frac{50}{49} = 123.7 \text{ lb H}_2\text{SO}_4 \text{ as CaCO}_3 \text{ acidity}$$

$$85.7 \times \frac{50}{40} = 107.1 \text{ lb NaOH as CaCO}_3 \text{ alk}$$

$$7 \text{ Kgr/lb} \times 123.7 = 865.9 \text{ Kgr H}_2\text{SO}_4 \text{ as CaCO}_3$$

$$7 \text{ Kgr/lb} \times 107.1 = 749.7 \text{ Kgr NaOH as CaCO}_3$$

865.9 Kgr H₂SO₄ as CaCO₃ put into cation unit

-193.2 Kgr H₂SO₄ as CaCO₃ used in resin

672.7 Kgr H₂SO₄ as CaCO₃ not used (in regeneration)

749.7 Kgr NaOH as CaCO₃ put into anion unit

-168.0 Kgr NaOH as CaCO₃ used in resin

581.7 Kgr NaOH as CaCO₃ not used (in regeneration)

-25.2 Kgr H₂SO₄ as CaCO₃ from H⁺ water rinse

556.5 Kgr NaOH as CaCO₃ not used

$$672.7$$

$$-581.7$$

$$91.0 \text{ Kgr H}_2\text{SO}_4 \text{ as CaCO}_3 \text{ acidity}$$

or

$$\begin{array}{r} 672.7 \\ -556.5 \\ \hline 116.2 \text{Kgr H}_2\text{SO}_4 \text{ as CaCO}_3 \text{ acidity} \end{array}$$

With 4% NaOH

8% H₂SO₄

$$\frac{85.7}{.04 \times 8.34} = 257 \text{ gal}$$

$$\frac{121.2}{.08 \times 8.34} = \frac{182}{439} \text{ gal}$$

$$\frac{91,000 \text{ gr}}{439} = 207.3 \text{ gr/gal acidity as CaCO}_3 \text{ or } 3549 \text{ mg/L}$$

$$\frac{116,200 \text{ gr}}{439 + 720} = 100.3 \text{ gr/gal acidity as CaCO}_3 \text{ or } 1716 \text{ mg/L}$$

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