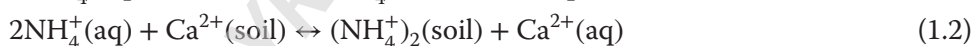


## 1

## Ion Exchange and Ion Exchangers: An Introduction

### 1.1 Historical Perspective

Evolution is traditionally viewed to occur in a slow but continuous manner for living organisms and creatures gradually acquiring new traits. To the contrary, many areas of “science” undergo periods of rapid bursts of fast development separated by virtual standstill with no significant activity. The first historically recorded use of ion exchange phenomenon is from the Old Testament of the Holy Bible in Exodus 15:22–25 describing how Moses rendered the bitter water potable by apparently using the process of ion exchange and/or sorption. Another often quoted ancient reference is to Aristotle’s observation that the salt content of water is diminished or altered upon percolation through certain sand granules. From a scientific viewpoint, however, the credit for recognition of the phenomenon of ion exchange is attributed to the English agriculture and soil chemists, J.T. Way and H.S. Thompson. In 1850, these two soil scientists formulated a remarkably accurate description of ion exchange processes in regard to removal of ammonium ions from manure by cation exchanging soil [1,2]. They essentially simulated the following naturally occurring cation exchange reactions as follows:

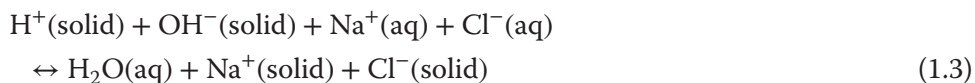


Some of the fundamental tenets of ion exchange resulted from this work: first, the exchange of ions differed from true physical adsorption; second, the exchange of ions involved the exchange in equivalent amounts; third, the process is reversible and fourth, some ions were exchanged more favorably than others.

*As often with many groundbreaking inventions, the findings of Way and Thompson cast doubts, disbeliefs and discouragement from their peers. In the following years, these two soil scientists discontinued persistent research in this field.* As a result, the evolution of ion exchange process progressed rather slowly due to the difficulties in modifying or manipulating naturally occurring inorganic clayey materials with low cation exchange capacities.

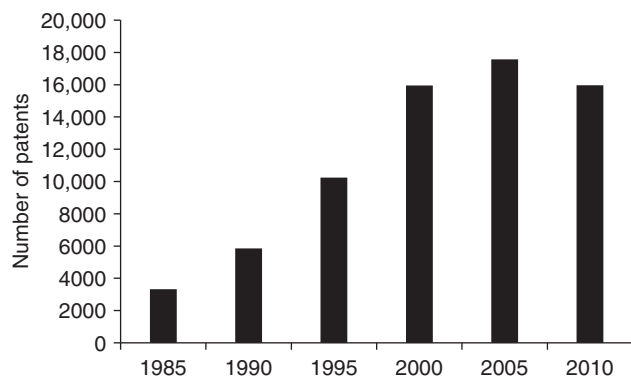
Inorganic zeolites (synthetic or naturally occurring aluminosilicates) later found wide applications in softening hard waters, that is, removal of dissolved calcium and magnesium through cation exchange. However, the anion-exchange processes remained unexplored and practically unobserved. Even at that time, it was not difficult to conceptualize that the availability of both cation exchangers and anion exchangers

in the ionic forms of hydrogen and hydroxyl ions, respectively, would create a new non-thermal way to produce water free of dissolved solids as indicated below:



The biggest obstacle to realize this concept was to identify and/or synthesize ion exchangers which will be chemically stable and durable under the chemically harsh environments at very high and low pH. The immense potential of ion exchange technology scaled a new height when the first organic-based (polymeric) cation exchanger was synthesized by Adams and Holmes [3]. In less than ten years, D’Alelio prepared the first polymeric, strong/weak cation and anion exchangers [4–6]. Since then, synthesis of new ion exchangers never seemed to slow down and application of ion exchange technology in industries as diverse as power utilities, biotechnology, agriculture, pharmaceuticals, pure chemicals, microelectronics, etc. are continually growing. No specialty grows in isolation; ion exchange fundamentals, ion exchange resins and ion exchange membranes continue to find new and innovative applications globally. Figure 1.1 includes the number of ion exchange related US patents issued during the last three decades, illustrating continued inventions in new products and processes.

Ironically, the Second World War and, more specifically, the race for nuclear technology helped catalyze the growth and maturity of the field of ion exchange at an accelerated pace. Ion exchange was found to be a viable process for separating some of the transuranium elements and, for understandable reasons, its application aroused a great deal of interest. In fact, some of the most fundamental works on ion exchange equilibria and kinetics were carried out during the Second World War period by Boyd *et al.* and reported afterwards in the open literature [9–11]. All along, the scientific understanding of ion exchange fundamentals consistently lagged well behind its applications. Table 1.1 attempts to summarize milestones in regard to the development and application of ion exchange technology over time.



**Figure 1.1** Number of patents per year for “anion exchange” and “cation exchange” per a Google Patents search. *Source:* Data taken with permission from Google [7,8].

**Table 1.1** Historical milestones in ion exchange.

Year	Description	Patent #	Authors
1850	Discovery of ion exchange properties of soil	N/A	Thompson and Way [1,2]
1876	Zeolites or aluminosilicates recognized for base exchange and equivalence of exchange is proved	N/A	Lemberg [12,13]
1906–1915	Industrial manufacture of sodium permutit for hardness removal	914,405; 943,535; 1,131,503	Gans [14]
1934	Invention of sulfonated condensation polymers as cation exchangers	2198378A	Ellis
1935	First synthetic organic ion exchangers	2104501A, 2151883A	Adams and Holmes [15]
1938	Mixed-bed ion exchange process or duplex ion exchanger	2275210A	Stemen, Urbain, and Lewis
1939	Invention of sulfonated polystyrene polymerization as cation exchangers Invention of aminated polystyrene polymerization as anion exchangers	2283236A 2304637A	Soday Vernal
1942	Cation exchange resin beads made from polymerized acrylic acids Cation exchange resins with sulfonated, polymerized poly-vinyl aryl parent resin	2340110A, 2340111A 2366007A	D'Alelio
1947	Anion exchange resins with aminated, polymerized poly-vinyl aryl parent resin Element 61 (Promethium) was discovered by ion exchange of the by-products of fission	2366008A N/A	Marinsky, Glendenin, and Coryell [16]
1953	Use of zeolites as molecular sieves Magnetic ion exchange resin for NOM removal (MIEX process) Invention of weak acid cation exchangers	2882243A 2642514A 2838440A	Milton Herkenhoff Thurmon
1954	First countercurrent ion exchange using suspended/agitated beds of resin Higgins countercurrent ion exchange contactor invented	N/A 2815322A	Swinton and Weiss [17] Higgins [18]
1955	Ligand exchange	2839241A	Albisetti
1956	Pellicular ion exchange resin	2933460A	Richter and McBurney
1958	Agitated bed contactor for semicontinuous ion exchange Ion exchange in drug delivery	N/A 2990332A	Arden, Davis, and Herwig [19] Keating

(Continued)

**Table 1.1** (Continued)

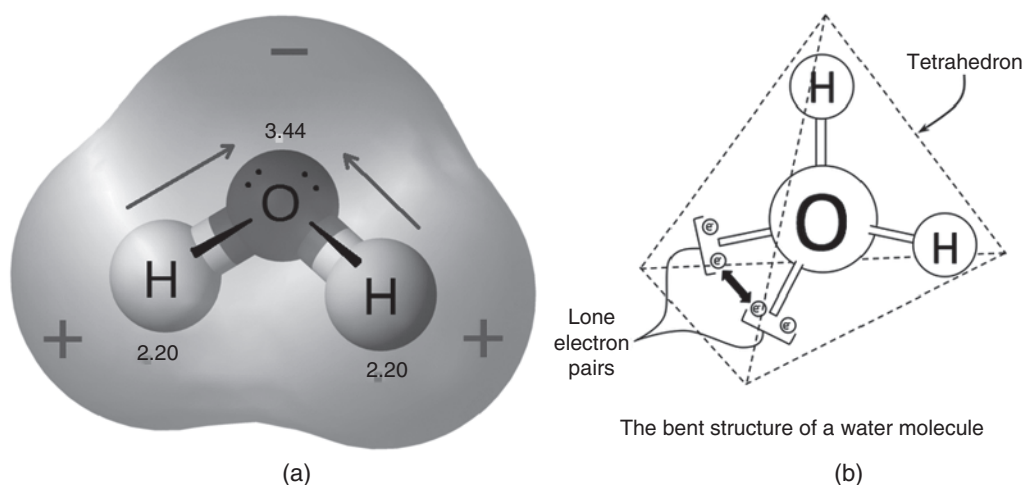
<b>Year</b>	<b>Description</b>	<b>Patent #</b>	<b>Authors</b>
1958 (publicly released)	Uranium separation, intraparticle diffusion (Manhattan Project)	2956858A	Powell
1959–1960	The book on “Ion Exchange” by Friedrich Helfferich was printed and laid the theoretical foundations for the field of ion exchange	N/A	Helfferich [20]
1962–1971	Cloete–Streat countercurrent contactor invented	3551118A (1962) 3738814A (1969) 3957635A (1971)	Cloete and Streat [21]
1964	Cellulosic ion exchange fibers synthesized	3379719A	Rulison
1965	Sirotherm process – thermally regenerable ion exchange resins	274-029; 59,441/65 (Australia)	Bolto, Weiss, and Willis
1966	Partially functionalized cation exchange (shallow-shell technology)	3252921A	Hansen and McMahon
1968	Macroporous ion exchange resin	3418262A	Grammont and Werotte
1969	Boron selective resin	20110108488A1	Chemtob
1969	Development of poly(methyl methacrylate) anion exchange resins or macroreticular polymers that reduced fouling by natural organic matter	N/A	Kressman and Kunin [22,23]
1971	Continuous moving bed ion exchange	3751362A	Probststein, Schwartz, and Sonin
1972	Phenolic ion exchange fibers	3835072A	Economy and Wohrer
1973	Iminodiacetic acid chelating resin	3936399A	Hirai, Fujimara, and Kazigase
	Metal-selective biosorbents	CA1036719A1	Stamberg, Prochazka, and Jilek
1973	Iminodiacetic acid chelating resin	3936399A	Hirai, Fujimara, and Kazigase
	Metal-selective biosorbents	CA1036719A1	Stamberg, Prochazka, and Jilek
1975	“Himsley contactor” multistage fluidized bed continuous counter-current ion exchange contactor	CA980467A1	Himsley
1976	Solvent impregnated resins	4220726A	Warsawsky <i>et al.</i> [24,25]

1980	Monosphere ion exchange resin (Dow Chemical Co.)		4444961A	Timm
1979	Ion exchange induced supersaturation (IXISS)		N/A	Muraviev [26,27]
1981	Radium selective resins		EP0071810 A1	Hatch
1983	Nitrate selective resin CARIX (carbon dioxide regenerated ion exchange) process for brackish water desalination		4479877A EP0056850 B1	Guter Kiehling and Wolfgang
1985	Short bed ion exchanger		EP0201640 B2	Brown
1990	Selective anion exchange for gold from cyanide solution with a simple and straightforward chemical regeneration		N/A	Schwellnus and Green [28]
1991	Bifunctional ion exchange resins (Diphonix)		EP0618843 A1	Alexandratos, Chiarizia, and Gatrone
1997	Polymeric ligand exchange		6136199A	SenGupta and Zhao
2003	Fluoride selective resins: strong acid cation exchange resin in aluminum form		WO2005065265A2	Jangbarwala and Krulik
2004	Donnan principle-based hybrid ion exchanger		7291578 B2	SenGupta and Cumbal
2007	(Ion Exchange) Membrane capacitive deionization (MCDI)		6709560 B2	Andelman and Walker
2008	Macroporous copolymers with large pores (0.5–200 µm)		20080237133A1	Dale, Sochilin, and Froment
2009	Rapid sensing of toxic metals with hybrid inorganic materials		WO2008151208A1	Chatterjee and SenGupta
	Removal of alkyl iodides by strong acid cation exchange resin loaded in Ag <sup>+</sup> -form		7588690B1	Tsao
2010	Separation of ionic aqueous mixtures with ion exchange materials in an immiscible organic phase		8940175B2	Khamizov
2013	Hybrid ion exchange-reverse osmosis processes		WO2014193955A1	SenGupta and Smith
	Fluoride-selective resins: hybrid anion exchange resin with zirconium oxide nanoparticles		20130274357A1	SenGupta and Padungthorn

*Note:* Patents are issued from the USA, unless mentioned otherwise.

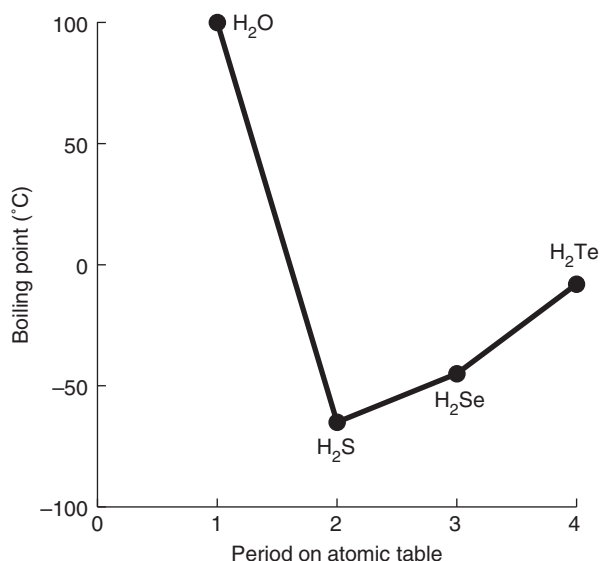
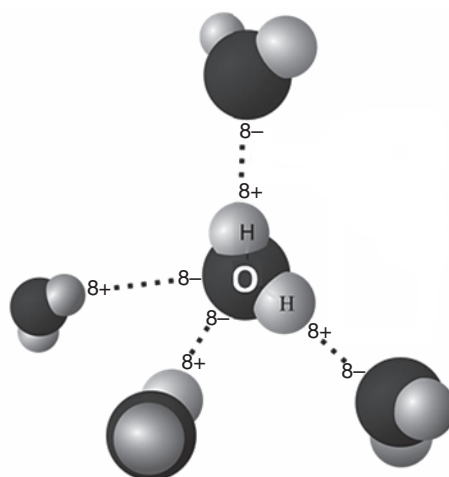
## 1.2 Water and Ion Exchange: An Eternal Kinship

Ion exchange is a heterogeneous process where water, the most abundant polar solvent in our planet, is inevitably present. Even the ion exchange processes involving gases or solids require the presence of water. It is imperative that we understand the fundamental properties of water in order to follow the science of ion exchange. Oxygen is present in Group VIA of the periodic table and water ( $\text{H}_2\text{O}$ ) is essentially a dihydride of oxygen. Note that sulfur (S) and selenium (Se) are also in the same group with oxygen but their dihydride, namely  $\text{H}_2\text{S}$  and  $\text{H}_2\text{Se}$  are volatile at room temperature. In contrast, water is liquid and an excellent solvent for salts with ionic bonds. In the electronegativity scale, hydrogen and oxygen are far apart. While hydrogen is electropositive, oxygen is strongly electronegative. Thus, covalent O—H bonds in water molecules are polar due to unequal sharing of bonding electrons with residual negative and positive charges on oxygen and hydrogen atoms, respectively. Hence, water molecules are essentially dipoles (dipole moment = 1.85 D), as shown in Figure 1.2a. The electronic structure of the water molecule corresponds to the tetrahedral arrangement with the oxygen atom having two lone pairs of electrons as presented in Figure 1.2b. The dipolar water molecules experience a torque when placed in an electric field and this torque is called a dipole moment. When molecules have dipole moments, their intermolecular forces are significantly greater, especially when dipole–dipole interactions or hydrogen bonding is possible. Water molecules are particularly well suited to interact with one another because each molecule has two polar O—H bonds and two lone pairs on the oxygen atom. This can lead to the association of four hydrogen atoms with one oxygen through a combination of covalent and hydrogen bonding as shown in Figure 1.3. Water molecules thus exist as trimers ( $\text{H}_6\text{O}_3$ ) and boiling requires a high heat of vaporization to break the intermolecular hydrogen bonds among water molecules. Thus, water has the highest boiling point among the entire Group VIA hydrides as shown in Figure 1.4.



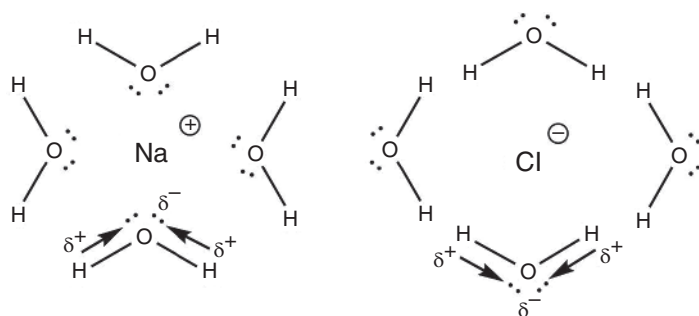
**Figure 1.2** Shape of water molecules (a) Dipolar O—H bonds with electronegativity values; (b) Electronic structure with tetrahedral arrangement.

**Figure 1.3** Interaction of water molecules through association of four hydrogen atoms with each oxygen atom.



**Figure 1.4** Anomalous boiling point behavior of H<sub>2</sub>O in Group VIA hydrides.

Like dissolves like. Ionic compounds such as sodium chloride (NaCl) are highly soluble in water, which is an excellent polar solvent. When sodium chloride is added to water, the dipolar water molecules separate sodium from chloride ions forming a cluster of solvent molecules around them due to the ion–dipole interaction as presented in Figure 1.5. This interaction is known as hydration and the hydrated ionic radius of an ion is always greater than its ionic radius. The degree of hydration depends primarily on the charges and the atomic mass of the ions. Ions with higher charges, and similar masses, always are more hydrated, that is, divalent calcium ion (Ca<sup>2+</sup>) is more hydrated than monovalent sodium ion (Na<sup>+</sup>). For monatomic ions with identical charges, hydrated ionic radius increases with a decrease in atomic mass or crystal



**Figure 1.5** Illustration of ion–dipole interaction: Sodium chloride (ionic compound) solution in water (polar solvent).

**Table 1.2** Hydrated ionic radius and atomic mass of typical monatomic ions of interest.

Ions	Atomic mass	Crystal ionic radii (pm)	Hydrated ionic radii (pm)
Li <sup>+</sup>	6.94	59	382
Na <sup>+</sup>	22.99	102	358
K <sup>+</sup>	39.09	151	331
Rb <sup>+</sup>	85.46	161	329
F <sup>-</sup>	18.99	133	352
Cl <sup>-</sup>	35.45	181	332
Br <sup>-</sup>	79.9	196	330
Be <sup>2+</sup>	9.01	27	459
Mg <sup>2+</sup>	24.3	72	428
Ca <sup>2+</sup>	40.07	100	412
Sr <sup>2+</sup>	87.62	126	412
Ba <sup>2+</sup>	137.33	142	404

Source: Conway 1981 [29]. Reproduced with permission of Elsevier.

ionic radius as illustrated in Table 1.2. Since the process of heterogeneous ion exchange inevitably involves hydrated ions, the following observations are universally true:

- (i) Binding of an ion onto a rigid ion exchanger requires partial shedding of water of hydration and hence, all other conditions remaining identical, an ion with lower hydrated ionic radius shows higher affinity. For example, both K<sup>+</sup> and Na<sup>+</sup> are monovalent cations, but K<sup>+</sup> is preferred over Na<sup>+</sup> by cation exchange resins due to its lower hydrated ionic radius.
- (ii) An ion with a larger hydrated ionic radius is less mobile, that is, it has a lower diffusion coefficient. The kinetics of ion exchange are often a diffusion-controlled process. Thus, binding of an ion with a higher hydrated ionic radius is always a kinetically slower process.



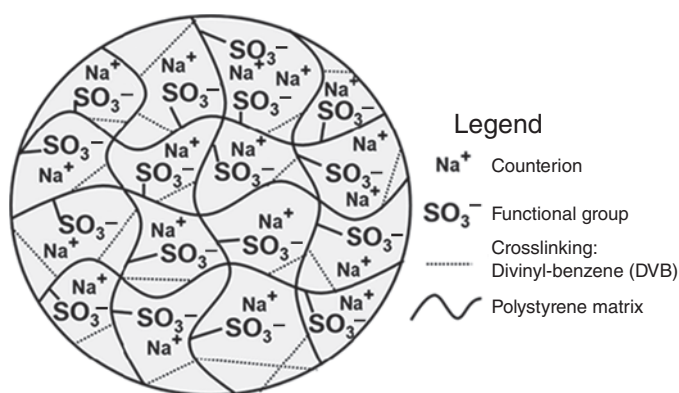
### 1.3 Constituents of an Ion Exchanger

An ion exchanger is ideally defined as a framework of fixed coions, which can be permeated and electrically neutralized by mobile counterions from the aqueous (liquid) phase. The underlined terms in the foregoing definition require further elaboration.

FRAMEWORK is much like a skeleton that constitutes a continuous phase, which is held together by covalent bonds or lattice energy. For polymeric ion exchangers, covalent bonds predominate and the framework is often referred to as the matrix. In inorganic ion exchangers, the lattice energy helps retain the ion exchange sites in the solid phase and the framework is constituted by amorphous or crystalline structures. FIXED COIONS are electric surplus charges (positive or negative) on the framework, or the matrix, unable to leave their phase. This surplus charge is due to covalent bonding for polymeric ion exchangers and isomorphous substitution for zeolites and clays. MOBILE COUNTERIONS are solutes with charges opposite to the fixed coions. They compensate the charges of fixed coions in the exchanger phase and can also be replaced by other ions of the same sign on an equivalent basis. Unlike fixed coions, the counterions can permeate in and out of the exchanger phase and by doing so, they maintain electroneutrality in both the liquid and the solid phase.

For synthetic ion exchangers, fixed coions are known as functional groups or ionogenic groups, while the exchanging ions are known as counterions. To readily grasp the underlying concept without loss of generality, let us consider a polymeric ion exchanger where the three-dimensional cross-linked polymer constitutes a separate insoluble phase or matrix. The covalently attached functional group is essentially the fixed coion that is permeated and electrically balanced by an exchangeable counterion. Figure 1.6 shows a simple schematic of a cation exchanger with sulfonic acid functional groups loaded with sodium counterions.

Thermodynamically, the activity or concentration of an ion exchanger is not a unique number, but it varies with the type and concentration of the counterion in the

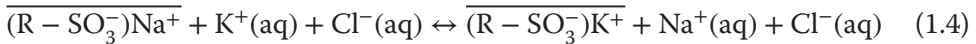


Commonly represented as:  $\text{R-SO}_3^-\text{Na}^+$

**Figure 1.6** Schematic illustration of a strong acid cation exchange resin bead where matrix/framework is represented by R, fixed coions or functional groups by  $\text{—SO}_3^-$  and counterions/exchanging ions by  $\text{Na}^+$ .

exchanger phase. However, the fixed coions in an ion exchanger are always balanced by permeating counterions, that is, the ion exchanger is always electrically neutral. Ideally, the ion exchange capacity is equal to the concentration of the fixed coions. We will later see that the capacity is not a constant and it depends, to some extent, on the external liquid phase concentration.

To be familiar with the basic premise and terminologies of ion exchange processes, let us consider the following cation exchange reaction between potassium and sodium ions:



where the overbar denotes the exchanger phase; sulfonic acid functional group ( $-\text{SO}_3^-$ ) is the fixed, non-diffusible coion and  $\text{Na}^+$  and  $\text{K}^+$  are the permeable or exchanging counterions. The chloride ion does not participate in the cation exchange reaction and is referred to as a mobile coion. Both the exchanger and aqueous-phase electroneutrality remain undisturbed at every stage of the cation exchange reaction. Likewise, the anion exchange process is fundamentally the same, but the exchanger phase has positively charged fixed coions (e.g., quaternary ammonium functional groups,  $\text{R}_4\text{N}^+$ ) as shown for the nitrate-chloride exchange reaction below:

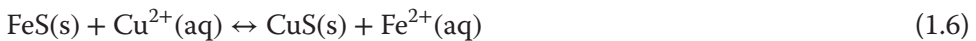


While  $\text{NO}_3^-$  and  $\text{Cl}^-$  are the permeating counterions,  $\text{R}_4\text{N}^+$  and  $\text{Na}^+$  are the fixed and mobile coions, respectively.

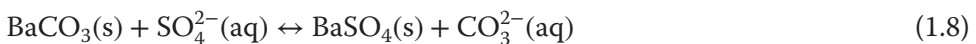
## 1.4 What is Ion Exchange and What is it Not?

Prior to getting into the details of the various materials presented in this book, it is imperative that we present a scientifically coherent definition of what we call “ion exchange.” A list of reactions, as shown below, are often mistakenly presented in the open literature as ion exchange simply because the process appears to involve an exchange of equivalent amounts of cations or anions:

*Pseudo-cation exchange:*



*Pseudo-anion exchange:*



These are essentially precipitation–dissolution and redox reactions involving a pure solid phase denoted by “(s).” Since the activity of a pure independent solid phase (e.g., crystalline) is unity, the equilibrium constant of Reaction 1.6, considering ideality, is given by

$$K = \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]} \quad (1.9)$$

All the foregoing reactions are identical in the sense that the equilibrium constants are influenced only by the dissolved species and are independent of the composition of the pure solid phases. Ion exchange phenomena are distinctly different from the above in this regard. An ion exchanger is a separate phase from the aqueous solution with a different dielectric constant and the exchanging counterions can be present at varying proportions to produce a continuous solid solution. The thermodynamic activity of an ion exchanger phase is not equal to unity, but is dependent on its composition. For the cation exchange reaction in (1.4), the idealized equilibrium constant is

$$K_{IX} = \frac{\overline{[RK^+]}[Na^+]}{\overline{[RNa^+]}\overline{[K^+]}} \quad (1.10)$$

where overbar with a bracket represents the exchanger phase molar concentration while the bracket alone represents the aqueous phase concentration. Note that ion-exchanger phase activity is not unity and its relative proportion of  $Na^+$  or  $K^+$  will vary with the extent of each ion exchange reaction. Also, the mobile coion,  $Cl^-$ , does not influence the ion exchange equilibrium constant,  $K_{IX}$ . Mole or equivalent fraction (they are the same for monovalent ions) of  $Na^+$  or  $K^+$  in the exchanger phase is given by:

$$y_{Na} = \frac{\overline{[RNa^+]}}{\overline{[RNa^+]} + \overline{[RK^+]}} \quad (1.11)$$

$$y_K = \frac{\overline{[RK^+]}}{\overline{[RNa^+]} + \overline{[RK^+]}} \quad (1.12)$$

Since sodium and potassium are the only counterions present in the exchanger, the total capacity,  $Q$ , of the cation exchange is

$$Q = \overline{[RNa^+]} + \overline{[RK^+]} \quad (1.13)$$

Therefore,

$$y_{Na} = \frac{\overline{[RNa^+]}}{Q} \quad (1.14)$$

$$y_K = \frac{\overline{[RK^+]}}{Q} \quad (1.15)$$

$$y_{Na} + y_K = 1.0 \quad (1.16)$$

Thus, the equivalent fraction of  $Na^+$  or  $K^+$  ( $y_{Na}$  or  $y_K$ ) in the exchanger phase is free to vary from zero to unity in accordance with Eq. (1.16). An ion exchanger, be it inorganic, polymeric or liquid, is essentially a separate phase or continuum, the composition of which can vary due to ion exchange reaction. An ion exchanger is thus distinctly different from a pure solid phase of single chemical composition. Instead, for an insightful understanding of diverse ion exchange phenomena, an ion exchanger may be viewed as a condensed and cross-linked polyelectrolyte where the anions (for a cation exchanger) or cations (for an anion exchanger) are immobilized and cannot permeate out of the condensed state.

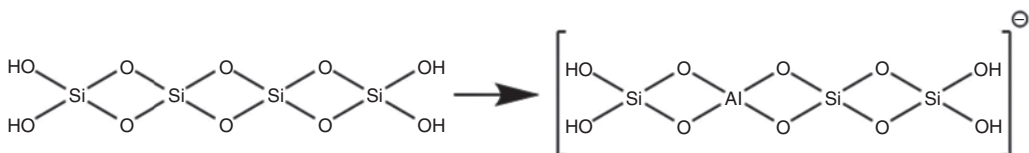
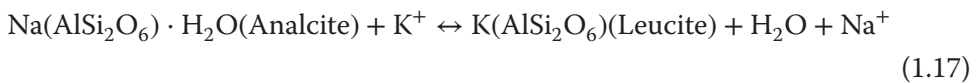
## 1.5 Genesis of Ion Exchange Capacity

### 1.5.1 Inorganic

In accordance with the generalized definition of an ion exchanger, fixed coions are the true origins of ion exchange capacity. From a historical perspective, naturally occurring inorganic silicate minerals were the first materials to be studied for their ion exchange or, more specifically, cation exchange behavior. In such naturally occurring crystalline silicate materials with three-dimensional Si—O chains, a silicon atom, having an oxidation state of four, is often replaced by an aluminum atom having an oxidation state of three. Thus, there is a charge deficiency (excess negative charge) in the crystalline lattice at the defect location. To preserve electroneutrality, this deficiency must be balanced by the presence of a cation. It is this cation that becomes the exchangeable counterion. The above-mentioned defects are truly the seats of fixed coions. The higher the number of such defects per unit mass or volume in the silicate phase, the greater will be the cation exchange capacity. The process of such defect formation is often referred to as “Isomorphous Substitution.” Since aluminum and silicon are the two most abundant elements in soil after oxygen, such substitutions are widespread in natural minerals, and these materials are often called zeolites.

Figure 1.7 provides a general schematic showing the formation of fixed coions through isomorphous substitutions in naturally occurring silicate phase or zeolites. It is to be noted that the substitution of Mg(II) for Al(III) gives rise to the same effect (i.e., generation of excess negative charges) as the substitution of Al(III) for Si(IV). The general stoichiometry of such silicate based inorganic ion exchangers or zeolites is given empirically as  $M_{2/n}O \cdot Al_2O_3M_{2/n} \cdot xSiO_2 \cdot yH_2O$  where M is a cation of valence  $n$  (commonly  $n = 1$  or  $2$ ) and  $x$  and  $y$  are integer values of coefficients.

The zeolites such as chabazite ( $CaAl_2Si_6O_{16} \cdot 8H_2O$ ) and analcite ( $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$ ) are essentially crystalline silicates with defects (fixed charges) to which sodium or calcium ions (counterions) are easily accessible through a three-dimensional network of pores. In the latter part of the nineteenth century, it was demonstrated that the zeolite mineral analcite could be converted stoichiometrically into leucite [ $K(AlSi_2O_6)$ ] simply by leaching with an aqueous solution of potassium chloride, a synthesis step driven solely by ion exchange.



**Figure 1.7** Charge acquisition through isomorphous substitution of Al for Si (formation of defects of fixed coions in naturally occurring silicates).

**Table 1.3** List of some common inorganic ion exchangers.

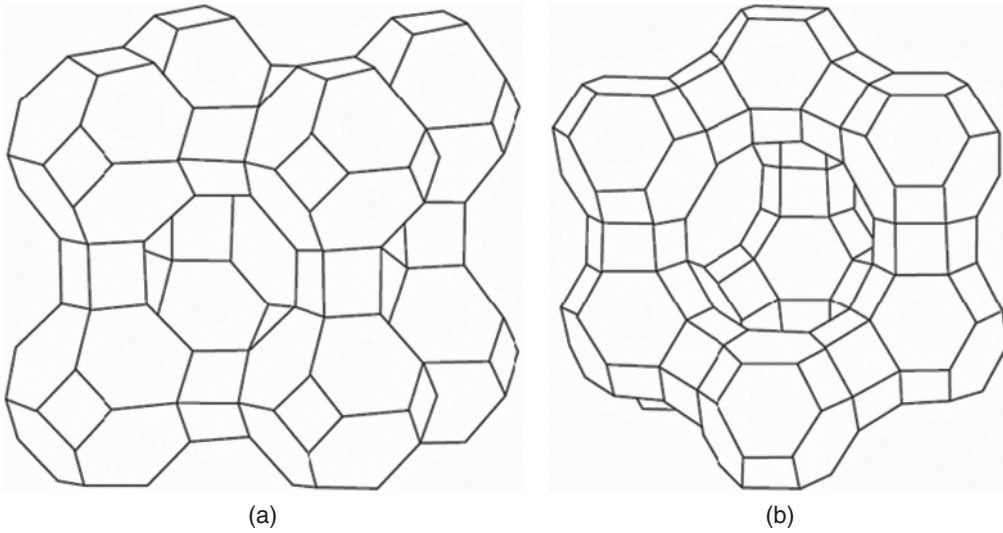
Type of ion exchanger	Example
Smectite clays	Montmorillonite: $M_{x/n}^{n+} [Al_{4-x}Mg_x]Si_8O_{20}(OH)_4$
Zeolites	$Na_x(AlO_2)_x(SiO_2)_y \cdot zH_2O$
Substitute Aluminum Phosphates	Silica aluminum phosphates; metal aluminum phosphates ( $M_x^{n+}Al_{1-x}O_2)(PO_2)(OH)_{2x/n}$ )
Phosphates of Gr IV elements	$Zr(HPO_4)_2 \cdot H_2O$ ; $Sn(HPO_4)_2 \cdot H_2O$
Metal oxides	$Fe_2O_3 \cdot xH_2O$ ; $ZrO_2 \cdot xH_2O$ ; $Al_2O_3 \cdot xH_2O$
Ferrocyanides	$M_{4/n}^{n+}Fe(CN)_6$ , $M = Ag^+, Zn^{2+}, Cu^{2+}, Zr^{4+}$
Titanates	$Na_2Ti_nO_{2n+1}$ ; $n = 2-10$
Apatites	$Ca_{10-x}H_x(PO_4)_6(OH)_{2-x}$
Heteropolyacid salts	$M_nXY_{12}O_{40} \cdot xH_2O$ ; ( $M = H, Na^+$ ; $X = P, As, Ge, Si, B$ ; $Y = Mo, W$ )
Fast ion conductors	$\beta$ -Aluminum oxides, $Na_{1+x}Al_{11}O_{17+x/2}$ ; NASICON, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$
Anion exchanger	Hydrotalcite – $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$

In recent years, zeolites with regular crystal structures have been synthesized and applied as ion-exchangers, catalysts and molecular sieves. Although chemical compositions of inorganic ion exchangers may be quite diverse, they are typically mixed metal oxides, insoluble salts of polyvalent metals and metal ferrocyanides [20,30,31]. Amorphous structures do exist, but inorganic ion exchangers are mostly crystalline polymers with a microporous framework. Table 1.3 provides a list of some common inorganic ion exchangers.

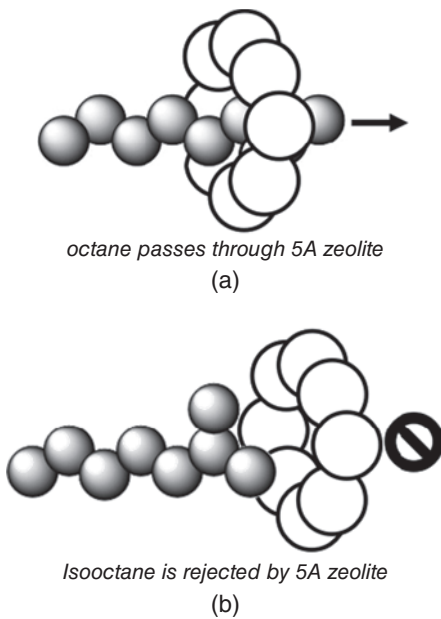
As ion exchangers, zeolites are of minor significance due to their chemical instability and poor regenerability. However, due to their narrow, rigid and strictly uniform pore structure, the zeolites act as “molecular sieves” and are capable of selectively sorbing molecules lower than specific sizes, while rejecting larger ones. Several types of molecular sieves are now commercially available both as microcrystalline powders and as pellets which consist of microcrystals in a clay binder [30,32,33]. Linde Sieve Type X and Type A have pore diameters of about 10 and 5 Å, respectively. Figure 1.8 shows structures of Zeolite A and Zeolite X and their cavities. Figure 1.9 illustrates how molecular sieves can effectively separate straight chain organic molecules from their branched-chain counterparts [33]. Since molecular sieves are essentially cation exchangers, the pore sizes can be adjusted to a certain degree by converting the materials into different ionic forms, resulting in other potential applications [31,35,36].

### 1.5.2 Organic/Polymeric Ion Exchanger

The advent of ion exchange technology began with the preparation and large-scale synthesis of polymeric ion exchangers, commonly referred to as ion exchange resins.

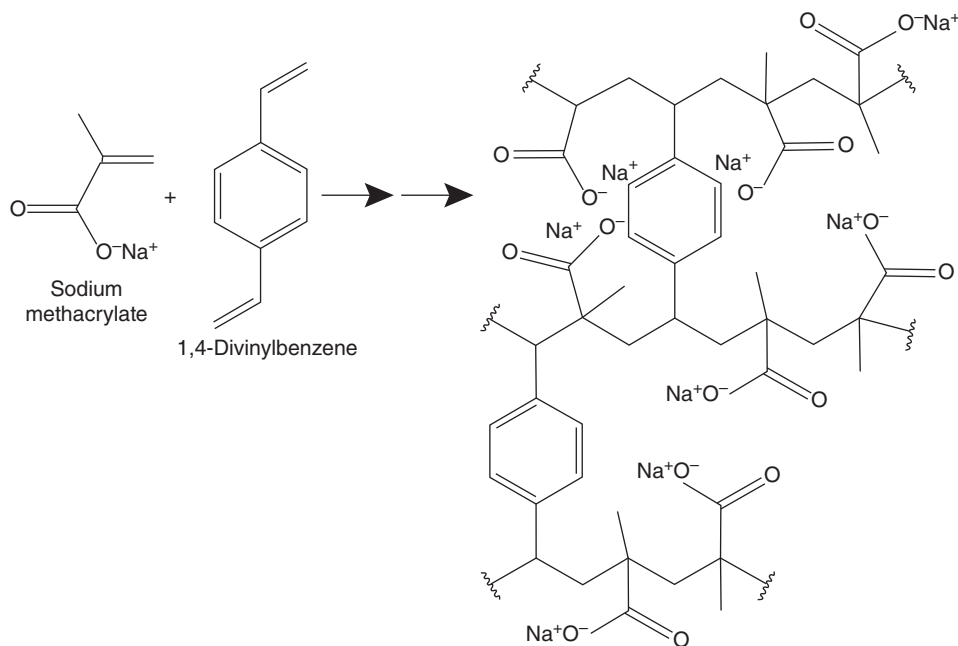


**Figure 1.8** Zeolite A (a) and faujasite-type zeolites X and Y (b) formed by sodalite cages. Source: From Lutz 2014 [34].



**Figure 1.9** Illustration of molecular sieves for the separation of straight chain organic molecule. Straight chain normal octane molecule (a) passes through the eight-ring aperture of 5A zeolite; branched molecule of isooctane cannot (b). Source: From Bekkum *et al.* 1991 [33].

Ion exchange resins are cross-linked polyelectrolytes and their ion exchange capacities originate from functional groups covalently attached to the matrix or framework. Although details pertaining to chemical synthesis of polymeric ion exchange resins is beyond the scope of this book, Figures 1.10–1.13 provide the step-wise preparation of the four most widely used ion exchange resins, namely, weak-acid cation, strong-acid cation, weak-base anion and strong-base anion exchangers. The four ionogenic



**Figure 1.10** Synthesis of weak-acid cation exchanger by polymerization of sodium methacrylate with divinyl-benzene crosslinking.

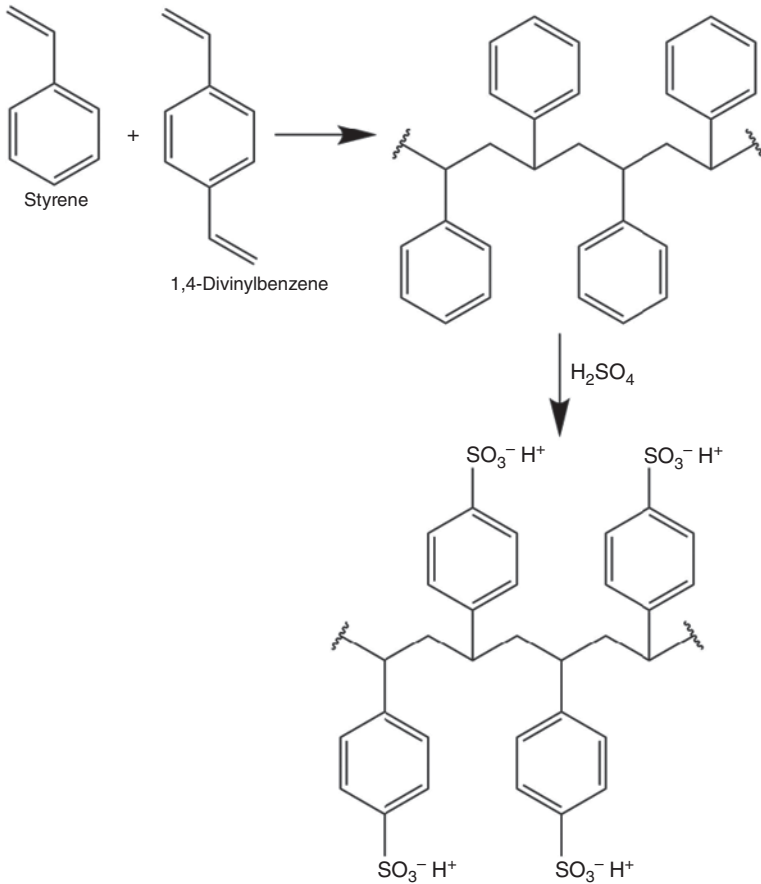
groups or fixed coions are: carboxylic ( $R - \text{COO}^-$ ), sulfonic ( $R - \text{SO}_3^-$ ), tertiary amine ( $R - \text{N}^+\text{R}_2\text{H}$ ) and quaternary ammonium ( $R - \text{N}^+\text{R}_3$ ).

It is only appropriate to note some distinct differences in the synthesis process of these ion exchangers:

- For the weak-acid cation exchanger, the carboxylate ionogenic group is already present in the repeating methacrylic acid monomer prior to polymerization. Divinylbenzene or DVB introduces the cross-linking to attain the three-dimensional polymer network during the single-step synthesis process.
- For the strong-acid cation exchanger, the styrene–divinylbenzene copolymer is synthesized first and then sulfonated to introduce the ionogenic groups. The synthesis is a two-step process.
- Synthesis of both strong and weak-base anion exchange resins involve three consecutive steps; first synthesis of styrene–divinylbenzene copolymer; second, chloromethylation of the copolymer; and third, amination of the chloromethylated copolymer, culminating in positively charged functional groups.

The repeating unit for each ion exchanger without divinylbenzene cross-linking is provided in Table 1.4. Theoretical ion exchange capacity for an ion exchanger can be calculated from the molecular weight of the repeating unit. Example 1.1 shows theoretically calculated ion exchange capacity of each type of polymeric ion exchanger and discusses why the real ion exchange capacity of an anion exchanger is significantly less than its theoretical value. Since ion exchange takes place on an equivalent basis, the capacities should preferably be expressed in equivalent units such as equivalent/liter

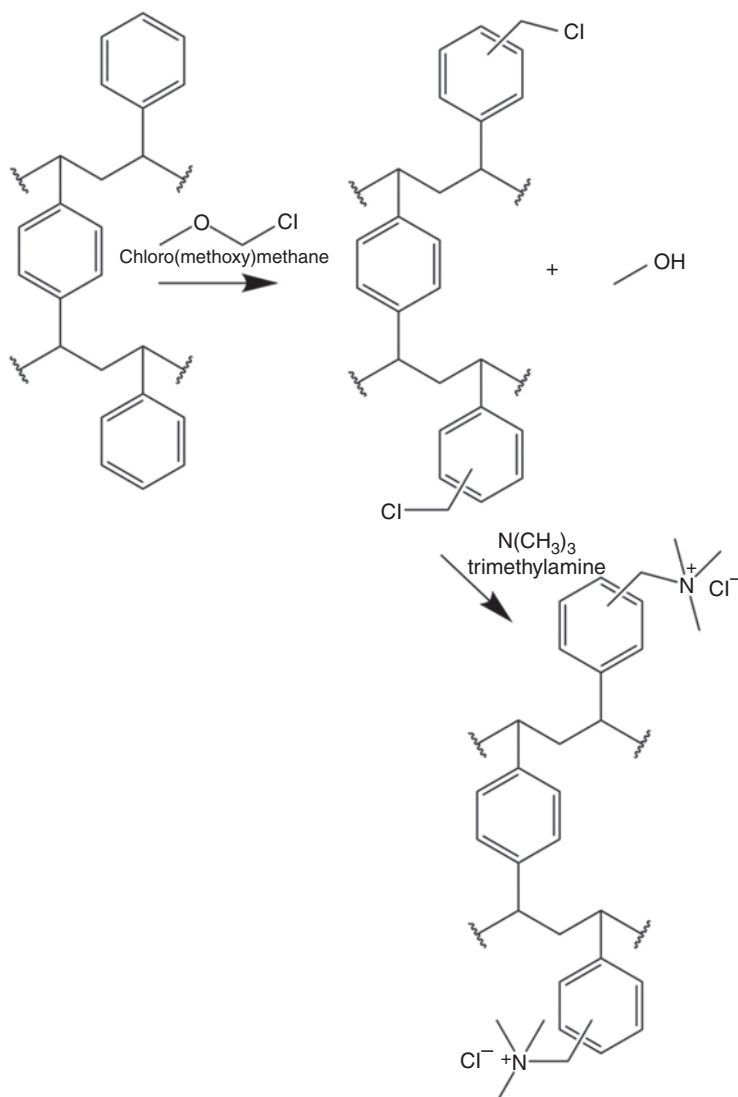




**Figure 1.11** Synthesis of strong-acid cation exchange resin by polymerization of styrene with cross linking of divinyl benzene followed by sulfonation.

(eq/L) or milliequivalents/gram (meq/g). The commonly used abbreviated dimensions are eq/L, meq/mL, and meq/g. To avoid confusion, universally accepted conventions should be followed while expressing ion exchange capacity. The ionic form, that is, the specific type of counterion present will change the mass of the ion exchanger, all other conditions remaining identical. For example, the equivalent weight of sodium ( $\text{Na}^+$ ) is 23 while that of lead ( $\text{Pb}^{2+}$ ) is 103. Thus, the same ion exchanger (inorganic or organic) while loaded with lead will weigh much more than when it is in sodium form, that is, its specific gravity will increase. So, equivalent capacity per unit mass will vary. Capacity expressions for engineered applications thus need to be consistent with the ionic forms of the ion exchangers. In general, the capacity of strong-acid cation exchanger is expressed in Na-form, weak-acid cation in H-form, strong-base anion in chloride form and weak-base anion in OH or free base form.

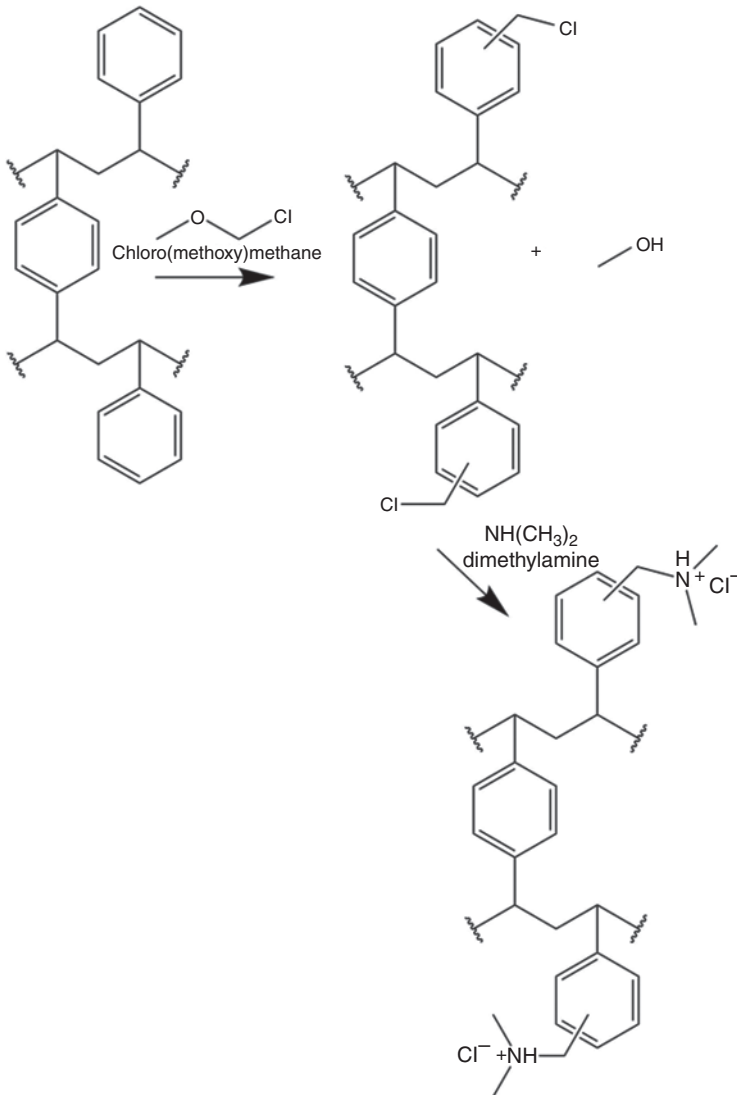




**Figure 1.12** Synthesis of strong-base anion exchange resin through chloromethylation followed by amination with tertiary amine.

**Example 1.1** Compare the relative capacity of each ion exchanger using the information in Table 1.4 and explain any discrepancy with respect to anion exchangers. Comment on any anomaly.

*Weak-acid cation (WAC) exchanger with carboxylate functional group:* For every ion exchange site, the repeating unit from Figure 1.10 contains – C: 4, O: 2, H: 5; Corresponding molecular mass =  $12 * 4 + 16 * 2 + 1 * 5 = 85$ .



**Figure 1.13** Synthesis of styrenic weak-base anion exchange resin through chloromethylation followed by amination with secondary amine.

*Strong-acid cation (SAC) exchanger with sulfonic group:* For every ion exchange site, the repeating unit contains – C: 8, O: 3, S: 1, H: 7; Corresponding molecular mass =  $12 \cdot 8 + 16 \cdot 3 + 32 \cdot 1 + 1 \cdot 7 = 183$ .

*Weak-base anion (WBA) exchanger with tertiary amine functionality:* In a similar manner, the repeating unit contains – C: 11, N: 1, H: 15; Corresponding molecular mass =  $12 \cdot 11 + 14 \cdot 1 + 1 \cdot 15 = 161$ .

*Strong-base anion (SBA) exchanger with quaternary amine:* The repeating unit contains – C: 12, N: 1, H: 17; Corresponding molecular mass =  $12 \cdot 12 + 14 \cdot 1 + 1 \cdot 17 = 175$ .

**Table 1.4** Repeating units of some common ion exchangers (without divinylbenzene crosslinking).

Type of ion exchanger	Functional group	Repeating units with functional group
Weak-acid cation	Carboxylate ( $R - \text{COO}^-$ )	
Strong-acid cation	Sulfonate ( $R - \text{SO}_3^-$ )	
Weak-base anion	Tertiary amine ( $R - \text{N}^+\text{R}_2\text{H}$ )	
Strong-base anion	( $R - \text{N}^+\text{R}_3$ )	

Ratio of the molecular mass of the four resins are WAC:SAC:WBA:SBA = 85:183:161:175.

Bulk densities of the fully ionized ion exchangers are nearly the same and equal to 1.0 g/mL. The lowest molecular mass of the WAC for each ion exchange site should render it the highest capacity, that is, ion exchange capacity is inversely proportional to the repeating molar mass. Thus, the ratio of the capacity when normalized with respect to the molecular weights of SBA, becomes

$$\text{WAC:SAC:WBA:SBA} = 2.05:0.96:1.1:1$$

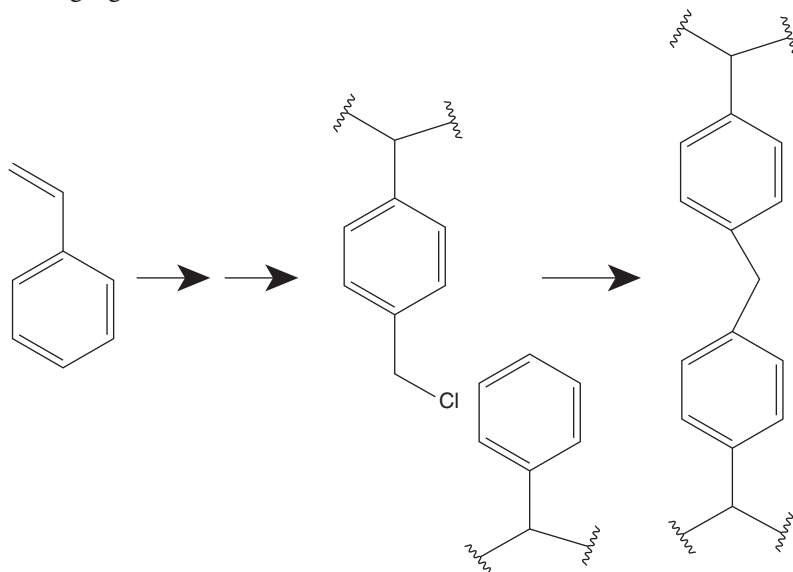
Ion exchange capacities of the commercial gel resins are available in the open literature; the ratio of the volume-based capacities corresponds to the following trend:

$$\text{WAC:SAC:WBA:SBA} = 2.75:1.7:1:1$$

### Agreement and Anomaly

The theoretical capacity thus calculated agrees reasonably well with the trend obtained from experimental/analytical determination for cation exchangers. However, for anion exchangers, actual ion exchange capacity is found to be significantly less than its theoretical value and this anomaly is due to the phenomenon of “methylene bridging.” During the chloromethylation step, even with strictest control of process parameters,

secondary cross-linking takes place between neighboring styrene molecules through methylene bridging as shown below:

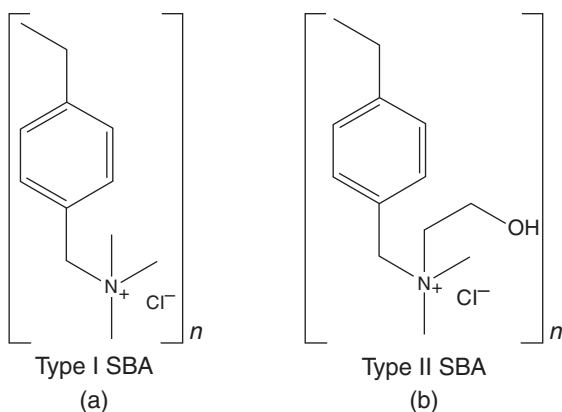


**Figure 1.** Secondary cross-linking during chloromethylation of polystyrene.

The styrene groups undergoing methylene bridging are difficult to be aminated (i.e., functionalized) during the next step due to enhanced steric hindrance. Hence, the total exchange capacity per unit mass or volume, all other parameters remaining identical, for anion exchange resins is relatively low.

### 1.5.3 Strong-Base Type I and Type II Anion Exchanger

Strong-base anion exchange resins possess quaternary amine functional groups corresponding to the general composition of  $R_4N^+$ . During the final stage of synthesis of an anion exchanger, chloromethylated copolymer is aminated with alkyl substituted amine. Use of trimethylamine,  $(R - N^+(CH_3)_3)$ , yields the quaternary benzyltrimethyl ammonium functional group which is called Type I strongly basic anion exchange resin, as represented in Figure 1.14a in chloride form. If instead, the amination step



**Figure 1.14** (a) Type I and (b) Type II functional groups of SBA resins.

is carried out by using dimethylethanolamine or  $(R - N^+(\text{CH}_3)_2(\text{C}_2\text{H}_4\text{OH}))$ , Type II strongly basic anion exchange resin is formed, as shown in Figure 1.14b.

Substitution of a methyl group with ethanol makes Type II anion exchange resins more hydrophilic. Hence, the efficiency of regeneration with NaOH is significantly greater for Type II SBA resins compared to its Type I counterpart. Conversely, relative chloride ( $\text{Cl}^-$ ) affinity with respect to  $\text{OH}^-$  is greater for Type I resins compared to Type II resins.

**Example 1.2** A glass column containing 1.0 L of a strong-acid cation exchanger with sulfonic acid functional group is being tested in the laboratory for removal of trace lead ( $\text{Pb}^{2+}$ ) from an industrial wastewater. At the start of the run the exchanger is in sodium form with bulk density 1.1 kg/L.

- (i) What is the approximate molecular weight of a bead with 1 mm diameter?
- (ii) If the exchange capacity is 1.5 eq/L, how is the mass of the ion exchange bed expected to change upon saturation (i.e., specific gravity)?
- (iii) For a resin bead of 1 mm diameter, how does the settling velocity change if the bead is fully converted into  $\text{Pb}^{2+}$  form?

State assumptions if any and briefly discuss the implications of ion exchanger density from an application viewpoint.

- (i) Volume of the bead of  $r = 0.05$  cm is

$$V = \frac{4}{3}\pi r^3 = 5.23 \times 10^{-4} \text{ cm}^3 \cdot \frac{1 \text{ L}}{1000 \text{ cm}^3} = 5.23 \times 10^{-7} \text{ L}$$

Capacity of the bead

$$q = 5.23 \times 10^{-7} \text{ L} \cdot 1.5 \frac{\text{eq}}{\text{L}} = 7.85 \times 10^{-7} \text{ eq}$$

One equivalent consists of Avogadro's number of charges or in this case the same number of repeating units shown in Table 1.4 for strong-acid cation exchanger. Number of repeating units in one bead:

$$N = q \cdot 6.022 \times 10^{23} \frac{\text{repeating units}}{\text{eq}} = 4.73 \times 10^{17} \text{ repeating units}$$

Molecular weight of each repeating unit from Example 1.1 is 183 Da per unit. Molecular weight of each spherical bead is

$$M = N \cdot 183.2 = 8.66 \times 10^{19} \text{ Da}$$

- (ii) Volume of resin = 1.0 L, initial bed mass =  $1.1 \frac{\text{kg}}{\text{L}} \times 1.0 \text{ L} = 1.1 \text{ kg}$  or 1100 g  
During ion exchange 1.5 eq  $\text{Na}^+$  (eq wt 23) is exchanged by 1.5 eq  $\text{Pb}^{2+}$  (eq wt 103.6)

Mass decrease from  $\text{Na}^+$ :

$$1.5 \frac{\text{eq}}{\text{L}} \times 1.0 \text{ L} \times 23 \frac{\text{Na}^+}{\text{eq}} = 34.5 \text{ g}$$

Mass increase from  $\text{Pb}^{2+}$ :

$$1.5 \frac{\text{eq}}{\text{L}} \times 1.0 \text{ L} \times 103.6 \text{ g} \frac{\text{Pb}^{2+}}{\text{eq}} = 155.4 \text{ g}$$

Final mass of

$$1 \text{ L resin} = (1100 - 34.5 + 155.4) \text{ g} \approx 1221 \text{ g; density} = 1.221 \text{ kg/L}$$

Upon saturation mass of 1 L resin increases by =  $1221 - 1100 = 121 \text{ g}$

- (iii) The settling of the resin bead is assumed to follow Stoke's law,  $V_s = \frac{D^2 g (\rho_s - \rho_f)}{18 \mu}$ , where,  $V_s$  = settling velocity,  $D$  = diameter of the bead (1 mm),  $g$  = acceleration due to gravity ( $9.81 \text{ m/s}^2$ ),  $\rho_s$  = density of solid bead,  $\rho_f$  = density of fluid (water  $\sim 0.997 \text{ kg/L}$ ),  $\mu$  = dynamic viscosity ( $0.891 \times 10^{-3} \text{ N s/m}^2$  at 298 K).

$V_s$  in  $\text{Na}^+$  form:

$$V_s = \frac{\left(1 \text{ mm} * \frac{1 \text{ m}}{1000 \text{ mm}}\right)^2 (1100 \text{ kg/m}^3 - 997 \text{ kg/m}^3) (9.81 \text{ m/s}^2)}{18 (0.891 \times 10^{-3} \text{ N}\cdot\text{s/m}^2)}$$

$$V_s = 0.063 \text{ m/s}$$

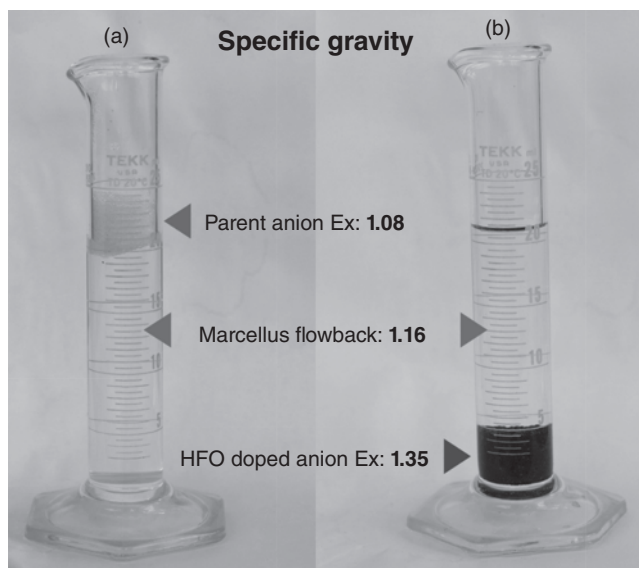
$V_s$  in  $\text{Pb}^{2+}$  form:

$$V_s = \frac{\left(1 \text{ mm} * \frac{1 \text{ m}}{1000 \text{ mm}}\right)^2 \left(1221 \frac{\text{kg}}{\text{m}^3} - 997 \frac{\text{kg}}{\text{m}^3}\right) \left(9.81 \frac{\text{m}}{\text{s}^2}\right)}{18 \left(0.891 \times 10^{-3} \frac{\text{N}\cdot\text{s}}{\text{m}^2}\right)}$$

$$V_s = 0.137 \text{ m/s}$$

Resin bead in  $\text{Pb}^{2+}$ -form settles  $2.17\times$  faster ( $V_{s,\text{Pb}}/V_{s,\text{Na}}$ ) than  $\text{Na}^+$ -form. Differential settling can be a technique to separate resins in different ionic forms.

Some applications may require specially designed high specific gravity resins. High specific gravity resins require the presence of non-polymeric, immobilized materials, such as metal oxide nanoparticles. Raw and waste drilling fluids can have very high specific gravities, such that typical ion exchange resins float on top of the fluids, making flow-through operations challenging and ion exchange unsuccessful. By doping hydrated ferric oxide (HFO) nanoparticles, it is possible to increase the specific gravity of the resins to significantly greater than the drilling fluids. Figure 1(a) shows how a commercial anion exchange resin floats on Marcellus flowback wastewater collected from a gas well in Pennsylvania that has a total dissolved solids (TDS) of 150,000 mg/L; the resin is unusable in fixed bed operation. By doping iron oxide nanoparticles, the density of the anion exchanger can be appropriately increased to enable its use in fixed-bed columns, Figure 1(b), without any noticeable loss in exchange capacity.



**Figure 1.** Specific gravity comparison of two different resins and Marcellus Shale flowback water. (a) Raw Purolite A850 resin; (b) Purolite A850 resin loaded with HFO nanoparticles to increase the specific gravity and to prevent floating during up-flow of high TDS and high specific gravity waste water.

## 1.6 Biosorbent, Liquid Ion Exchanger, and Solvent Impregnated Resin

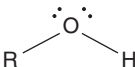
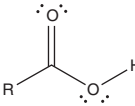
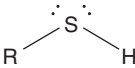
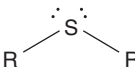
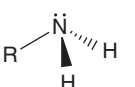
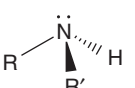
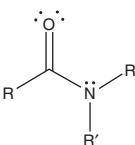
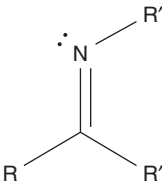
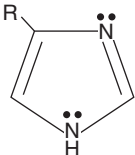
Fundamentals of all organic and inorganic ion exchanging materials, including membranes, have a unifying commonality. Yet, it is imperative that we also become familiar with other types of ion exchangers and note their pros and cons for applications.

### 1.6.1 Biosorbent

Biosorption is defined as the *passive uptake* of cations and/or anions by dead microbial matter or other renewable biomass, including seaweed, chitosan and/or agricultural carbonaceous byproducts. “*Passive uptake*” is distinguished from bioaccumulation which is active and metabolically mediated by living cells. Many independent recent studies indicate that the biosorptive metal uptake mechanism heavily relies on ion exchange and is very sensitive to solution pH [37,38]. Functionally, biosorbents are quite similar to chelating ion exchangers and exhibit strong affinity toward transition metal ions through Lewis acid–base interactions. The ability of a biosorbent to sequester metal ions arises from the presence of lone electron pair donor atoms within its structure, namely, oxygen, nitrogen, phosphorus and sulfur. Table 1.5 provides the list of several commonly occurring metal-binding groups in biomass.

Note that the binding groups have weak-acid and weak-base functional groups and, so, metal sorption onto biosorbents is reversible through pH swings. A reducing environment persists inside the biomass due to anaerobic activity. Thus, metal sorption

**Table 1.5** Metal-binding groups in biosorbents.

Binding group	Structural formula	$pK_a$	Donor atom	Occurrence in biomolecules
Hydroxyl (phenolic)		9–10	O	Polysaccharides
Carboxyl		1.7–4.7	O	Humic acid, alginate
Sulfhydryl (thiol)		8–10	S	Amino acid, protein
Thioether		–	S	Amino acid, protein
Primary amine		9–10	N	Amino acid, chitosan
Secondary amine		9–11	N	Amino acid, peptide bond
Amide		–	N	Amino acid
Imine		11.6–12.6	N	Amino acid
Imidazole		6.0	N	Amino acid

followed by reduction, for example, Cr(VI) to Cr(III), is also quite feasible. Besides metal sorption, chitin-based materials also have shown great promise as substrates for catalysis and nanotechnology [39,40].

The primary attribute of biosorbent materials is that they are biorenewable and hence attractive from a sustainability viewpoint. Poor chemical stability under extreme pH conditions and lack of mechanical strength are major impediments for large-scale application of biosorbent materials in flow-through or packed bed systems.



Through appropriate incorporation of cross-linking, significant progress is underway to improve the cost-effectiveness of biosorbents for specific applications [39,41].

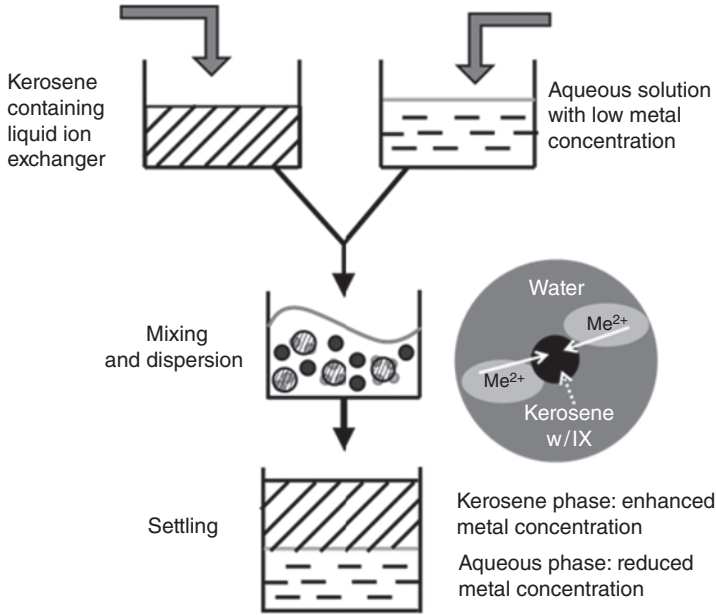
### 1.6.2 Liquid Ion Exchange

The book is devoted primarily to solid-phase functionalized polymers and ion exchangers, both inorganic and organic. However, it is only appropriate that we briefly discuss the field of liquid ion exchange and its distinctive properties in comparison with solid-phase ion exchange. Liquid ion exchange is essentially a special case of solvent extraction where the principle of ion exchange is employed for transfer (or selective exchange) of solutes between two immiscible liquid phases, namely, an aqueous and an organic phase. The organic phase is the liquid exchanger and it contains highly hydrophobic ionogenic compounds dissolved in solvents like kerosene, trichloroethylene, chloroform and xylene that are immiscible with water. The most successful anion exchangers of this type are high molecular weight amine derivatives, while as cation exchangers, organophosphoric and carboxylic acids have proved particularly successful [42]. Over the years, liquid ion exchange has found major applications in extractive metallurgy for recovering metals from ore leachates.

The process of ion exchange is the same in both liquid and solid ion exchangers. Nevertheless, one major fundamental difference exists. For liquid ion exchangers, the exchange occurs at the phase boundaries formed between two immiscible liquids, such as kerosene, containing the liquid exchanger, and an aqueous phase, containing the counterions. On the contrary, the interior of a solid ion exchanger is permeable to the aqueous phase. Liquid ion exchangers have several advantages over their polymeric counterparts. Ion exchange rates are significantly higher due to efficient dispersion of the organic phase into the aqueous phase and rapid mobility of the functional groups within the organic phase. While for solid ion exchangers, polymeric or inorganic, functional groups are rigidly attached to the matrix through covalent or ionic bonds and hence, immobile. Intraparticle diffusion-limited ion exchange processes with solid ion exchangers are thus relatively slow.

Liquid ion exchangers can be easily prepared and their capacity can be varied by changing the relative volumes in the solvent organic phase. In principle, preparation and application of liquid ion exchange is in the public domain and requires no proprietary synthesis process. Figure 1.15 illustrates the three primary steps of liquid ion exchange for metal extraction from a dilute aqueous solution.

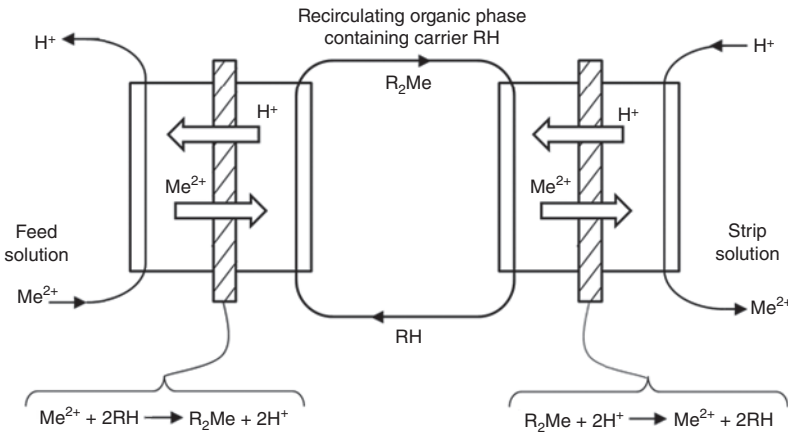
The primary disadvantages of liquid ion exchange are that the phase separation is difficult and not 100% efficient. Thus, the loss of ion exchange material escaping into the aqueous phase cannot be avoided. This shortcoming is particularly conspicuous if the components of the organic phase are partly soluble in water. With stricter environmental regulations, the presence of kerosene, xylene or chlorinated hydrocarbon in the treated aqueous phase is unacceptable and necessitates additional downstream treatment. In comparison, solid ion exchangers do not leach or impart any impurity into the aqueous phase and pose no environmental hazards. In a single-step process, the solid ion exchangers can achieve intended separation or removal of target ions without requiring any post-treatment. This attribute is the primary reason why synthesis



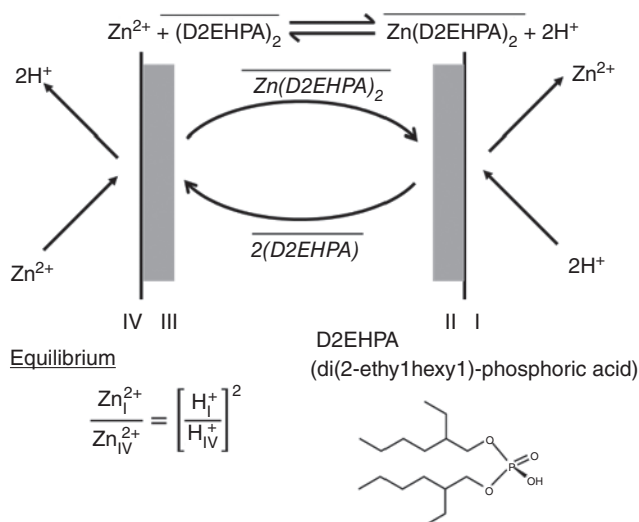
**Figure 1.15** Illustration of a typical liquid ion exchange process followed by phase separation.

and application of functionalized polymers and solid ion exchangers have grown so steadily in every field during the last four decades.

More recently, membrane contactors have been used to improve the overall stability of liquid ion exchangers where the exchanger material dissolved in an organic solvent acts as a shuttle between the aqueous phases. Figures 1.16 and 1.17 show the general arrangement of a liquid ion exchange process to recover metals ( $M^{2+}$ ) from a dilute stream using membrane contactors. In the first contactor on the left-hand side, metal



**Figure 1.16** An illustration of facilitated transport in liquid ion exchange for recovering metals using two membrane contactors.



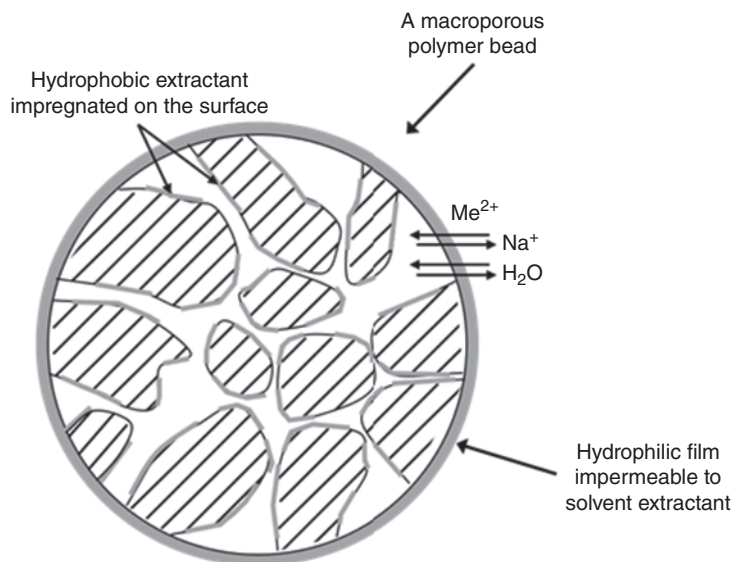
**Figure 1.17** Zinc recovery with D2EHPA metal extractant.

ions diffuse across the microporous membrane into the liquid ion exchanger, exchanging hydrogen ions ( $\text{H}^+$ ). The organic carrier solution containing the liquid exchanger is then brought in contact with the second membrane reactor on the right where the reaction is reversed and the metal ions are liberated into the strip solution. Similar systems, based on the principle of facilitated transport, have been used to separate metal ions, especially copper and zinc, using two steps, namely, sorption (i.e., uptake) and stripping (i.e., regeneration) [43,44].

Figure 1.17 illustrates recovery of zinc using liquid ion exchanger D2EHPA. While at the I/II interface,  $\text{Zn}^{2+}$  is finally recovered, separation of  $\text{Zn}^{2+}$  from the contaminated aqueous stream takes place at III/IV interface. Overall, hydrogen ions from the strip solution are transferred to the feed solution, exchanging equivalent amounts of metal ions. Loss of carrier solvent and instability of the membrane are two major hurdles for both facilitated and coupled transport processes in liquid ion exchange. Still, significant progress occurred during the last three decades to arrest solvent leakage primarily through the development of appropriate hydrophobic/hydrophilic contact materials.

### 1.6.3 Solvent-Impregnated Resins

In general, metal sorption onto polymeric chelating exchangers is quite selective, but kinetically very slow. Due to the rigid structure and tortuous pathways, the intraparticle diffusion rates for metals within solid ion exchangers are several orders of magnitude lower than they are in the solvent phase. Solvent impregnated resins (SIRs) can greatly overcome this shortcoming and SIRs are a compromise between solid ion exchange resins and liquid solvent extraction. Even more important, SIRs do not require covalent attachment of organic functional groups onto the parent polymer beads and, thus, conveniently avoid major steps in chemical synthesis for their preparation. SIRs can be easily deployed in packed-bed systems (i.e., plug flow reactor configuration) and are quite suitable for removal of trace concentrations of target metals. Liquid ion exchange



**Figure 1.18** An illustration of the characteristic features of the modified solvent-impregnated resin (SIR).

processes, in comparison, use continuous stirred tank reactors (CSTRs) and require multiple reactor stages for low concentrations of target solutes.

In SIR, an organophilic complexant is sorbed within macroporous copolymer beads, and the combined material serves as the selective adsorbent [24,25]. The organic chelating agent is neither chemically bound nor physically entrapped within the matrix of the porous polymer. Instead, they remain attached to the hydrophobic surface of the parent adsorbent through weak van der Waals force. This phenomenon is confirmed by the ability for organic complexants to be removed completely from SIRs by washing with an appropriate organic solvent. One critical disadvantage of SIRs is the gradual loss of complexant through aqueous phase dissolution or physical separation from the parent polymer for flow-through conditions. This phenomenon is a significant problem and often precludes adaptations of SIRs in environmental applications. To eliminate the loss of complexant, a new SIR has been prepared wherein a thin coating is formed around each bead [45]. This coating is hydrophilic and prevents the transport of the hydrophobic complexant out of the bead, while permitting transport of hydrophilic cations and anions into the bead. Figure 1.18 illustrates the characteristic features of the modified SIR. Despite its potential ease and versatility in applications, use of SIRs has so far remained very limited.

## 1.7 Amphoteric Inorganic Ion Exchangers

Unlike zeolites, amphoteric inorganic ion exchangers are non-siliceous materials; they are hydrated oxides of polyvalent metals, namely, Al(III), Fe(III), Zr(IV) and Ti(IV). Traditional ion exchange literature does not include them as ion exchangers for their relatively low capacity. However, these materials, as will be shown here and in

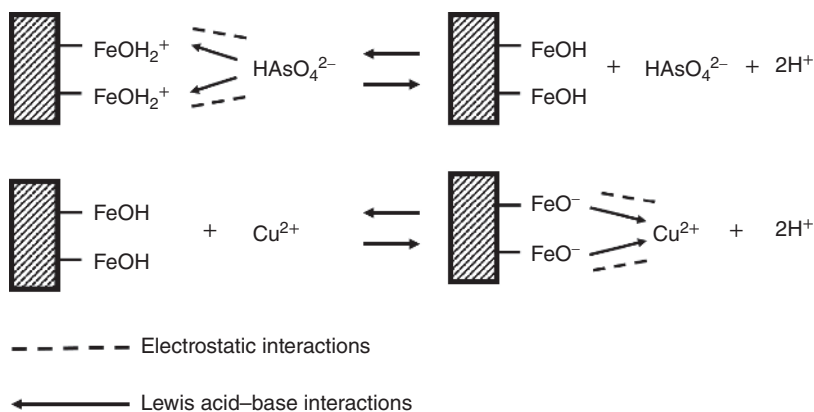
Chapter 6, provide unique sorption behaviors for a host of different types of trace contaminants, mostly metals and ligands. These metal oxide surfaces exhibit concurrent Lewis acid–base (i.e., metal–ligand) interaction along with ion exchange. Depending on the pH at the solid–water interface, the surface metal hydroxyl groups, commonly referred to as  $\overline{\text{MOH}}$ , can undergo protonation or deprotonation accompanied by ion exchange as shown hereunder:



where  $K_{a1}$  and  $K_{a2}$  are acid dissociation constants of the surface metal hydroxyl groups. One should be aware that the symbol  $\overline{\text{MOH}}$  is strictly conceptual and does not have a rigorous chemical entity from a scientific viewpoint. Nevertheless, the symbol allows treatment of an amphoteric hydrated metal oxide as a diprotic weak acid with dissociation constants  $K_{a1}$  and  $K_{a2}$ . In most systems, there is no evidence of definite hydrates, but MOH groups have been identified by IR spectroscopy [46,47]. Water molecules are strongly bound to the MOH groups through hydrogen bonding and are given off only at elevated temperatures [46]. It is noteworthy that depending on pH, hydrated metal oxide surfaces may possess fixed positive charges, negative charges or be electrically neutral. Figure 1.19 shows how a protonated hydrated Fe(III) oxide selectively sorbs arsenate (an anionic ligand) and copper ion (transition metal cation) at different pH.

As ion exchangers, hydrated metal oxides possess some unique properties that are distinctive from zeolites and ion exchange resins:

1. Ion exchange or sorption properties of hydrated metal oxides essentially reside on the surface. Thus, the exchange capacity per unit mass increases with an increase in the surface area, that is, reduction of particle sizes. In contrast, zeolites and ion exchange resins have fixed ionic charges distributed through the entire mass. Thus, their ion exchange capacity per unit mass or volume is independent of size.
2. While in contact with water, every hydrated metal oxide surface has a characteristic pH value at which surface negative charges balance surface positive charges. This pH value is referred to as the pH at zero-point charge or  $\text{pH}_{\text{ZPC}}$ .



**Figure 1.19** Illustration of amphoteric ion exchange behavior of polyvalent hydrated oxides.

**Table 1.6** pH at zero-point charge (pH<sub>ZPC</sub>) for different metal oxides of interest.

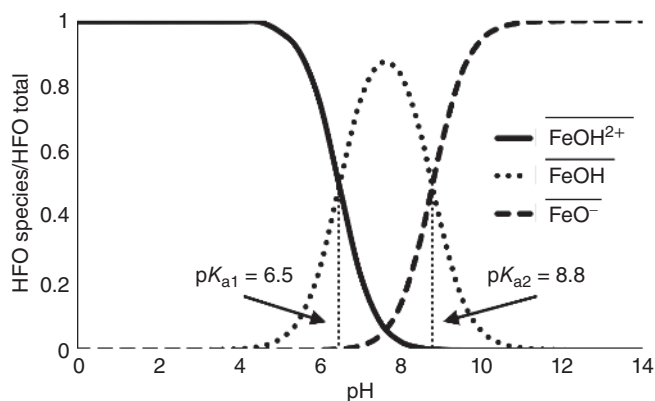
Oxide surface	pH <sub>ZPC</sub>
MgO (periclase)	11.5–12.3
α-Al <sub>2</sub> O <sub>3</sub> (corundum)	7.8–9.0
α-TiO <sub>2</sub> (rutile)	5.0–6.5
α-Fe <sub>2</sub> O <sub>3</sub> (hematite)	7.0–8.5
HFO (hydrated ferric oxide)	7.3–8.3
Calcite (mainly CaCO <sub>3</sub> )	8.0–9.0
Sepiolite (Mg <sub>4</sub> Si <sub>5</sub> O <sub>15</sub> (OH) <sub>2</sub> · 6H <sub>2</sub> O)	6.5–7.5
Feldspar (KAlSi <sub>3</sub> O <sub>8</sub> · NaAlSi <sub>3</sub> O <sub>8</sub> · CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> )	3.0–4.0
α-SiO <sub>2</sub> (quartz)	2.0–3.0
β-MnO <sub>2</sub>	6.5–7.5
ZrSiO <sub>4</sub>	5.0–6.0
ZrO <sub>2</sub>	6.5–7.5
Montmorillonite (Na,Ca) <sub>0.33</sub> (Al,Mg) <sub>2</sub> (Si <sub>4</sub> O <sub>10</sub> ) (OH) <sub>2</sub> · nH <sub>2</sub> O	2.0–3.0
Kaolinite (Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> )	4.0–5.0

Table 1.6 includes pH<sub>ZPC</sub> values for several metal oxides of interest [48]. There remain two common areas of misunderstanding or misinterpretation of pH<sub>ZPC</sub> values. First, the value of pH<sub>ZPC</sub> is not unique, it depends on the solution composition of the aqueous phase. The pH<sub>ZPC</sub> values in Table 1.6 represent conditions where electrolytes (cations and anions) in the aqueous phase have negligible specific affinities toward ion exchange sites besides through electrostatic or coulombic interactions. Second, metal oxides, although electrically neutral at pH<sub>ZPC</sub>, often exhibit high sorption capacities at pH = pH<sub>ZPC</sub>, that is, both positive and negatively charged functional groups may act independently.

3. Metal oxides exhibit strong Lewis acid–base characteristics during ion exchange processes; the central metal atom, that is, Fe(III), Zr(IV), Ti(IV) may act as a Lewis acid (electron acceptor) and the oxygen atoms as an electron donor (Lewis base). Thus, they can selectively bind both transition metal cations (Lewis acids) and anionic ligands (Lewis bases), which, incidentally, comprise a large group of trace contaminants of environmental interest. In fact, concurrent sorption of both transition metal cations and anionic ligands is also possible.

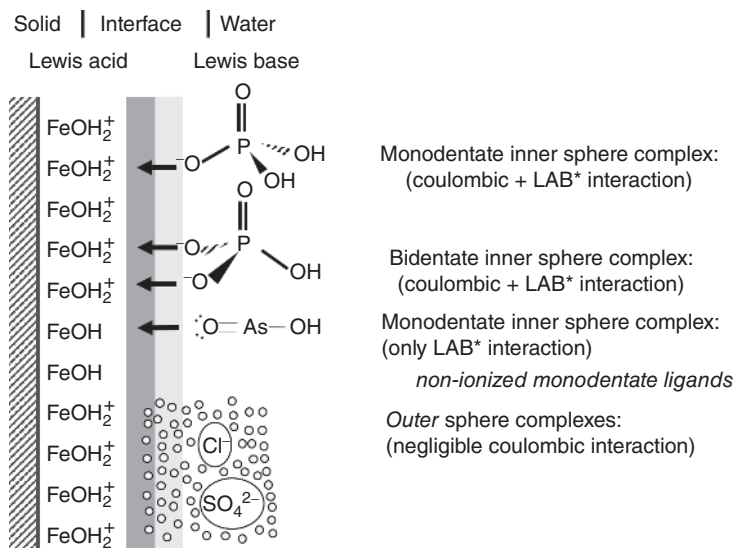
To further explore selective ion exchange properties of hydrated metal oxides of interest, let us take the case of hydrated Fe(III) oxides or HFO particles that have been rigorously investigated by geochemists and environmental engineers [49–54]. HFO is a weak diprotic acid with the following dissociation constants:





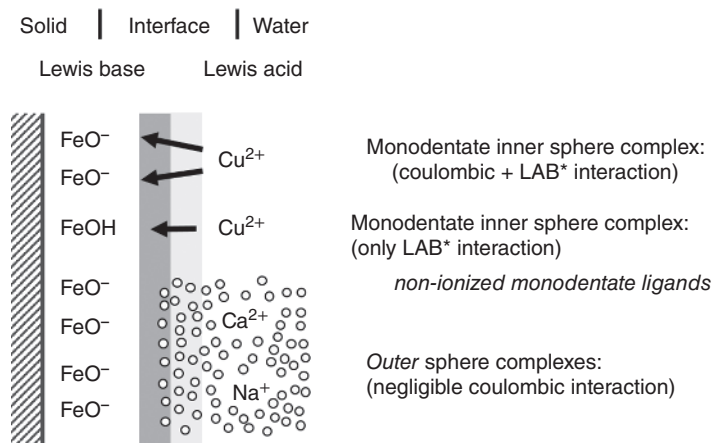
**Figure 1.20** Relative distribution of HFO surface functional groups as a function of pH ( $pK_{a1} = 6.5$ ,  $pK_{a2} = 8.8$ ). *Source:* Cumbal and SenGupta 2005 [52]. Reproduced with permission of American Chemical Society.

Figure 1.20 illustrates the distribution of the three surface functional groups of HFO (e.g.,  $\text{FeOH}_2^+$ ,  $\text{FeOH}$ , and  $\text{FeO}^-$ ) with respect to pH. At  $\text{pH} < 6.5$ , anionic ligands, such as arsenate, phosphate and citrate exhibit high sorption affinity toward positively charged surface hydroxyl groups. Such selective surface binding is often called formation of inner-sphere complexes because the solute-sorbent interaction involves an electron-pair donor (or Lewis base) and an electron-pair acceptor (or Lewis acid) as shown in Figure 1.21. Also, such Lewis acid–base interactions are often accompanied by electrostatic interactions. Note that commonly encountered anions, such as chloride, sulfate, and nitrate are poor ligands and, hence, unable to form inner-sphere



**Figure 1.21** An illustration of interaction of ligands (e.g., phosphate) with HFO surface functional groups in the presence of chloride. *Note:* LAB\* = Lewis acid–base. *Source:* Puttamaraju and SenGupta 2006 [53]. Reproduced with permission of American Chemical Society.





**Figure 1.22** An illustration of interaction of transition metal cation (e.g., Cu<sup>2+</sup>) with HFO surface in the presence of Ca<sup>2+</sup>. Source: Puttamaraju and SenGupta 2006 [53]. Reproduced with permission of American Chemical Society.

complexes; they undergo only electrostatic interactions and form weak outer-sphere complexes.

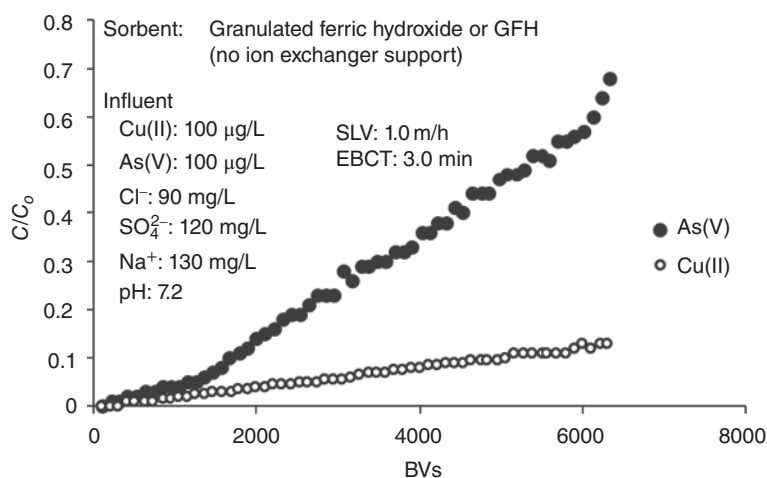
Likewise, at pH  $\geq 9.0$ , transition metal cations (e.g., Cu<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>) exhibit strong binding affinity toward negatively charged surface groups (FeO<sup>-</sup>) through formation of inner-sphere complexes accompanied by relatively weak electrostatic interaction. Surface FeO<sup>-</sup> groups act as sites for Lewis bases due to the presence of oxygen donor atoms while transition metal cations act as Lewis acids. Commonly encountered alkaline and alkaline-earth metal cations (e.g., Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>), on the contrary, form only outer-sphere complexes through electrostatic interactions. Figure 1.22 illustrates the underlying binding mechanism of Cu<sup>2+</sup>, a transition metal cation of environmental significance.

In the open literature, the selective binding of transition metal ions or ligands onto hydrated metal oxides through Lewis acid–base interactions is sometimes called *chemisorption*. From both the thermodynamic and kinetic standpoints, that is an overstatement. Selective surface binding of transition metals and ligands is reversible and the target solutes are easily desorbed simply through alteration of pH [52–56].

Temperature dependence of metal or ligand exchange onto amphoteric metal oxides is rather minimal. Activation energy requirement is always less than 50 kJ/mol. Kinetically, these heterogeneous surface ion-exchange reactions are diffusion-controlled; chemical reactions are rarely the rate-limiting steps. Due to their amphoteric behaviors and preference for both trace ligands and metals, hydrated metal oxides have much potential as selective sorbent materials. However, their low mechanical strength and chemical instability are the primary obstacles against wide range of applications. Chapter 6 reports preparation and characterization of hybrid ion exchangers that combine attributes of polymeric ion exchange resins and hydrated metal oxides to overcome these deficiencies.

It is worth noting that hydrated metal oxides can selectively and simultaneously remove both a toxic metal cation (e.g., Cu<sup>2+</sup>) and an anionic ligand (e.g., HAsO<sub>4</sub><sup>2-</sup>). Figure 1.23 shows the effluent histories of Cu(II) and As(V) during a fixed-bed column run using granular ferric hydroxide (GFH) sorbent. Note that both copper





**Figure 1.23** Effluent histories for As(V) and Cu<sup>2+</sup> for a fixed bed column run with GFH. SLV = Superficial Liquid Velocity; EBCT = Empty Bed Contact Time. *Source:* Puttamaraju and SenGupta 2006 [53]. Reproduced with permission of American Chemical Society.

and arsenate are removed for several thousand bed volumes, while cations and anions (e.g., Na<sup>+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) that form only outer-sphere complexes are poorly sorbed. In a succeeding chapter, we will discuss the preparation of tunable hydrated metal oxide materials that may remove either the ligands or the transition metals in accordance with the demand of the intended applications.

## 1.8 Ion Exchanger versus Activated Carbon: Commonalities and Contrasts

Activated carbon is probably the most widely used adsorbent and, expectedly, an enormous body of knowledge and scientific information is available about its properties and usage in the open literature. Activated carbon and ion exchangers have several properties in common: both are heterogeneous processes; fixed-bed column is the most common form of equipment configuration; both are diffusion-controlled processes; both have finite capacity and require reactivation/regeneration following exhaustion; and both exhibit different affinities to different solutes. Expectedly, there is often an inclination to interpret and understand ion exchange phenomena through the lens of activated carbon adsorption processes. As similar as they may seem to be, we need to be aware of the following distinct differences:

1. An ion exchanger, as already stated, is essentially a cross-linked polyelectrolyte with charged functional groups balanced by counterions, thus maintaining electroneutrality. Hence, it swells or shrinks very significantly due to the phenomenon of osmosis, which depends on the ionic strength and pH of the solution with which it is in contact. On the contrary, activated carbon barely exhibits any swelling/shrinking property in water.
2. Activated carbon adsorption is a surface phenomenon; so, adsorption capacity increases with an increase in surface area for a specific solute. The capacity of an ion exchanger is determined by the number of functional groups (i.e., fixed

coions) covalently attached per unit volume or mass of the ion exchanger. Thus, the capacity is not dependent on surface area. In fact, gel-type ion exchangers with practically no pores offer higher capacity than their macroporous counterparts with significantly higher surface area.

3. Activated carbon adsorption normally pertains to uncharged organic solutes and there is no electric potential gradient at the liquid/solid interface. So, solutes including ions of any sign and valence may permeate in and out of the porous solid phase. In contrast, there remains an electric potential gradient, often termed Donnan potential, at the ion exchanger/water interface inhibiting access of ions of specific charge inside the exchanger. The phenomenon is known as the Donnan exclusion effect. Several new and innovative processes have been developed through intelligent application of the Donnan exclusion effect and the subject has been adequately addressed in the succeeding chapters.

## 1.9 Ion Exchanger Morphologies

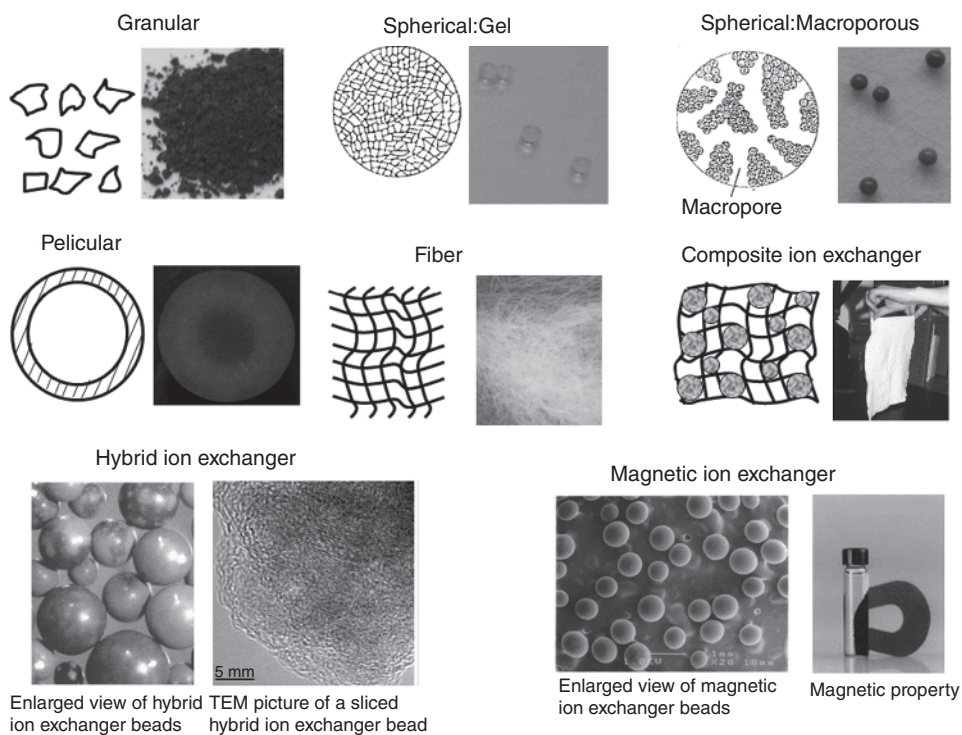
It is well recognized that the sorption behavior of an ion exchanger, inorganic or organic, is governed by its chemical makeup, that is, type of functional groups, matrix material and cross-linking. However, morphology or physical configuration of the ion exchanger also plays a significant role in deciding the success or appropriateness of an ion exchanger for an intended application. Type of reactor configuration, degree of pre-treatment required, environmental consideration, regenerability, durability and cost often decide the relative advantages of different types of ion exchanger morphologies that are available commercially. The following provides a broad classification of them [20,46,57–66]:

- a. Granular
- b. Spherical: Gel
- c. Spherical: Macroporous
- d. Pellicular
- e. Ion exchange fibers (IXFs)
- f. Composite ion exchanger (CIX) cloth
- g. Hybrid ion exchanger (HIX)
- h. Magnetic ion exchanger (MIEX)

Figure 1.24 provides a schematic and/or a photograph for each morphology depicting its physical configuration. Several succeeding chapters emphasize their distinctive properties and application opportunities.

## 1.10 Widely Used Ion Exchange Processes

Before leaving this chapter on *Introduction*, it is only appropriate that we briefly discuss the two most widely used ion exchange processes: Softening and Demineralization. These processes have been in use globally for over five decades, but the adverse



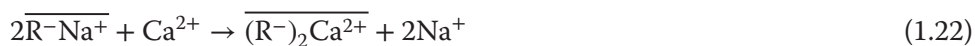
**Figure 1.24** Illustration of morphologies of different ion exchange materials.

environmental impact of these processes from a sustainability viewpoint is currently under severe scrutiny. The primary intent of this section is to briefly discuss the key elements of these processes and highlight their major shortcomings and areas warranting improvement.

### 1.10.1 Softening

Softening is a process to remove hardness from water, that is,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The presence of hardness in water increases the consumption of detergent and soap during cleaning and laundering. More importantly, hardness is highly undesirable in any heat exchanging equipment, including boilers, to avoid fouling and scaling. Membrane desalination of high hardness brackish water or sea water by reverse osmosis (RO) often requires the water to be pretreated by softening to avoid scaling of membrane surfaces. Lime and lime-soda softening processes can remove hardness, but the processes produce large volumes of sludge and is unable to remove hardness completely.

Complete softening may be achieved by sodium cycle cation exchange on a single fixed bed unit. As the feed or raw water containing hardness is passed through the fixed bed column, hardness causing cations (e.g.,  $\text{Ca}^{2+}$ ) displace sodium per the following ion exchange reaction:

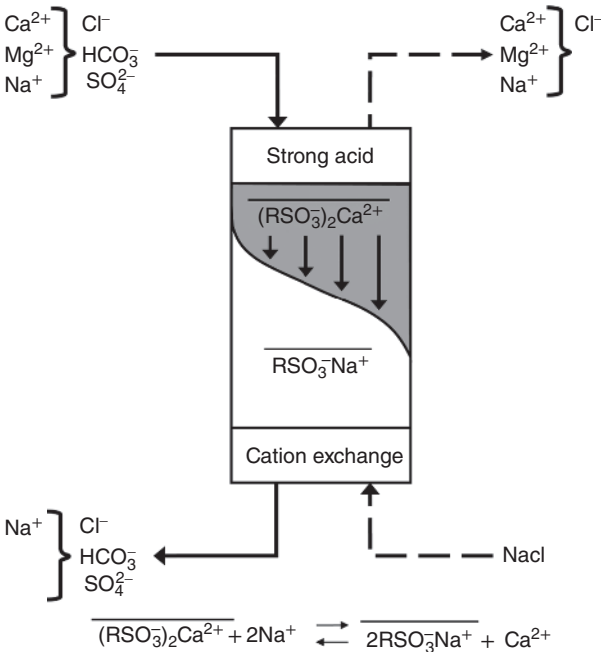


Calcium is removed from the feed water and the treated water is soft and in compliance with the specifications for the intended applications. Once the capacity is exhausted and calcium in the treated water starts increasing, the cation exchanger in the fixed bed warrants regeneration to desorb  $\text{Ca}^{2+}$  and return the cation resin to  $\text{Na}^+$ -form for the next cycle as shown below:

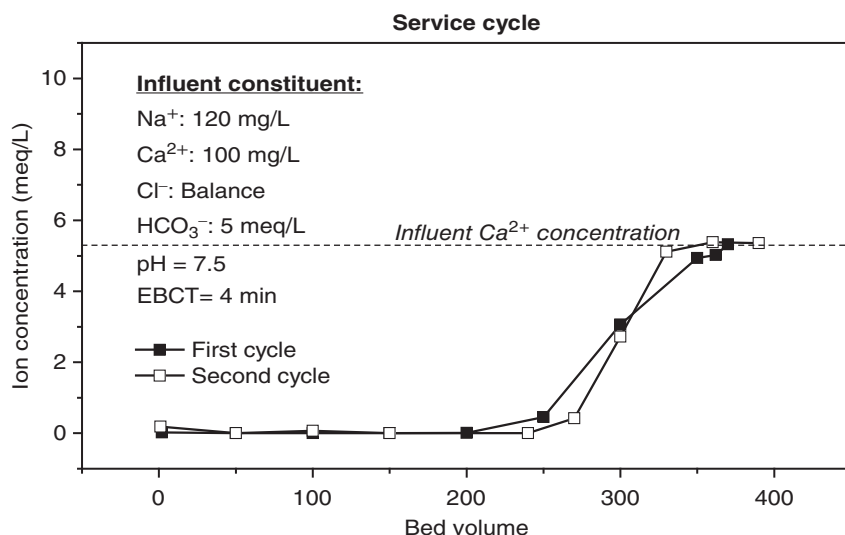


The regeneration of the exhausted resin is often, if not always, carried out by brine or  $\text{NaCl}$  solutions. The regeneration step is often accomplished in  $<10$  BVs (bed volumes). *One bed volume or BV corresponds to the volume of the cation exchange resin in the fixed bed.* Equivalents of  $\text{NaCl}$  solution used for regeneration are always greater than the equivalents of  $\text{Ca}^{2+}$  removed by the bed during the service or sorption cycle. Thus, the spent regenerant contains a significant excess of brine in addition to the calcium removed. From a sustainability or efficiency viewpoint, the softening process is poor-performing, because it invariably delivers more electrolytes to the surrounding waterways than it removes. To appropriately assess the overall sustainability of the softening process, let us consider the following example.

Figure 1.25 shows the schematic of the cation exchange softening process in a fixed-bed system where the solid line shows the service/sorption cycle and the



**Figure 1.25** A schematic of the cation exchange softening process in a fixed-bed system. The solid line shows the service/sorption cycle and the dashed line represents regeneration with brine.



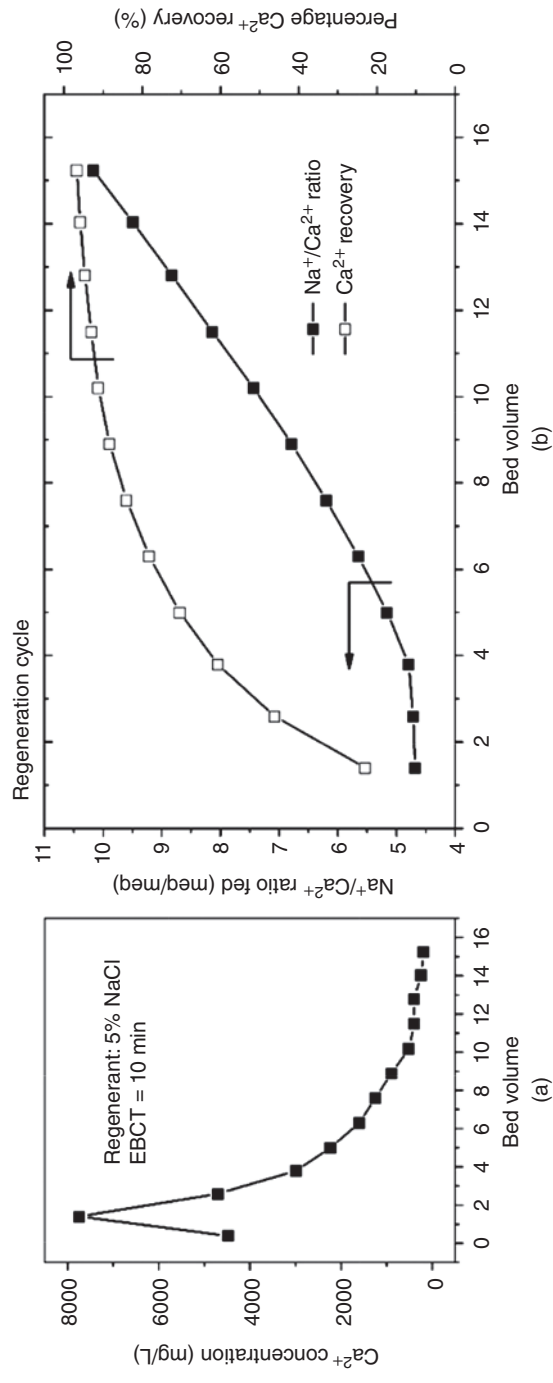
**Figure 1.26** Calcium history of two consecutive service cycles by a strong-acid cation exchange softener.

dashed line represents regeneration with brine. Figure 1.26 presents the effluent or breakthrough history of calcium from the cation exchange column in sodium form for two consecutive runs. The feed water composition is also included in the figure [67].

Between the two successive runs, the column was regenerated with 5% NaCl. Figure 1.27a shows elution or desorption profiles of calcium during regeneration: over 90% calcium is recovered after 15 BVs of regeneration.

It is apparent that from an operational viewpoint, the cyclic process – sorption followed by regeneration and rinsing – is sustainable and can be carried out for tens of cycles with desired hardness removal. From an environmental sustainability viewpoint, however, a critical question is now being asked: How many equivalents of  $\text{Na}^+$  are consumed and/or discharged to the environment per equivalent of  $\text{Ca}^{2+}$  removed from the hard water? This sustainability parameter is of great consequence, particularly in arid areas with low rainfall or precipitation. High volumes of spent regenerant could cause adverse effects by elevating the salinity level in natural water bodies in the region. Ideally, based on the stoichiometry of the exchange reactions in Eqs (1.22) and (1.23), one equivalent of  $\text{Na}^+$  is needed for removal of one equivalent of hardness.

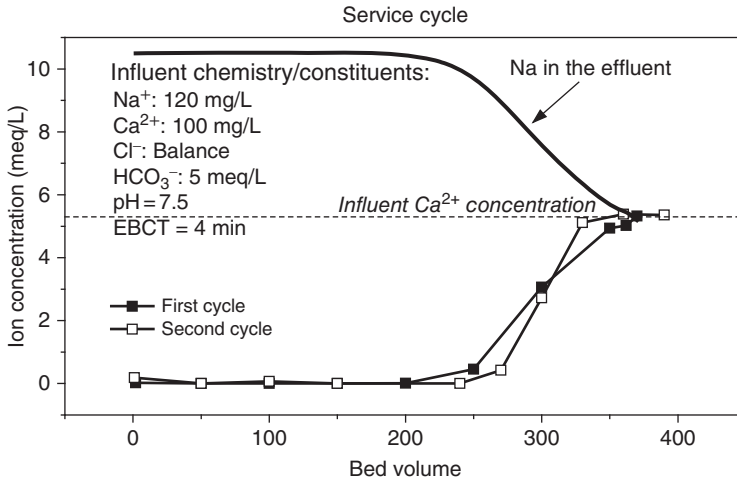
Figure 1.27b presents the ratio of equivalents of  $\text{Na}^+$  used per equivalent of  $\text{Ca}^{2+}$  removed during the regeneration cycle. Note that the ratio after 12 BVs is 8.5 implying that the process consumes and discharges several times more equivalents of NaCl to the environment than is stoichiometrically required. This inefficiency is embedded in an ion exchange softening process and is the sole reason why brine regeneration is being banned in many places, including the state of California [68].



**Figure 1.27** (a) Regeneration curve for exhausted strong-acid cation exchange resin with 5% NaCl; (b) A comparison of regeneration efficiency ( $\text{Na}^+ : \text{Ca}^{2+}$ ) versus  $\text{Ca}^{2+}$  recovery. Source: Reprinted with permission from Li et al. 2016 [67].

**Example 1.3** Consider the effluent history of calcium in Figure 1 during the softening cycle. Superimpose the  $\text{Na}^+$  effluent history in the same figure. What is the chloride concentration at the exit of the column after 100 BVs?

**Solution:**



**Figure 1.** Calcium and sodium history of two consecutive service cycles by a strong-acid cation exchange softener. *Source:* Li *et al.* 2016 [67]. Reproduced with permission of American Chemical Society.

The sodium concentration in the treated water can be calculated by applying the principle of electroneutrality. Same equivalent amount of  $\text{Na}^+$  was released to the effluent as  $\text{Ca}^{2+}$  was removed.  $\text{Ca}_{\text{effluent}}^{2+}$  was read from the figure provided.

$$\begin{aligned} \text{Na}^+_{\text{effluent}} &= \text{Na}^+_{\text{initial}} + \text{Ca}^{2+}_{\text{initial}} - \text{Ca}^{2+}_{\text{effluent}} \\ \text{Na}^+_{\text{effluent}} &= \left( \frac{120 \text{ mg}}{\text{L}} \times \frac{1 \text{ mmol}}{23 \text{ mg}} \times \frac{1 \text{ meq}}{\text{mmol}} \right) + \left( \frac{100 \text{ mg}}{\text{L}} \times \frac{\text{mmol}}{40 \text{ mg}} \times \frac{2 \text{ meq}}{\text{mmol}} \right) \\ &\quad - \text{Ca}^{2+}_{\text{effluent}} \\ \text{Na}^+_{\text{effluent}} &= 5.22 \frac{\text{meq}}{\text{L}} + 5 \frac{\text{meq}}{\text{L}} - \text{Ca}^{2+}_{\text{effluent}} \end{aligned}$$

Thus, for each data point corresponding to  $\text{Ca}^{2+}_{\text{effluent}}$  in Figure 1,  $\text{Na}^+_{\text{effluent}}$  can be computed. Figure 1 includes the effluent history of  $\text{Na}^+$  during the column run.

Chloride concentration may also be computed using the principle of electroneutrality. Concentration of  $\text{H}^+$  and  $\text{OH}^-$  can be ignored at  $\text{pH} = 7.5$ .

*Cations:*

$$\text{Na}^+ = \frac{120 \text{ mg/L}}{23 \text{ mg/mmol}} \times 1 \text{ meq/mmol} = 5.22 \text{ meq/L}$$

$$\text{Ca}^{2+} = \frac{100 \text{ mg/L}}{40 \text{ mg/mmol}} \times 2 \text{ meq/mmol} = 5 \text{ meq/L}$$

*Anion:*

$$\text{HCO}_3^- = 5 \text{ meq/L}$$

Thus,

$$\text{Cl}^- = (5.22 + 5 - 5) \frac{\text{meq}}{\text{L}} \times 1 \frac{\text{mmol}}{\text{meq}} \times 35.5 \frac{\text{mg}}{\text{mmol}} = 185.3 \text{ mg/L}$$

There is no anion exchange during the process. Thus, the chloride concentration remains the same throughout and is equal to 185.3 mg/L.

### 1.10.2 Deionization or Demineralization

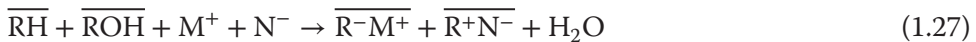
Deionization or demineralization is a process of removing electrolytes by ion exchange to produce pure water, that is, removal of all cations and anions. In the simplest form of this process, two ion exchange units in series constitute the heart of the process; a cation exchange bed in hydrogen form is followed by an anion exchange bed in hydroxyl form. As the water to be treated is passed through the two-bed system, all the cations (say monovalent  $M^+$ ) are exchanged releasing equivalent amounts of hydrogen ions:



Thus, at the exit of the cation exchange column, the water is essentially a dilute acid containing all the anions ( $N^-$ ) that were originally present in the feed water balanced by equivalent  $H^+$  cations. Upon passing through the anion exchange column, all anions are exchanged for  $OH^-$ , which then associates with  $H^+$  to produce pure water or  $H_2O$ .



Thus, the overall reaction is



Dissolved solutes that are not ionized cannot be removed by the deionization process. Also, the product water is not free of electrolytes due to early “leakage” or “break-through” of ions from the ion exchange columns. Once the capacities are exhausted, the columns need to be regenerated: cation exchangers with an acid ( $HCl$  or  $H_2SO_4$ ) and the anion exchanger with a base ( $NaOH$ ). The regeneration process is often not efficient, that is, the consumption of acid and base is significantly more than their stoichiometric requirement.

As the electrolyte concentration in the feed water increases, regeneration is needed more frequently, as capacity is a function of equivalents of electrolytes removed. The general guideline is that once the TDS of the feed water increase beyond 500 mg/L, conventional deionization becomes economically less viable. From an environmental sustainability viewpoint, spent regenerant from the demineralization process is a challenge that requires innovation and improvement both in the efficiency of the regeneration process and choice of the regenerant chemicals. The following example attempts to illustrate several pertinent issues.

#### Example 1.4 Design of a Two-Bed Deionizer

*Given: Raw water of the following quality:*

Hardness = 3.0 meq/L

Bicarbonate = 2.0 meq/L



pH = 7.8  
 Chloride = 1.0 meq/L  
 Sulfate = 2.0 meq/L  
 Sodium = to balance anions

*Find:* The design parameters for a two-bed, 400 L/min deionizer system which must run for 8 hours before breakthrough.

- The volume of cation resin required if the two-bed deionizer has a capacity of 1.0 eq/L of resin after regeneration with  $\text{H}_2\text{SO}_4$  at 162 g/L (100% basis) and a concentration of 2.0 N.
- The volume of anion resin required if it has a capacity of 0.7 eq/L of resin after regeneration with NaOH at 120 g/L of resin (100% basis) and a concentration of 1.0 N.
- The analysis in mg/L for all the ions in the mixed waste regenerant solution after neutralization. Assume that the slow rinses are collected with the regenerants and that they comprise 2 BV for each bed. Deionized water is used to make up the regenerant solutions. Neutralization is done with the same acid or base as used for regeneration.
- In the above two-bed deionization system, do you anticipate any problem if the anion-exchanging unit precedes the cation exchanging unit?
- Draw a sketch of the process and indicate approximate pH at different locations of the systems during exhaustion run.
- Find the electrolyte concentration in the spent regenerant and compare this to the amount of removed contaminants to find a measure of the ion exchange efficiency.

**Solution:**

- (a) *Concentration of cations:*

$$\text{Hardness} = [\text{Ca}^{2+}] + [\text{Mg}^{2+}] = 3.0 \text{ meq/L}$$

$$\text{Total anions} = \text{Bicarbonate} + \text{Chloride} + \text{Sulfate} = 5.0 \text{ meq/L} \quad [\text{Na}^+] = 2.0 \text{ meq/L}$$

$$\text{Total cations} = 5.0 \text{ meq/L}$$

*Total mass of exchanged cation:*

$$5.0 \frac{\text{meq}}{\text{L}} \cdot 400 \frac{\text{L}}{\text{min}} \cdot 60 \frac{\text{min}}{\text{h}} \cdot 8 \text{ h} = 9.60 \times 10^5 \text{ meq} = 960 \text{ equivalents}$$

*The volume of cation exchange resin needed:*

$$\frac{960 \text{ equivalents}}{1.0 \frac{\text{eq}}{\text{L}}} = 960 \text{ L} = 0.96 \text{ m}^3$$

- (b) *Concentration of anions:*

$$2.0 \frac{\text{meq}}{\text{L}} (\text{HCO}_3^-) + 2.0 \frac{\text{meq}}{\text{L}} (\text{SO}_4^{2-}) + 1.0 \frac{\text{meq}}{\text{L}} (\text{Cl}^-) = 5.0 \frac{\text{meq}}{\text{L}}$$

Total equivalents of exchanged anion same as cations: 960 eq

*The volume of anion exchange resin needed:*

$$\frac{960 \text{ eq}}{0.7 \frac{\text{eq}}{\text{L}}} = 1370 \text{ L} = 1.37 \text{ m}^3$$

- (c) First, let us identify and record the volumes of separate streams in the mixed waste regenerant. Note that the mixed waste will contain: (i) all the electrolytes removed during the 8-h period of the service cycle, (ii) excess  $H_2SO_4$  and NaOH used during the regeneration of the cation exchanger and anion exchanger, (iii) excess acid and/or base added to neutralize the pH from the previous steps.

*Volume of rinse water ( $V_1$ ):*

$$V_1 = 2 \text{ BVs} \cdot 0.96 \frac{\text{m}^3}{\text{BV}} + 2 \text{ BVs} \cdot 1.37 \frac{\text{m}^3}{\text{BV}} = 4.66 \text{ m}^3$$

*Volume of  $H_2SO_4$  ( $V_2$ ):*

$$V_2 = \frac{162 \frac{\text{g}}{\text{L}_{\text{resin}}} \cdot 960 \text{ L}_{\text{resin}}}{49 \frac{\text{g}}{\text{eq}} \cdot 2 \frac{\text{eq}}{\text{L}}} = 1587 \text{ L} = 1.59 \text{ m}^3$$

*Volume of NaOH ( $V_3$ ):*

$$V_3 = \frac{120 \frac{\text{g}}{\text{L}_{\text{resin}}} \cdot 1370 \text{ L}_{\text{resin}}}{40 \frac{\text{g}}{\text{eq}} \cdot 1 \frac{\text{eq}}{\text{L}}} = 4110 \text{ L} = 4.11 \text{ m}^3$$

*Volume of acid for neutralizing base ( $V_4$ ):*

*Excess of acid*

$$\frac{162 \frac{\text{g}}{\text{L}_{\text{resin}}} \cdot 960 \text{ L}_{\text{resin}}}{49 \frac{\text{g}}{\text{eq}}} - 960 \text{ eq} = 2214 \text{ eq}$$

*Excess of base*

$$\frac{120 \frac{\text{g}}{\text{L}_{\text{resin}}} \cdot 1370 \text{ L}_{\text{resin}}}{40 \frac{\text{g}}{\text{eq}} \cdot 1 \frac{\text{eq}}{\text{L}}} - 960 \text{ eq} = 3150 \text{ eq}$$

*Acid needed to neutralize base*

$$3150 - 2214 \text{ eq} = 936 \text{ eq}$$

$$V_4 = \frac{936 \text{ eq}}{2 \frac{\text{eq}}{\text{L}}} = 468 \text{ L} = 0.47 \text{ m}^3$$

*Total volume:*

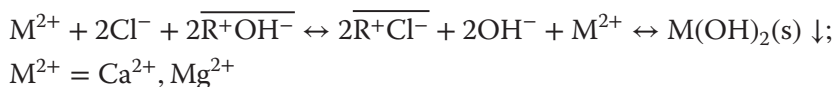
$$V_T = V_1 + V_2 + V_3 + V_4 = 10.8 \text{ m}^3$$

*Concentration in mixed solution:*

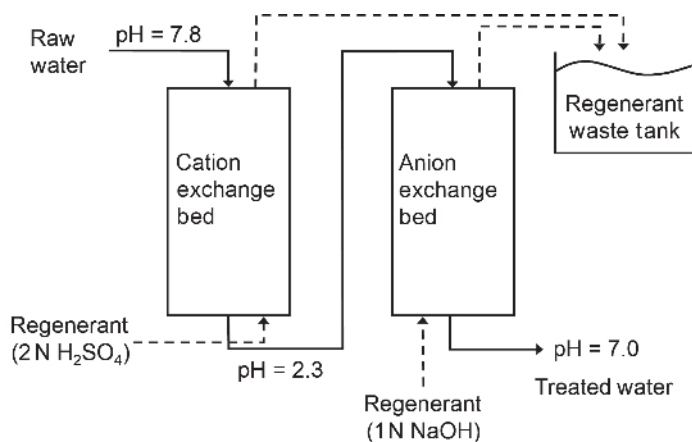
$$\begin{aligned} [\text{Ca}^{2+}] + [\text{Mg}^{2+}] &= \frac{3 \frac{\text{meq}}{\text{L}} \cdot 400 \frac{\text{L}}{\text{min}} \cdot 60 \frac{\text{min}}{\text{h}} \cdot 8 \text{ h}}{10.8 \text{ m}^3 \cdot 10^3 \frac{\text{L}}{\text{m}^3}} = 52.8 \frac{\text{meq}}{\text{L}} \\ &= 1057 \frac{\text{mg}}{\text{L}} \text{ as Ca}^{2+} \end{aligned}$$

$$\begin{aligned}
 [\text{Na}^+] &= \frac{2 \frac{\text{meq}}{\text{L}} \cdot 400 \frac{\text{L}}{\text{min}} \cdot 60 \frac{\text{min}}{\text{h}} \cdot 8 \text{ h} + 4110 \text{ L} \times 10^3 \frac{\text{meq}}{\text{L}}}{10.8 \text{ m}^3 \times 10^3 \frac{\text{L}}{\text{m}^3}} \\
 &= 412 \frac{\text{meq}}{\text{L}} = 9483 \frac{\text{mg}}{\text{L}} \\
 [\text{HCO}_3^-] &= \frac{2 \frac{\text{meq}}{\text{L}} \cdot 400 \frac{\text{L}}{\text{min}} \cdot 60 \frac{\text{min}}{\text{h}} \cdot 8 \text{ h}}{10.8 \text{ m}^3 \times 10^3 \frac{\text{L}}{\text{m}^3}} = 35.2 \frac{\text{meq}}{\text{L}} = 2149 \frac{\text{mg}}{\text{L}} \\
 [\text{Cl}^-] &= \frac{1 \frac{\text{meq}}{\text{L}} \cdot 400 \frac{\text{L}}{\text{min}} \cdot 60 \frac{\text{min}}{\text{h}} \cdot 8 \text{ h}}{10.8 \text{ m}^3 \times 10^3 \frac{\text{L}}{\text{m}^3}} = 17.6 \frac{\text{meq}}{\text{L}} = 625 \frac{\text{mg}}{\text{L}} \\
 [\text{SO}_4^{2-}] &= \frac{2 \frac{\text{meq}}{\text{L}} \cdot 400 \frac{\text{L}}{\text{min}} \cdot 60 \frac{\text{min}}{\text{h}} \cdot 8 \text{ h}}{10.8 \text{ m}^3 \times 10^3 \frac{\text{L}}{\text{m}^3}} = 35.2 \frac{\text{meq}}{\text{L}} = 1690 \frac{\text{mg}}{\text{L}}
 \end{aligned}$$

- (d) If an anion exchange bed precedes the cation exchange bed,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  will probably precipitate in the anion exchange bed due to the low solubility of their hydroxide and carbonate salts at high pH.



(e)



During an exhaustion run,  $\text{H}^+$  in the effluent from the cation exchange bed is  $5.0 \times 10^{-3} \text{ M}$  ( $\text{pH} = 2.3$ ).

- (f) Part c of the solution provides various concentrations and total masses of different cations and anions present in the spent regenerant. Ideally, the most efficient deionization system would be when the equivalents removed from the feed water during the service cycle is equal to the equivalents present in the spent regenerant. Equivalents in the spent regenerant are always greater than what have been

removed. Thus, a dimensionless sustainability indicator for ion exchange,  $SI_{IX}$ , can be presented as the ratio of the equivalents in the spent regenerant over equivalents removed.

Cations and anions removed per L of water treated

$$\begin{aligned} &= [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{HCO}_3^-] + [\text{Cl}^-] + [\text{SO}_4^{2-}] \\ &= 5.0 \frac{\text{meq}}{\text{L}} \text{cations} + 5.0 \frac{\text{meq}}{\text{L}} \text{anions} = 10 \frac{\text{meq}}{\text{L}} \end{aligned}$$

Regenerant added =  $[\text{H}^+]_{\text{added}} + [\text{OH}^-]_{\text{added}}$

$$= 2214 \text{ eq H}^+ + 3150 \text{ eq OH}^- = 5364 \text{ eq}$$

pH neutralization requirement =  $[\text{OH}^-]_{\text{added}} - [\text{H}^+]_{\text{added}}$

$$= 3150 \text{ eq OH}^- - 2214 \text{ eq H}^+ = 936 \text{ eq}$$

$$= \frac{\text{Regenerant Added} + \text{pH Neutralization Requirement}}{\text{Cations and Anions Removed}}$$

$$= \frac{([\text{H}^+]_{\text{added}} + [\text{OH}^-]_{\text{added}}) + ([\text{OH}^-]_{\text{added}} - [\text{H}^+]_{\text{added}})}{[\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{HCO}_3^-] + [\text{Cl}^-] + [\text{SO}_4^{2-}]}$$

$$= \frac{2214 \text{ eq H}^+ + 3150 \text{ eq OH}^- + 936 \text{ eq H}^+}{10 \frac{\text{meq}}{\text{L}} \cdot \frac{1 \text{ eq}}{1000 \text{ meq}} \cdot 400 \frac{\text{L}}{\text{min}} \cdot 60 \frac{\text{min}}{\text{h}} \cdot 8 \text{ h}} = 3.28$$

$SI_{IX}$  values greater than unity represent the deviation of the process from its theoretical limit – the process in this example is very inefficient. Later in Chapter 2, we will see how the regeneration efficiency can be significantly improved and  $SI_{IX}$  value lowered by modifying the deionization process.

## Summary

- The phenomenon of cation exchange was first recognized and reported in 1850 by two British soil scientists, J.T. Way and H.S. Thompson, while investigating properties of natural soils. They provided experimental evidence that the process of ion exchange is reversible and takes place through equivalent exchange of ions. Also, different cations have different selectivity toward the soil. In general, natural materials were found to have very poor anion exchange behavior.
- In 1935, Adams and Holmes synthesized the first organic-based (polymeric) cation exchanger. In less than 10 years, D'Alelio prepared the first synthetic anion exchange resin. Since then, synthesis of new ion exchange resins has never slowed down. The Second World War and, more specifically, the race for nuclear technology helped catalyze the growth and maturity of the field of ion exchange.
- Ion exchange resins have charged functional groups (positive or negative) that are covalently attached to a cross-linked polymer, often called matrix. Inorganic ion

exchangers, namely clays or zeolites, have cation exchange capacity that is obtained through isomorphous substitutions of silicon with aluminum.

- Many redox and precipitation–dissolution reactions have the appearance of ion exchange reactions, but they are not. An ion exchanger is not a pure solid phase. It contains counterions at varying distributions, like a continuous solid solution.
- The large-scale synthesis of polymeric ion exchangers has been standardized and is practiced globally. The four most widely used ion exchange resins are: weak-acid cation exchange resins, strong-acid cation exchange resins, weak-base anion exchange resins and strong-base anion exchange resins. Due to uncontrolled methylene bridging, anion exchange resins possess lower capacity than their cation counterparts.
- Biosorbent materials often exhibit high sorption affinity toward heavy metals and other trace contaminants of environmental concern. They are biorenewable and attractive from a sustainability viewpoint. Poor chemical stability under extreme pH and redox conditions and lack of mechanical strength are major impediments for large-scale application of biosorbent materials.
- Liquid ion exchangers have exchange at the phase boundaries of the immiscible liquids and have much faster kinetics versus solid phase ion exchangers that are controlled by intraparticle diffusion. But effluent solutions are often contaminated with organic solvent. SIRs use an organophilic extractant and are easy to synthesize. However, the gradual loss of complexant during lengthy fixed-bed processes is a major shortcoming of the SIRs.
- Oxides of polyvalent metals, namely, Fe(III), Zr(IV) and Ti(IV) are amphoteric. They exhibit high sorption affinity toward both transition metal cations and anionic ligands.
- Activated carbon and ion exchange resins are the two most commonly used adsorbent materials for packed-bed water treatment processes and have similar operating procedures. But the genesis of their sorption capacity is distinctly different. While carbon adsorption is a surface phenomenon, the ion exchange capacity is derived from the functional group density, that is, the number of covalently attached functional groups per unit volume of the ion exchanger.
- Softening and demineralization (DM) are the two most common applications of ion exchange. These industrial processes improve system efficiency through hardness scaling prevention and TDS elimination, respectively. Both have sustainability concerns due to poor regeneration efficiency on an equivalent basis and consequent production of spent regenerant with large amounts of very high TDS.

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