Tech Fact

Ion Exchange Resins

Fundamentals of Ion Exchange

Introduction

Ion exchange is the reversible interchange of ions between a solid (ion exchange material) and a liquid in which there is no permanent change in the structure of the solid. Ion exchange is used in water treatment and also provides a method of separation in many non-water processes. It has special utility in chemical synthesis, medical research, food processing, mining, agriculture and a variety of other areas.

The utility of ion exchange rests with the ability to use and reuse the ion exchange material. For example, in water softening:

$$2\overline{R}Na^{+} + Ca^{2+} \$ \overline{R}_2Ca^{2+} + 2Na^{+}$$

The exchanger $\overline{R}$ in the sodium ion form is able to exchange for calcium and thus, to remove calcium from hard water and replace it with an equivalent quantity of sodium. Subsequently, the calcium loaded resin may be treated with a sodium chloride solution, regenerating it back to the sodium form, so that it is ready for another cycle of operation. The regeneration reaction is reversible; the ion exchanger is not permanently changed. Millions of liters of water may be softened per cubic meter of resin during an operating period of many years.

Ion exchange occurs in a variety of substances and it has been used on an industrial basis since circa 1910 with the introduction of water softening using natural and later, synthetic zeolites. Sulfonated coal, developed for industrial water treatment, was the first ion exchange material that was stable at low pH. The introduction of synthetic organic ion exchange resins in 1935 resulted from the synthesis[1] of phenolic condensation products containing either sulfonic or amine groups which could be used for the reversible exchange of cations or anions.

A variety of functional groups have been added to the condensation or addition polymers used as the backbone structures. Porosity and particle size have been controlled by conditions of polymerization and uniform particle size manufacturing technology. Physical and chemical stability have been modified and improved. As a result of these advances, the inorganic exchangers (mineral, greensand and zeolites) have been almost completely displaced by the resinous types except for some analytical and specialized applications. Synthetic zeolites are still used as molecular sieves.

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Physical Properties of Resins

Conventional ion exchange resins consist of a cross-linked polymer matrix with a relatively uniform distribution of ion-active sites throughout the structure. A cation exchange resin with a negatively charged matrix and exchangeable positive ions (cations) is shown in Figure 1. Ion exchange materials are sold as spheres or sometimes granules with a specific size and uniformity to meet the needs of a particular application. The majority are prepared in spherical (bead) form, either as conventional resin with a polydispersed particle size distribution from about 0.3 mm to 1.2 mm (50-16 mesh) or as uniform particle sized (UPS) resin with all beads in a narrow particle size range. In the water- swollen state, ion exchange resins typically show a specific gravity of 1.1-1.5. The bulk density as installed in a column includes a normal 35-40 percent voids volume for a spherical product. Bulk densities in the range of 560-960 g/l (35-60 lb/ft^3) are typical for wet resinous products.

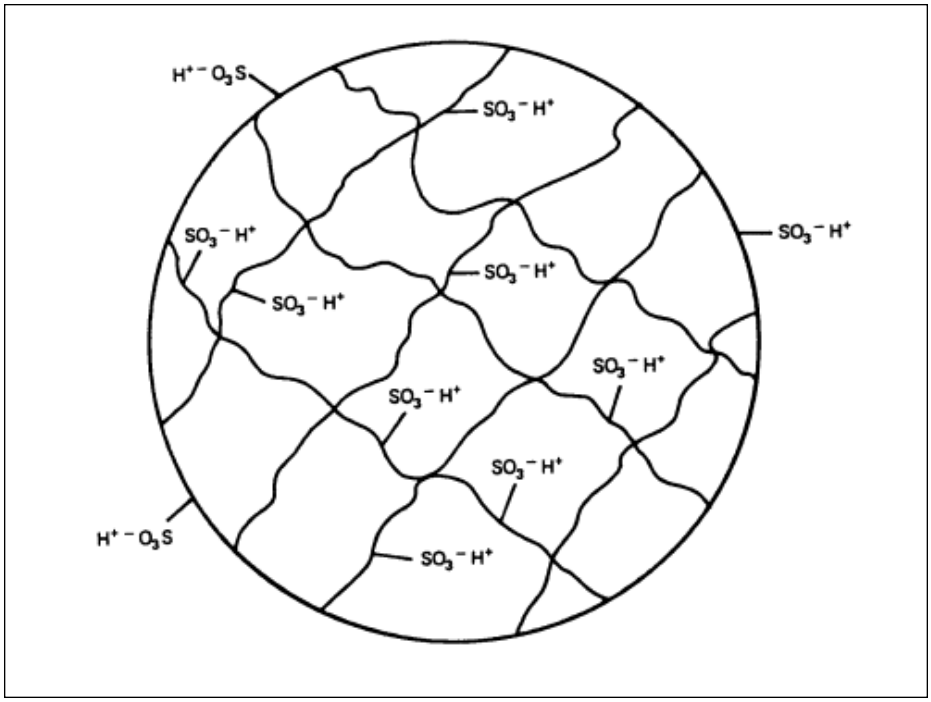

Figure 1: Cation Exchange Resin Schematic Showing Negatively Charged Matrix and Exchangeable Positive Ions

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Chemical Properties of Resins

Capacity. Ion exchange capacity may be expressed in a number of ways. Total capacity, i.e., the total number of sites available for exchange, is normally determined after converting the resin by chemical regeneration techniques to a given ionic form. The ion is then chemically removed from a measured quantity of the resin and quantitatively determined in solution by conventional analytical methods. Total capacity is expressed on a dry weight, wet weight or wet volume basis. The water uptake of a resin and therefore its wet weight and wet volume capacities are dependent on the nature of the polymer backbone as well as on the environment in which the sample is placed. Variations of dry weight and wet volume capacities with cross-linkage are shown in Figure 2 for a sulfonic resin.

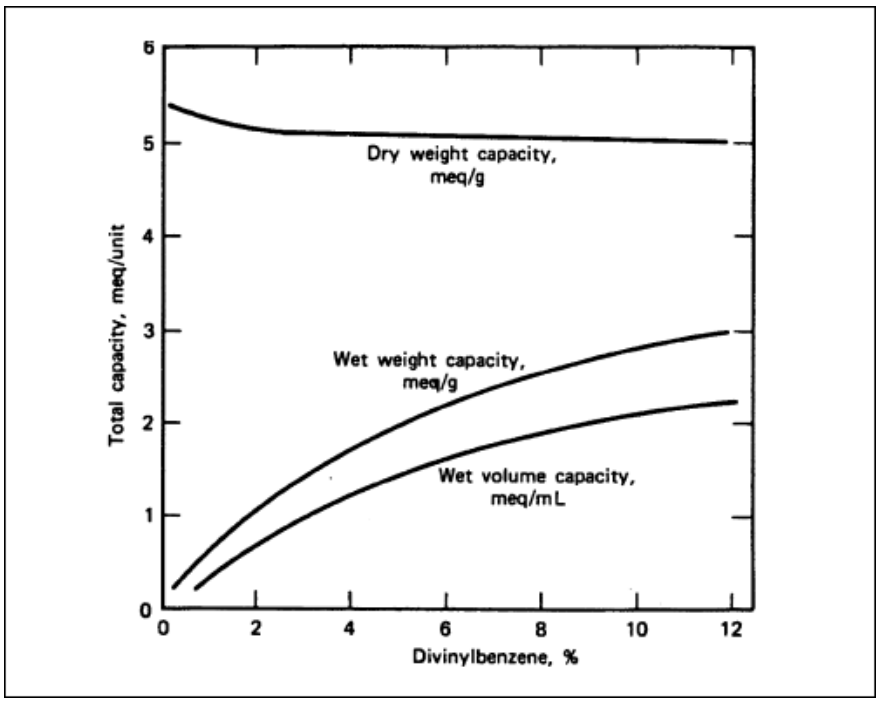

Figure 2: Total Capacity vs. Cross-Linkage (Percent DVB) Polystyrene Sulfonic Acid Resin, H^+ Form

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Chemical Properties of Resins (Cont.)

Operating capacity is a measure of the useful performance obtained with the ion exchange material when it is operating in a column under a prescribed set of conditions. It is dependent on a number of factors including the inherent (total) capacity of the resin, the level of regeneration, the composition of solution treated, the flow rates through the column, temperature, particle size and distribution. An example is shown in Figure 3 for the case of water softening with a standard sulfonic resin at several regenerant levels.

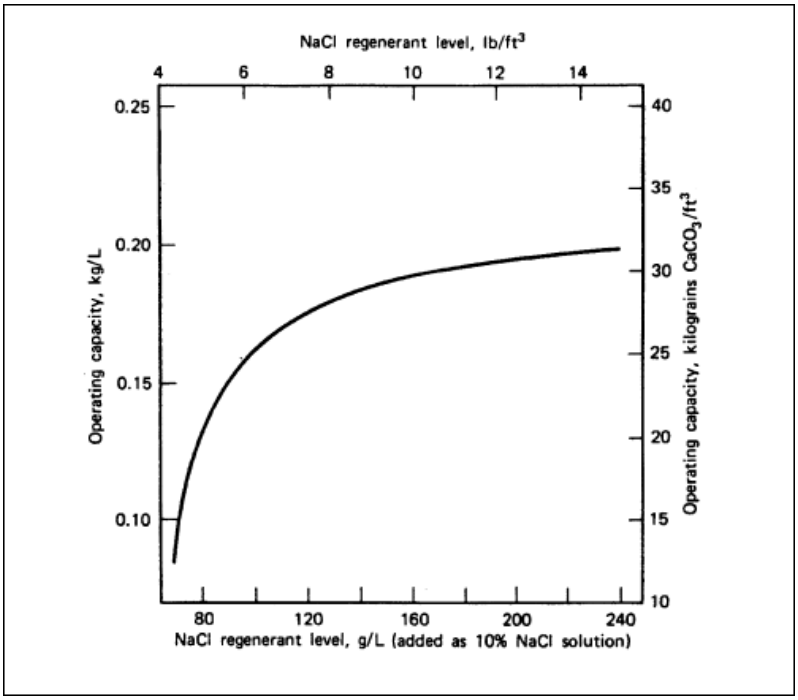

Figure 3: Operating Capacity vs. Regenerant Level for Sodium-Cycle Operation, Sulfonic Acid Resin

Swelling. Water swelling of an ion exchanger is primarily a hydration of the fixed ionic groups and increases with an increase in capacity to the limits imposed by the polymer network. Resin volumes change with conversion to ionic forms of differing degrees of hydration; thus, for a cation exchanger, there is a volume change with the monovalent ion species, $Li^+ > Na^+ > K^+ > Cs^+ > Ag^+$. With polyvalent ions, hydration is reduced by the cross-linking action; therefore, $Na^+ > Ca2^+ > Al^{3+}$. In more concentrated solutions, less water is taken up owing to greater osmotic pressure.

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Chemical Properties of Resins (Cont.)

Selectivity. Ion exchange reactions are reversible. By contacting a resin with an excess of electrolyte (B^+ in the following reaction), the resin can be converted entirely to the desired salt form:

$$\overline{R}A^+ + B^+ \rightarrow \overline{R}B^+ + A^+$$

However, with a limited quantity of B^+ in batch contact, a reproducible equilibrium is established which is dependent on the proportions of A^+ and B^+ and on the selectivity of the resin. The selectivity coefficient, KB, for this reaction is given by:

$$K_A^B = \frac{m_B}{\overline{m}_A} \cdot \frac{m_A}{m_B}$$

where m and m refer to ionic concentrations in solution and resin phase, respectively. Resin selectivity coefficients have been determined for a range of ionic species and related to H^+ for cations and OH– for anions, which are assigned selectivity values of 1.00.

Kinetics. The speed with which ion exchange takes place. The ion exchange process involves diffusion through the film of solution that is in close contact with the resins and diffusion within the resin particle. Film diffusion is rate-controlling at low concentrations and particle diffusion is rate-controlling at high concentrations. Whether film diffusion or particle diffusion is the rate- controlling mechanism, the particle size of the resin also is a determining factor. Uniform particle sized resins exhibit enhanced kinetic performance compared to conventional polydispersed resins due to the absence of kinetically slow larger beads.

Stability. Strong oxidizing agents, such as nitric or chromic acid, rapidly degrade ion exchange resins. Slower degradation with oxygen and chlorine may be induced catalytically. For this reason, certain metal ions, for example, iron, manganese and copper, should be minimized in an oxidizing solution. With cation exchangers, attack is principally on the polymer backbone. Highly cross-linked cation resins have an extended useful life because of the great number of sites that must be attacked before swelling reduces the useful volume-based capacity and produces unacceptable physical properties, for example, crush strength reduction and pressure drop increase. With anion exchangers, attack first occurs on the more susceptible functional groups, leading to loss of total capacity and/or conversion of strong base to weak base capacity.

The limits of thermal stability are imposed by the strength of the carbon-nitrogen bond in the case of anion resins. This strength is sensitive to pH and low pH enhances stability. A temperature limitation of 60°C (140°F) is recommended for hydroxide cycle operations. Cation resin stability also is dependent on pH; the stability to hydrolysis of the carbon-sulfur bond diminishes with a lowering of pH. They are much more stable than anions however and can be operated up to 150°C (300°F).

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Resin Structure and Manufacture

The manufacture of ion exchange resins involves the preparation of a cross-linked bead copolymer followed by sulfonation in the case of strong acid cation resins, or chloromethylation and the amination of the copolymer for anion resins.

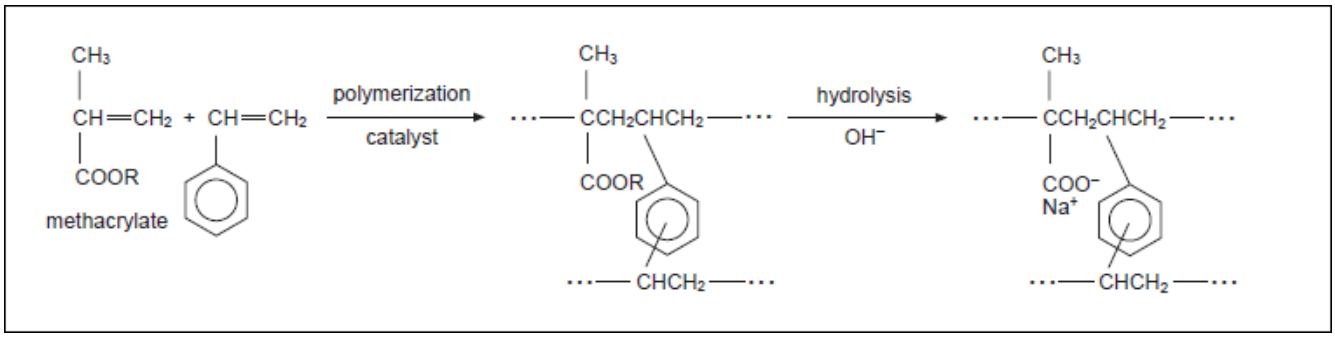
Cation Exchange Resins. Weak acid cation exchange resins are based primarily an acrylic or methacrylic acid that has been cross- linked with a di-functional monomer (usually divinylbenzene [DVB]). The manufacturing process may start with the ester of the acid in suspension polymerization followed by hydrolysis of the resulting product to produce the functional acid group.

Weak acid resins have a high affinity for the hydrogen ion and are therefore easily regenerated with strong acids. The acid-regenerated resin exhibits a high capacity for the alkaline earth metals associated with alkalinity and a more limited capacity for the alkali metals with alkalinity. No significant salt splitting occurs with neutral salts. However, when the resin is not protonated (e.g., if it has been neutralized with sodium hydroxide), softening can be performed, even in the presence of a high salt background.

Strong acid resins are sulfonated copolymers of styrene and DVB. These materials are characterized by their ability to exchange cations or split neutral salts and are useful across the entire pH range.

Anion Exchange Resins. Weak base resins do not contain exchangeable ionic sites and function as acid adsorbers. These resins are capable of sorbing strong acids with a high capacity and are readily regenerated with caustic. They are therefore particularly effective when used in combination with a strong base anion by providing an overall high operating capacity and regeneration efficiency.

Strong base anion resins are classed as Type 1 and Type 2. Type 1 is a quaternized amine product made by the reaction of trimethylamine with the copolymer after chloromethylation.



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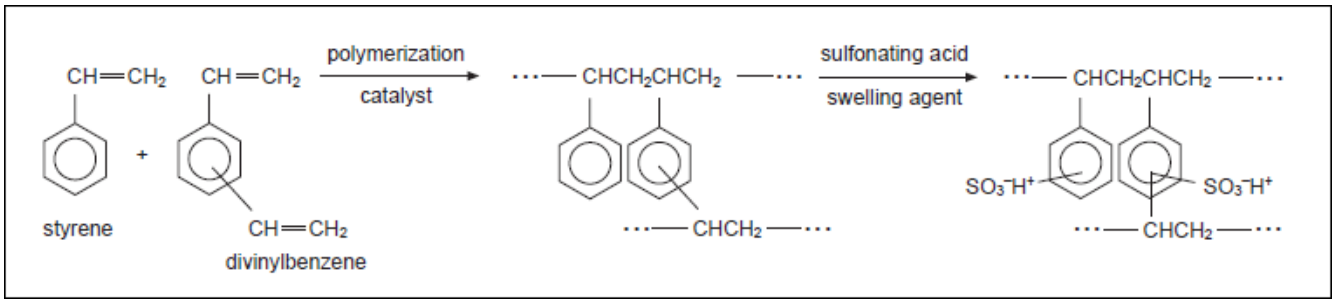

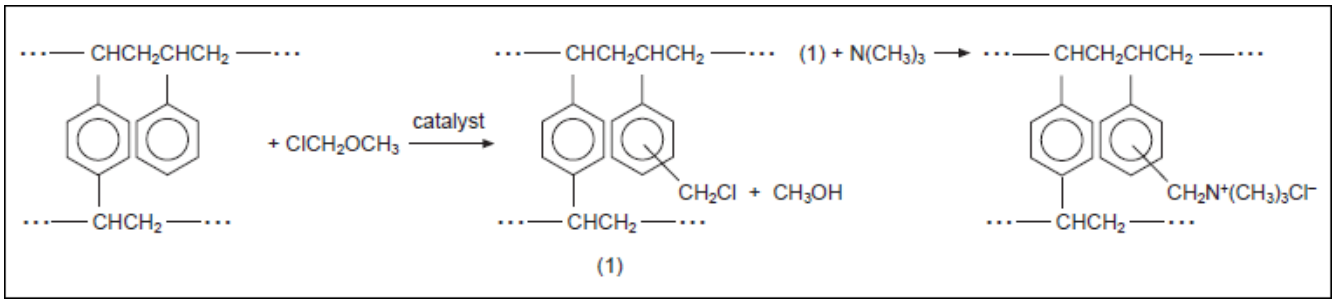

The Type 1 functional group is the most strongly basic functional group available and has the greatest affinity for the weak acids such as silicic acid and carbonic acid, that are commonly present during a water demineralization process. However, the efficiency of regeneration of the resin to the hydroxide form is somewhat lower, particularly when the resin is exhausted with monovalent anions, such as chloride and nitrate. The regeneration efficiency of a Type 2 resin is considerably greater than that of Type 1. Type 2 functionality is obtained by the reaction of the styrene-DVB copolymer with dimethylethanolamine. This quaternary amine has lower basicity than that of the Type 1 resin, yet it is high enough to remove the weak acid anions for most applications. The chemical stability of the Type 2 resins is not as good as that of the Type 1 resins, the Type 1 resins being favored for high temperature applications.

Other Functional Groups. Ion exchange resins with special functional groups have been made for specific applications. Of interest to the hydrometallurgical industry are a variety of resins having chelating ability and which are particularly applicable for the selective exchange of various heavy metals from alkaline earth and alkali metal solutions[2].

Polymer Matrix. The structure and porosity of an ion exchange resin are determined principally by the conditions of polymerization of the backbone polymer. Porosity determines the size of the species, molecule or ion, that may enter a specific structure and its rate of diffusion and exchange. There also is a strong interrelationship between the equilibrium properties of swelling and ionic selectivity.

For example, a conventional gel type, styrenic ion exchanger is built on a matrix prepared by co-polymerizing styrene and DVB. In these systems, porosity is inversely related to the DVB cross-linking. Gel resins exhibit microporosity with pore volumes typically up to 10 or 15 Ångstroms.

Resin Structure and Manufacture (Cont.)

Macroporous (macroreticular) ion exchange resins have pores of a considerably larger size than those of the gel type resins with pore diameters up to several hundred Ångstroms. Their surface area may reach 500 m^2/g or higher. Macroporous polymers are generally highly cross-linked and therefore exhibit little volume change (swelling). Because of the high cross-linkage in the matrix, the apparent oxidation stability of macroporous resins is improved. However, at similar cross-linkages, macroporous resins have greater exposure to potential oxidants than gel resins due to their greater porosity and surface area.

Poorer regeneration efficiencies, lower capacities and higher regeneration costs are the penalties paid for the use of the macroporous resins. Macroporous resins may be used as catalysts, particularly in non- polar media where gel resins do not perform satisfactorily because of their inaccessibility to the reactants.

Ion Exchange Regeneration Technologies

Ion exchange regeneration technology has developed over the years from the early co-flow regenerated systems to counter-flow block systems and through to packed bed technology, including the UPCORE™* process. Counter-current regeneration systems have reduced chemical costs, improved water quality and less waste volumes compared to traditional co-flow regenerated systems. They are also more productive, utilizing smaller vessels, faster regenerations and fewer mechanical failures.

Co-Current Regeneration System. This is the simplest system where a resin is regenerated in the same direction as the service flow (downwards). The vessel has a large freeboard to allow expansion of the resin bed when backwashing is carried out to remove suspended solids and resin fines.

Counter-Current Regeneration Systems. In these systems, the regenerant is applied in the opposite direction to the service flow. This has the advantage of providing better water quality (lower ionic leakage), higher chemical efficiency and reduced waste water. In order to obtain low leakage levels from a counter-flow regenerated resin system, the contaminating ions must be kept from the effluent end of the column during re-generation and rinse. This requires avoidance of conditions that would disrupt the resin bed configuration. Backwash frequency also must be minimized.

The difference between ion leakage for co-current and counter-current regeneration is illustrated in Figure 4. Re-exchange of the contaminating Na^+ ion occurs from the base of the co-flow regenerated bed when the incoming salt solution (feed) is converted to the corresponding dilute acid. When this acid solution contacts the sodium ion, re-exchange of hydrogen ions for sodium ions occurs and the sodium ions exit the column as leakage (Figure 4a). Leakage in counter-flow regeneration is substantially reduced as the resin bed is predominantly in the regenerated form at the bottom of the vessel Figure 4b).

Ion Exchange Regeneration Technologies (Cont.)

There are two main types of counter-current systems:

Blocked Systems. This includes air hold down, water hold down and inert mass blocked. The service flow is downwards and regeneration upflow. To avoid disturbance of the resin polishing zone at the bottom of the vessel, the resin bed is held down (blocked) during regeneration by air pressure, water flow or an inert mass in the top part of the vessel. The regenerant passes up through the resin and out of a collector system in the middle part of the vessel.

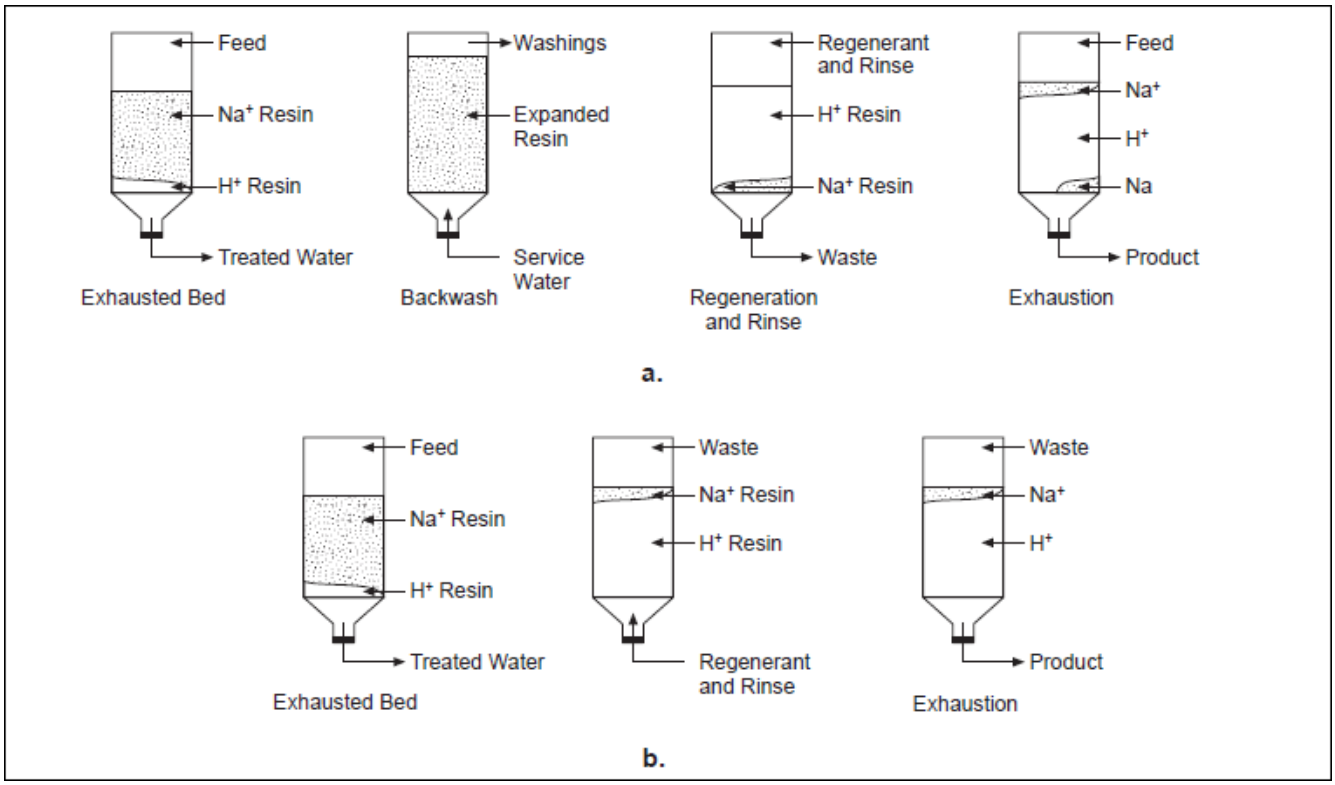

Figure 4: Ion Leakage: a. Co-flow and b. Counterflow Regenerated Fixed-Bed Column Contractors (H+ Form Cation Resin; Na+ Removal)

Packed Bed Systems. These may be up-flow service with down-flow regeneration or down-flow service with up-flow regeneration, such as the UPCORE™ system.

Semi-Continuous and Continuous. Semi-continuous and continuous contactors operate as intermittently moving packed beds as typified by the Higgins contactor[3] or as fluidized staged (compartmented) columns such as the Himsley contactor[4-6]. Flow is counter-current, and their use is in increased resin utilization and high chemical efficiency. Commercial installations include those for phosphoric pickle acid recovery, water softening and ammonium nitrate recovery.

Resin Applications

Water Softening. Water softening accounts for the major tonnage of resin sales. Hard waters, which contain principally calcium and magnesium ions, cause scale in power plant boilers, water pipes and domestic cooking utensils. Hard waters also cause soap precipitation which forms an undesirable gray curd and a waste of soap. Water softening involves the interchange of hardness for sodium on the resin. Typically, hard water is passed through a bed of a sodium cation exchange resin and is softened.

$$2\overline{R}Na^{+} + Ca^{2}+ \rightarrow \overline{R}_2Ca^{2+} + 2Na^{+}$$

Regeneration of the exchanger involves the passage of a fairly concentrated (8-12 percent) solution of sodium chloride through the resin.

$$\overline{R}_2Ca^{2+} + 2Na^{+} \rightarrow 2\overline{R}Na^{+} + Ca^{2+}$$

Dealkalization. Many industrial processes require that hardness and alkalinity be removed from a raw water before the water is used in the process. Two main processes involving ion exchange are used for dealkalizing:

1. Dissolved solids are removed to the extent of the alkalinity in the raw water by passing the raw water through a bed of weak acid cation resin in the hydrogen form. The 100 percent utilization of regenerant acid that is characteristic of this process decreases operating costs and greatly minimizes the waste disposal problem. A weak acid cation resin creates no free mineral acidity in the effluent when regenerated at a level of not more than 105-110 percent of the theoretically required amounts for the cations picked up.
2. Chloride anion dealkalizing involves passing the raw water through a Type 2 anion exchange resin that is in the chloride form to remove alkalinity.

Demineralization. Ion exchange demineralization[7] is a two step process involving treatment with both cation and anion exchange resins. Water is passed first through a column of strong acid cation exchange resin that is in the hydrogen form ($\overline{R}H^{+}$) to exchange the cation in solution for hydrogen ions:

$$\overline{R}H^{+} + C^{+} \rightarrow \overline{R}C^{+} + H^{+}$$

where C^{+} represents common cations, for example, Ca^{2+}, Mg^{2+} and Na^{+}. This effluent is passed to a column of anion exchange resin in the hydroxide form $\overline{R}\,OH^{-}$) to replace anions in solutions with hydroxide:

$$\overline{R}OH^{-} + A^{-} \rightarrow \overline{R}A^{-} + OH^{-}$$

where A^{-} represents common anions, for example, Cl^{-}, SO_4^{2-} and NO^{3-}.

The hydrogen ions from the cation resin neutralize the hydroxide ions from the anion resin:

$$H^{+} + OH^{-} \rightarrow H_2O$$

The net effect is the removal of electrolytes and a yield of purified water.

Resin Applications (Cont.)

Alternatively, the impure water may be passed through an intimately mixed bed of cation and anion exchange resins where both types of exchange occur simultaneously:

$$\overline{R}H^+ + \overline{R}OH^- + C^+A^- \rightarrow \overline{R}C^+ \overline{R}A^- + H_2O$$

The choice of the ion exchange system for demineralization depends on the water quality desired, operating and capital economics and composition of the raw water.

Condensate Polishing. Single or mixed bed ion exchange resins are used in deep bed filter demineralizers for reduction of particulate matter and dissolved contaminants in utility power plant condensates.

Ultra Pure Water. Ultra pure water (UPW) is essential to the proper fabrication of integrated circuit boards in the semiconductor industry. As the degree of integration becomes increasingly more complex, the semiconductor industry requires higher levels of water purity. Single beds, mixed beds and also reverse osmosis are used in the production of ultra pure water.

Nitrate Removal. Ion exchange is used for the removal of nitrates from nitrate polluted waters[8]. Strong base anion exchange resins operating in the chloride ion form (salt solution regenerated) have been successfully used for this service.

Waste Treatment – Radioactive. Radiation waste systems in nuclear power plants include ion exchange systems for the removal of trace quantities of radioactive nuclides from water that will be released to the environment. The primary resin system used is the mixed bed.

Chemical Processing – Catalysis. Since ion exchange resins are solid, insoluble (but reactive) acids, bases, or salts, they may replace alkalis, acids and metal ion catalysts in hydrolysis, inversion, esterification, hydration or dehydration, polymerization, hydroxylation and epoxidation reactions. The advantages of ion exchange resins as catalysts include easy separation from the products of reaction, repeated reuse, reduction of side reactions and lack of need for special alloys or lining of equipment.

Purification. Purification by ion exchange is used to remove contaminating acids, alkalis, salts or mixtures from non-ionized or slightly ionized organic or in-organic substances. Examples include formic acid removal from 50 percent formaldehyde solutions, removal of amines from methanol, removal of iron from steel pickling operations, purification of aluminum bright dip baths and removal of iron in the purification of hydrochloric acid[9].

Metal Extraction, Separation and Concentration. In aqueous or solvent mixtures containing large amounts of contaminants and small amounts of a desired solute, ion exchange resins can be used to selectively isolate and concentrate the desired solute, for example, the recovery of uranium from sulfuric acid leach solution with strong base anion resins. Other specific chelating resins can be used for metals recovery such as copper, nickel, cobalt and precious metals.

Resin Applications (Cont.)

Desiccation. Ion exchange resins, particularly strong acid cation exchange resins in the dry state, are useful as desiccants[10]. Ion exchange resins show their greatest capability as desiccants in the drying of hydrophobic solvents, for example, hydrocarbons and chlorinated hydrocarbons.

Sugar Separations and Purifications. Ion exchange resins are used as an integral part of corn syrup, high-fructose corn syrup (HFCS) processing and other starch-based syrups. In sucrose processing, the resins are often used for softening feed streams, recovering sugar from molasses streams, or decolorization. They are also used in the production of non-nutritive sweeteners such as sorbitol or mannitol. Resins and adsorbents are used in four major unit processes in corn sweetener processing: deashing, chromatographic separation of glucose and fructose, mixed bed polishing and color removal. In deashing, a bed of strong acid cation resin is typically followed by a bed of weak base anion resin. The resins used are macroporous, as their large porous structure allows syrup components to move freely into the bead.

Chromatographic Separation. Chromatographic separation is a manufacturing process using ion exchange resins to separate one dissolved component from another. It is applied in the sugar industry for the purification of compounds such as sucrose, glucose, fructose, oligosaccharides, sorbitol and mannitol. It can be used to separate salt from glycerol and in purifying amino acids and various organic acids. Most industrial chromatography today utilizes simulated moving bed (SMB) technology to minimize solvent use, leading to a significantly reduced cost of operation when compared to traditional batch chromatography.

Pharmaceuticals and Fermentation. Ion exchange resins are useful as carriers for medicinal materials and in slow release applications. In some cases, the ion exchange resin has the medicinal affect desired, for example, Cholestyramine, a dried and ground strong base anion resin used to bind bile acids for reducing blood cholesterol. Ion exchange resins also are used in a variety of fermentation and biotechnology processes, such as the isolation and purification of lysine, streptomycin and neomycin and other similar antibiotics.

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