

Sybron Chemicals Inc.

IONAC®
ION-EXCHANGE
RESINS

**INTRODUCTION TO
INDUSTRIAL
ION EXCHANGE**

by
F. X. McGarvey

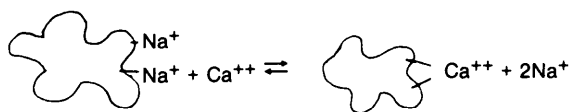
**Sybron Chemicals Inc.
Birmingham, New Jersey**

INTRODUCTION TO INDUSTRIAL ION EXCHANGE

Ion exchange is a natural phenomenon occurring continually in inorganic substances and in living bodies on the earth's surface. Apparently, ion exchange materials were used in biblical times to remove salts and poisons from water. However, the first scientific observations of the phenomenon were reported by Thomas and Way, English agriculturists. Various minerals called permutites were discovered and industrial use for water softening was started about 1906.

Prior to 1940, synthetic gel zeolites and sulfonated coal were produced at the present location of Sybron Chemicals Inc. at Birmingham, New Jersey. In the middle 1940's, a cooperative agreement with American Cyanamid resulted in purchase of rights to produce organic ion exchangers under the trade name Ionac. Since that time, research and development in new polymer structures has continued, resulting in a complete series of modern ion exchange resins.

The ion exchange reaction can best be described as the interchange of ions between a solid phase and a liquid surrounding the solid. Initially, ion exchange was confined to surface reactions, but these were gradually replaced by gel type structures where the exchange sites were available throughout the particle. The process is shown graphically as follows:



The Ion Exchange Reaction

The sites exhibit affinity for certain ions over others and this phenomenon is very helpful in removing objectionable ionic materials from process streams. The affinity relationships have been the subject of many papers and certain simple rules have been developed. First, ions with multiple charges are held more strongly than those of lower charge. Ions with the same charge are held according to their atomic weight with the heavier elements held more strongly. Some affinity relationships follow:

Cation Exchangers

Monovalent—Cs > Rb > K > Na > Li

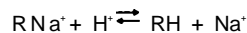
Divalent—Ra > Ba > Sr > Ca > Mg ≫ Na

Anion Exchangers

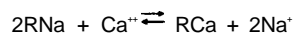
Monovalent—I > Br > NO₃ > Cl > HCO₃ > F > OH

Divalent—CrO₄ > SO₄ > CO₃ > HPO₄

The affinity relationship can also be expressed by equilibrium (selectivity) equations based on the reversibility of ion exchange reactions and the law of mass action.



and for the divalent-monovalent reactions



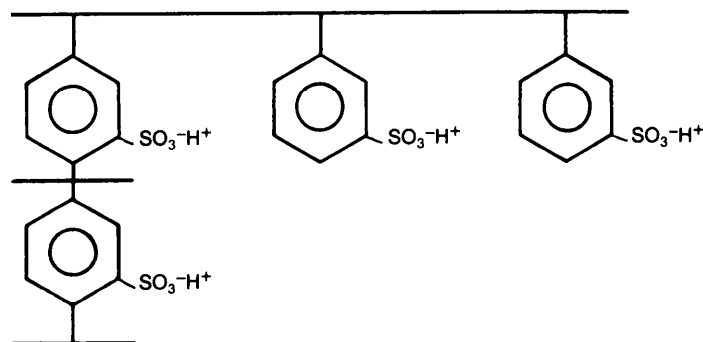
$$K_{\text{Ca}} = \frac{[\text{RCa}] [\text{Na}^+]^2}{[\text{RNa}]^2 [\text{Ca}^{++}]}$$

$$KQ = \frac{y(1-x)^2}{x(1-y)^2}$$

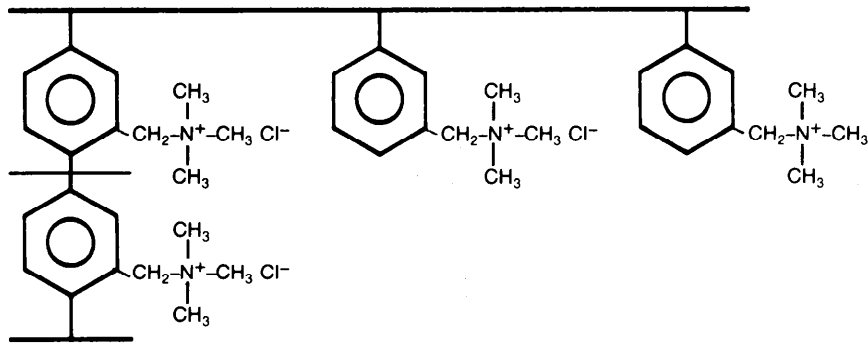
In these equations, the brackets represent concentration of ions in the resin and in the liquid phase. The y, x notation expresses the reactions as equivalent ratios. For the divalent-monovalent reaction, Q is the resin capacity and C_o is the total concentration of the electrolyte in solution. These equations can be plotted, usually as y vs x plots, to give an understanding of the exchange processes occurring in the exchange zone or in a batch contactor.

NATURE OF EXCHANGE SITE

Modern ion exchange materials are prepared from synthetic polymers such as styrene-divinylbenzene copolymers which have been sulfonated to form strongly acidic cation exchangers, or aminated to form strongly basic anion exchangers. Weakly basic anion exchangers are similar to the strong base except for the choice of amines. Weakly acidic cation exchangers are usually prepared from crosslinked acrylic copolymers. Typical examples are shown in the following structural diagrams:

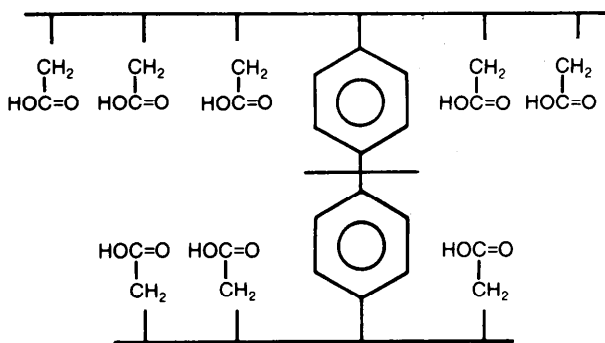
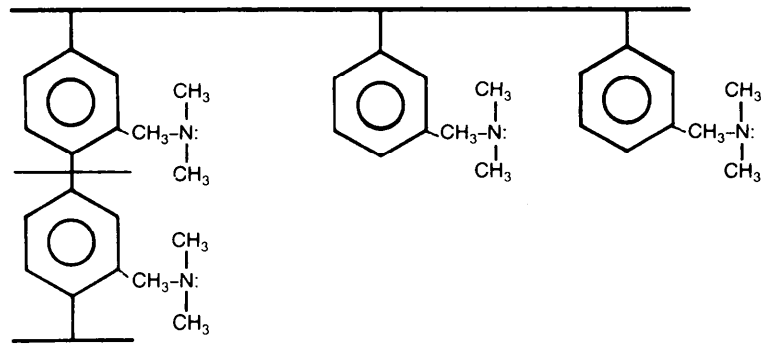


Strong Acidic Cation Exchanger Structure (Styrene-Divinylbenzene Matrix)



Strong Base Type 1 Anion Exchanger Structure (Styrene-Divinylbenzene Matrix)

Weakly Basic Anion Exchanger Structure (Styrene-Divinylbenzene Matrix)



Weakly Acidic Cation Exchanger Structure (Acrylic Divinylbenzene Matrix)

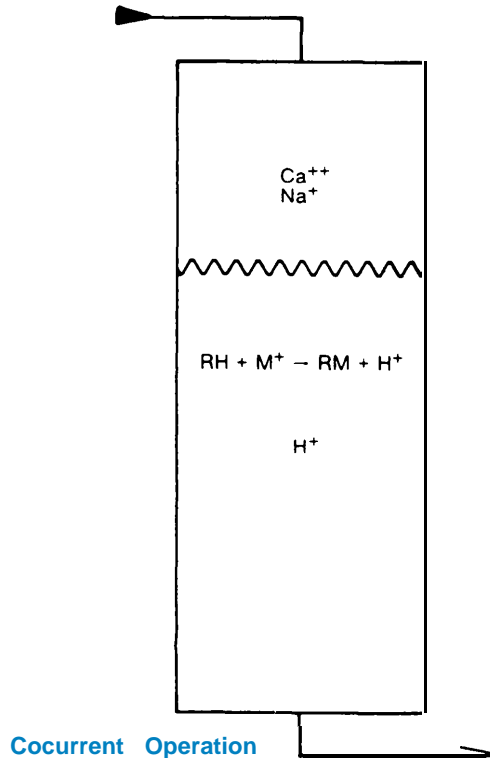
These exchange sites have chemical properties quite similar to those expected from analogous monomeric compounds in solutions. For example, the strong acid cation exchanger in the hydrogen form as shown in the diagram has a titration curve quite like that of sulfuric acid. On the other hand, the weakly acidic cation exchanger gives a titration curve rather like acetic acid. The exact acid strength is influenced by the nature of polymer matrix crosslinkage and steric factors caused by the polymer.

The strongly basic anion exchangers when in the OH⁻ form give titration curves similar to NaOH. Depending on the amine, the weakly basic and intermediate basic anion exchangers give curves which do not show significant inflection points in their titration curves. Generally they show very little exchange capacity above pH 8 or 9.

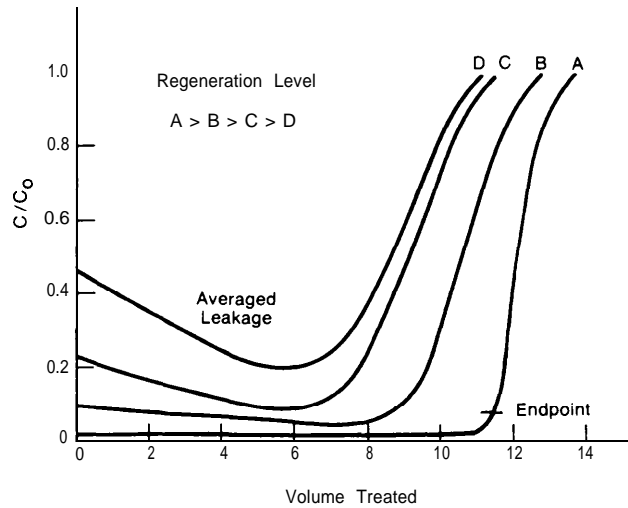
PROCESS APPLICATION

Ion exchange processes are usually practiced in columns which were initially designed in a fashion similar to gravity filters. Modern ion exchange still employs columns which now have well defined distribution systems and may be operated in either a cocurrent or countercurrent fashion, the cocurrent operation still the most prevalent.

The cocurrent column employs downflow for both exhaustion and regeneration. The process follows the schematic shown.



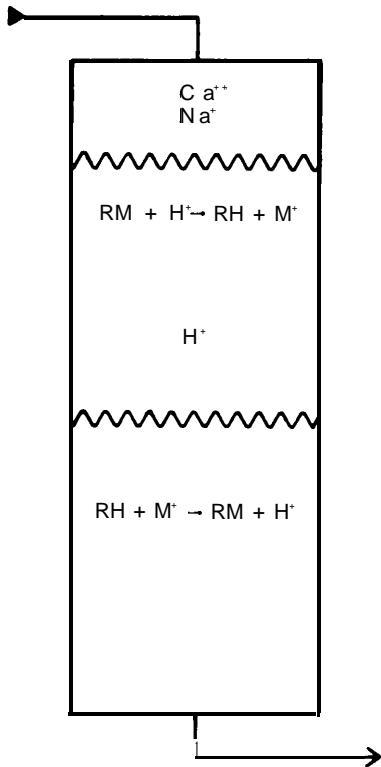
Cocurrent operation leaves a residue of ions from the previous regeneration. In the case shown, the hydrogen ion generated during exchange in the upper portion of the bed (the exchange zone) will tend to strip the ion with least affinity which is held in the residual zone at the exit of the bed. The site of the residual zone depends on the regeneration level and the amount employed. Typical leakage curves due to sodium leakage in the hydrogen cycle are shown in the following curves.



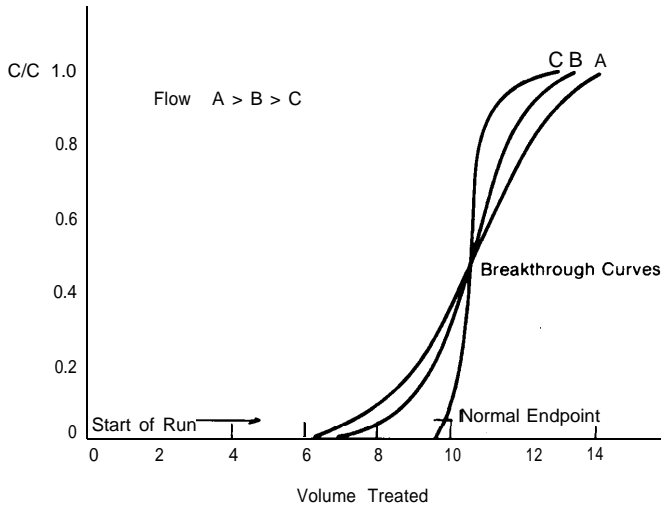
Typical Cocurrent Exhaustion Curves

Recent years have seen the development of countercurrent regeneration techniques where the regeneration is applied in a flow opposite from the feed flow, usually upflow. This obvious technique was held up for many years due to difficulty in holding the bed in place during regeneration. This has been accomplished by use of inert fillers above the bed, by gas pressure and most commonly by a counter flow of water to hold the bed in place. The reactions expected in a countercurrent operation are shown in the following diagram.

Since there are no residual ions at the exit portion of the bed, the bed will not leak and breakthrough curves similar to those shown for typical countercurrent exhaustion can be achieved.



Countercurrent Operation



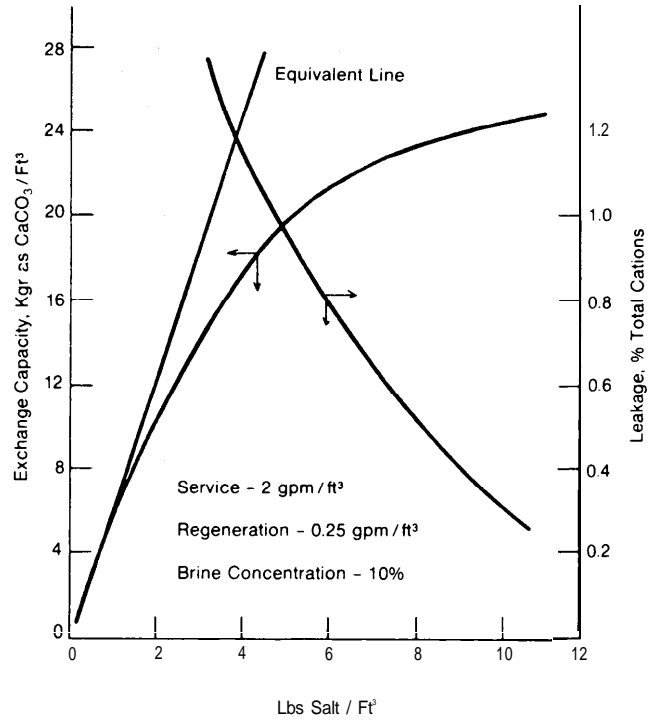
Typical Countercurrent Exhaustion Curves

Previously the concept of regeneration has been mentioned indicating that it is possible to **reverse** the exchange reactions as shown in the following equations representing softening of water.



These reactions show that the divalent cations

are exchanged effectively for sodium on the column. If the reaction were not reversible, no water softening would be possible. Fortunately, concentrated sodium chloride, about 10% usually, can reverse the reaction and the bed can be used over and over again. For this reaction, about twice as much sodium chloride is required as hardness removal from the bed. Typical results for softening are given in the following graph.



Typical Loading Curve-Softening Cycle

While ion exchange processes are used in many applications, the main use continues to be water treatment. The four major classes of the commercially available ion exchange materials are used in a variety of arrangements depending on the composition of substances in the water supply, the flow demand and the effluent requirement. The water composition is basic to the design and determines the proper way to produce the desired effluent. Flow is important to the size of the plant and may dictate the way in which the water is treated.

A typical water analysis is shown in the following table:

Composition of a Typical Water

Composition	ppm as Ion	Conversion Factor	ppm as CaCO ₃	Equivalents Per Million**
Calcium	45	2.500	113	2.26
Magnesium	20	4.107	82	1.64
Sodium	30	2.174	65	1.30
Total Cations	-		260	5.20
Chloride	50	1.408	70	1.40
Sulfate	68	1.042	71	1.42
Bicarbonate	146	0.820	120	2.40
Silica	11	0.833	9*	0.18
Total Anions			261	5.22

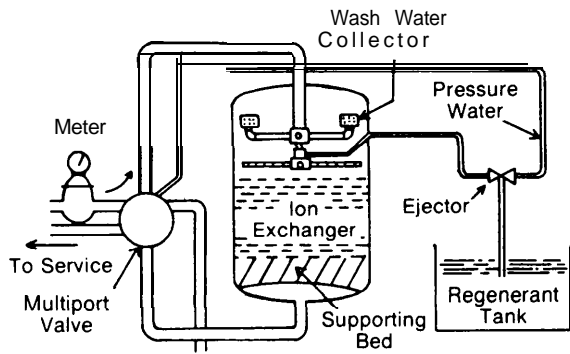
*Silica may be present as (SiO₃)_x and may not have any cations associated with it

**Typical conversion

$$\text{ppm [Ca]} = 45 \left(\frac{50}{20} \right) \frac{112.5}{50} \text{ ppm as CaCO}_3 = 2.25 \text{ eq./million}$$

The major cations and anions are listed and shown to equal each other. In practice, water composition may not add up due to methods of analysis and matters related to pH and dissolved gases. The method of conversion is shown in the example. In the United States the unit parts per million as calcium carbonate is used almost exclusively.

The ion exchange process is usually performed in some type of column. Beds are usually between two and eight feet in depth and may be as large as 12.5 feet in diameter. The various components involved in the equipment are shown in the cutaway figure.



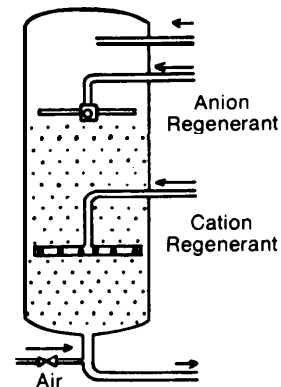
Single-Bed Ion Exchange Unit

This unit is a typical manual softener, but completely automatic units are commonly used in the modern systems. Units of this design are used also in deionization processes where they are joined in various combinations depending on the water composition.

There are exceptions to these cocurrently operated units. These involve countercurrent flow of the regenerants while the bed is held in place hydraulically or by other restrictions. In addition

to countercurrent operations, there are several modifications employing layered bed concepts with weak acid resin layered on top of the strong acid resins or weak base resins on top of strong base resins. These units may be practically regenerated upflow depending on the purpose of the process.

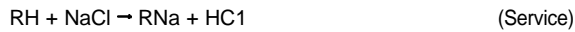
High purity water, treatment of nuclear process waters and other uses are frequently accomplished by use of mixed bed units where the anion and cation components are held in the same unit. They are separated to regenerate and mix usually with air or inert gas for service. A schematic drawing of a mixed bed is shown in the figure.



Mixed Bed Ion Exchange Unit

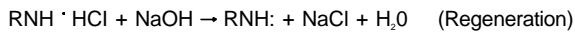
The reactions involved in the deionization of demineralization processes are similar to those mentioned previously for softening.

Cation Exchange Step

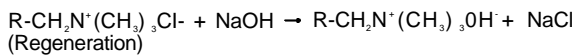
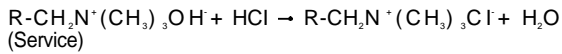


Anion Exchange Step

Weak Base

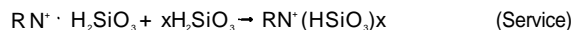
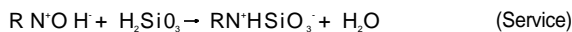


Strong Base

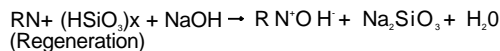


These equations show that the cation exchanger coupled with an anion exchange bed can remove all cations and anions producing an effluent which can be classed as a demineralized or deionized water. To achieve removal of silica, the strong base resins are required. These reactions are summarized in the following equations:

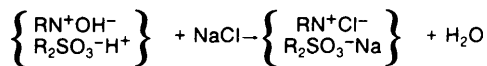
Silica Removal



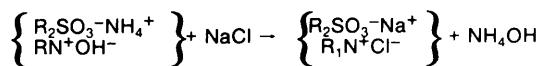
Silica Regeneration



The mixed bed reactions are similar to the previous ones except that they occur in localized areas in the column so that they go to completion with water as the chief product:



An interesting application of mixed bed processes involves the use of certain forms of the individual components to yield products which act as corrosion control agents and also nuclear moderators in reactors. The following equation illustrates these processes:

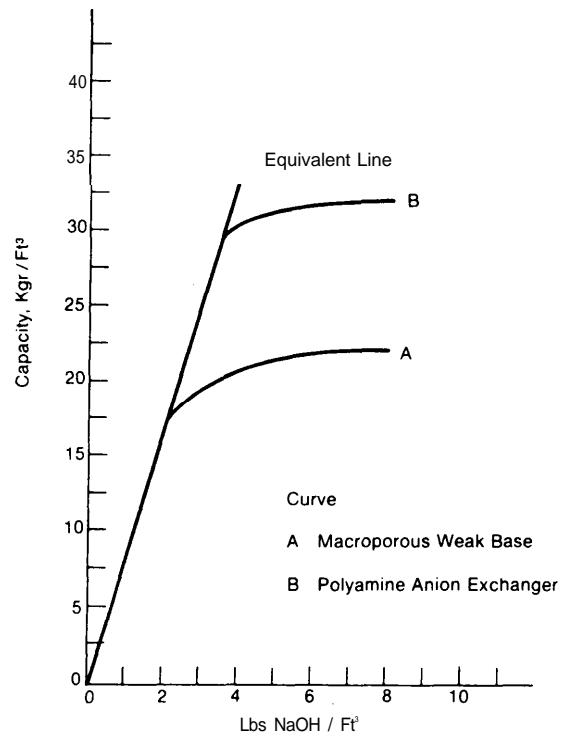


where ammonium hydroxide equivalent to the amount of sodium chloride removed will be generated in the effluent.

The design of equipment for ion exchange processes needs a knowledge of capacity, regenerant requirements, flow rate limitations and several other factors. Loading curves, i.e. capacity as a function of regenerant consumption, has been used for the softening process. Similar curves are also obtained for the use of sulfuric acid and hydrochloric acid.

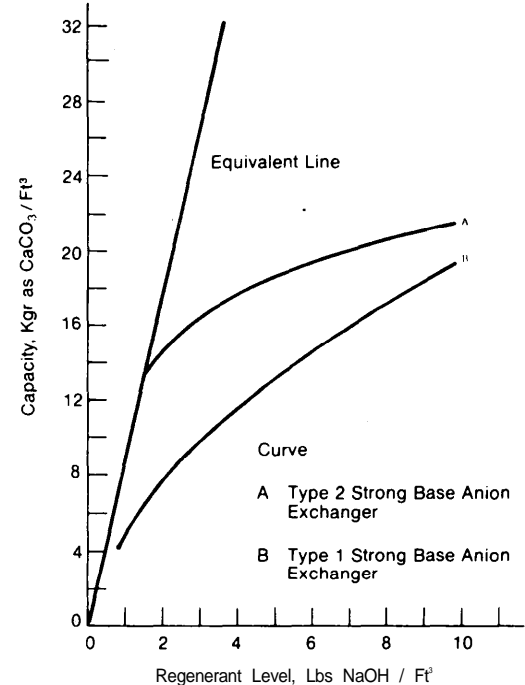
The anion exchanger beds are also rated on

capacity and regenerant consumption. Weakly basic anion exchangers are regenerated very efficiently with alkali solutions including ammonia. The relationships are shown in the following figure.



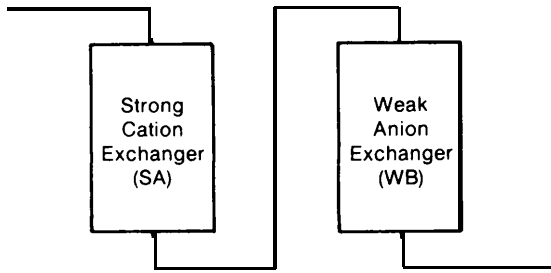
Capacity of Weakly Basic Anion Exchanger as a Function of Regenerant Consumption

The strongly basic anion exchangers are less efficiently regenerated using only caustic. Typical loading curves are shown in the following figure.



Capacity of Strong Base Anion Exchangers as a Function of Regeneration Level

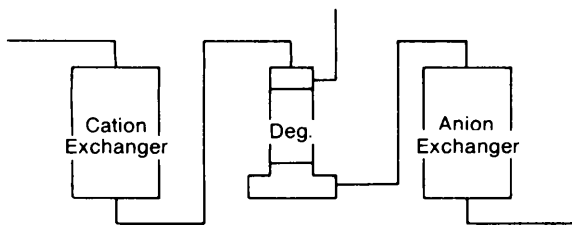
The arrangement of cation and anion exchangers in the process depends largely on the components in the water, but they can be classified in several typical process arrangements. These are discussed in the following sections.



Typical Two Bed System

Configuration A

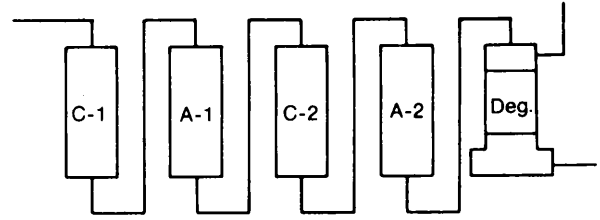
Configuration A is the typical two-bed system with no provision to reduce carbon dioxide generated by the cation exchanger. All equipment must be corrosion resistant. Rubber lined mild steel tanks are usually employed. Regeneration initiated when either the cation or anion exchanger shows breakthrough. Normally the cation exchanger will break first with a reduction in acidity entering the anion bed. Since the anion exchanger has no capacity for cations, these cations will leave the anion bed as some salt, usually bicarbonate. The conductivity will increase and the pH may show a slight increase on degassed samples. If the anion capacity is exceeded, the pH will show a decrease along with a conductivity increase.



Two Bed System with Degasification

Configuration B

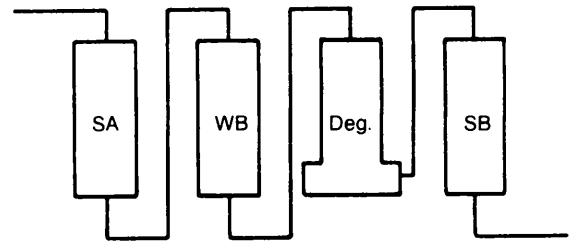
Configuration B shows the two-bed system with a degasification unit prior to the anion bed. This step reduces carbon dioxide content to about 5 ppm and avoids accumulation of gas in the anion bed. This will also reduce the pressure required on the pressurizing pumps. Since the degasification unit is operated either under a vacuum or at atmospheric pressure, it is necessary to install a pump after the degasification reservoir.



Four Bed System with Degasification

Configuration C

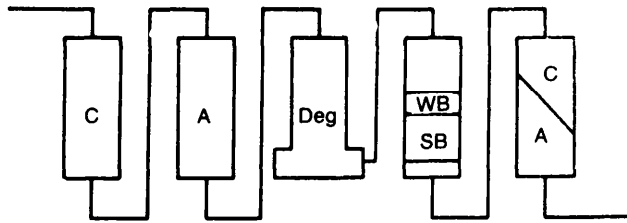
Configuration C shows a double set of strongly acidic cation and weakly basic anion columns operating in series. This arrangement is designed to provide reduced leakage when high solids waters are being treated. Various methods for regenerating the second unit with sufficient acid to provide a high level in that column and a reduced amount in the primary can be practiced. Sometimes a single weak base column will treat the effluent from a double cation column. Systems to recycle rinse waters are also practical.



Typical Three Bed Deionization Flow Sheet

Configuration D

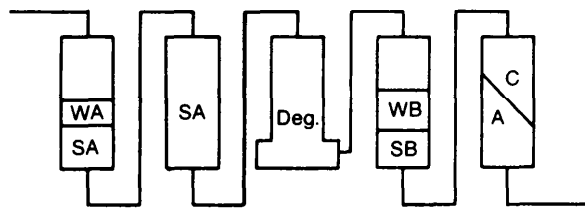
Configuration D shows a typical three-bed system with a degasifier. The weak base bed removes mineral acidity while weak acids are picked up on the strong base. Since strong base resins are exhausted by carbon dioxide, the degasifier should always be placed ahead of the strong base anion exchanger. In this plant, leakage from the cation exchanger would appear in the effluent as the hydroxide. The endpoint of the cycle would be usually based on silica leakage from the strong base resin.



Typical Deionization Process Sheet
with Mixed Bed Polisher

Configuration E

Configuration E shows a complex system with a weak base resin ahead of the degasifier and a layered bed after the degasifier and finally a mixed bed to polish the effluent. This system places special emphasis on protection of strongly basic anion exchanger from fouling with organic matter by using a weakly basic anion exchanger bed. Macroporous weak base resins are usually used in the layered bed due to their low density. Type 2 macroporous strong bases are also used in place of the layered bed.

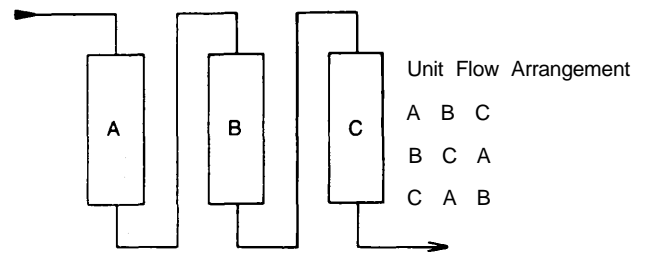


Typical Deionization Process with Layered Beds

Configuration F

Configuration F uses a layered bed of carboxylic and sulfonic cation exchangers ahead of a strongly acidic bed to increase regenerant efficiency. This system is followed by a degasifier, a layered bed of anion exchangers and a polishing mixed bed. Various other combinations can be selected depending on the water analysis and plant size.

Plants operating on high solids waters or those where continuous operations are needed can meet these demands with a merry-go-round concept where individual units or sets of units are operated in such a fashion that there is always sufficient capacity on stream to meet demand. The arrangement for a typical three-bed merry-go-round is given below.



Merry-go-round Processes

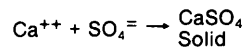
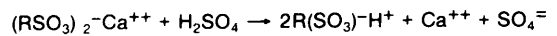
SPECIAL TOPICS

There are several problems which affect the performance of ion exchange resins in field use. The following sections will discuss some of these problems starting with the cation exchanger and following through the process. Some problems may be due to the resins, but the majority are related to mechanical failures in the equipment including leakage in the valves, failure in pump controls, etc. These are not discussed in these sections.

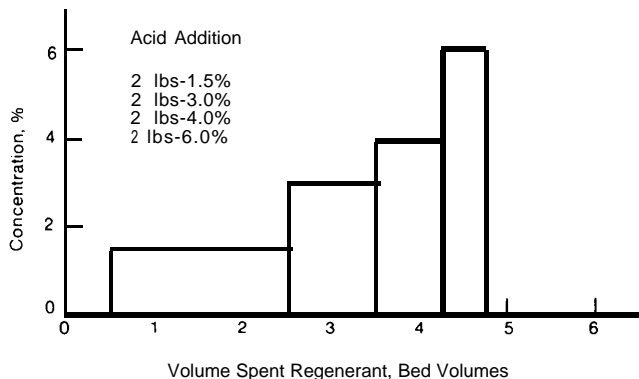
Cation Exchanger Problems

Cation exchangers are quite stable and with good treatment can last 20 years. They are subject to attack from oxidizing agents including chlorine, ozone, peroxide, high temperature oxygen, and others. Generally this will result in an increase in moisture content of the resin due to attack of the oxidant on the crosslinkage. The rate of degradation will depend on temperature, concentration of oxidant, presence of metals as well as crosslinkage of the resin.

A common problem with cation exchangers is the generation of calcium sulfate during regeneration with sulfuric acid. Avoiding this problem requires good control of acid strength reaching the bed. The following equation illustrates the problem:

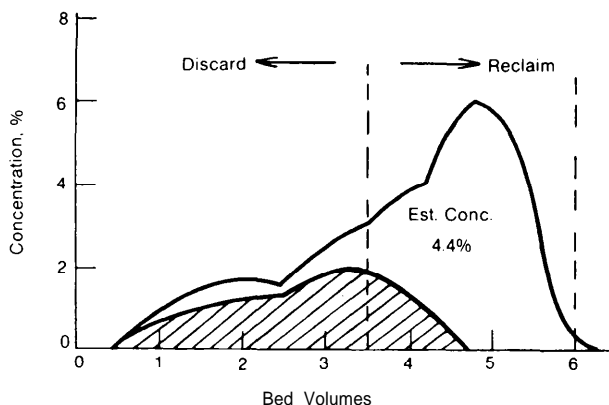


Calcium sulfate has a solubility of about 2000 ppm, but a certain amount of super saturation can exist in the spent regenerant provided the acid leaves the bed in about 15 minutes. By adding sulfuric acid initially at low concentration and gradually increasing strength, it is possible to have an effective regeneration. A typical program for this is shown in the figure below. Normally the flow is rapid initially and is decreased when the bed has been depleted of calcium.



Avoidance of Calcium Sulfate Precipitation

Acid saving is practical for cation exchangers and caustic saving for strong base anion exchangers. This procedure requires a knowledge of the composition of the spent regenerant so that the volume to be saved can be determined. A typical situation is given in the following figure. Generally about 40% of the acid can be recycled in a cocurrent process. Efficient countercurrent processes would not require a regenerant saving operation.



Acid Recovery

Anion Problems - Weak Base

Since these resins regenerate quite efficiently, there is a tendency to over regenerate which will result in long rinse and a waste of chemicals. These resins are also attacked by oxidants and will pick up organic substances. As the resins age, rinse volumes increase and may reach the point where the beds will not rinse to design quality. These resins can be expected to have a life of about 500,000 to a million gallons treated water volume per cubic foot.

Strong Base Resins

One of the chief demands on strong base resins is their ability to remove silica to low levels (less than 25 parts per billion). This requires that the resin retains strong base capacity throughout the design life of the bed. Methods to control leakage have been developed.

Silica leakage can be controlled and reduced to the parts per billion range by the use of warm (105-120°F) caustic with long contact and slow displacement. A regeneration process requiring about 90 minutes for caustic addition and displacement rinse is widely used. Under good conditions, silica leakages of less than 10 ppb can be guaranteed recognizing of course that the resin removes only dissolved silica. Field studies indicate that some strong base macroporous resins can reduce the concentration of colloidal silica by providing a surface which can retain the particles, probably by an electrostatic mechanism.

Another serious problem is the fouling of the strong base resins with organic materials resulting from the degradation of natural products, leaves, industrial waters, etc.

Organic fouling is a problem confined largely to strong base resins, although any resin can be fouled with various organic contaminants including oil. The commonplace organic fouling was first clearly demonstrated at the Barnstead Still and Sterilizer Laboratories in Boston about 1950. Boston water could not be processed successfully with mixed beds, while water from other sources could easily be treated. The problem grew from these tests to a worldwide one, particularly in northern climates where partially oxidized natural organic matter usually as a humic acid component existed in most supplies.

Organic fouling is observed as a gradual decrease in the pH of treated water accompanied by a serious drop in resistance values from 5 megohms-cm to less than 1 megohm-cm. Efforts to recover resin capacity include treatment with oxidants, particularly dilute sodium hypochlorite (bleach). Modern high surface porous resins have shown resistance to these problems. The fouling mechanism can be viewed as the gradual diffusion of large molecules into the resin polymer structure. Since the regeneration step is shorter in time than the exhaustion step, the molecules continue to accumulate in the bed. Reduction in organic contamination by coagulation, chlorination and carbon treatment will help the problem, but some organic fouling almost always occurs with surface waters. One source is the degradation products from the cation exchanger.

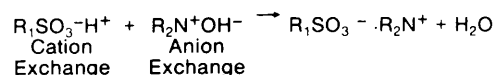
The life of strong base resins is related to thermal conditions. The Type 1 strong base is more resistant to degradation than is the Type 2 by a factor of at least two. These reactions tend to degrade the strong base group initially to weak base sites so that the ability to remove strong acids from chlorides and sulfates is normally not

reduced until the resin is seriously degraded. Usually the strong base groups will be lost and silica leakage will be noticeable. Recommendations on maximum operating temperature have been made so that there will be a balance between thermal life and operating cost. Usually Type 1 strong base resins will last for about 750,000 gallons water per cubic foot, while the Type 2 will last about 300,000 to 400,000 gallons water per cubic foot. In any case, specific operating conditions will have a bearing on resin life.

Mixed Bed Problems

The mixed beds have problems similar to those of the components. Since these resins are usually used for high purity polishers, slight changes in mixed bed performance will be noticed quickly. Operational steps are more complex since it is necessary to completely separate the resin components for regeneration. To do this properly, the bed must expand at least 100%. Also it should be possible to observe the separation and mixing in the unit.

One difficulty in mixed bed operation is known as clumping. This occurs when the resins are new and results in a condition where resin components are electrostatically attracted and cannot be separated. The following equation shows this effect:



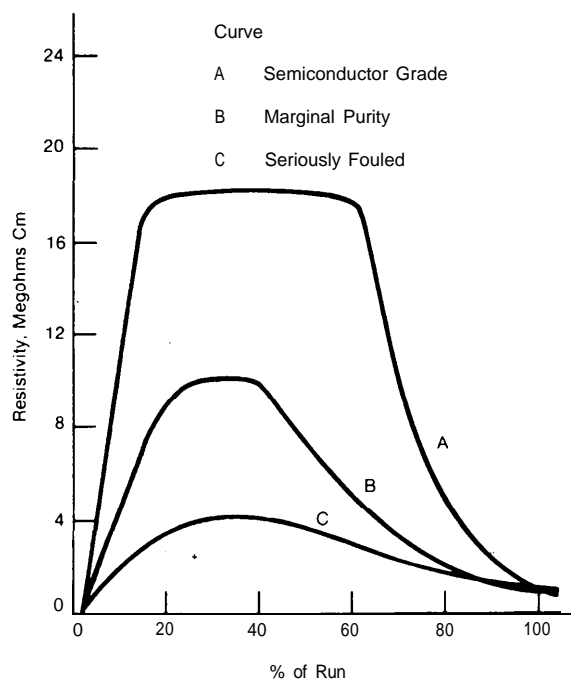
While this condition can be overcome by discharging the particles with a dilute salt solution, the problem may go undetected giving a very poor performance with difficulty in rinse down. A related condition can result if the cation exchanger or the anion exchanger tends to mix after separation. This can result in poor effluent quality, particularly sodium leakage. Efforts to overcome this problem and to avoid poor separation have resulted in the development of inert resin separators which can clearly mark the point of separation between the two zones. These materials are separated as a result of density differences during backwash.

High Purity Water

The preparation of large quantities of high purity water requires a well designed process to overcome all the various problems discussed in the previous sections. The testing and sampling of water having resistivity greater than about 5 megohms requires considerable skill. This water cannot be allowed in contact with the atmosphere or its resistivity will drop to less than one megohm in a few seconds. This water also should be evaluated with a resistivity meter and

not a conductivity bridge which does not read well near zero.

High purity water is generally measured in excess of 10 megohms-cm and actually 18 megohms-cm water is usually required in the electronics industry. Normally the water supply has elaborate pretreatment including ultrafiltration, reverse osmosis, carbon treatment and deionization equipment ahead of the final polisher. Some typical curves are shown in the figure to illustrate that the selection of resin for 18 megohm-cm performance must be selected properly so that the expected purity can be achieved. The resins in the figure which do not deliver quality still give an adequate capacity performance.



Typical Curves for High Purity Water in Test Unit-1 Megohm Endpoint

Summary

This introduction to ion exchange technology highlights major areas of resin use. The selection of the most suitable resin for a particular situation requires a careful balance of physical and chemical properties of the resins as well as of the fluid which is to be treated. For example, the hydraulic properties of the resins will dictate selection in cases where high flow rates are involved. In many cases the resin volume will be based on flow rate limitation rather than on capacity. Thermal stability, particularly of anion exchangers, will be a major consideration in some installations while the ability to resist organic fouling may be a major consideration in other cases. Increased resistance to attrition and to osmotic shock is required for resins in processes where such problems are likely to be encountered. The ability to produce ultrapure water is a frequent requirement in the manufacture of semiconductors and in the electric utilities. The demand to meet ever stricter specifications is a continual challenge to the resin producer.

Ion exchange resins have applications in many other areas of technology. Processes to recover and purify antibiotics are frequently encountered in the pharmaceutical industry. Hydrometallurgical recovery of valuable minerals including gold, silver, platinum and uranium have found wide acceptance throughout the world. Ion exchange resins have been used extensively to reduce the concentration of toxic elements such as cadmium, cobalt, copper and zinc in waste streams. Many analytical methods including those for amino acids, trace metals and nucleic acids are based on ion exchange.

Additional Reading Material

Applebaum, S. B., *Demineralization by Ion Exchange*, Academic Press, New York, N.Y., 1968

Dorfner, K., *Ion Exchangers, Properties and Applications*, Ann Arbor Science, Ann Arbor, Michigan, 1972

Kunin, R., *Ion Exchange Resins*, Robert E. Krieger Publ. Co., Huntington, N.Y., 1957

Nachod, F. C. and Schubert, J., editors, *Ion Exchange Technology*, Academic Press, New York, N.Y., 1957

