

**ION
EXCHANGE
PRIMER**

SYBRON

Sybron Chemicals Inc.

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ION EXCHANGE PRIMER

ION EXCHANGE

England: The year, 1850. Harry Stephen Meysey Thompson, an agriculturist, and John Thomas Way, a chemist, report to the Royal Agricultural Society they have observed that when a solution of ammonium sulfate was passed through a layer of certain soils, the effluent solution contained calcium sulfate.

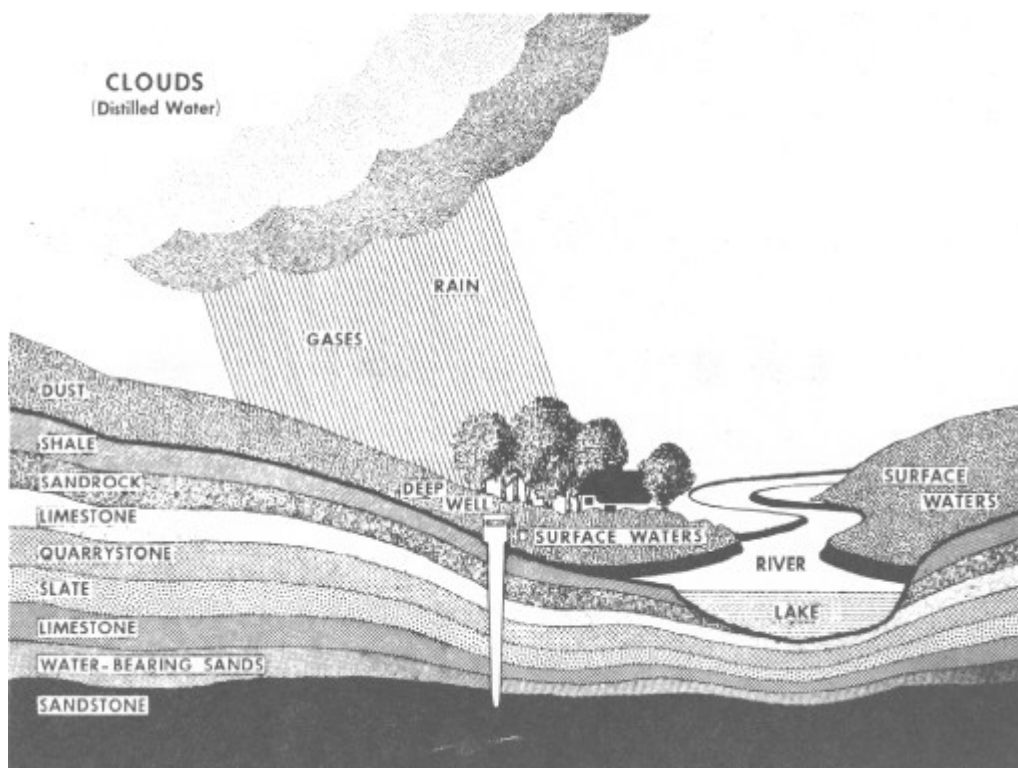
Germany: The year, 1905. Dr. R. Gans first makes use of a zeolite type soil for removing hardness from water on a commercial scale.

U.S.A.: The year, 1913. The first American synthetic zeolite is marketed by The Permutit Company of New York. The capacity of such material for hardness removal from water is greater than that of the natural zeolites.

It was from these beginnings that an industry developed in this country which today produces millions of cubic feet of ion exchange materials for use in water treatment and for many other purposes.

IONS AND ION EXCHANGE. The smallest units which make up chemical compounds, and still retain the properties of the compounds, are molecules. Molecules are, in turn, made up of atoms or groups of atoms and if these atoms or groups of atoms carry electrical charges, they are known as *ions*. The charge of a single ion may be positive or negative: ions of metals and of hydrogen are usually positively charged and are called *cations*. Their charges are balanced by negatively charged *anions* such as chloride, sulfate, etc. Hydrogen ions and anions combined constitute acids (e.g. two hydrogen ions and one sulfate ion is sulfuric acid) while metal ions in combination with anions give salts (e.g. one sodium ion and one chloride ion give sodium chloride), but if the anion is hydroxide then it is a base. Acids and bases react, i.e. the hydrogen ion of the acid and the hydroxide ion of the base unite to give HOH (H_2O), which is water. Acids, bases and salts are known as *electrolytes* as they conduct electricity.

Certain insoluble materials are made up of large ions forming a skeletal structure to which are attached other ions of opposite electrical charges. The latter ions may be exchanged for others carrying charges similar to their own. Such insoluble materials are called *ion exchangers*, and may be both natural and synthetic products. They may further be *cation exchangers* or *anion exchangers* depending on the charge on the skeleton or matrix of the exchanger.



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IONS IN WATER - Rain water falling from the clouds through the atmosphere may dissolve traces of acidic gases from the air (carbon dioxide, sulfur dioxide, etc.). When the water reaches the ground, it percolates through the soil and will dissolve certain components of the soil, which are either water-soluble or which become soluble by virtue of the slight acidity of the dissolved gases in the water. Ground waters (wells, springs) as well as so-called surface waters (rivers, lakes, oceans) all contain greater or smaller amounts of dissolved matter, most of which, as a rule, are electrolytes and, therefore, ionize.

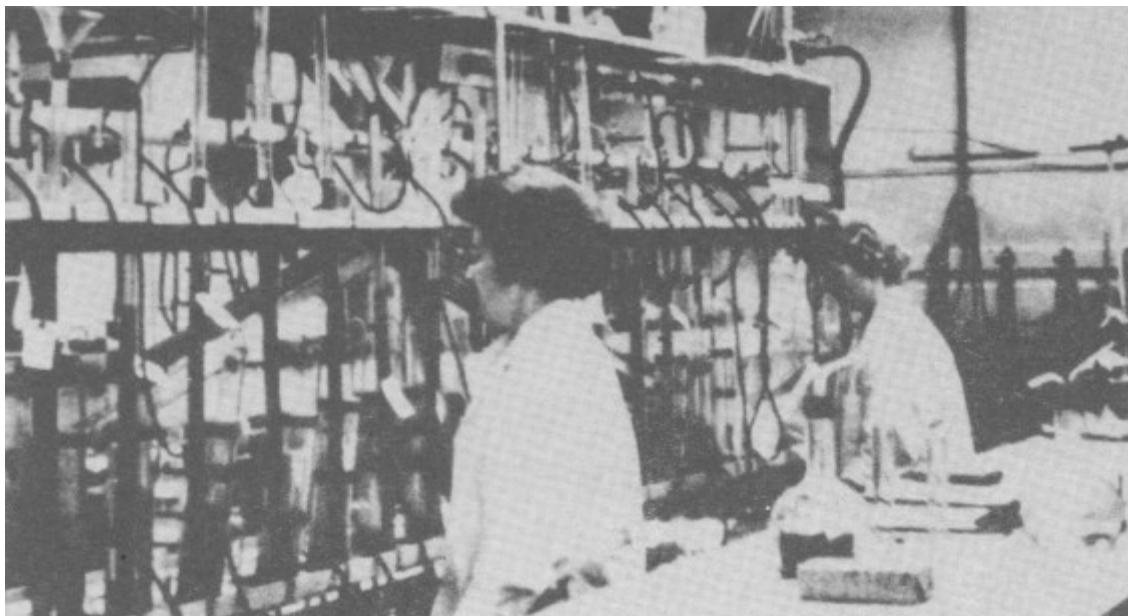
Two of the most commonly occurring ions in natural waters are calcium and magnesium, both of which are positively charged *cations* each carrying two unit charges. The presence of calcium and magnesium in a natural water is the cause of *hardness*, which will produce scaling in appliances (kettles, steam irons, etc.) and in boilers form a scum or precipitates with soap. Other cations present may include sodium and potassium and, in trace amounts, iron, manganese and other metallic components.

Anions present in waters include the alkalinity-producing bicarbonate and carbonate ions (and hydroxide, e.g. in boiler waters) as well as chloride, sulfate, nitrate and sometimes fluoride, phosphate, etc.

SOFTENING OF WATER (*Hardness Removal*) - A hard water, as mentioned above, can cause scaling in boilers and in household appliances. It will produce a curd with soap before it will produce a lather, thus soiling kitchen and bathroom fittings, giving laundry a less clean appearance, and wasting soap.

Early attempts at removing hardness included boiling to remove that part of the hardness which is due to calcium and magnesium bicarbonates, and the commercial process known as Clarke's or the lime-softening process. Modifications of the latter are widely used even today but, like boiling, it will not remove calcium and magnesium salts such as chlorides, sulfates, etc.

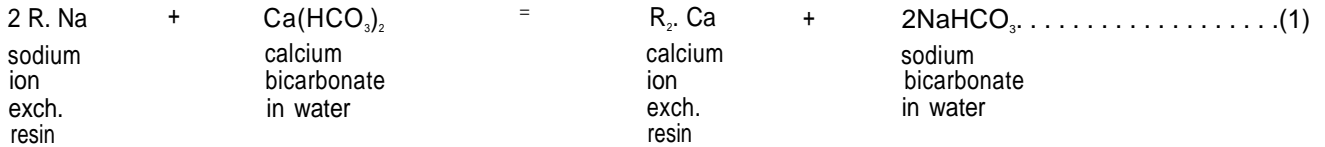
The first commercial applications of ion exchange was the softening of water by Dr. Gans in 1905. Since that time, the ion exchange (or as previously called: base exchange) method of softening has become a widespread treatment process and the original natural and synthetic zeolite type materials were replaced over the years by newer and more versatile ion exchangers, such as the sulfonated coals, the sulfonated phenol formaldehyde (bakelite) type resins and, more recently, within the last ten years or so, by the physically and chemically resistant, high-capacity materials of the sulfonated polystyrene bead type.



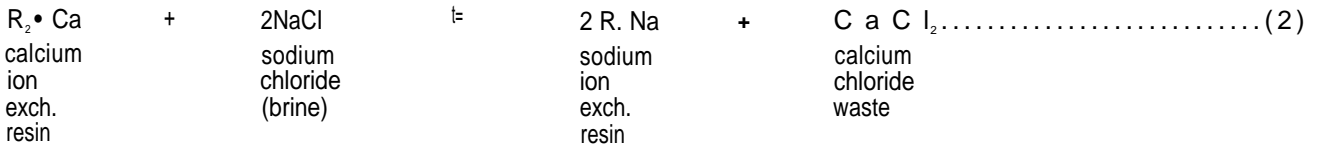
Here's where we find out how much soft water an i/e resin produces per pound of salt. We test for total capacity, but more important, operating efficiency under conditions as close as possible to field use. Salt economy is especially important now, with the trend toward automation of water softeners. That's why manufacturers who use Ionac i/e resins needn't worry about the inconveniences of "short capacity."

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The softening of water by ion exchange relies on the replacement of the calcium and magnesium ions in the water by an equivalent number of sodium ions. This eliminates the undesirable characteristics of hard water, as sodium salts do not form scale, nor a scum with soap, only lather. Chemically, the process of *softening* may be illustrated by the following equation:

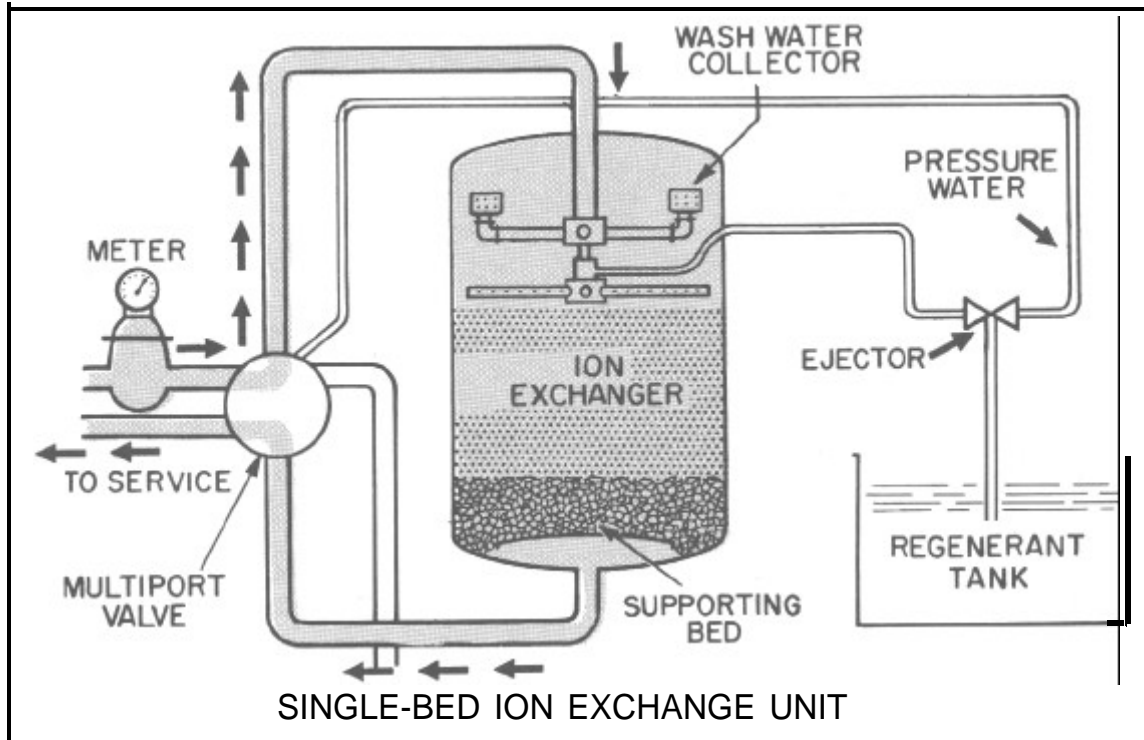


It will be self-evident that a certain quantity of sodium ion exchanger will contain only a finite number of exchangeable sodium ions. This number is known as the capacity of the resin. When this capacity has been *exhausted*, i.e., all sodium ions have been replaced by calcium or magnesium, regeneration of the resin back to the sodium form is necessary. This is done by passing through the resin a solution of sodium chloride (brine), as may be illustrated by this equation:



The total number of exchangeable sodium ions, which can be present in a fully sodium-form ion exchanger, i.e. its *total capacity*, can only be made use of if a very large excess of brine is used each time for regeneration. As a rule, more economical quantities of brine are used and at each regeneration quantity, a certain *operating capacity* is obtained. In this respect, the *efficiency* of the regeneration is important, i.e. the total amount of hardness removed per pound of salt used. This factor is of greater importance in the industrial use of ion exchange softening than it is in the case of the household applications, because of the quantities of salt used and water treated, which are involved.

Capacities of ion exchangers for softening are usually expressed in engineering terminology as grains of hardness (as calcium carbonate) removed per cubic foot of resin, or in scientific terms: Milliequivalents per liter.

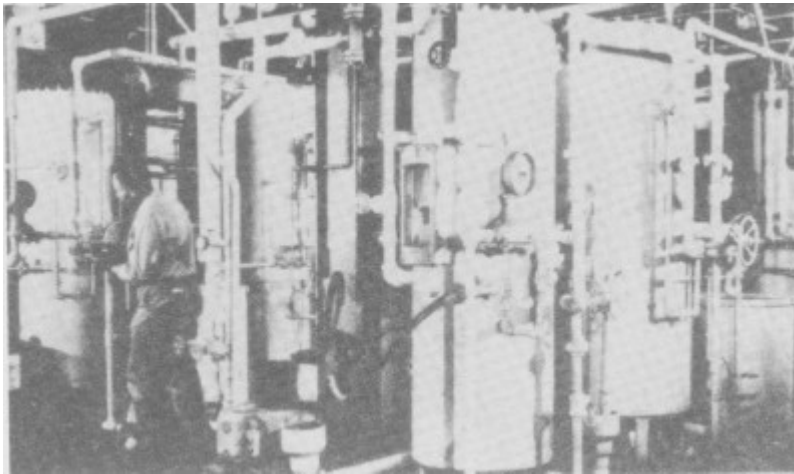


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IRON AND MANGANESE - These two trace elements frequently found in ground waters are undesirable for many reasons; among them possible staining of clothes and textiles, formation of deposits in bathroom and other fittings, pipes, tanks, etc., promotion of corrosion of pipes, etc. They can be removed from waters by ion exchange provided they are in the ionic form, i.e. not precipitated, but this procedure is subject to certain limitations. It, and available alternatives, are discussed in a separate booklet in this series.

DEMINERALIZATION OF WATER - It is desirable to remove all the dissolved ionic impurities from the water used for feeding to very high pressure boilers, or for use in the production of electronic components (such as television tubes, transistors, etc.) in delicate plating operations, the production of pharmaceuticals, and many other process applications. In addition, in some isolated cases, a water may contain excessive amounts of nitrate ions. This is undesirable if that water is to be used for preparing baby food. Infants fed excessive nitrates are subject to methaemoglobinemia, which can be fatal.

Before the development of the ion exchange process, the only way to obtain such ion-free water was by distillation, an expensive process. By means of ion exchange processes, water can be demineralized at low cost and will then be comparable or superior in quality to distilled water for most purposes. The process depends upon two reaction stages. In the first, all metal ions are removed and replaced by hydrogen ions, using a cation exchange resin regenerated with an acid; and in the second stage, acids produced are removed by an anion exchange resin, which has been regenerated with an alkali such as sodium hydroxide (caustic soda) or sodium carbonate (soda ash). The equations on page 7 illustrate these reactions.



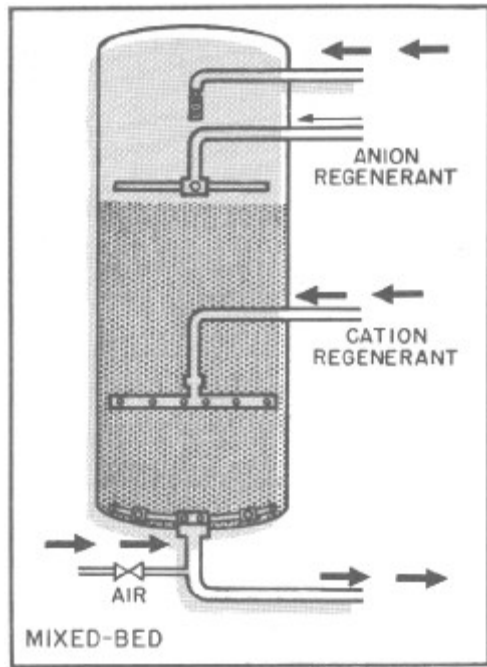
Typical high purity water treatment systems include these single-bed, two-step demineralizers.

TWO TYPES OF ANION EXCHANGERS

Anion exchange resins can be weakly or strongly basic.

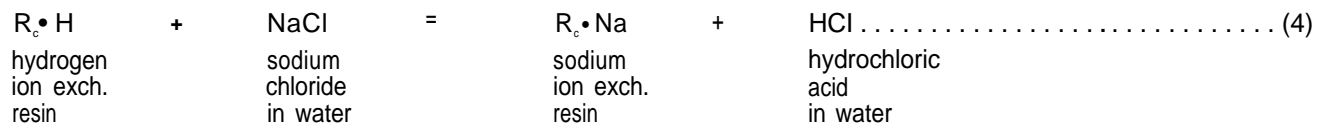
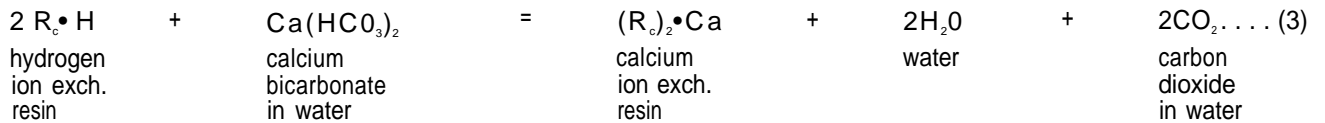
A *weak base* anion exchanger will absorb strong acids, such as hydrochloric, sulfuric or nitric acid, but will not remove weak acids, such as carbonic (carbon dioxide) or silica, from water. It may be regenerated with soda ash, or sometimes ammonia, or caustic soda.

A strong base anion exchanger is usually regenerated with sodium hydroxide (caustic soda) and it will exchange all anions, those of carbonic and silicic acid as well as those of hydrochloric, sulfuric or nitric acid.

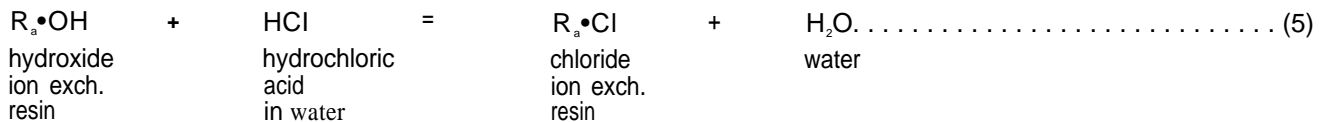


MULTI-STAGE DEMINERALIZING

The first stage in this process involves, as pointed out above, the replacement of all cations by hydrogen ions, thus obtaining the free acids corresponding to the various salts dissolved in the raw water. The materials employed for this purpose are strongly acidic, of the sulfonic acid type, and the reactions may be illustrated thus:



For the second stage, a *weak base* resin could be employed, in which case the strong acids in the hydrogen ion exchange treated water, e.g. the hydrochloric acid shown above, will just be absorbed by the resin. If a *strong base* resin is used, however, the chloride ion of the hydrochloric acid above, the carbon dioxide (as bicarbonate ion), and any other anions (including silica) will be removed and replaced by hydroxide, as follows:



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Although the carbon dioxide, produced by the hydrogen ion exchanger from any bicarbonates (or carbonates) present in the raw water, can be taken up by a strong base anion exchanger, in large commercial installations it is mostly found to be more economical to remove this gas by passing the water as a spray downward through a tower filled with packing rings and contacting it with a counter current of air.



An ion exchange resin must have consistent particle size distribution so it offers minimum resistance to water flow. It's also important for suitable backwash expansion characteristics. That's why we test every production batch of Ionac ion exchangers by sifting them through standard wire mesh screens to assure the correct particle size distribution.

THE MIXED BED PROCESS

If a water were to be demineralized by a two-stage process as above, and the treated water were to be passed through a second, and possibly third or fourth pair of such demineralizing units, the effluent from each pair of units would be slightly better quality than that from the preceding pair. Taking this principle ad infinitum, it was found that a completely demineralized water can be obtained by passing the same raw water through a single column containing an intimate mixture of strongly acidic cation and strongly basic anion exchange resins. In this case the individual beads of the two resins alternate and essentially act as an infinite series of two-stage demineralizers. This type of process is especially useful for producing ultra-pure water for use in rinsing of transistors and other electronic equipment and for critical pressure boilers.

Although the two resins are used mixed, they can also be regenerated after exhaustion by separating them hydraulically into two layers with an upward flow of water, (their densities are slightly different), regenerating each layer separately and then, after rinsing, remixing the two materials by bubbling air through them upwards.

QUALITY OF DEMINERALIZED WATER

Demineralized water obtained using strong base materials, especially in the mixed bed process, will meet quality standards set for "Purified Water" in the U.S. Pharmacopoeia. To illustrate the quality of water obtainable by the various combinations, we may consider a raw water having a specific electrical conductance of about 450 micromhos/cm³, with about 300 parts per million dissolved solids* (as calcium carbonate), of which the analysis would approximate as follows.

Total Hardness:	250 ppm	Alkalinity:	200 ppm
Sodium Salts:	50 ppm	Chlorides, sulfates:	100 ppm
Conductance:	450	Silica:	16 ppm

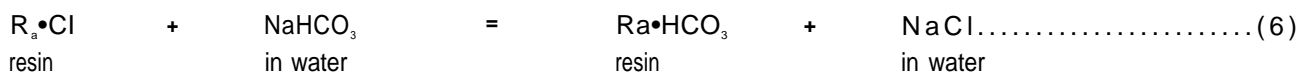
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Treated Water	Conductance	Silica
Hydrogen exch.		
+weak base	12 - 15	16
+weak base +degassing	7 - 8	16
+strong base	5 - 7	< 0.1
Mixed Bed	< 0.5	< 0.1
Distilled	2.5	

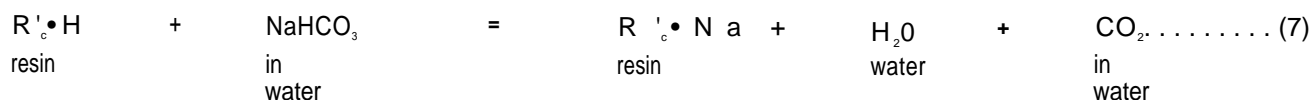
*Note: the higher the concentration of dissolved solids (electrolytes),
the higher is the conductance and vice versa.

ALKALINITY REMOVAL - In the case of high alkalinity waters, i.e. waters containing considerable concentrations of bicarbonates, such as occur in some parts of the Mid-West, it may be desirable to remove or destroy the bicarbonate part only without completely demineralizing the water. Two processes have been used for the purpose.

The *chloride-anion exchange* process relies on replacing the bicarbonate ions present in the water with chloride ions, using a strongly basic anion exchanger, regenerated with sodium chloride. While this is a convenient method, and uses a cheap regenerant which is easy to handle, it does not reduce the total solids dissolved in the water.



The second process relies on the use of a *weak acid cation exchange* resin which, if incompletely regenerated with acid, will replace the cations of weak acid salts, such as bicarbonates, with hydrogen but will not exchange the cations of neutral salts, such as sodium chloride. The reactions of the two processes may be illustrated by this equation:



The carbon dioxide produced in the second process can be removed by degassing.

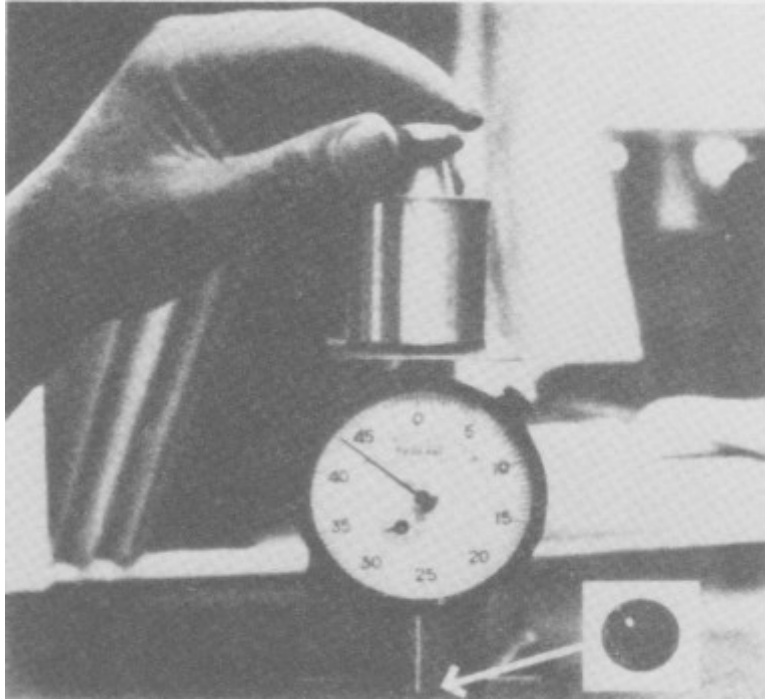
OTHER APPLICATIONS OF ION EXCHANGE

Although the chief application of ion exchange today is still the treatment of water, the principle offers almost unlimited possibilities in other fields. Commercial installations already include such processes as the purification of sugar solutions and wines, separation and purification of drugs and fine chemicals, purification of waste effluents and the recovery of valuable wastes, e.g. in the metallurgical industries, the extraction and quantitative separation of elements and metallic complexes which have hitherto been achieved only with great difficulty and tedium.

A striking example of the last mentioned application is the separation by ion exchange of the rare earth elements, making use of their citrate, or other complexes. In the drug industry, can be cited the separation of Vitamin B12 from streptomycin.

Purification of coke oven effluents and the recovery of chromate from plating liquors are also among the special applications and the resins have found their uses in analytical work in the laboratory, as well as in medical clinical tests.

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The life of an ion exchanger is determined largely by its physical strength. It has to be strong to last. At Ionac, the tiny ion exchanger beads are subjected to direct mechanical pressures many thousands of times their own weight. Strength is one of the characteristics of Ionac's polystyrene sulfonic acid resins. It's regularly checked by our Quality Control Laboratory.

OPERATION OF ION EXCHANGE PROCESSES

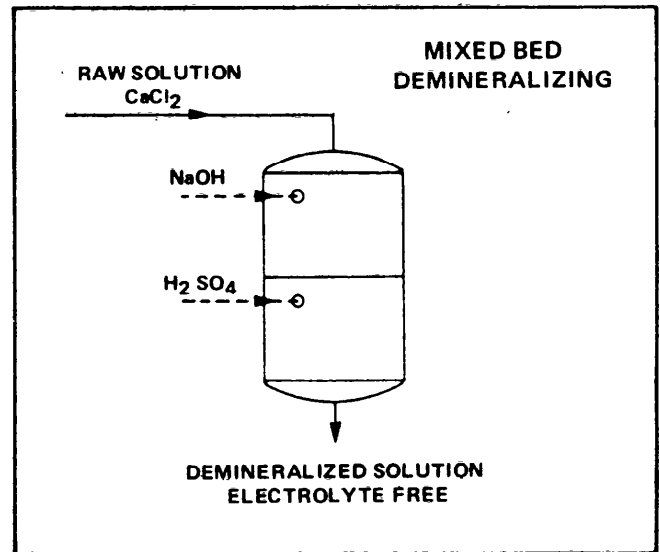
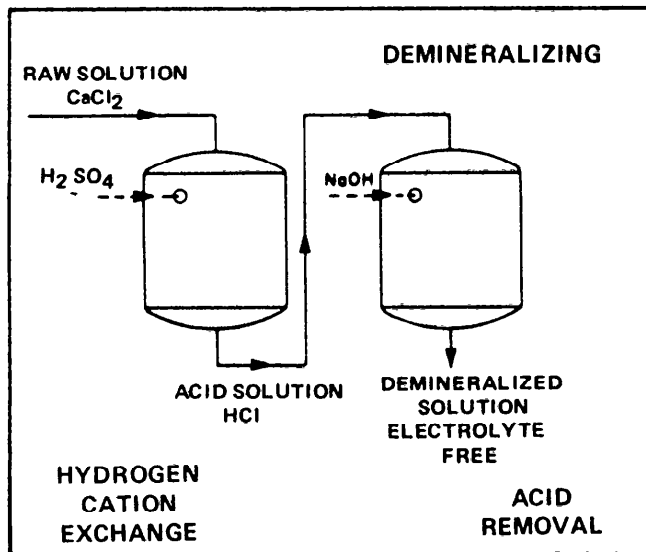
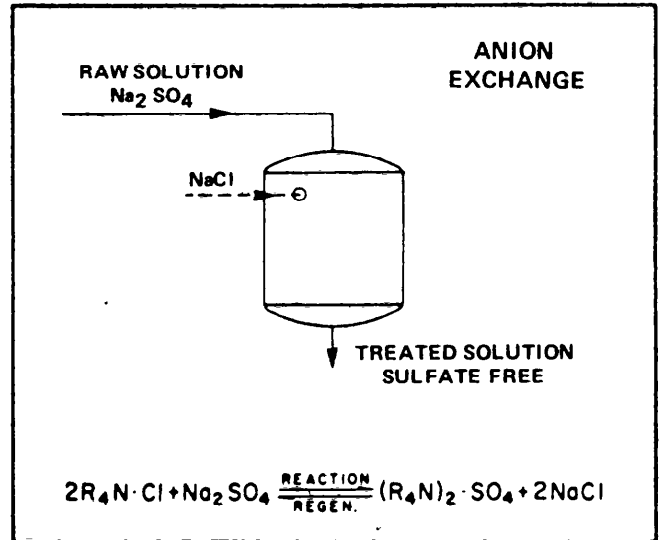
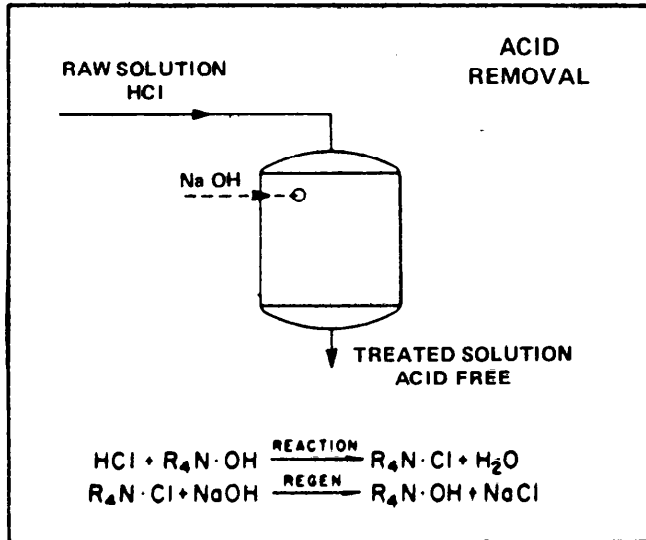
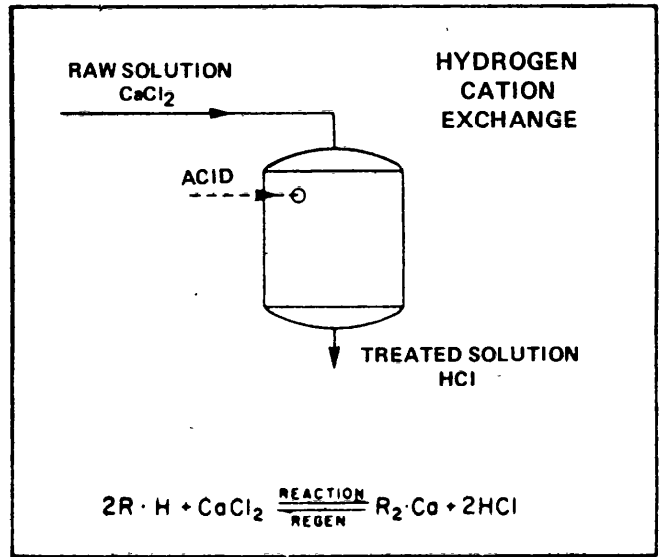
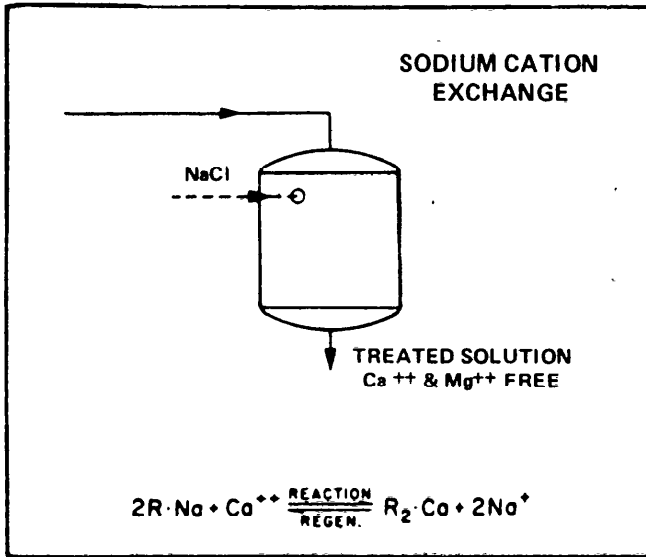
In general, the sequence customary in water treatment applications is applied to ion exchangers.

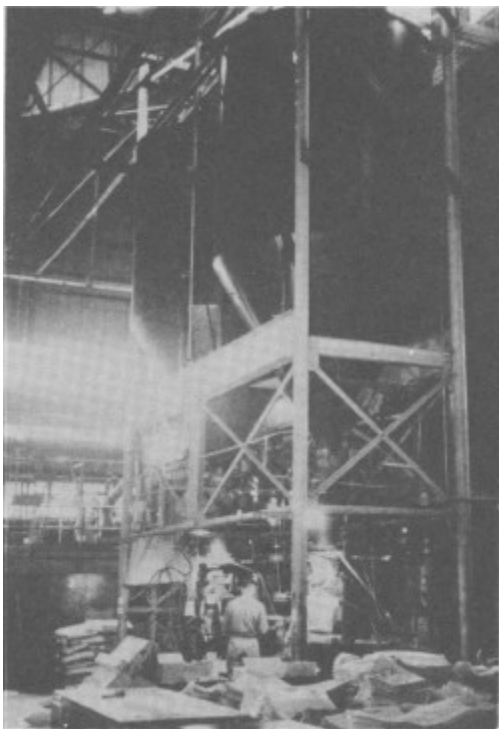
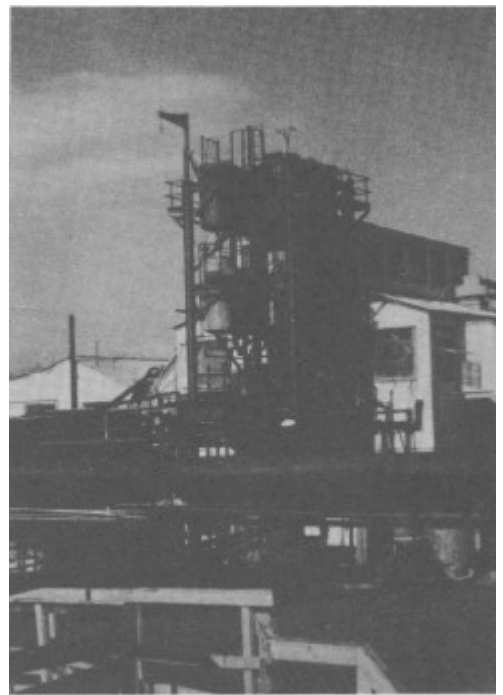
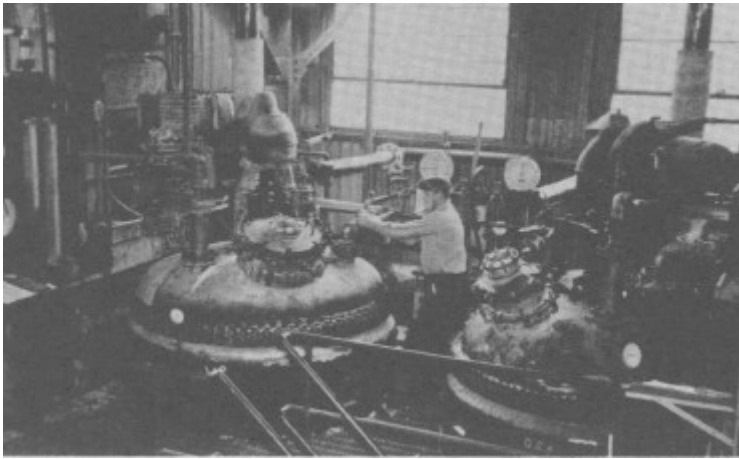
1. Backwashing: The resin bed is loosened up by an upward flow of water. Any channelling or air bubbles are removed together with any suspended matter which may have accumulated. The resin is then allowed to settle.
2. Regeneration: The necessary regenerant solution is passed through the resin bed with the flow rate recommended.
3. Rinse: Excess regenerant and unwanted impurities, removed from the resin by the regenerant, are removed.
4. Treatment run (Exhaustion step): Usually carried out in the same direction of flow as the regeneration and rinse, but in certain cases counter-current operation may be desirable.

AVAILABLE ION EXCHANGERS

Currently available ion exchangers include granular and bead type materials, such as natural and synthetic aluminosilicates, and various strong and weak cation and anion exchange resins.

THE SIX BASIC ION EXCHANGE PROCESSES





SYBRON

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