ION EXCHANGE RESINS

Ion exchange resins are polymers that are capable of exchanging particular ions within the polymer with ions in a solution that is passed through them. This ability is also seen in various natural systems such as soils and living cells. The synthetic resins are used primarily for purifying water, but also for various other applications including separating out some elements.

In water purification the aim is usually either to soften the water or to remove the mineral content altogether. The water is softened by using a resin containing Na^+ cations but which binds Ca^{2+} and Mg^{2+} more strongly than Na^+. As the water passes through the resin the resin takes up Ca^{2+} and Mg^{2+} and releases Na^+ making for a 'softer' water. If the water needs to have the mineral content entirely removed it is passed through a resin containing H^+ (which replaces all the cations) and then through a second resin containing OH^- (which replaces all the anions). The H^+ and OH^- then react together to give more water.

The process has some disadvantages in that there are substances occuring in some water (such as organic matter or Fe^{3+} ions) which can foul the resin, but in general the advantages of the process (long life of resins, cheap maintainance etc.) outweigh the disadvantages. In addition, the process is very environmentally friendly because it deals only with substances already occuring in water.

INTRODUCTION

Ion exchange materials are insoluble substances containing loosely held ions which are able to be exchanged with other ions in solutions which come in contact with them. These exchanges take place without any physical alteration to the ion exchange material. Ion exchangers are insoluble acids or bases which have salts which are also insoluble, and this enables them to exchange either positively charged ions (cation exchangers) or negatively charged ones (anion exchangers). Many natural substances such as proteins, cellulose, living cells and soil particles exhibit ion exchange properties which play an important role in the way the function in nature.

Synthetic ion exchange materials based on coal and phenolic resins were first introduced for industrial use during the 1930's. A few years later resins consisting of polystyrene with sulphonate groups to form cation exchangers or amine groups to form anion exchangers were developed (**Figure 1**). These two kinds of resin are still the most commonly used resins today.

How ion exchange resins work
The resins are prepared as spherical beads 0.5 to 1.0 mm in diameter. These appear solid even under the microscope, but on a molecular scale the structure is quite open, **Figure 2**. This means that a solution passed down a resin bed can flow through the crosslinked polymer, bringing it into intimate contact with the exchange sites.

The affinity of sulphonic acid resins for cations varies with the ionic size and charge of the cation. Generally the affinity is greatest for large ions with high valency. For dilute solutions
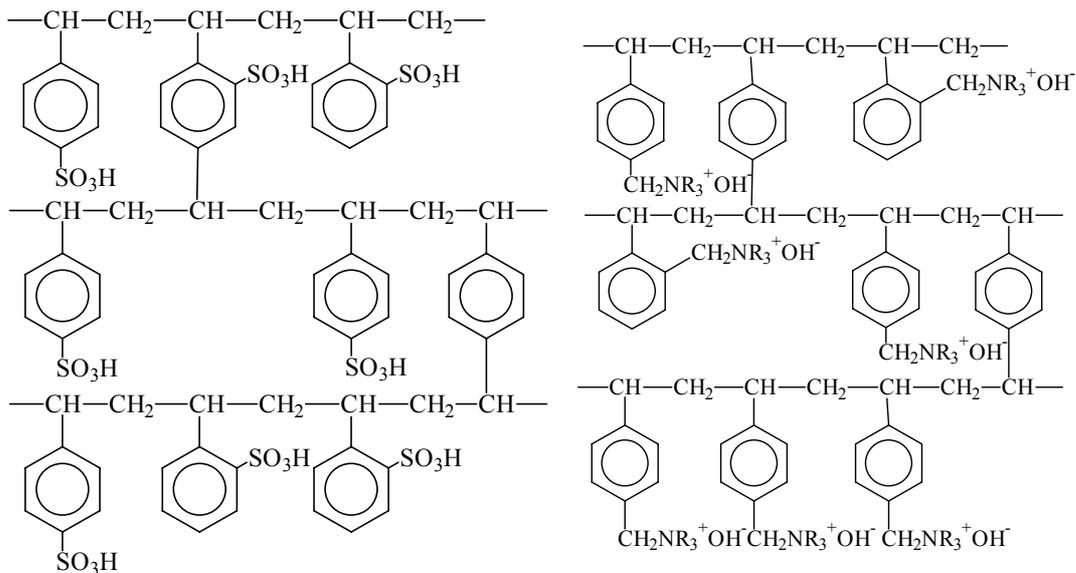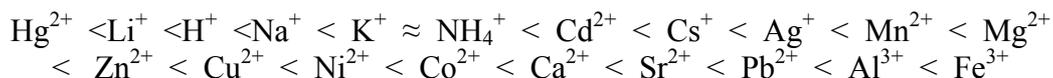
A strongly acidic sulphonated polystyrene cation exchange resin

A strongly basic quaternary ammonion anion exchange resin

Figure 1 - Some examples of ion exchange resins

the order of affinity for some common cations is approximately:

$$Hg^{2+} < Li^+ < H^+ < Na^+ < K^+ \approx NH_4^+ < Cd^{2+} < Cs^+ < Ag^+ < Mn^{2+} < Mg^{2+}$$
$$< Zn^{2+} < Cu^{2+} < Ni^{2+} < Co^{2+} < Ca^{2+} < Sr^{2+} < Pb^{2+} < Al^{3+} < Fe^{3+}$$

A corresponding list for amine based anion exchangers is:

$$OH^- \approx F^- < HCO_3^- < Cl^- < Br^- < NO_3^- < HSO_4^- < PO_4^{3-} < CrO_4^{2-} < SO_4^{2-}$$

Suppose a resin has greater affinity for ion B than for ion A. If the resin contains ion A and ion B is dissolved in the water passing through it, then the following exchange takes place, the reaction proceeding to the right (R represents the resin):

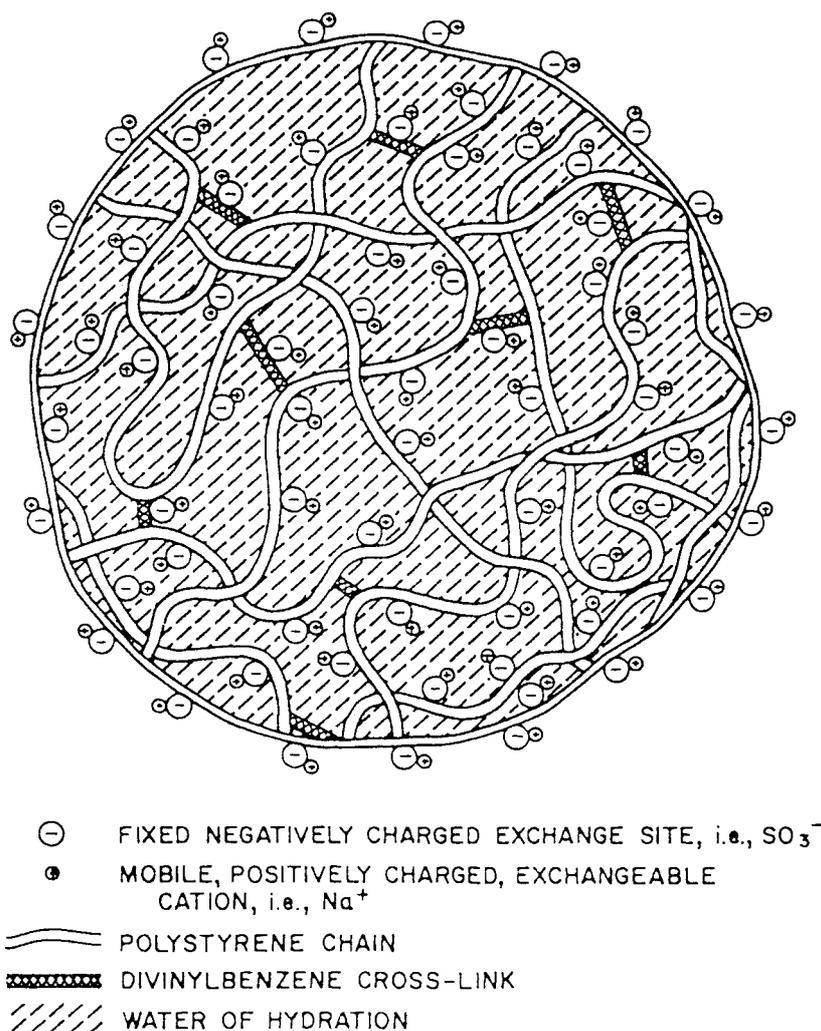$$AR + B^{n\pm} \leftrightarrows BR + A^{n\pm}$$

When the resin exchange capacity nears exhaustion, it will mostly be in the BR form.

A mass action relationship applies where the bracketed entities represent concentrations:

$$\frac{[BR][A]}{[AR][B]} = Q$$

Q is the equilibrium quotient, and is a constant specific for the pair of ions and type of resin. This expression indicates that if a concentrated solution containing ion A is now passed through the exhausted bed, the resin will regenerate into the AR form ready for re-use, whilst ion B will be eluted into the water. All large scale applications for ion exchange resins involved such exhaustion and regeneration cycles.

$\ominus$	FIXED NEGATIVELY CHARGED EXCHANGE SITE, i.e., SO_3^-
$\oplus$	MOBILE, POSITIVELY CHARGED, EXCHANGEABLE CATION, i.e., Na^+
	POLYSTYRENE CHAIN
	DIVINYLBENZENE CROSS-LINK
	WATER OF HYDRATION

Figure 2 - Expanded view of polystyrene bead

Uses
A bed of resin can be used either to remove unwanted ions from a solution passed through it or to accumulate a valuable mineral from the water which can later be recovered from the resin. Examples of the removal of unwanted ions are the removal of heavy metals from metal trade wastes, the demineralistion of the whey used to manufacture specialized dairy products and the removal of salts from fruit juices.

Strong cation resins in the hydrogen form are used for the hydrolysis of starch and sucrose.

Resins also find many uses in the laboratory where the chemist's ingenuity is less constrained by economic considerations. They can be used to remove interfering ions during analysis or to accumulate trace quantities of ions from dilute solutions after which they can be concentrated into a small volume by elution. A cation resin in the hydrogen form can be used to determine the total concentration of ions in a mixture of salts. The sample passing through a column is converted to the equivalent quantity of acid and the amount readily found by titration.

One of the earliest applications of ion exchange was the separation of rare earth elements during the 1940's. These metals occur naturally as mixtures and have almost identical

chemical properties. The equilibrium quotents for cationic resin were found to vary sufficiently for separation to be achieved chromatographically by adding a solution of the mixture to a resin column and eluting the metals with an acid wash. This work lead first to the discovery of promethium (element 61) and later to the discovery of five new elements in the actinide series.

WATER TREATMENT

Far more resin is used for water purification than for any other purpose. It is therefore appropriate to discuss water treatment examples when outlining the application of the principles of ion exchange technology. Industrial ion exchange units are produced in sizes ranging from a few litres up to vessels holding several tonnes of resin. Service runs between regenerations usually range from 12 to 48 hours.

The two major types of treatment applied to water are water softening - the replacement of 'hard' ions such as Ca^{2+} and Mg^{2+} by Na^+ - and demineralisation - the complete removal of dissolved minerals. Both of these treatments are outlined below.
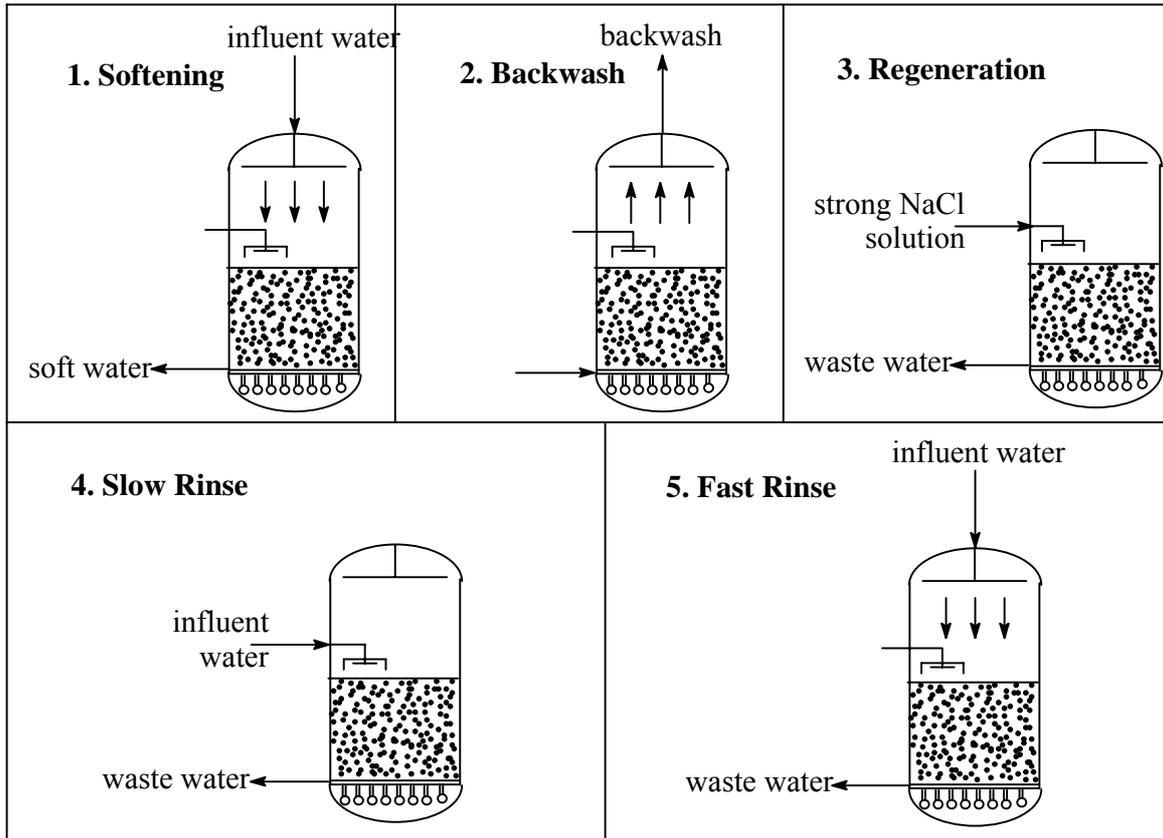
Water softening

In water softening a cation resin in the sodium form is used to remove hard metal ions (calcium and magnesium) from the water along with troublesome traces of iron and manganese, which are also often present. These ions are replaced by an equivalent quantity of sodium, so that the total dissolved solids content of the water remains unchanged as does the pH and anionic content. At regular time intervals the resin is cleaned (**Figure 3**). This involves passing influent water back up through the resin to remove suspended solids, passing a regenerant solution down through the resin to replace the ions that have bound to the resin and then rinsing again with water to remove the regenerant solution. In water softening the regenerant is a strong solution of sodium chloride.

Demineralisation

Virtually all the dissolved matter in natural water supplies is in the form of charged ions. Complete deionization (i.e. demineralisation) can be achieved by using two resins. The water is first passed through a bed of cation exchange resin contained in a vessel similar to that described for softeners. This is in the hydrogen ion form brought about by the use of a strong acid regenerant (either hydrochloric or sulphuric). During service, cations in the water are taken up by the resin while hydrogen ions are released. Thus the effluent consists of a very weak mixture of acids. The water now passes through a second vessel containing anion exchange resin in the hydroxide form for which sodium hydroxide is used as the regenerant. Here the anions are exchanged for hydroxide ions, which react with the hydrogen ions to form water. Such twin bed units will reduce the total solids content to approximately 1-2 mg L^{-1}.

With larger units it is usual to pass water leaving the cation unit through a degassing tower. This removes most of the carbonic acid produced from carbon dioxide and bicarbonate in the feed water and reduces the load on the anion unit. Without degassing the carbonic acid would be taken up by the anion bed after conversion to carbonate.

Figure 3 - Using and cleaning a water softening ion exchange system

If complete demineralization is required this is achieved by passing the twin bed effluent through a third vessel containing either cation resin in the hydrogen form or a bed of mixed resin consisting of both anionic and cationic resin which has been intimately combined. Mixed resin is a very efficient demineraliser and can produce water with much lower levels of dissolved material than can be achieved by distillation. For small supplies, such as in laboratories, mixed resin is often used in disposable cartridges. These are only used once, but larger mixed resin units can be regenerated. After exhaustion the bed is subjected to an up flow of water. Anionic resin beads are less dense than the cationic ones and they rise to the top so that the bed is separated into two layers of resin. Each is regenerated in situ with the appropriate regenerant then rinsed with clean water. The internal pipe work of the vessel is arranged so that regenerants and washes enter at the point separating the two resins and flow either up or down as required. An upflow of compressed air then mixes the resins up again.

Detection of resin exhaustion
A resin is considered to be exhausted when the ions in the resin have mostly been replaced by the ions that are being removed from the solution. Exhaustion of demineraliser is usually detected by an electrical conductivity cell installed at the outlet. When the conductivity rises to indicate ionic break through, a regeneration cycle can be initiated automatically. With small units it is possible to incorporate a pH indicator on the anion resin of a mixed bed cartridge. Exhaustion can be followed down the side of a transparent cartridge as the alkaline anion resin is converted to the neutralised salt form.

REGENERATING AN ION-EXCHANGE RESIN

As stated earlier, an ion-exchange resin in industrial use is usually regenerated every 12 to 48 hours. Depending on the use of the resin, this can be done in several different ways, each with their own advantages and disadvantages depending on both chemical and economic factors.

Regeneration is important because reducing the regenerant level lowers water quality by allowing a small proportion of the ions which are being taken up by the resin to slip through without exchange. For example, with twin bed deionisers, incomplete regeneration of the cation resin to the hydrogen form allows leakage of some sodium (the least held of the cations commonly found in natural supplies) into water passing to the anion exchange vessel. Consequently the water leaving the anion unit still contains this sodium in the form of a sodium hydroxide solutions usually of pH 8 to 9. However, the excessive amounts of regenerant required for complete regeneration means that this is rarely practical. In practice a compromise is usually reached, and commonly resins are regenerated to about two thirds of the total capacity. In addition, for many uses total purification is not necessary. For example, the water with a pH of 8 to 9 mentioned earlier is highly suitable for use in boilers, as they require slightly alkaline water.

Some impurities such as silica can only be removed by a strongly basic resin. For example, dissolved silica is a major component of most water supplies. Normally it exists as a neutral polymer, and it becomes negatively charged only at high pH levels. This means that it can only be removed from water in the highly alkaline environment of a strong base resin in the hydroxyl form.

The exchange process is often made more efficient by introducing the regenerant at the bottom of the resin column and passing it upwards through the bed (counter current regeneration). This ensures that the resin at the bottom becomes more highly regenerated than that above it. Treated water leaving the column flowing downwards then comes in contact with this resin last and undergoes the highest possible degree of exchange.

ADVANTAGES AND DISADVANTAGES IN THE USE OF ION-EXCHANGE RESINS

The advantages of ion exchange processes are the very low running costs. Very little energy is required, the regenerant chemicals are cheap and if well maintained resin beds can last for many years before replacement is needed. There are, however, a number of limitations which must be taken into account very carefully during the design stages. When itemised these limitations appear to represent a formidable list and the impression can be given that ion exchange methods might have too many short comings to useful in practice. However, this is not the case as the advantages mentioned above are very great and compensation can readily be made for most restrictions.

Calcium sulphate fouling
Sulphuric acid is the cheapest cation resin regenerant for demineralisers and is used where possible. Some water supplies contain a high proportion of calcium and when this acid is used calcium sulphate precipitates can form during regeneration. This fouls the resin and blocks drain pipes with a build up of scale. Under such circumstances, hydrochloric acid must be substituted.

Iron fouling

Bores yielding anaerobic water from underground supplies nearly always contain soluble iron in the Fe^{2+} state. Small amounts are readily removed by sodium cycle softeners but care must be taken to prevent contact with air prior to treatment. Aeration allows oxidation of Fe^{2+} to Fe^{3+} and consequent precipitation of ferric hydroxide which clogs resin beads and prevents ion exchange. Iron fouling is the commonest cause of softener failure.

Adsorption of organic matter

One of the commonest problems results from the presence of organic matter in water supplies. Untreated water from lakes and rivers usually contains dissolved organic material derived from decaying vegetation which imparts a yellow or brown colour. These substances can become irreversibly adsorbed within the anion beads, reducing their exchange capacity and leading to a reduction in treated water quality. Removal of organics prior to demineralisation is usually achieved by flocculation with alum or ferric salts followed by filtration which removes the metal hydroxide floc and the coprecipitated organic compounds. This treatment also removes any fine silt which represents another source of resin fouling. Both organic and iron fouled units can be chemically cleaned on site but complete removal of impurities is rare and resin performance usually suffers after fouling.

Organic contamination from the resin

The resins themselves can be a source of non-ionized organic contamination. New commercial grade resin often contains organics remaining after manufacture, while very old resin will shed organic fragments as the polymer structure opens up very slowly (de-crosslinkage). Such contamination may be disregarded for many uses, but when removal is needed, the demineralised water can be passed through an ultra filtration membrane.

Bacterial contamination

Resin beds do not act as filters for the removal of bacteria or other micro-organisms. They very often tend to worsen such contamination as traces of organic matter, which invariably accumulate, constitute a nutrient source for continued growth. When sterile water is required it can be obtained by treating the demineralised water by non-chemical means such as heat, ultra violet irradiation or very fine filtration. Resins beds can be decontaminated with disinfectants such as formaldehyde, but heat or oxidising disinfectants such as chlorine must not be used as these damage resins.

Chlorine contamination

As stated above, chlorine damages resins. This means that even town supply water is an unsuitable demineraliser feed because of the trace of chlorine it contains. It is customary to treat such feeds by passing them through activated carbon which removes chlorine very efficiently.

ENVIRONMENTAL IMPLICATIONS

The waste water for disposal after regeneration contains all the minerals removed from the water plus salt from the spent regenerants. These are concentrated into a volume equivalent to 1-5% of the treated water throughput. Disposal is not usually a problem as the load on waste treatment systems is low compared with at from many other industrial processes.

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