

# METHODS OF PURIFICATION

## (B) ION-EXCHANGE

### The process of Ion-Exchange

In the context of water purification, ion-exchange is a rapid and reversible process in which impurity ions present in the water are replaced by ions released by an ion-exchange resin. The impurity ions are taken up by the resin, which must be periodically regenerated to restore it to the original ionic form. (An ion is an atom or group of atoms with an electric charge. Positively-charged ions are called cations and are usually metals; negatively-charged ions are called anions and are usually non-metals).

The following ions are widely found in raw waters:

#### Cations

Calcium ( $\text{Ca}^{2+}$ )

Magnesium ( $\text{Mg}^{2+}$ )

Sodium ( $\text{Na}^+$ )

Potassium ( $\text{K}^+$ )

\* [Hydrogen ( $\text{H}^+$ )]

#### Anions

Chloride ( $\text{Cl}^-$ ) Bicarbonate ( $\text{HCO}_3^-$ )

Nitrate ( $\text{NO}_3^-$ ) Carbonate ( $\text{CO}_3^{2-}$ )

Sulphate ( $\text{SO}_4^{2-}$ )

†Carbon dioxide ( $\text{CO}_2$ )

†Silica ( $\text{SiO}_2$ )

\* [Hydroxide ( $\text{OH}^-$ )]

\* Although these ions are not present in any significant amounts in water, they are, nevertheless, very important in the process of ion exchange.

† Both of these compounds, when dissolved in water, form weak acids which are weakly ionised.

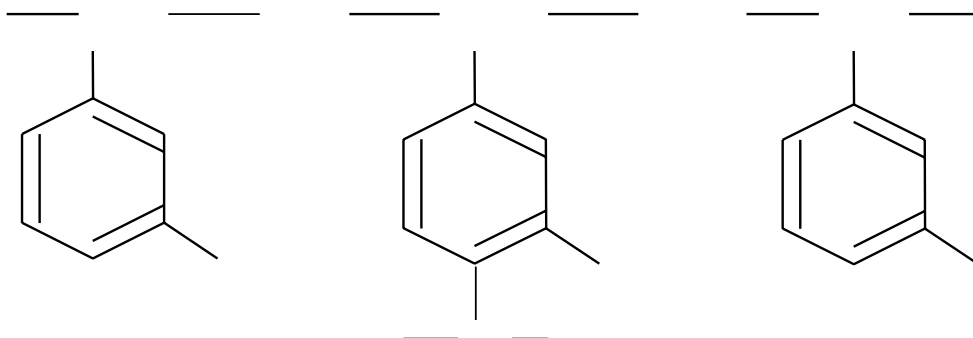
### Ion Exchange Resins

There are two basic types of resin - cation-exchange and anion-exchange resins. Cation exchange resins will release Hydrogen ( $\text{H}^+$ ) ions or other positively charged ions in exchange for impurity cations present in the water. Anion exchange resins will release hydroxyl ( $\text{OH}^-$ ) ions or other negatively charged ions in exchange for impurity anions present in the water.

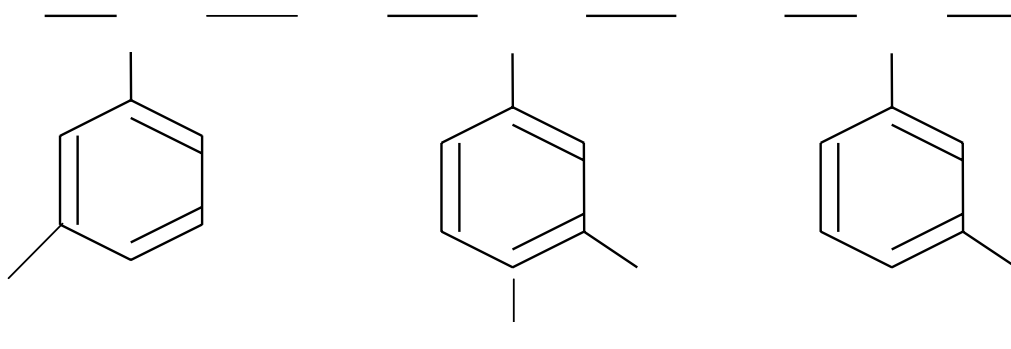
Today's modern ion-exchange resins are prepared from synthetic polymers such as styrene-divinylbenzene copolymers which have either been sulphonated to form strongly acidic cation-exchangers or aminated to form strongly basic or weakly basic anion-exchangers. See Figure 6 which illustrates typical structures of cation and anion resins.

**Figure 6: Structural diagrams of ion-exchange resins:**

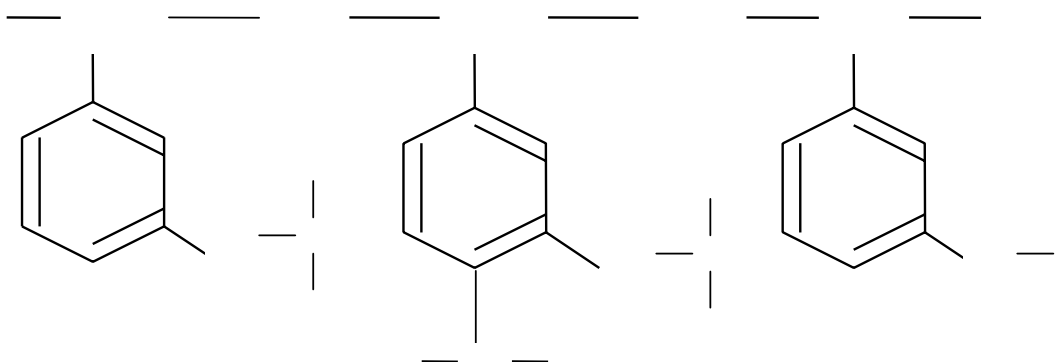
**(a) Strongly-acidic cation resin**



**(b) Strongly-basic anion resin**



**(c) Weakly-basic anion resin**



The resins are in the form of insoluble, porous, spherical beads, approximately 0.5mm in diameter.

## **The application of ion-exchange to water treatment and purification**

These are three ways in which ion-exchange technology can be used in water treatment and purification: first, cation-exchange resins alone can be employed to soften water by base exchange; secondly, anion-exchange resins alone can be used for organic scavenging or nitrate removal; and thirdly, combinations of cation-exchange and anion-exchange resins can be used to remove virtually all the ionic impurities present in the feedwater, a process known as deionisation.

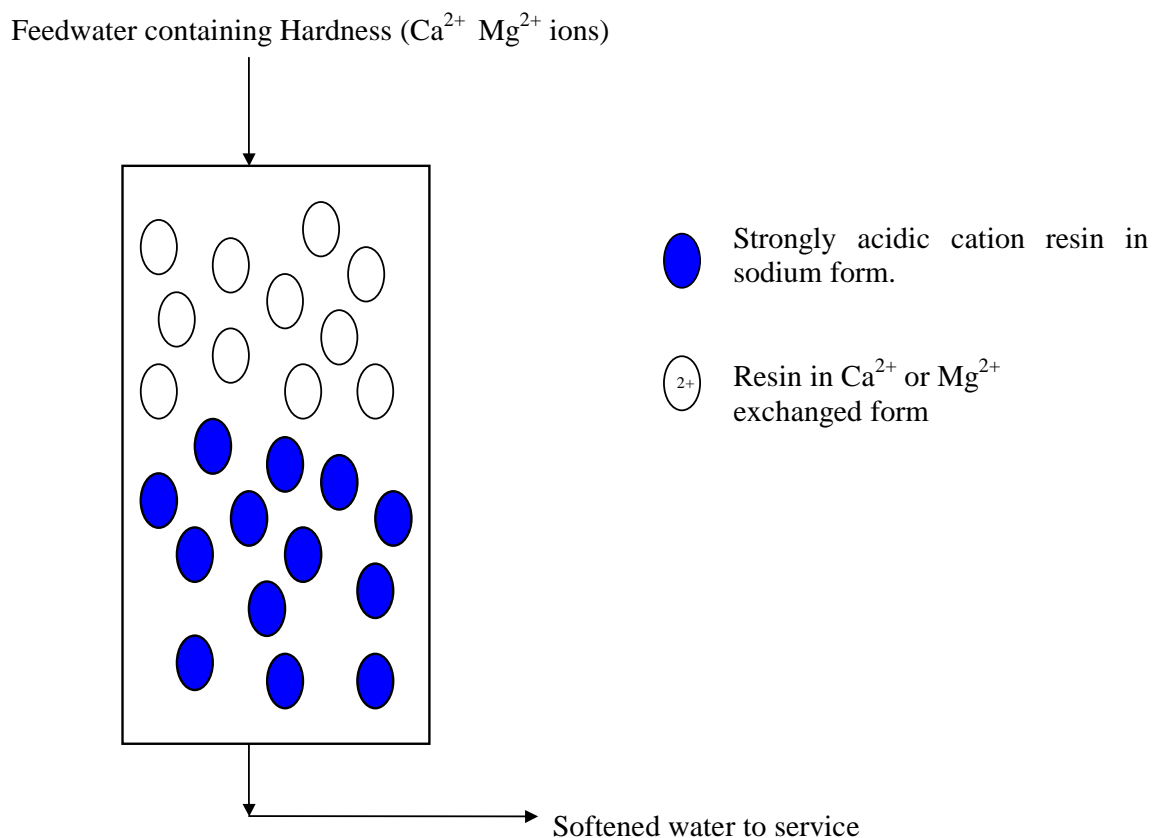
The first two technologies are forms of water treatment in which either the chemical nature of the impurities is changed (as in base-exchange softening) or certain impurities are selectively removed (as in organic scavenging or nitrate removal). By contrast, deionisation is a purification process which can produce water of exceptionally high quality.

## B(i) BASE-EXCHANGE SOFTENING

Softening was the first industrial application involving ion exchange. The process was first proposed by Gans in 1905. Except for certain improvements in the type of ion exchange material and the equipment, Gans' process is still one of the simplest methods for softening water.

The process involves passing water containing hardness ions, namely calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) through a column containing a strongly acidic cation exchange resin in the sodium ( $\text{Na}^+$ ) form (i.e. the exchangeable cations are sodium). The calcium and magnesium ions are exchanged for an equivalent number of sodium ions. The resin, once exhausted, (i.e. all the available sodium ions have been exchanged) must be re-charged. This entails passing a solution containing a high concentration of sodium salts such as brine (sodium chloride) through the ion exchange resin - a process known as regeneration. Figure 7 below illustrates the process of softening using ion-exchange i.e. base-exchange softening.

**Figure 7: Base-exchange softening**



### **Main usage of softened water**

1. To prevent scale formation in boilers, immersion heaters, steam irons and glass-washing machines etc.
2. To eliminate the production of insoluble 'scums' formed as a result of the reaction between calcium and magnesium ions with fatty acids found in soaps - in the textile industry, washing machines etc.
3. To prevent unsightly stains on glassware, mirrors, double glazing etc.
4. To pre-treat reverse osmosis feed water to prevent fouling of reverse osmosis membranes.

## **B(ii) ORGANIC SCAVENGING**

Organic scavengers are fully automatic plants designed primarily to remove naturally-occurring

organic contaminants - mainly humic and fulvic acids - from water supplies. These are weakly-ionised compounds which can irreversibly foul normal anion resins and reverse osmosis membranes, but which can readily be removed from water by a combination of adsorption and ion-exchange.

Organic scavengers contain special macroporous anion-exchange resins operated in the chloride form. They have an open structure with large pores that allow the bulky organic anions to be removed from the feedwater and then eluted out again during regeneration. (See also the section Adsorption: (ii) Synthetic ion-exchange resins).

Regeneration is initiated automatically by a clock cycle timer. The regenerant is sodium chloride in the form of a 10% brine solution which is drawn into the scavenger from a brine tank. From time to time a solution of sodium hydroxide is added to the brine to strip out the gross contamination and clean the resin bed.

### **B(iii) NITRATE REMOVAL**

Nitrates are a particular hazard to infants under six months old. The nitrates are reduced to nitrites in the child's gastro-intestinal system, reducing the capacity of the blood to carry oxygen ('blue baby syndrome'). The simplest and most cost-effective method of removing nitrates from water is by anion-exchange, using resins operated in the chloride form and regenerated with brine. Special resins are available to treat sulphate-rich waters. (Conventional resins have a stronger affinity for sulphate than nitrate, reducing their capacity for nitrate removal).

## B(iv) DEIONISATION

For many laboratory and industrial applications, high-purity water which is essentially free from ionic contaminants is required. Water of this quality can be produced by deionisation.

The two most common types of deionisation are:

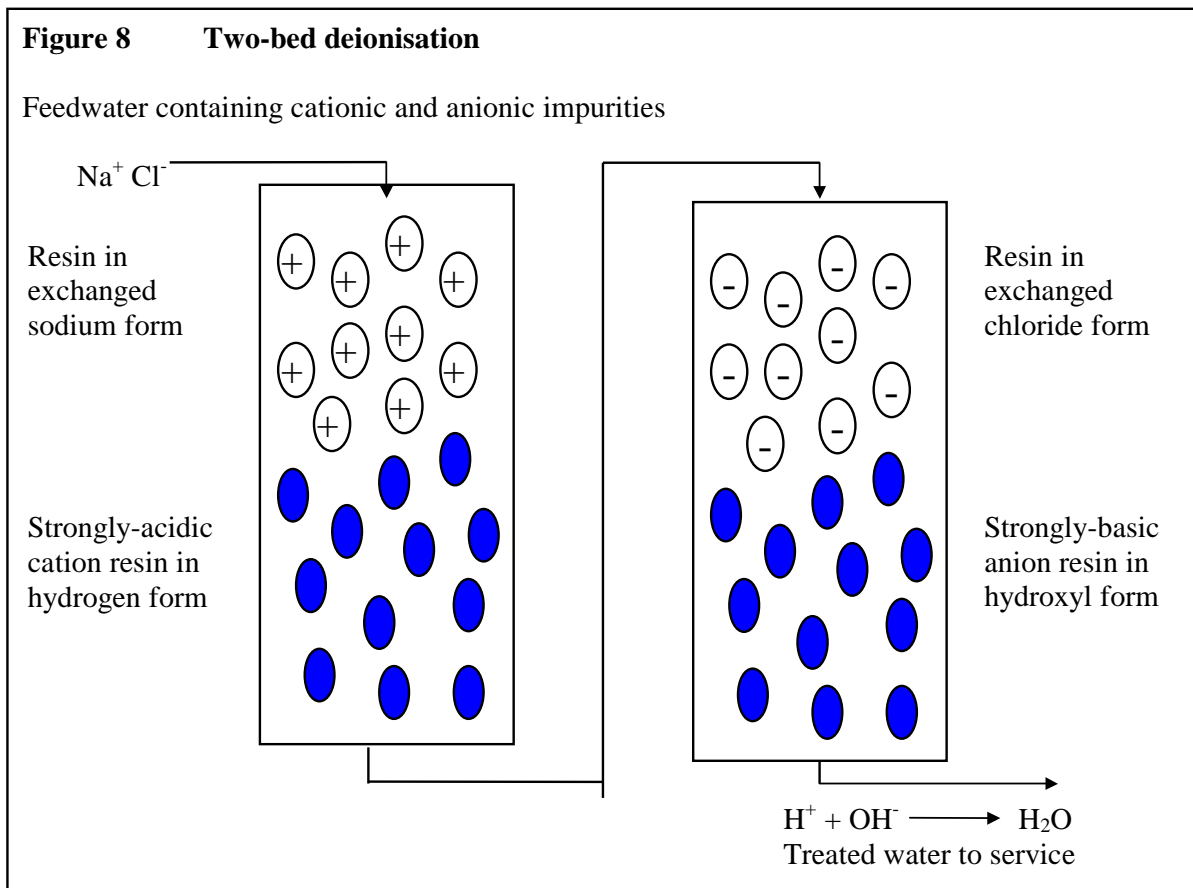
- i. Two-bed
- ii. Mixed-bed

### Two-bed deionisation

The two-bed deioniser consists of two vessels - one containing a cation-exchange resin in the hydrogen ( $H^+$ ) form and the other containing an anion resin in the hydroxyl ( $OH^-$ ) form. Water flows through the cation column, whereupon all the cations are exchanged for hydrogen ions.

NB. To keep the water electrically balanced, for every monovalent cation, e.g.  $Na^+$ , one hydrogen ion is exchanged and for every divalent cation, e.g.  $Ca^{2+}$ , or  $Mg^{2+}$ , two hydrogen ions are exchanged. The same principle applies when considering anion-exchange.

The decationised water then flows through the anion column. This time, all the negatively charged ions are exchanged for hydroxide ions which then combine with the hydrogen ions to form water ( $H_2O$ ). See Figure 8 below which illustrates the principles of two-bed deionisation.





## **Mixed-bed Deionisation**

In mixed-bed deionisers the cation-exchange and anion-exchange resins are intimately mixed and contained in a single pressure vessel. The thorough mixture of cation-exchangers and anion-exchangers in a single column makes a mixed-bed deioniser equivalent to a lengthy series of two-bed plants. As a result, the water quality obtained from a mixed-bed deioniser is appreciably higher than that produced by a two-bed plant.

The vessel can be in the form of a large stainless steel or reinforced fibreglass column containing many hundreds of litres of resin, or a small disposable/regenerable cartridge which, when exhausted, can either be thrown away or sent back to the original supplier for regeneration. The large deionisers - whether two-bed or mixed-bed - regenerate themselves automatically, in situ, when the water quality drops to a pre-set level.

Although more efficient in purifying the incoming feedwater, mixed-bed plants are more sensitive to impurities in the water supply and involve a more complicated regeneration process. Mixed-bed deionisers are normally used to 'polish' the water to higher levels of purity after it has been initially treated by either a two-bed deioniser or a reverse osmosis unit.

The deionisers used in laboratory applications are almost invariably small mixed-bed units containing exchangeable or disposable cartridges of resin. Large, self-generating deionisers are sometimes used in water purification systems supplying substantial volumes of water to suites of laboratories, or providing large quantities of industrial process water.

Three types of resin systems can be used in mixed-bed laboratory deionisers:

1. Standard strong mix.
2. Standard weak mix.
3. Nuclear grade.

The choice of resin system is dictated by the end-users' water requirements.

### Type 1

The standard strong mix range of disposable/exchangeable deionisers are filled with an intimate mix of a strongly acidic cation and strongly basic anion resins designed to remove all major ionic impurities.

From a single pass, this type of resin will produce water with a quality of between 1-10 MΩ.cm at 25°C when fed with either potable water or a pre-purified source.

## Type 2

The standard weak mix range of disposable/exchangeable deionisers are filled with an intimate mix of a strongly acidic cation resin and a weakly basic anion resin.

The weak base anion resin has little affinity for weak anions, e.g. silica (SiO<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>), and therefore, the treated water will contain silica and carbon dioxide at the same concentration as the feedwater. Therefore, the water quality in terms of conductivity expected from a weak base unit will be between 1-50 µS/cm. This quality is suitable for applications such as battery top-up.

## Type 3

Nuclear grade resin cylinders/cartridges are intended as final polishing mixed-bed units.

They are normally fed with deionised water of better quality than 1MΩ.cm resistivity, whereupon they will remove any remaining ionic impurities down to trace levels (sub-ppm) and polish the water to almost absolute purity of 18.24 MΩ.cm @ 25°C.

The resins employed are of a very high quality and as such, can only be used once as nuclear grade. When exhausted, the cylinder is recharged with new resin, and the exhausted nuclear grade resin is returned to the general pool of resin for regeneration.

## **Summary**

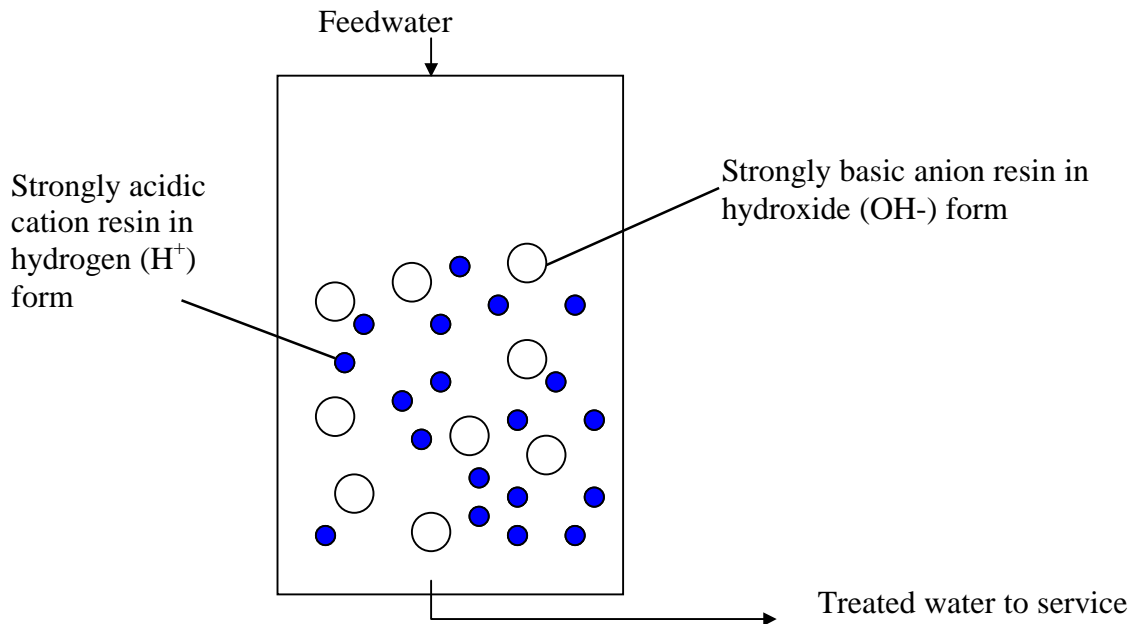
	Treated Water Quality	Comments
1. Standard strong (exhaustion point 1 µS/cm)	1-10 MΩ.cm @ 25°C	Single pass with potable or purified feedwater.
2. Standard weak (exhaustion point 50 µS/cm)	1-50 µS/cm @ 25°C	Silica & carbon dioxide levels same as influent.
3. Nuclear grade (exhaustion point usually set by customer's requirements)	18 MΩ.cm @ 25°C	Deionised feed - ionic impurities removed down to trace levels on recirculation.

Industrial mixed-bed deionisers usually feature strongly basic anion resins and regenerate themselves automatically in situ. By contrast, laboratory deionisers are either regenerated externally in a regeneration station, or the resins are discarded.

There are four distinct stages in the operation of an industrial mixed-bed deioniser:

- i. Service/exhaustion
  - ii. Backwashing
  - iii. Regeneration
  - iv. Rinse/remix
- 
- i. Service/exhaustion

**Figure 9. Mixed-bed deionisation - service/exhaustion**



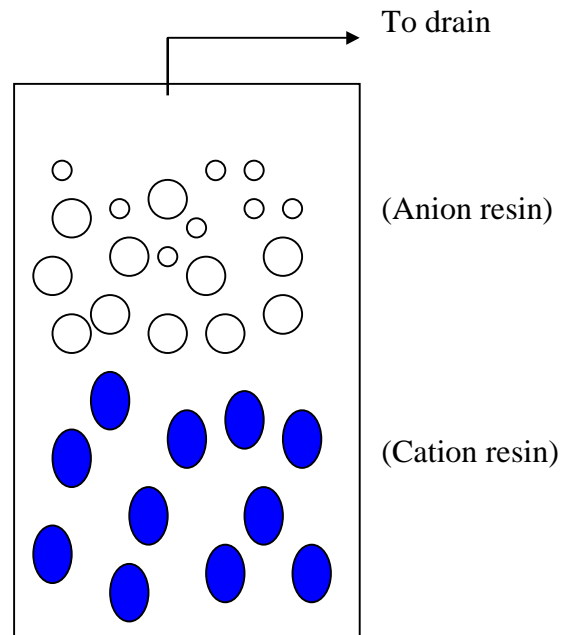
- ii. Backwashing

**Figure 10. Mixed-bed deionisation - backwashing**

Once the resins are exhausted, the bed is backwashed. Backwashing is initiated by introducing a uniform upward flow of water through the resin bed. The backwash step serves two important functions:

Firstly, it expands the resin bed releasing any entrapped particulate matter and resin fines.

Secondly, the backwash flow separates the denser cation resin from the lighter anion resin, forming two distinct layers in the vessel.

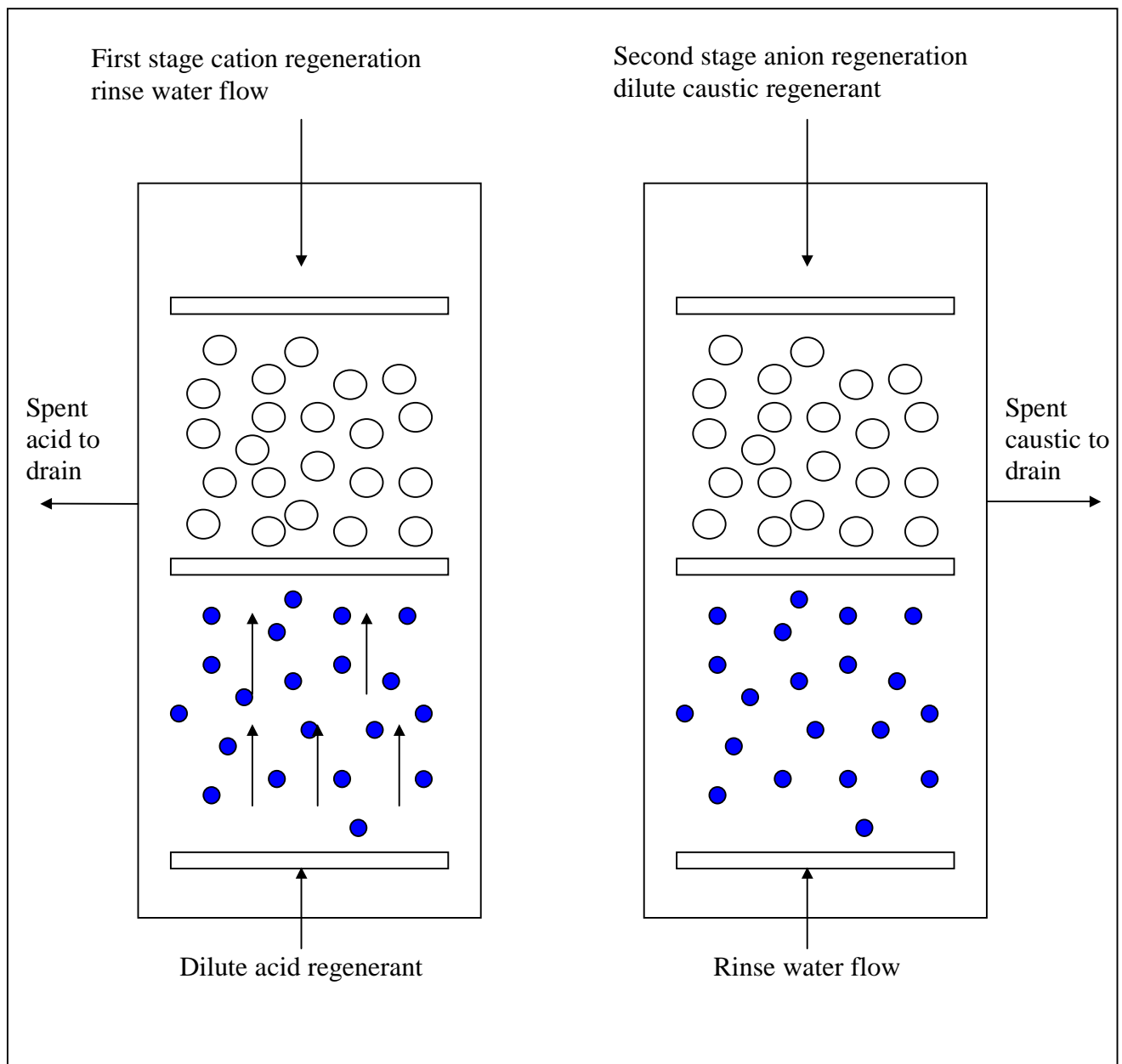


iii. Regeneration

↑  
Backwash water flow

The first stage in the process of regeneration involves passing a dilute solution of acid, usually hydrochloric, through the cation bed. After the cation resin has been regenerated, the anion resin is regenerated by passing a dilute solution of caustic (sodium hydroxide) through the anion resin bed. As a result, the cation resin is reconverted to the hydrogen form and the anion resin to the hydroxyl form.

**Figure 11. Mixed-bed deionisation - in situ regeneration**



iv. Rinse/remix

The final stage of regeneration is to rinse the resins of excess regenerant and then remix with air.