ION EXCHANGERS	GE 7

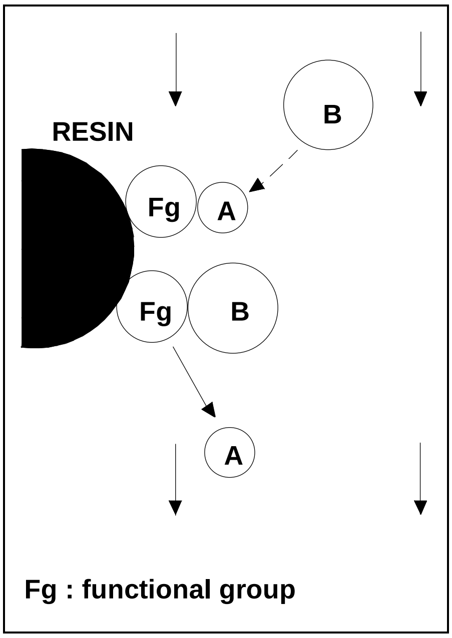
Principle

Ion exchangers are insoluble solid compounds having a basic chemical structure to which mobile ions are bonded by chemical groups known as « functional groups ».

The basic structure is acquired by organic synthesis (by polymerisation of a compound or co-polymerisation of several organic compounds). Ion exchangers are therefore synthetic resins. That is why they are frequently known as « ion-exchange resins » or simply « resins ».

Functional groups are either acquired directly during polymerisation or during post-treatment of the polymer beads.

Each ion exchanger has different affinities for the various ions with which it comes into contact. Whenever a resin bearing **A** ions for which it has little affinity comes into contact with a liquid containing **B** ions for which it has greater affinity, the **B** ions are absorbed by the resin in exchange for **A** ions. The liquid trickling over the ion exchanger therefore loses **B** ions and gains **A** ions. At the same time, the resin loses **A** ions and gains **B** ions (fig. 1 below).



- Fig. 1 : Ion-exchange principle

Exchange capacity

When a given volume of resin has released all its mobile ions, ion exchanging can no longer take place. The resin is then said to be " **saturated** ". The composition of the water recovered from the resin bed is identical to that of the water being treated.

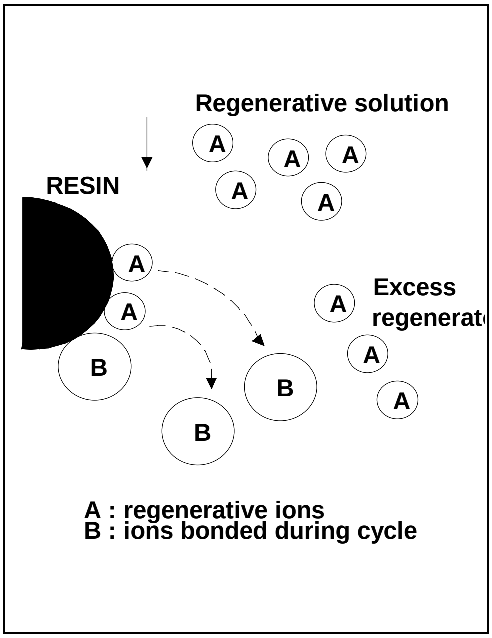
The saturated resin can then either be simply replaced by the new resin, or undergo treatment to restore its original chemical structure. Such treatment is known as " ***regeneration*** " (see below).

The term *exchange capacity* refers to the quantity of ions that a given volume of resin can absorb between two regenerations.

Each resin has a distinctive exchange capacity. This capacity is measured in cubic meter degrees or equivalents per litre of resin.

Regeneration of ion exchangers

During regeneration, a solution rich in regenerating ions is trickled over the saturated resin in such a way that the regenerating ions replace bonded ions during the production cycle (fig. 2 below).



- Fig. 2 : Regeneration of ion exchangers -

Because the resin has less affinity for regenerative ions than for the ions bonded to it during its production cycle, it is necessary to :

- use solutions with a relatively high concentration of regenerative ions,

- trickle the regenerative solution slowly over the resin.

The regenerative solution is stored in concentrated form in a container called the " reagent tub" (or " salt tub " in the case of sodium softening).

Life span of resins

In theory, resins should have an indefinite life span. In practice, three factors may, with time, alter a resin's exchange capacity :

- *Destruction of the basic structure*

Certain chemical compounds may react with the basic structure and lead to its partial or total destruction. This is the case with certain solvents and highly oxidising compounds in particular. This accidental phenomenon can be avoided by eliminating solvents or limiting the dose and contact time of oxidising compounds, particularly when disinfecting resins (see below).

- *Resin poisoning*

Ion exchangers are likely to bond with inert compounds (organic substances or metal oxides). Ion exchangers can also be a breeding ground for living organisms (algae, mould, bacteria). Deposits may therefore form on the resins and lead to a phenomenon known as « poisoning » : the granules are then coated with inert gangue which resists the desired ion exchange and reduces the resin's active surface.

- *Cracked resin beads*

The ions bonded to the resin in their working phase are not of the same size as those which bond during regeneration. As a result, the resin is subjected to internal swelling or deflation stress which eventually causes the resin beads to crack and fine particles to appear. These are easily drawn towards the drain during the regeneration phase.
Cracks in the resin beads can also be observed after freezing.

These phenomena lead to a gradual reduction in the volume of resin and a simultaneous diminution of the apparatus' exchange capacity.

Principal ion exchangers

Cationic exchangers

The functional groups of these resins are acid radicals, some being highly acidic while others are slightly acidic.

Highly acidic cationic exchangers

These resins have a low affinity for H^+ hydrogen ions, a slightly higher affinity for alkaline ions sodium Na^+ and potassium K^+, a high affinity for alkaline-earth ions magnesium Mg^{2+} and calcium Ca^{2+}, and a very high affinity for aluminium Al^{3+} and iron Fe^{3+}.

These resins are used in three forms for water treatment purposes :

- *sodium ($R\text{-}Na^+$)*

The resin bonds with alkaline-earth cations Ca^{2+} et Mg^{2+} and substitutes them for the cation Na^+. This is known as sodium softening. Regeneration is ensured by the sodium chloride (refined salt).

- *hydrogen ($R\text{-}H^+$)*

The resin bonds with all cations in the water and replaces them with the cation hydrogen H^+. In this form, the resins constitute one of the elements of the total demineralisation chain. Regeneration is carried out using a strong acid, usually hydrochloric acid, and sometimes sulphuric acid.

- *ammonium ($R\text{-}NH_4^+$) or potassium ($R\text{-}K^+$)*

Having been regenerated with a brine of ammonium chloride or potassium chloride, the resin can be used to soften water without a sodium build-up.

In most cases, this type of regeneration has horticultural applications (irrigation of calciphobic and sodiphobic plants).

Slightly acidic cationic exchangers

These resins are commonly referred to as carboxylic resins.

The carboxylic group gives these resins very specific properties :

- high affinity for the cation hydrogen H^+ ,
- very high affinity for cations other than H^+ having a pH in excess of 4.5, this affinity decreasing as soon as the pH falls under 4.5.

A pH of 4.5 is obtained when all hydrogencarbonates are transformed into carbonic acid by substituting the cation H^+ for alkaline-earth (Ca^{2+} and Mg^{2+}) and alkaline (Na^+ et K^+) ions.

It can thus be said that these resins bond with other cations besides H^+ up to the TAC (CDR?).

In addition, their practical exchange capacity is highly dependent on the TH / TAC ratio, the ionic current and the temperature.

These resins are almost always used in the form of H^+ (with regeneration by hydrochloric acid) for simultaneous softening and decarbonisation ; the carbonic acid released by the hydrogencarbonates breaks up into CO_2 and H_2O immediately.

Softening is :

- total if the TH is lower than the TAC,
- partial if the TH is higher than the TAC.

Anionic exchangers

These ion exchangers have a polystyrene or polyacrylic-type basic structure with basic functional groups. Some of these are highly alkaline while others are slightly alkaline.

Highly alkaline anionic exchangers

These resins have a very high affinity for strong anions (nitrates, sulphates, chlorides), an average affinity for hydrogencarbonates and carbonates, a slightly lower affinity for hydrogensilicate ions (ionised silica), and a much lower affinity for hydroxyl anions (OH^-).

They are mainly used in the form of $R\text{-}OH^-$ (regeneration by caustic soda NaOH) in total demineralisation treatments downstream from a highly acidic cationic exchanger.

In the $R\text{-}OH^-$ form, highly alkaline anionic exchangers must not be fed with hard water, in order to prevent the formation of magnesium oxide $Mg(OH)_2$ deposits at the beginning of the cycle and calcium carbonate deposits in the middle and at the end of the cycle.

Slightly alkaline anionic exchangers

These resins have functional groups of the tertiary amine type (dimethylamine). They have a very high affinity for strong anions (nitrates, sulphates, chlorides) and an average affinity for hydroxyl anions (OH^-).

However, they do not bond with weak anions (hydrogencarbonates and hydrogensilicates), and lead to the production of water with a pH under 7.

They are used in total demineralisation after a highly acidic cationic exchanger, or alone when the presence of CO_2 and silica in the treated water does not jeopardise the use of this water, or in pre-treatment prior to a highly alkaline anionic exchanger. In the latter case, only weak anions must be bonded to the highly alkaline finisher.

Regeneration rate

The term «regeneration rate », mainly expressed in percentages, refers to the ratio between the quantity of regenerative ions employed for one regeneration process and the quantity of ions to which the resin will bond during the production cycle following the regeneration process.

This rate varies according to a number of criteria :

- type of resin ;
- quantity of regenerator used per litre of resin ;
- concentration of the regenerative solution on contact with the resin ;
- mode of regeneration (see below) ;
- rate at which regenerator flows over resin ;
- saturation of the resin at the time of regeneration;
- temperature of regenerative solution.

The regeneration rate is also influenced by the efficiency of the distribution and recovery devices in the filter frame, inasmuch as these devices distribute the regenerator evenly or unevenly over the whole resin bed.

Lastly, the empty spaces between the resin beads during the flow of the regenerator play an important role because when the beads are spaced too far apart, some of the regenerator does not come into contact with the resin.

In practice, the regeneration rate varies from 20 % to 95 % according to the type of resin and operating conditions.

There are two main regeneration modes :

– *Downstream regeneration*

In this mode, the regenerator flows through the resin bed in the same direction as the water in the production cycle, i.e. downstream as in conventional procedures.

This mode has the advantage of not requiring an elaborate upstream distributing device as the regenerator flow is automatically distributed almost evenly by the upper layers of the resin bed.

– *Upstream regeneration*

In this mode, the regenerator moves against the flow of the water being treated : for conventional ion exchangers treating the water in a downstream movement, the regenerator flows upstream.

Fluidised beds

Fluidised beds are exchanger devices for ions regenerated upstream, with the treated water flowing upstream during the production cycle, and regeneration taking place downstream.

Recently developed, the main advantage of this method over conventional downstream methods, is a significant improvement in the regeneration rate and quality of the treated water, with the volume of regeneration effluents being considerably reduced.

Again with regard to the conventional downstream method, this method eliminates problems involving regenerator distribution and resin accumulation during regeneration which takes place downstream.

A number of systems have been developed and patented. These include three Bayer beds called “Schwebebett ”, “ Rinsebett ” and“ Liftbett ”.

Mixed beds

The « mixed bed » principle consists of filling an ion exchanger vessel with an optimally uniform mixture of two resins, one of these being a « strong cationic » resin in the form of $R\text{-}H^{+}$, and the other being a « strong anionic » resin in the form of $R\text{-}OH^{-}$.
The resin bed makes up a very long chain in which each link is a "strong cation-anion » pair.

Mixed bed regeneration

The two types of resin cannot be regenerated without first being perfectly separated. The anionic resin would be saturated by the anions in the acid used for regenerating the cationic resin, while the cationic resin would be saturated by the sodium used to regenerate the anionic resin.

The resins can be separated properly by lifting them under a strictly controlled flow, using the slight difference in real density between the saturated resin beads, the anionic resin being lighter than the cationic resin. It should be noted that this difference in density is not enough to separate the resins properly if they are not totally saturated.

Regeneration in situ

The two resins are regenerated separately thanks to a network of interposed strainers. After regeneration, the resins are mixed again using compressed air (dry, oil-free air).

Non-regenerated resins

When the volumes of resin are very small and/or the treated water is intended for applications requiring the mixed resin to be extremely pure, non-regenerated resins after saturation are used.

Exhausted resins can be dumped (if they have not bonded with toxic substances or undesirable pollutants) or incinerated.