ION EXCHANGE FOR DUMMIES

An introduction

Water

Water is a liquid.

Water is made of water molecules (formula H_2O).

All natural waters contain some foreign substances, usually in small amounts. The water in the river, in a well or from your tap at home is not just H_2O, it contains a little of:

- Solid, insoluble substances, such as sand or vegetal debris. You can in principle filter these solid substances out.
- Soluble substances, that you most often cannot see and that cannot be filtered out. These substances can be inorganic or organic, they can be ionised (electrically charged) or not.

The soluble, **non-ionised** substances are present in the water in form of **molecules** of various sizes and formulas, for instance:

- Carbon dioxide is a small molecule with a simple formula: CO_2.
- Sugar is a larger molecule with a complicated formula abbreviated as $C_{12}H_{22}O_{11}$.

You may want to remove these foreign substances from the water. You can remove the ionised substances by ion exchange.

Ions

The soluble, **ionised** substances are present in water as **ions**, which are electrically charged atoms or molecules. The positively charged ions are called **cations**, and the negatively charged ions are called **anions**. Because water is globally neutral electrically (otherwise you would get an electric shock when you put your hand in water) the number of positive charges is identical to the number of negative charges.

Ions can have one charge or more, the most usual range being 1 to 3. Ions can be made of one atom only, or several atoms linked permanently together, like molecules.

Examples:

- A monovalent atomic cation: the sodium ion Na^+
- A divalent atomic cation: the calcium ion Ca^{++}
- A monovalent molecular cation: the ammonium ion NH_4^+
- A monovalent atomic anion: the chloride ion Cl^-
- A monovalent molecular anion: the nitrate ion NO_3^-
- A divalent molecular anion: the carbonate ion $CO_3^=$
- A divalent complex anion: the chromate ion $CrO_4^=$
- The trivalent aluminium cation Al^{+++} exists only in very acidic solution, not in normal water.

Ions are able to move around in water, they are not fixed, and they are not attached to ions of the opposite charge. Only to sum of the charges is the same for all cations and all anions. See figure 1 for a schematic representation of ions in water.

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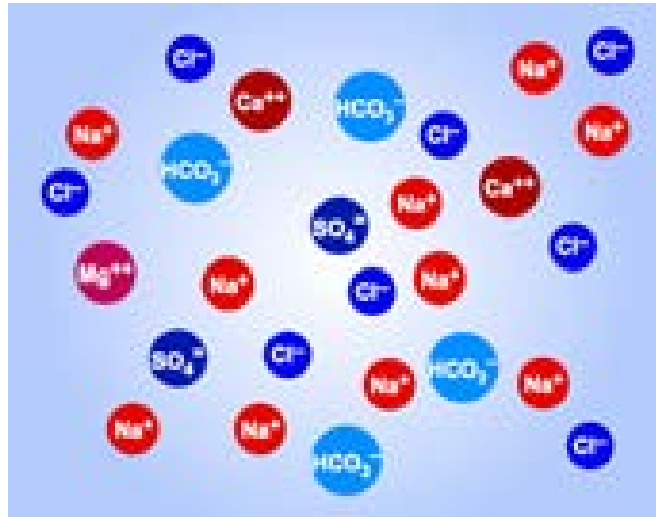www.lenntech.com   Fax. +31-152-616-289

Figure 1: Ions in water are not attached. The sum of charges is constant.

Salts are crystallised substances containing a fixed proportion of cations and anions. For instance, table salt has exactly the same number of sodium cations (Na^+) and chloride anions (Cl^-). Its formula is given as NaCl. When you dissolve a salt into water, its cations and anions are free to wander as seen on figure 1.

Ions in water are loosely connected to water molecules. They are said to be hydrated, the cations being attracted by the O atom, anions by the H atoms of the water molecule, as shown in figure 2.
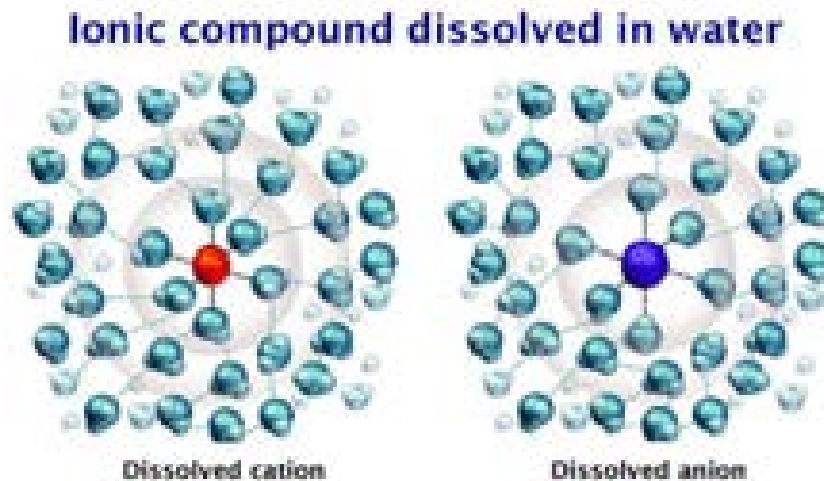

Figure 2: Ions in water e.g. Na^+ and Cl^- (table salt NaCl)

Magnesium sulphate is a salt with exactly the same number of magnesium cations (with double charge: Mg^{++}) and sulphate anions (also with double charge, $SO_4^=$) so that the formula is $MgSO_4$.

Calcium chloride is made of calcium ions (with 2 charges, Ca^{++}) and chloride ions (with 1 charge only, Cl^-). You need 2 chloride anions to balance each calcium cation. Therefore the formula of calcium chloride is $CaCl_2$.

Similarly, in sodium carbonate you have sodium cations Na^+ and carbonate anions $CO_3^=$, so that you need 2 sodium ions for each carbonate ion, and the formula is Na_2CO_3.

When you boil and evaporate water for a long time, you are left with a dry residual which is made of salts and possibly other residues, such as silica and organic compounds. Only in sea water do you have a sizeable quantity of dry residual, 35 to 40 g dry residual for one litre of sea water. In river or tap water, the dry residual is usually very low, ranging from 50 to 500 mg/L. The dry residual is also called **Total Dissolved Solids** and abbreviated as TDS.

Ion Exchange

Impurities in water

Water, as we have seen, contains small amounts of foreign substances. In many cases, these substances cause no problem. Drinking water containing some salinity is much better for health than ultra-pure water. For specific applications, however, these foreign substances are regarded as **impurities** and must be removed from water.

Insoluble substances (sand etc.) can be removed by filtration. There are many different sorts of filtration technologies, down to ultrafiltration that can remove sub-micron particles. For soluble substances other techniques must be used.

Soluble ionised substances can be removed by ion exchange.

Ion exchange resins

These are very small plastic beads, with a diameter of about 0.6 mm. These beads are porous and contain invisible water inside the beads, measured as "humidity" or "moisture content". The structure of the resin is a polymer (like all plastics) on which a **fixed ion** has been permanently attached. This ion cannot be removed or displaced; it is part of the structure. To preserve the electrical neutrality of the resin, each fixed ion must be neutralised with a **counterion**. This counterion is mobile and can get into and out of the resin bead. Figure 3 shows schematic cation and anion exchange resin beads. The dark lines represent the polymeric skeleton of the resin bead: it is porous and contains water. The fixed ions of this cation exchange resin are sulphonates (SO_3^-) that are attached to the skeleton. In this picture, the mobile ions are sodium (Na^+) cations. Cation exchange resins such as Amberjet 1200 are often delivered in the sodium form.
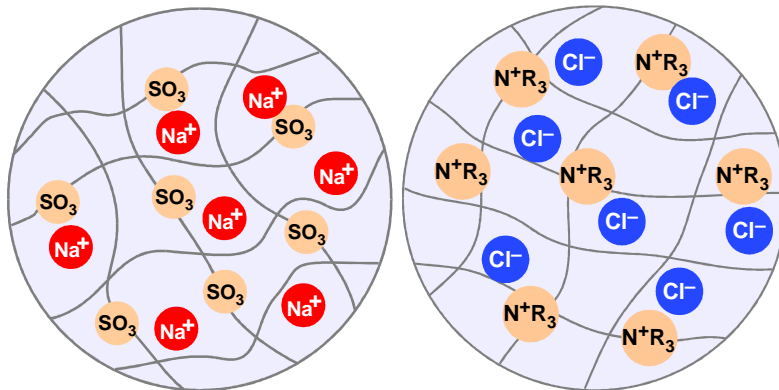

Figure 3: Schematic cation and anion exchange resin beads

The anion resin bead has a very similar skeleton. The functional groups are here quaternary ammonium cations shown in the picture as N^+R_3; a more accurate formula would be $CH_2-N^+-(CH_3)_3$. The mobile ions in the anion resin bead are chloride anions (Cl^-). This is also the standard delivery form for many anion resins. Each ion going into the bead has to be replaced by an ion getting out of the bead, again to preserve electrical neutrality. This is what is called **ion exchange**. Only ions of the same electric sign are exchanged. You cannot make a resin that can exchange cations as well as anions, because the fixed cations inside the resin beads would neutralise the fixed anions and no exchange with the outside world would be possible. Therefore you need separate cation exchange resins and anion exchange resins.

Water softening

Among the substances dissolved in water, **hardness** is very commonly found. Hardness is a popular word to represent principally calcium and magnesium dissolved in the water; these ions can precipitate under certain conditions and form the scale that you may have seen in your boiling pan, and that can obstruct pipes and damaged water boilers. The "softening" of water is the exchange of the hardness cations (Ca^{++} and Mg^{++}) for another cation that cannot form scale because it is much more soluble: the sodium ion Na^+.

To soften water, you take a cation exchange resin on which the mobile ion inside the beads is sodium (Na^+) and you pass the hard water through a column filled with the sodium form resin. The hardness ions Ca^{++} and Mg^{++} move into the resin beads and each of these divalent cations is replaced by two sodium ions getting out of the resin. The exchange reaction can be written as:
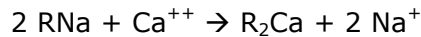
$$2\ RNa + Ca^{++} \rightarrow R_2Ca + 2\ Na^+$$

Figure 4 illustrates the reaction: the resin beads are initially loaded with sodium (Na^+) ions. As shown schematically, each calcium or magnesium ion entering the resin bead is compensated by two sodium ions leaving it. Anions from the water (not shown) cannot enter the resin bead because they would be repelled by the fixed sulphonate (SO_3^-) anions inside the beads.
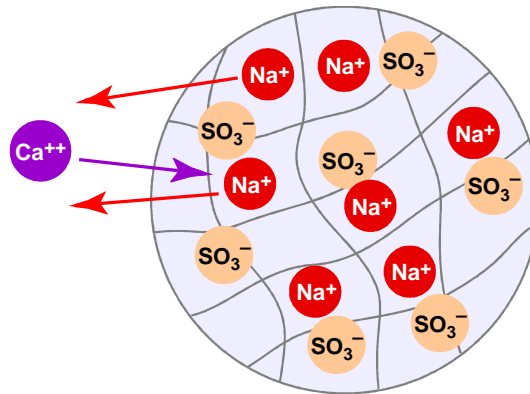

Figure 4: Softening (sodium exchange) in a single resin bead

This cation exchange can only take place efficiently because the cation exchange resin has a higher **affinity** for the hardness ions than for sodium. In plain English, the resin prefers calcium and magnesium over sodium. The result of the softening process is not a net removal of the hardness ions from water, it is the replacement of the hardness ions by sodium ions. The salinity of the water has not changed, only the constituents of the salinity are different at the end of the softening process.

Obviously, this exchange is not unlimited: when the resin has removed so much hardness from the feed water that no room is left on the resin for removing more, the exhaustion run has to be stopped. At this stage, the resin will be replaced by a fresh resin, or regenerated.

Demineralisation

If you replace all cations dissolved in water by H^+ ions and all anions by OH^- ions, these will recombine and form new molecules of water. To do this, you need a cation exchange resin in the H form and an anion exchange resin in the OH form. All cations and anions will be exchanged, and in this case the net result is a complete "disappearance" of the ionic contaminants. The cation exchange reactions will be:

$$2\ R'H + Ca^{++} \rightarrow R_2Ca + 2\ H^+$$

$$R'H + Na^+ \rightarrow R'Na + H^+$$
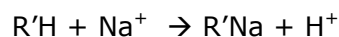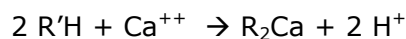
In these equations, R' represents the cation resin. This is shown on figure 5. The resin is initially in the hydrogen (H^+) form. In this picture the anions in water are not shown. You can see that one Ca^{++} ion getting in causes two H^+ ions to leave the resin, whilst one Na^+ cation is exchanged for one H^+ ion.

Ion exchange introduction

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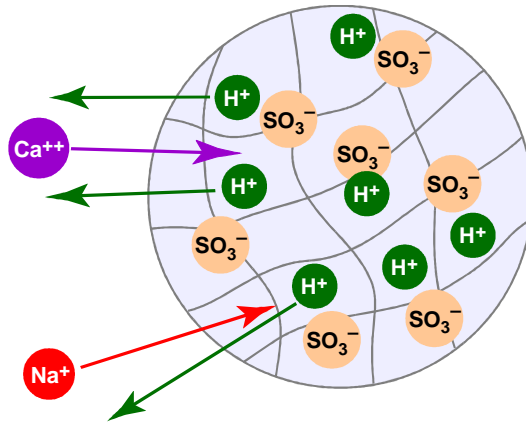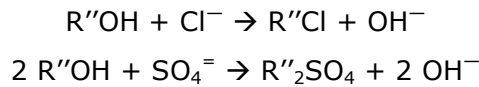
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Figure 5: Decationisation (all cations replaced by H⁺)

Similarly, an anion exchange resin initially in the OH form can remove all anions. The anion exchange reactions will be:

$$R''OH + Cl^- \rightarrow R''Cl + OH^-$$

$$2\ R''OH + SO_4^= \rightarrow R''_2SO_4 + 2\ OH^-$$

where R'' represents the anion exchange resin. All anions are replaced by hydroxide (OH⁻) ions. There is no picture for this anion exchange, as it is very similar to the cation exchange picture in figure 5 above.

At the end of the exchange process, the resin beads have loaded all cations and anions from the water and released H⁺ and OH⁻ ions. The resin beads are nearly exhausted (fig. 6 shows them completely exhausted).
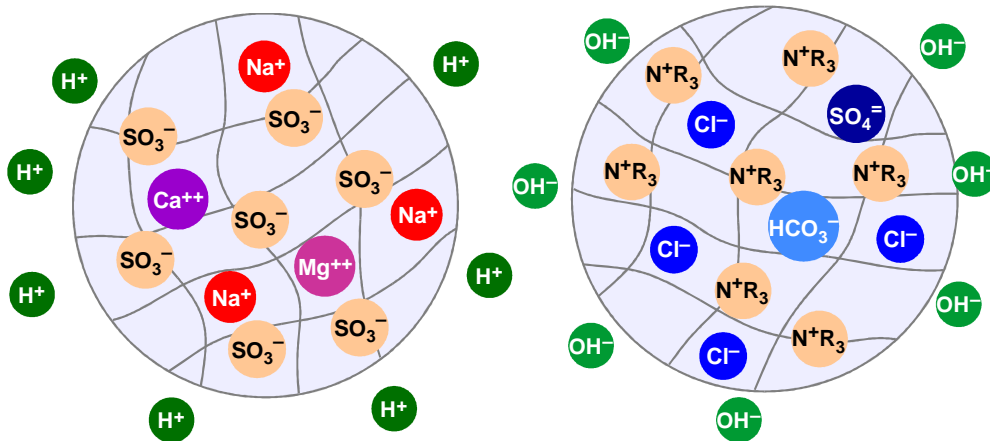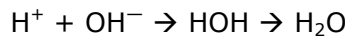

Figure 6: Resin beads are exhausted. H⁺ and OH⁻ ions have been released into the water

These ions will immediately combine and form water:

$$H^+ + OH^- \rightarrow HOH \rightarrow H_2O$$

The ionic contaminants are now sitting on the two resins (Na and Ca on the cation resin, Cl and SO₄ on the anion resin) and the water has been **completely demineralised**. Its salinity is reduced to almost nothing, a few ions that have "escaped" from the resin columns, and that are called **ion leakage**. So demineralisation can be summarised in the following picture:
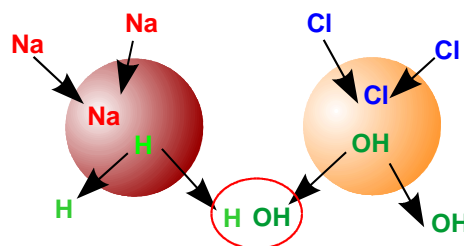

Figure 7: Demineralisation summary!

How resins look like

Figure 8: Sample of a macroporous cation resin

Figure 9: A gel-type Amberjet anion resin under the microscope

Column operation

In the laboratory as well as in industrial plants, ion exchange resins are used in columns. The water or solution to be treated flows through the resin. On figure 10, you see the fresh resin, then you see how the resin gets progressively loaded with the ions from the feed solution. Ions from the resin not shown on the picture are released into the treated solution. At the end some of the "blue" ions escape into the pure solution, and operation is stopped.
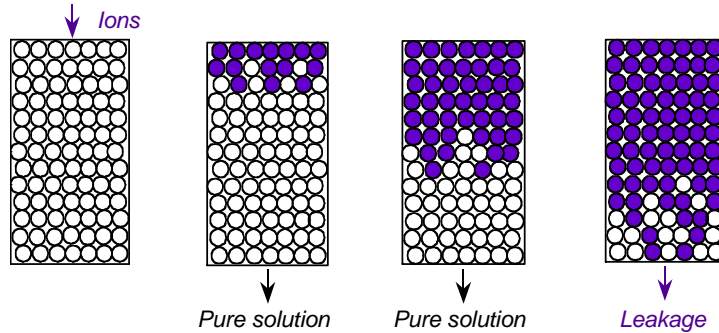

Figure 10: Column operation

Figure 11 shows a typical laboratory column, a simple industrial column and a photograph of an existing Amberpack plant.
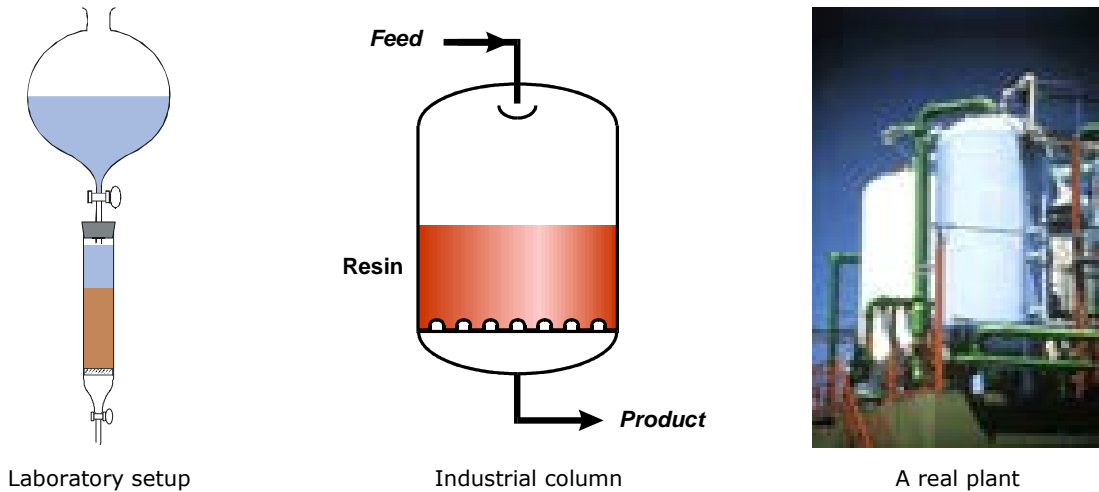

Laboratory setup   Industrial column   A real plant

Figure 11: Ion exchange columns

Regeneration

When the resins are exhausted, you can bring them back to the fresh state and start over again. Regeneration of ion exchange resins is a reversal of the exchange reactions shown above. For instance, the softening resin is regenerated with sodium (Na^+) ions supplied by a salt (common salt: NaCl) solution. The regeneration reaction is:

$$R_2Ca + 2\ NaCl \rightarrow 2\ RNa + CaCl_2$$
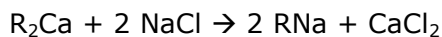
Regeneration can only be performed when the concentration of the regenerant is high, typically 1000 times higher than the concentration in normal water. For instance, salt is used as a brine with 10 % (about 100 g/L) concentration.

In the case of demineralisation, strong acids such as hydrochloric acid (HCl) or sulphuric acid (H_2SO_4) are fully dissociated and can supply H^+ ions to replace the cations that have been exchanged and are sitting in the cation exchange resin beads at the end of the exhaustion run:
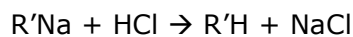
$$R'Na + HCl \rightarrow R'H + NaCl$$

Similarly, strong alkalis, of which in practice only caustic soda (NaOH) is used, can supply OH⁻ ions to replace the anions sitting on the anion exchange resins beads at the end of the run:

$$R''Cl + NaOH \rightarrow R''OH + NaCl$$
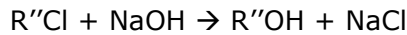
As can be seen from the regeneration reactions, the regeneration step produces saline waste. This is the principal disadvantage of ion exchange.

Limits of ion exchange

For ion exchange to be efficient there must be a **difference in affinity** between the ion in the resin and the ion or ions you want to remove from solution. The resin must have a higher affinity for the ion in solution compared to the ion in the resin.

The ion exchange technology is a perfect tool to remove or exchange contaminants present in **low concentrations**. In such a case the running time until the resin column is exhausted can be very long, ranging from a few hours to several months. When however the concentration of contaminants is high, say several grams per litre of water, the ion exchange cycles become exceedingly short and the quantity of regenerants increases to uneconomical levels. In the case of brackish water (underground water with high salinity as often found in arid countries) or sea water, ion exchange is not suitable and other technologies must be used, such as reverse osmosis or distillation.

Also, any contaminant that is not ionised cannot be removed by ion exchange. Other technologies are available for this purpose, using activated carbon, polymeric adsorbents, molecular sieves and other media.

Selective ion exchange

Thanks to differences of affinity for different ions, common ion exchange resins can be used to remove selectively ions from water. One of the most obvious examples is softening. You cannot soften water effectively with reverse osmosis; you have to demineralise it partially. Similarly, you can remove fairly selectively other ions from water, such as nitrate of sulphate, using an anion exchange resin in the chloride form. This works because the anion resin has more affinity for the nitrate or sulphate ion than for the chloride ion, the order of affinity being:

$$SO_4^= > NO_3^- > Cl^- > HCO_3^- > OH^- > F^-$$
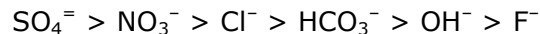
For cation resins used in softeners, the affinity is

$$Pb^{++} > Ca^{++} > Mg^{++} > Na^+ > H^+$$
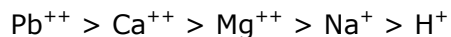
The Pb (lead) is shown here to indicate that any dissolved lead will be removed efficiently by a softening resin, as well as many other (but not all) heavy metals.

Some contaminants are not easy to remove by conventional ion exchange resins. In many cases, very specific resins have been developed for these contaminants. Selective resins are available today for the removal of:

- Boron
- Cadmium, mercury and other heavy metals
- Chromate
- Lead
- Nickel
- Nitrate
- Perchlorate

and some other contaminants.

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Conclusion

Ion exchange is a very powerful technology to remove impurities from water and other solutions. Many industries depend on ion exchange for the production of extremely pure water. Examples are

- Nuclear and thermal power stations
- Semiconductor, computer chips and display panel production
- Removal of toxic contaminants from drinking water

There are also many applications in areas other than water treatment, in the food industry, chemical processes, catalysis, mining, waste decontamination and a lot more…