ION EXCHANGE

- Similar in many ways to adsorption treatment, but chemical mechanism is *ion exchange* rather than adsorption.
- An ion exchanger is an insoluble substance containing loosely held ions which can be exchanged with other ions in solution which come in contact with it.
- These exchanges take place without any physical alteration to the ion exchange material.

During ion exchange mobile ions from an external solution are exchanged for ions that are electrostatically bound to the functional groups contained within a solid matrix.

Example :

$$R - H + Cs^+ \leftrightarrow R - Cs + H^+$$

where R represents the insoluble matrix of the ion exchange resin.

The cation exchanger will release its hydrogen ion into solution and pick up a caesium ion from the solution.

Example :

In the softening of water by the ion exchange process, the calcium and magnesium ions are removed from the solution and the exchanger solid releases sodium ions to replace the removed calcium and magnesium ions.

$$2RNa^{+} + Ca^{+2} \leftrightarrow RCa^{+2} + 2Na^{+}$$

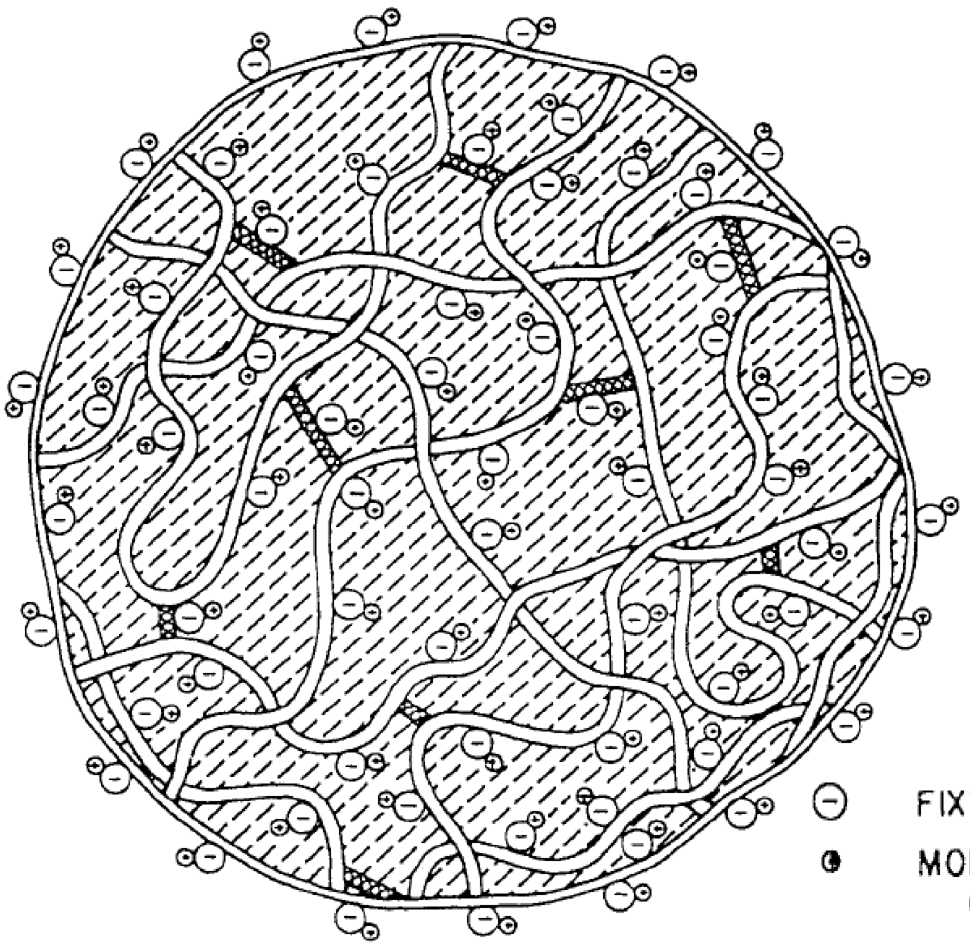
$$2RNa^{+} + Mg^{+2} \leftrightarrow RMg^{+2} + 2Na^{+}$$

- **functional groups are negatively charged**
  - exchange will involve cations
- **functional groups are positively charged**
  - exchange will involve anions

- The first commercially used ion exchange materials were naturally occurring porous sands that were commonly called **zeolites**.
- Zeolites were the first ion exchangers used to soften waters; however, they have been almost completely replaced in recent years by synthetic organic exchange resins that have a much higher ion exchange capacity.

Resin is a network of crosslinked hydrocarbons attached to ionic groups.

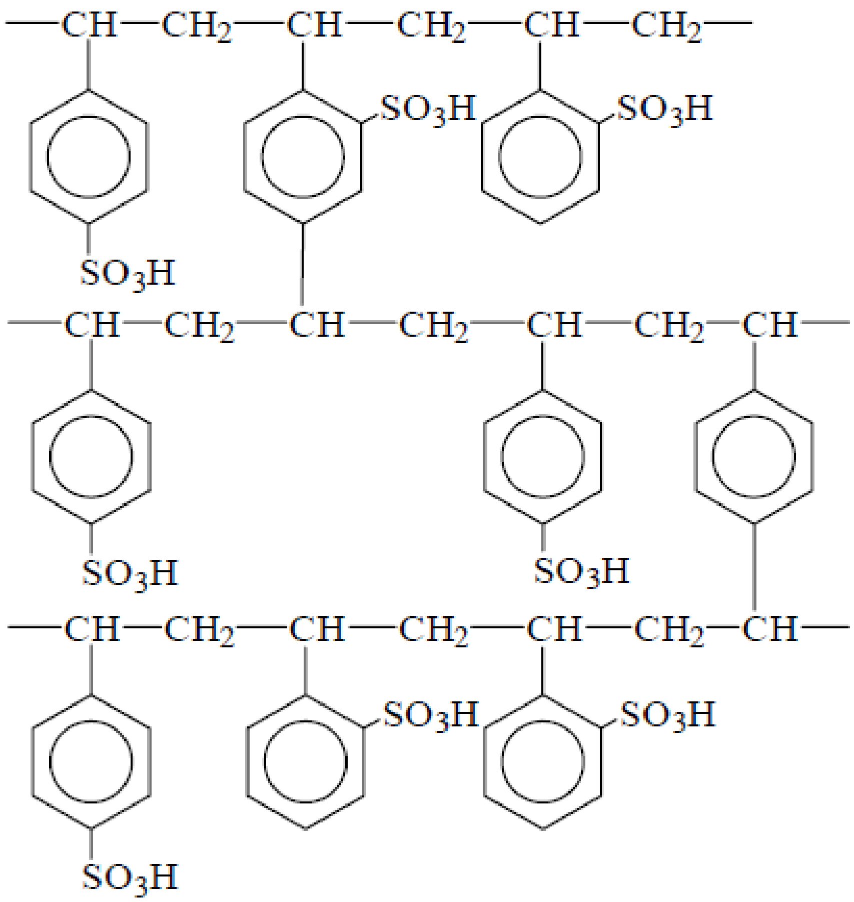
The resins are prepared as spherical beads 0.5 to 1.0 mm in diameter.



Synthetic cation exchange resins are polymeric materials that have reactive groups, such as the

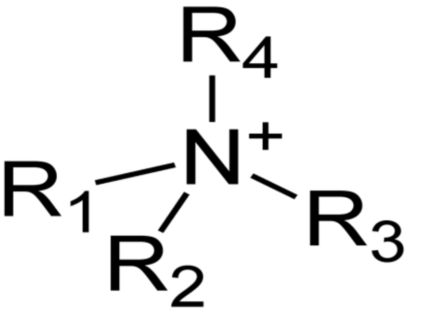
- Sulfo acidic groups ⇨ $-SO_3H$
- Phospho acidic groups
- Phenolic groups
- Carboxylic groups

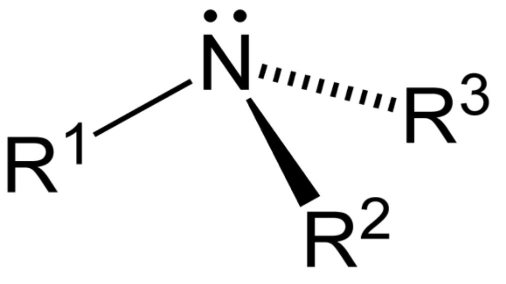
that are ionizable and may be charged with exchangeable cations.



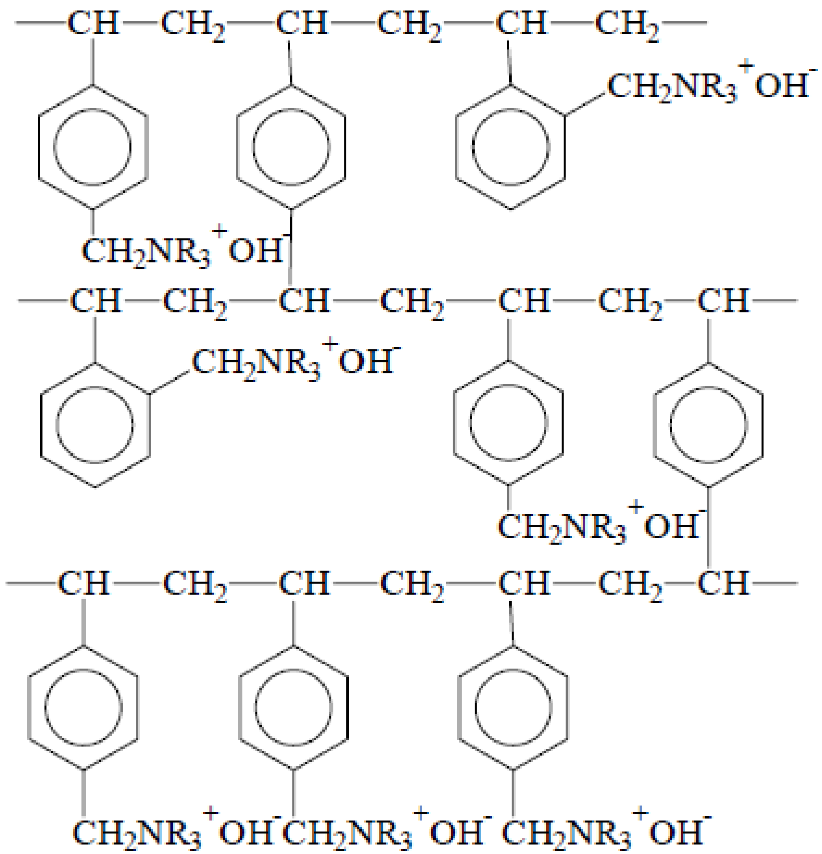
A strongly acidic sulphonated polystyrene cation exchange resin

Also, synthetic anion exchange resins are available that have ionizable groups, such as the

- quaternary ammonium  or

- amine groups, 

that may be charged with exchangeable anions.



A strongly basic quaternary ammonium anion exchange resin

Depending on the type of the functional group, ion exchangers can be divided into several types:

- strong acidic,
- strong basic,
- weak acidic,
- weak basic.

pk VALUES FOR THE MOST COMMON FUNCTIONAL GROUPS OF ORGANIC ION EXCHANGERS			
Cation Exchangers		**Anion Exchangers**	
Functional group	pK	Functional group	pK
$-SO_3H$ (strong acidic)	1-2	$\equiv N^+$(strong basic)	1-2
$-PO_3H_2$	2-5	$=N$	4-6
$-COOH$	4-6	$=NH$	6-8
$-OH$ (weak acidic)	9-10	$-NH_2$ (weak basic)	8-10

To achieve the removal of both positively and negatively charged ions from solution, a mixture of cation and anion resins in a mixed bed system is often used.

Example

For a NaCl solution the ion exchange process will be:

$$R_1 - H + Na^+ \Leftrightarrow R_1Na + H^+$$

$$R_2 - OH + Cl^- \Leftrightarrow R_2Cl + OH^-$$

$$2H^+ + OH^- \Leftrightarrow H_2O$$

Since H_2O is only weakly dissociated, the reactions of ion exchange are driven in this case to the right hand side of the equation.

SELECTIVITY

- Ion exchange media have a *greater affinity* for certain ionic species than for others. Thus, a separation of these species can be made.
- Certain ions in the solution are preferentially sorbed by the ion exchanger solid, and because electroneutrality must be maintained, the exchanger solid releases replacement ions back into the solution.

SELECTIVITY

The generalized equation for cation exchange by a resin may be represented by

$$M_1^+ + Re.M_2 \leftrightarrow M_2^+ + Re.M_1$$

where M_1^+, M_2^+ are cations of different species and Re is the resin.

The equilibrium constant for this reaction is ,

$$K_{M_2^+}^{M_1^+} = \frac{[\mathrm{Re}.M_1][M_2^+]}{[\mathrm{Re}.M_2][M_1^+]} = \left[\frac{M_1}{M_2}\right]_{solid} \times \left[\frac{M_2}{M_1}\right]_{solution}$$

Eqn.s 13.8 and 13.9 in Reynold's

where $K_{M_2^+}^{M_1^+}$ = selectivity coefficient

The greater the selectivity coefficient, *K*, the greater is the preference for the ion by the exchanger. An ion exchanger tends to prefer

1. ions of higher valence,
2. ions with a small solvated volume,
3. ions with greater ability to polarize,
4. ions that react strongly with the ion exchange sites of the exchanger solid, and
5. ions that participate least with other ions to form complexes.

However, it should be noted that selectivity coefficients are not constant and will vary with the experimental conditions such as concentration, temperature and the presence of other ions in the solution.

The determination of selectivity coefficients is a complicated task and is ordinarily not undertaken in the design of waste treatment systems; most of these parameters can be extracted from manufacturers' data or research literature.

For the usual cation exchangers, the preference series for the most common cations is as follows:

Ba^{+2}> Pb^{+2} > Sr^{+2} > Ca^{+2} > Ni^{+2} > Cd^{+2} > Cu^{+2} > Co^{+2} > Zn^{+2} > Mg^{+2} > Ag^{+} > Cs^{+} > K^{+} >NH_4^{+} >Na^{+} >H^{+}

This series is for strong acid resins - that is, those having strong reactive sites such as the sulfonic group ($-S0_3H$).

Weak acid resins such as the carboxylic group (-COOH) - will have the H^{+} position to the left of that shown here.
For very weak sites, the H^{+} may fall to the left as far as Ag^{+}.

For the usual anion exchangers the preference series for the most common anions is as follows:

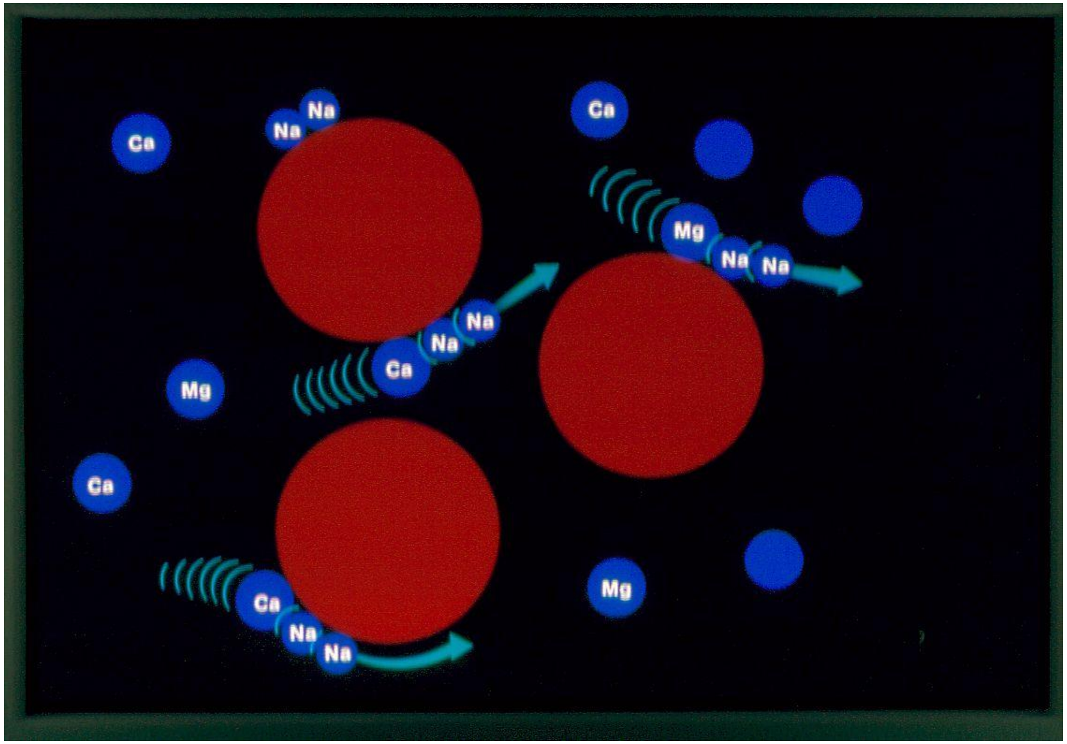
$S0_4^{-2} > I^- > NO_3^- > Cr0_4^{-2} > Br^- > Cl^- > OH^-$

This series is for strong base resins such as the quaternary ammonium group.

For weak base resins - such as the secondary or tertiary amine group - the OH^- will fall farther to the left.

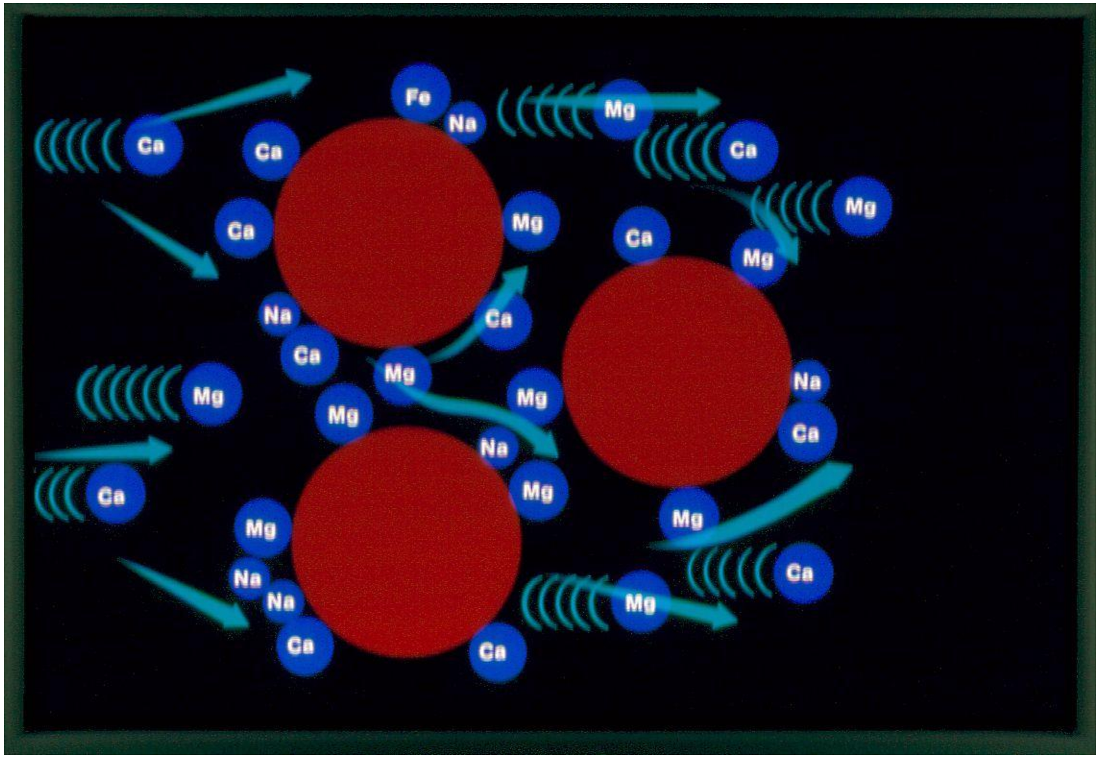
REGENERATION

www.waterking.com/presentations/PPT020



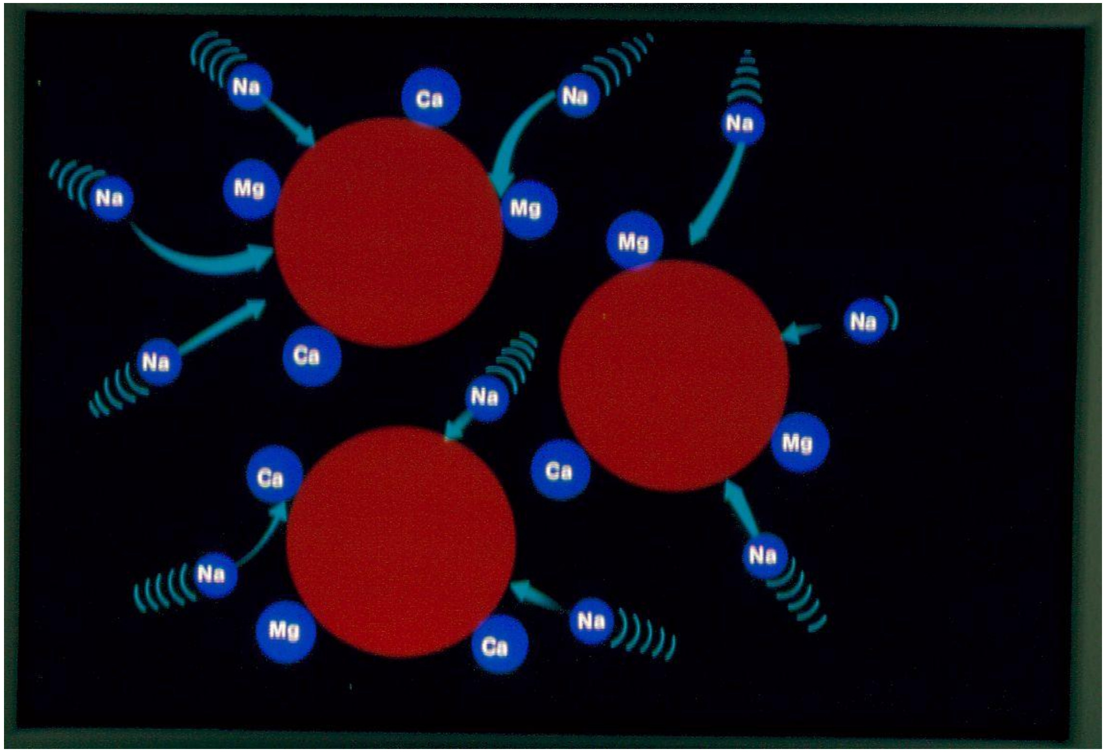
- Resin beads attract Ca^{+2} and Mg^{+2} ions and release Na^{+}.
- Water has been softened because the Ca^{+2} and Mg^{+2} concentrations, which cause water hardness have been reduced.

- After a vast number of Ca^{+2} and Mg^{+2} ions have become attached to the resin beads, and most of the Na^{+} ions have been released, the resin can no longer soften the water.



- If no new chemical reaction is set, the incoming Ca^{+2} and Mg^{+2} ions flow untouched through the unit because there is no room for them on the resin beads.

- The reaction can be reversed by greatly increasing the concentration of sodium in the solution.
- Reverse process drive the Ca^{+2} and Mg^{+2} ions off the resin beads and replace them with Na^{+} ions.



- This process is called **REGENERATION**.

REGENERATION

- At appropriate time, the resin beads are washed with a strong solution, also known as a BRINE SOLUTION.
- Although the resin beads prefer Ca^{+2} and Mg^{+2} ions, the excessive concentration of Na^{+} ions overcomes this affinity.
- The Ca^{+2} and Mg^{+2} are forced off of the resin beads and are discharged to waste.
- The resin beads are ready to remove more Ca^{+2} and Mg^{+2} from the water.
- The degree to which the resin is converted is dependent upon the concentration of sodium in the brine.

The softening reaction is given as:

$$2RNa^{+} + Ca^{+2} \longrightarrow RCa^{+2} + 2Na^{+}$$

$$2RNa^{+} + Mg^{+2} \longrightarrow RMg^{+2} + 2Na^{+}$$

The reverse reaction is give as:

$$2RNa^{+} + Ca^{+2} \longleftarrow RCa^{+2} + 2Na^{+}$$ High Sodium Concentration

$$2RNa^{+} + Mg^{+2} \longleftarrow RMg^{+2} + 2Na^{+}$$ High Sodium Concentration

NOTE: R represents the resin macro-molecule.

Regeneration of resin is by

- HCl or H_2SO_4 if resin exchanges H^+
- NaCl if resin exchanges Na^+
- NaOH if resin exchanges OH^-
- HCl if resin exchanges Cl^-