

Ion Exchange

10.1 INTRODUCTION

Ion exchange is the reversible interchange of ions between a solid ion-exchange medium and a solution. Cations may be exchanged for Na^+ or H^+ while anions are exchanged for OH^- . Most exchange media in current use are insoluble synthetic polymer resins, although some naturally occurring minerals such as greensand zeolites (analcite, clinoptilolite, montmorillonite and others) are used. Synthetic media possess a very large number of functional groups, such as $-\text{SO}_3^-$, and $-\text{NH}_3^+$, to which are loosely attached (by electrostatic forces) small mobile ions of opposite charge. These latter ions are exchanged for ions of the same sign (so-called counter ions) in solution. Ions of the same charge as the functional groups are known as co-ions.

Resins are designated as cation exchangers or anion exchangers, depending on the counter-ions they exchange. Some resins can exchange both cations and anions and are termed amphoteric ion exchangers.

Depending on bead structure and size, resins may be designated as gel resins, macroporous resins, isoporous resins and micro resins. Gel resins and macroporous resin beads are typically 0.3-1.2 mm in diameter and have a three-dimensional matrix of macromolecular hydrocarbon chains, usually consisting of a copolymer of styrene and divinylbenzene. Gel resins have a homogeneous non-porous structure. They imbibe water, which usually results in a swelling of the resin. Ions diffuse through the imbibed water and are exchanged for mobile ions attached to the polystyrene chains. The matrix of the porous resins is of the same structure as that of the gel resins but the existence of pores allows a more ready access of water into the beads and thus reduces the resistance to diffusion and enables a higher rate of ion exchange. Micro resins are resins in powder form, used in a somewhat similar manner to powdered activated carbon and also requiring separation by a filtration process.

The properties of typical ion-exchange resin are given in Table 10.1.

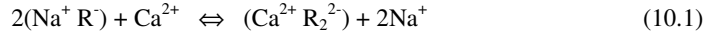
Table 10.1 Properties of a typical strong acid resin

		Gel structure	Macroporous structure
Resin bead diameter	(mm)	0.3-1.2	0.3-1.2
Bulk density	(kg m^{-3})	850	834
Moisture content	(%)	45-48	40-46
pH range		0-14	0-14
Maximum temperature	($^{\circ}\text{C}$)	120	150
Turbidity tolerance	(NTU)	5	5
Chlorine tolerance	(mg l^{-1})	1	1
Back-wash rate	(m h^{-1})	12	15
Back-wash period	(min)	20	20
Service rate	($\text{m}^3\text{h}^{-1}\text{m}^{-3}$)	16-50	16-50
Regeneration rate	($\text{m}^3\text{h}^{-1}\text{m}^{-3}$)	4	4
Rinse volume	(m^3m^{-3})	3	3-4
Total capacity	(keq m^{-3})	1.5	1.8

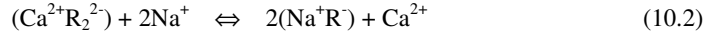
Source: Bolto and Pawlowski (1987)

10.2 EXCHANGE EQUILIBRIUM

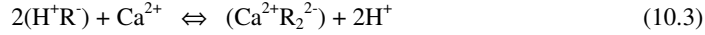
The selectivity and extent of exchange depend on the equilibrium relationships between ions in solution and those attached to the solid phase.



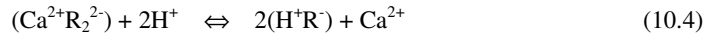
where R represents the negatively charged polymer. When the available exchange sites are effectively used up, the medium can be regenerated by passing a concentrated solution of Na^+ ions through the bed (5-10% NaCl):



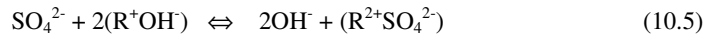
Similarly, for a hydrogen cation exchange medium:



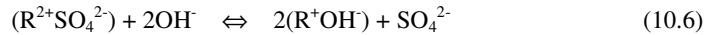
Regeneration with H_2SO_4 (2-10% solution):



An anion exchange medium replaces anions in solution by OH^- ions:



Regeneration with NaOH (5-10% solution):



The selectivity of an exchange medium for ions in solution can be quantified in equilibrium terms. The equilibrium expression corresponding to exchange equation (10.1) is

$$\frac{[\text{Ca}^{2+} \text{R}_2^{2-}][\text{Na}^+]^2}{[\text{Na}^+ \text{R}^-]^2 [\text{Ca}^{2+}]} = K_s (\text{NaR} \rightarrow \text{CaR}) \quad (10.7)$$

where K_s is a selectivity coefficient, defining the relative distribution of counter-ions when the cation exchanger in the Na^+ form is placed in a solution containing the Ca^{2+} cations. K_s typically has a value close to unity for the exchange of monovalent ions by monovalent ions and between 20 and 40 for the exchange of monovalent ions by bivalent ions, thus indicating, with some exceptions, a greater affinity for bivalent ions than for monovalent ions (Fair et al., 1968). It should be noted, however, that K_s is not a constant for all resins, being dependent on a number of factors, such as the degree of cross-linking in the resin, the valency of the ions and the concentration of the solution (Helfferich, 1962).

10.3 SELECTIVITY AND CAPACITY OF EXCHANGE RESINS

Information on the qualitative order of affinity for counter-ions is essential for practical design purposes. The following are typical examples (Bolto and Pawlowski, 1987):

sulphonic acid resin:	$\text{Fe}^{3+} > \text{Al}^{3+} > \text{Ca}^{2+}$
carboxylic acid resin:	$\text{H}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$
quaternary ammonium resin:	$\text{NO}_3^- > \text{CrO}_4^{2-} > \text{Br}^- > \text{Cl}^-$
polyamine resin:	$\text{OH}^- > \text{SO}_4^{2-} > \text{CrO}_4^{2-} > \text{NO}_3^- > \text{PO}_4^{3-} > \text{HCO}_3^- \geq \text{Br}^- > \text{Cl}^- > \text{F}^-$

It follows from equation (10.7) that the extent of the selective removal of Ca^{2+} ions from a solution containing Ca^{2+} and Na^+ ions depends on the relative concentrations of Ca^{2+} and Na^+ and increases greatly as the solution becomes more dilute. This is illustrated graphically in Fig 10.1.

The capacity of an ion-exchange medium is measured by the number of charges it can replace per unit volume of medium, the unit of measurement being eq l^{-1} . The exchange capacity of a given material can be determined experimentally by measuring the total quantity of ions exchanged, when the exchange reaction is driven to completion in a column containing a known volume of the medium. A

typical result of such an experiment is shown in Fig 10.2. The capacity of synthetic media is generally within the range 0.5-2.0 eq l⁻¹.

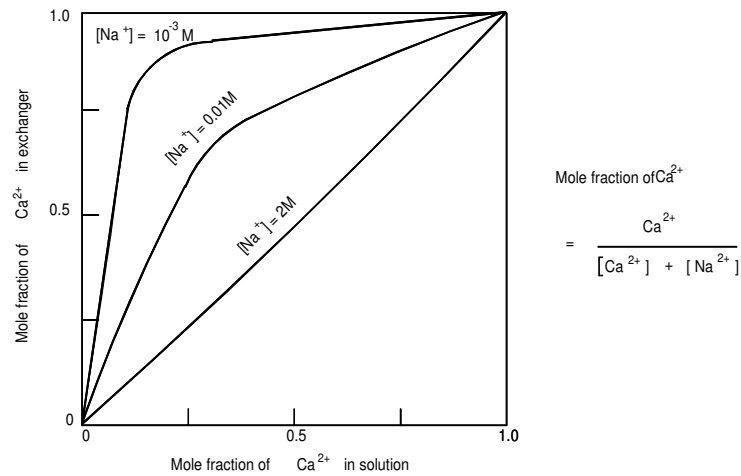


Fig 10.1 Influence of concentration on selective ion removal

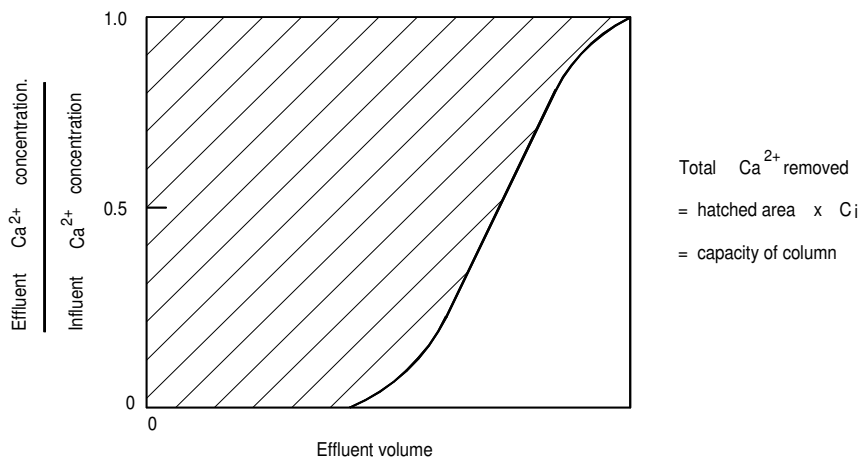


Fig 10.2 Exchange capacity of ion-exchange medium

10.4 ION EXCHANGE APPLICATIONS

In the water treatment field ion exchange is used for water softening and demineralisation. A common system in use is the down-flow fixed bed arrangement, using a granular medium, as illustrated in Fig 10.3. The typical properties of such a resin are given in Table 10.1.

In softening plants a strong acid sodium cation exchange medium is normally used, while in demineralising plants, beds of H⁺ and OH⁻ media may be used in series or in a single mixed bed. To avoid short-circuiting, beds are commonly not less than 0.8m in depth. The required bed volume for a particular application can be most reliably obtained from the results of a laboratory column study. Flow rates obtaining in practice generally fall within the range 0.2-1.0 m³ min⁻¹ m⁻³ of medium. When breakthrough occurs, the bed is generally back-washed with clean water to remove any accumulated

solids before regeneration is carried out. Regeneration and back-wash rates are generally as given in Table 10.1.

The influent to an ion exchanger must be low in turbidity and in organics, which might be adsorbed by the exchange medium, thus inactivating its exchange capability.

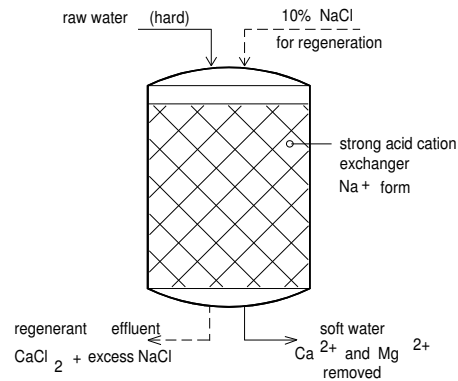


Fig 10.3 Schematic arrangement of ion-exchange column for water softening

REFERENCES

- Bolto, B. A. and Pawlowski, L. (1987) *Wastewater Treatment by Ion-exchange*, E & F Spon, London.
- Fair, G. M., Geyer, J. C. and Okun, D. A. (1968) *Water and Wastewater Engineering*, 2, John Wiley & Sons inc., New York
- Helfferich, F. (1962) *Ion Exchange*, McGraw-Hill Book Co., New York.