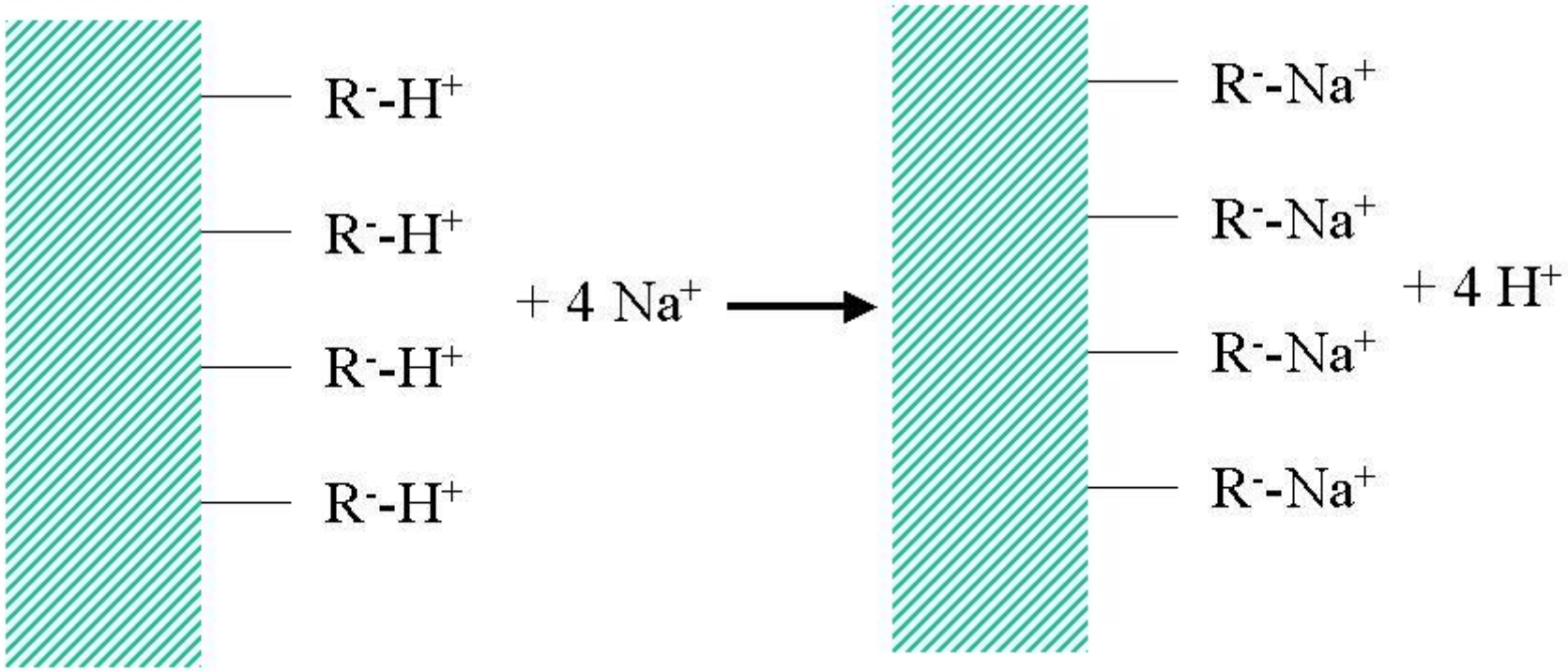
Ion Exchange

Ion Exchange

Ion exchange is an adsorption phenomenon where the mechanism of adsorption is electrostatic. Electrostatic forces hold ions to charged functional groups on the surface of the ion exchange resin. The adsorbed ions replace ions that are on the resin surface on a 1:1 charge basis. For example:


R-H+
R-H+
R-H+
R-H+
+ 4 Na+
R-Na+
R-Na+
R-Na+
R-Na+
+ 4 H+

Applications of ion exchange in water & wastewater

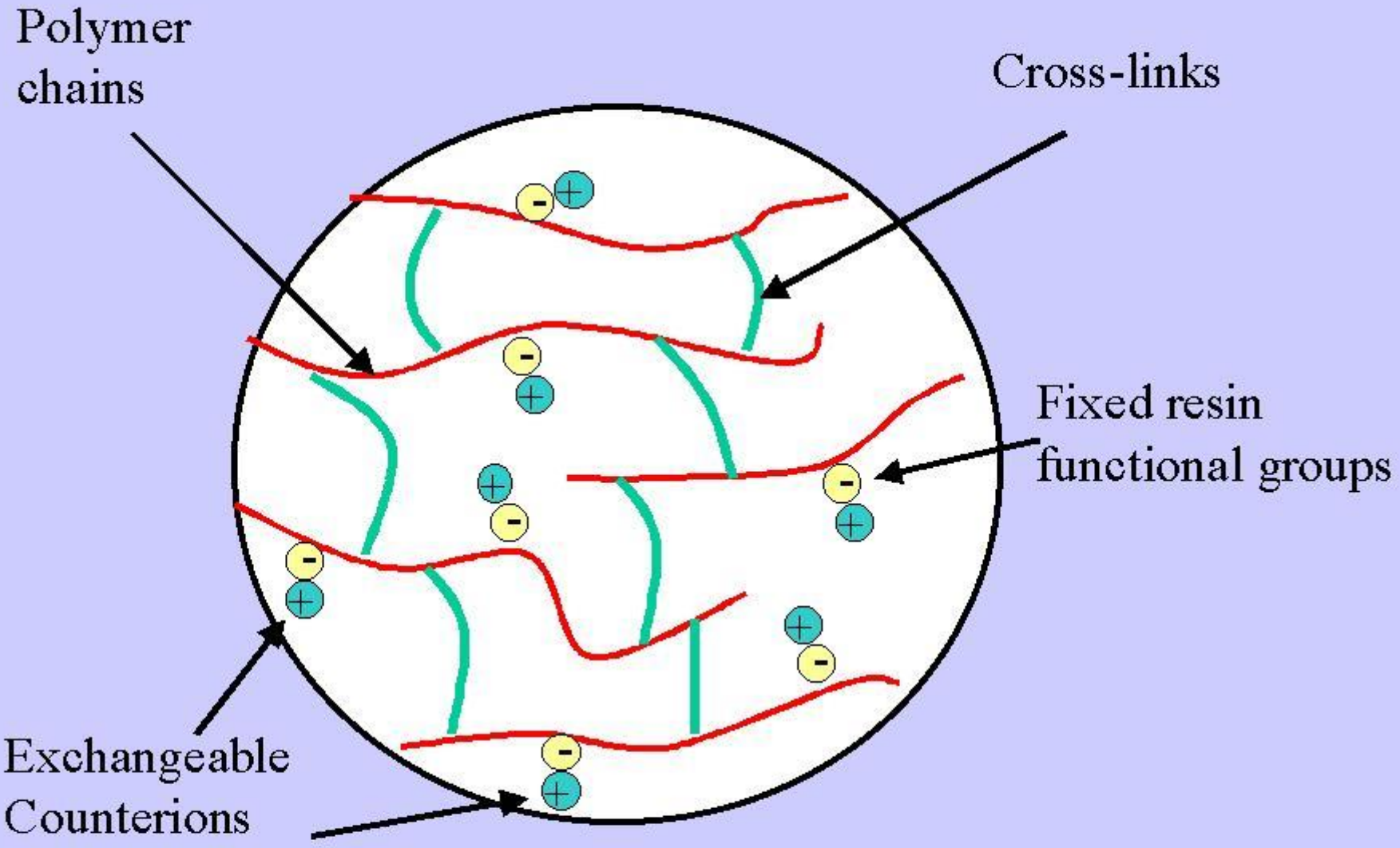
- Ca, Mg (hardness removal) exchange with Na or H.
- Fe, Mn removal from groundwater.
- Recovery of valuable waste products Ag, Au, U
- Demineralization (exchange all cations for H all anions for OH)
- Removal of NO_3, NH_4, PO_4 (nutrient removal).

Ion Exchangers (types)

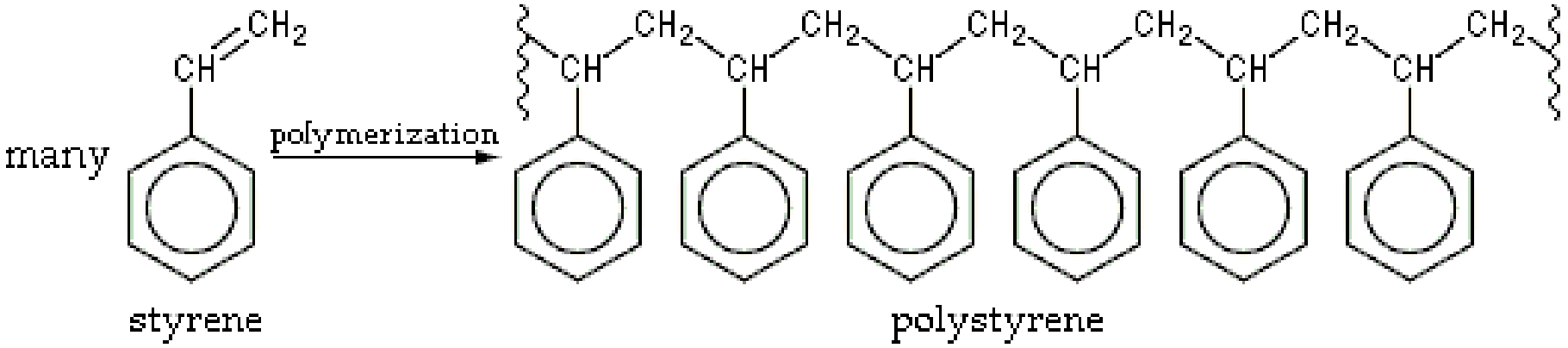
- Natural: Proteins, Soils, Lignin, Coal, Metal oxides, Aluminosilicates (zeolites) ($NaOAl_2O_3 \cdot 4SiO_2$).

- Synthetic zeolite gels and most common - polymeric resins (macroreticular, large pores).

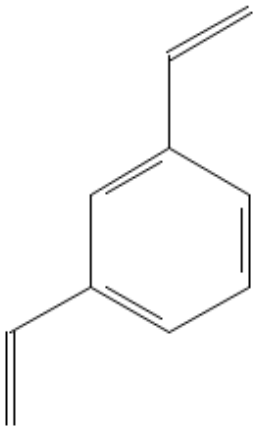
Polymeric resins are made in 3-D networks by cross-linking hydrocarbon chains. The resulting resin is insoluble, inert and relatively rigid. Ionic functional groups are attached to this framework.


Polymer chains
Cross-links
Fixed resin functional groups
Exchangeable Counterions

These resins are generally manufactured by polymerizing neutral organic molecules such as sytrene (to form polystrene) and then cross-linked with divinyl benzene (DVB). Functional groups are then added according to the intended use. For example the resin can be sulfonated by adding sulfuric acid to get the structure shown above.


many
polymerization
styrene
polystyrene

Divinylbenzene:



Ion Exchange Resin:

Resin classification:

Resins are classified based on the type of functional group they contain and their % of cross-linkages

Cationic Exchangers:

- Strongly acidic – functional groups derived from strong acids e.g., R-SO_3H (sulfonic).

- Weakly acidic – functional groups derived from weak acids, e.g., R-COOH (carboxylic).

Anionic Exchangers:

- Strongly basic – functional groups derived from quaternary ammonia compounds, R-N-OH.

- Weakly basic - functional groups derived from primary and secondary amines, R-NH_3OH or R-R'-NH_2OH.

Selectivity Coefficients

Preference for ions of particular resins is often expressed through an equilibrium relationship using the *selectivity coefficient.* The coefficient is described below.

For the exchange of A^+ in solution for B^+ on the resin:

$$A^+ + \overline{B} \leftrightarrow B^+ + \overline{A}$$

The barred terms indicate location on the resin (resin phase) as opposed to solution phase.

For this exchange an operational equilibrium constant can be defined.

$$K^{A^+}_{B^+} = \frac{\{\overline{A}\}\{B^+\}}{\{A^+\}\{\overline{B}\}}$$

The superscript and subscript on the selectivity coefficient indicate the direction of the reaction. The superscript is the reaction side and the subscript is the product side of the exchange reaction.

Selectivity coefficients are reported for various resins and various exchangeable ions. Selectivity coefficients can be combined to give a variety of new selectivity coefficients.

For example:

$$\frac{K_B^A}{K_B^C} = K_C^A$$

Also note that:

$$K_B^A = \frac{1}{K_A^B}$$

Neglecting activity corrections we can write:

$$K_{B^+}^{A^+} = \frac{[\overline{A}][B^+]}{[A^+][\overline{B}]}$$

Where:

$[A^+]$, $[B^+]$= moles A^+, B^+ per liter of <u>liquid</u>

$[\overline{A}]$, $[\overline{B}]$ = moles of A^+, B^+on resin per liter of <u>resin</u> (bulk volume basis).

This *selectivity coefficient* is not quite a thermodynamically defined equilibrium constant because of the strange choice of concentration units and the lack of activity corrections. So it is clearly an operational equilibrium constant.

Factors which affect the selectivity coefficient:

For a given resin type ion selectivity is a function of ionic charge and hydrated radius and functional group-ion chemical interactions.

In most cases the higher the ionic charge the higher the affinity for a site.

The smaller the hydrated radius of the ion the greater the affinity. This depends on the % cross-linkage of the resin. The reason that hydrated radius has an effect on selectivity is that macro-reticular pore spaces have limited volume as determined by % cross-linkage. Some exchanged ions can actually cause a swelling of the resin (it's relatively deformable). The swelling causes a backpressure that reduces the preference for ions with larger hydrated radii.

An example of this phenomenon is shown here for Li and Ag (Ag has a smaller hydrated radius). Numerical values are relative affinity, not selectivity coefficients.

% Crosslink

	4%	8%	16%
Li^+	1	1	1
Ag^+	4.73	8.51	22.9

By increasing the cross-linkages Ag^{+} is selected for adsorption (exchanged because of its smaller hydrated radius). Note that the absolute amount adsorbed for both Ag and Li will be lower with more cross-linkages, however there is a relative advantage for Ag.

In some cases there are more than electrostatic forces holding the ion to the functional group of the resin. For example for weakly acid functional groups such as carboxylic groups, hydrogen bonding is partially responsible for attracting H^+ ions. Another example is the strong bonding between Ca and PO_4 when PO_4 is used for a functional group.

All these factors show up in the apparent selectivity coefficient.

The selectivity coefficient is only applicable over a narrow range of concentrations because the activity coefficients vary with concentration.

Because we need to maintain a charge balance during the ion exchange process it is more convenient to express concentration of ions as equivalents instead of molar concentration. Therefore, we define:

C = total concentration of exchangeable ions in the liquid phase (eq/L).

For example,

if Ca^{2+} and Na^{+} are the only exchanged ions.

$$C = [Na^{+}] + 2[Ca^{2+}]$$

$\overline{C}$ = total concentration of exchangeable sites on resin . This is also known as the “exchange capacity” (eq/L of bulk volume). We can now define "equivalent fraction" for each ion in each phase.

$$X_{A^+} \quad \text{or} \quad X_{A^{2+}} = \frac{[A^+]}{C} \quad \text{or} \quad \frac{2[A^{2+}]}{C}$$

$$\overline{X}_{A^+} \quad \text{or} \quad \overline{X}_{A^{2+}} = \frac{[\overline{A}^+]}{\overline{C}} \quad \text{or} \quad \frac{2[\overline{A}^{2+}]}{\overline{C}}$$

with similar definitions for B.

For monovalent exchange:

$$A^+ + \overline{B}^+ \leftrightarrow B^+ + \overline{A}^+$$

$$K_{B^+}^{A^+} = \frac{[\overline{A}^+][B^+]}{[A^+][\overline{B}^+]}$$

$$[A^+] = C \cdot X_{A^+}$$

$$[B^+] = C \cdot X_{B^+} = C(1 - X_{A^+})$$

$$[\overline{A}^+] = \overline{C} \cdot \overline{X}_{A^+}$$

$$[\overline{B}^+] = \overline{C} \cdot \overline{X}_{B^+} = \overline{C}(1 - \overline{X}_{A^+})$$

Substitute in the mass action expression to get:

$$K_{B^+}^{A^+} = \frac{\overline{X}_{A^+} \cdot (1 - X_{A^+})}{X_{A^+} \cdot (1 - \overline{X}_{A^+})}$$

Rearranging gives:

$$\frac{\overline{X}_{A^+}}{(1 - \overline{X}_{A^+})} = K_{B^+}^{A^+} \frac{X_{A^+}}{(1 - X_{A^+})}$$

For monovalent – divalent exchange:

$$A^{2+} + 2\overline{B}^{+} \leftrightarrow 2B^{+} + \overline{A}^{2+}$$

$$\frac{\overline{X}_{A^{2+}}}{(1-\overline{X}_{A^{2+}})^2} = K_{B^{+}}^{A^{2+}} \frac{X_{A^{2+}}}{(1-X_{A^{2+}})^2} \frac{\overline{C}}{C}$$

In this form the equation gives the amount exchanged as a function of the amount in solution. It is very useful for process design as demonstrated below.

Exchange Isotherms -

Isotherms are an alternative to describing equilibrium by selectivity coefficients. These isotherms have the same format as those for carbon adsorption. i.e., Langmuir, Freundlich, etc.

In spite of the non-constant selectivity coefficient, calculations can be made with these coefficients to estimate process limits. Note that the most vulnerable (non-constant) selectivity coefficients are for those resins that have weak acid or base functional groups. These functional groups will protonate and de-protonate as a function of the solution pH as opposed to strong acid-base functional groups that tend to be fully deprotonated or protonated at most pH values.

Kinetics versus equilibrium.

Ion exchange adsorption is much faster than carbon adsorption and as a result we can use equilibrium assumption in design calculations.

Ion Exchange Design Example

Suppose we want to remove NO^-_3 by ion exchange on a strong base anionic resin of the Cl^- form. The resin has the following characteristics:

$$K^{NO_3^-}_{Cl^-} = 4$$

$$\overline{C} = 1.3\,\text{meq/L}$$

The influent has the following characteristics:

$[Cl^-] = 3$ meq/L

$[NO^-_3] = 1.5$ meq/L

Determine how much water can be treated per ft^3 of resin before the bed is exhausted. Assume equilibrium for the resin.

First we need to determine $\overline{X}_{NO_3^-}$ at equilibrium with the influent (need to estimate the column capacity relative to the influent composition).

$$X_{NO_3^-} = \frac{1.5}{3+1.5} = 0.33 \quad \text{(influent)}$$

$$\frac{\overline{X}_{NO_3^-}}{1-\overline{X}_{NO_3^-}} = K_{Cl^-}^{NO_3^-} \left(\frac{X_{NO_3^-}}{1-X_{NO_3^-}} \right) = 4 \left(\frac{0.33}{1 - 0.33} \right) = 1.97$$

Solve this equation for $\overline{X}_{NO_3^-} = 0.66$. This value (0.66) represents the maximum fraction of resin sites that can be occupied by NO^-_3 with these influent conditions. When this fraction has been reached the column is considered exhausted

Thus the total amount of NO^-_3 this resin can exchange is:

$$1.3\,\text{eq/L}(0.66) = 0.86\,\text{eq}\ NO^-_3\ \text{per liter of resin.}$$

Volume of water that can be treated assuming a fully Cl^- charged resin to begin is:

$$(0.86\ \text{eq/L-resin})/(0.0015\ \text{eq/L-water})$$

$$= 570\ \text{liters-water/liter-resin}$$

= 4300 gal/ft^3-resin (1 liter = 0.264 gal = 0.035 ft^3)

The effluent concentration of nitrate will be practically zero until breakthrough occurs if the column were initially fully charged with chloride, since $\bar{X}_{NO_3^-}$ is practically zero at the effluent end of the column. There are some other design factors that have to be considered though, namely *leakage and regeneration extent.* These are discussed next.

Regeneration

Spent or exhausted columns must be regenerated because of the cost of the resin would make one-time use prohibitive. Since ion exchange is a very reversible process regeneration can be accomplished by manipulation of solution composition.

Example:

A spent column used to remove Ca^{2+} is to be regenerated in a batch process to the Na^{+} form. A strong brine (mostly NaCl) is contacted with the exhausted resin to replace Ca with Na. The composition of the brine (regenerant) after equilibrating with the exhausted resin is:

NaCl = 2 eq/L (117 g/L)

$CaCl_2$ = 0.2 eq/L (11 g/L)

Most of the Ca is from the spent column. Na in the fresh brine would have been slightly higher than 2 eq/L.
For this resin:

$$\overline{C} = 2 eq / L$$

$$K_{Na^+}^{Ca^{2+}} = 4$$

What we need to determine is how effective this regeneration step is, i.e., what is the magnitude of $\overline{X}_{Ca^{2+}}$ after the regeneration is completed.

In the regenerant after equilibration :

$$X_{Ca^{2+}} = \frac{0.2}{2 + 0.2} = 0.091$$

$$\frac{\overline{X}_{Ca^{2+}}}{(1-\overline{X}_{Ca^{2+}})^2} = K_{Na^{+}}^{Ca^{2+}} \frac{\overline{C}}{C} \frac{X_{Ca^{2+}}}{(1-X_{Ca^{2+}})^2}$$

$$\frac{\overline{X}_{Ca^{2+}}}{(1-\overline{X}_{Ca^{2+}})^2} = \frac{4(2)}{2.2}\left(\frac{0.091}{(1-0.091)^2}\right) = 0.4$$

Solve for : $\overline{X}_{Ca^{2+}} = 0.235$

$$\overline{X}_{Na^{+}} = 1 - .235 = 0.765$$

Only 76.5% regeneration can be accomplished with this regenerant because even small amounts of Ca can have a significant effect because of the high selectivity coefficient in favor of Ca. To get higher regeneration need to make the NaCl concentration higher or make the total volume of regenerant higher to dilute the Ca that comes off the exhausted column . Both options cost money and there needs to be a tradeoff evaluated between higher column utilization and more costly regeneration. To formalize this trade-off problem define the following.

Theoretical or total capacity = $\overline{C}$ **(**eq/L of bulk volume).

Degree of column utilization = fraction or percent of $\overline{C}$ actually used during an exhaustion cycle. This is the difference between the fresh capacity (generally less than $\overline{C}$ **)** and the capacity at the end of the exhaustion cycle compared to $\overline{C}$ **.**

Operating exchange capacity = (degree of column utilization) x $\overline{C}$ (eq/L of resin).

Regeneration efficiency: ratio of actual regenerant (equivalents) exchanged divided by equivalents of regenerant applied times 100 (%).

The following example shows how all this works.

Assume we have a 1-liter column initially exhausted with Ca^{2+} . Assume that $\overline{X}_{Ca^{2+}} = 1$, although in reality it's likely to be less than this. For example, in the NO^-_3 /Cl^- problem above exhaustion occurred at $\overline{X} = 0.66$. This number depends on the selectivity coefficient and the influent composition). Regenerate with 1 liter of Na^+ at some high concentration to be determined. Assume that we have the following resin characteristics.

$$K_{Na^+}^{Ca^{2+}} = 3$$

$$\overline{C} = 2 \text{ eq/L}$$

Estimate the sodium concentration, C, in the regenerant required to get $\overline{X}_{Ca^{2+}} = 0.1$ after regeneration . Note that this represents 90% column utilization if the column is completely exhausted. Again, the influent composition will determine how much of the column capacity can be exhausted.

C, the regenerant strength, must remain constant before and after regeneration is complete so that electroneutrality is maintained. For the regenerant brine, assuming no initial Ca and 1 liter each of resin and regenerant:

$$X_{Ca^{2+}} = \frac{0.9 \cdot \overline{C}}{C} = \frac{1.8}{C} \qquad \text{(target is } \overline{X}_{Ca^{2+}} = 0.1\text{)}$$

$$\frac{X_{Ca^{2+}}}{(1-X_{Ca^{2+}})^2} = \frac{1}{K_{Na}^{Ca}} \frac{C}{\overline{C}} \frac{\overline{X}_{Ca^{2+}}}{(1-\overline{X}_{Ca^{2+}})^2}$$

$$\frac{1.8/C}{(1-1.8/C)^2} = \frac{C(0.1)}{3 \cdot 2(1-0.1)^2} = C(0.0206)$$

$$\frac{1.8}{C^2(1-1.8/C)^2} = 0.0206$$

$$C^2(1-1.8/C)^2 = 1.8/0.0206 = 87.38$$

$$C^2 - 3.6C - 84.14 = 0$$

Solve for the positive root:

C = 11.2 eq/L

Regeneration efficiency for this process = (Na exchanged/Na applied)x100. This is the same as Ca released/C x 100 (for 1 liter).

RE = (0.9(2)/11.2) x100 = 16.1 %

This calculation can be repeated for 50% column utilization using the same assumptions as above.

$$X_{Ca^{2+}} = \frac{0.5 \cdot \overline{C}}{C} = \frac{1.0}{C}$$ assuming complete exhaustion

$$\frac{1.0/C}{(1-1.0/C)^2} = \frac{C(0.5)}{3 \cdot 2(1-0.5)^2} = C(0.333)$$

$$3.00 = C^2(1-1.0/C)^2 = C^2 - 2C - 1$$

C = 3.34 eq/L

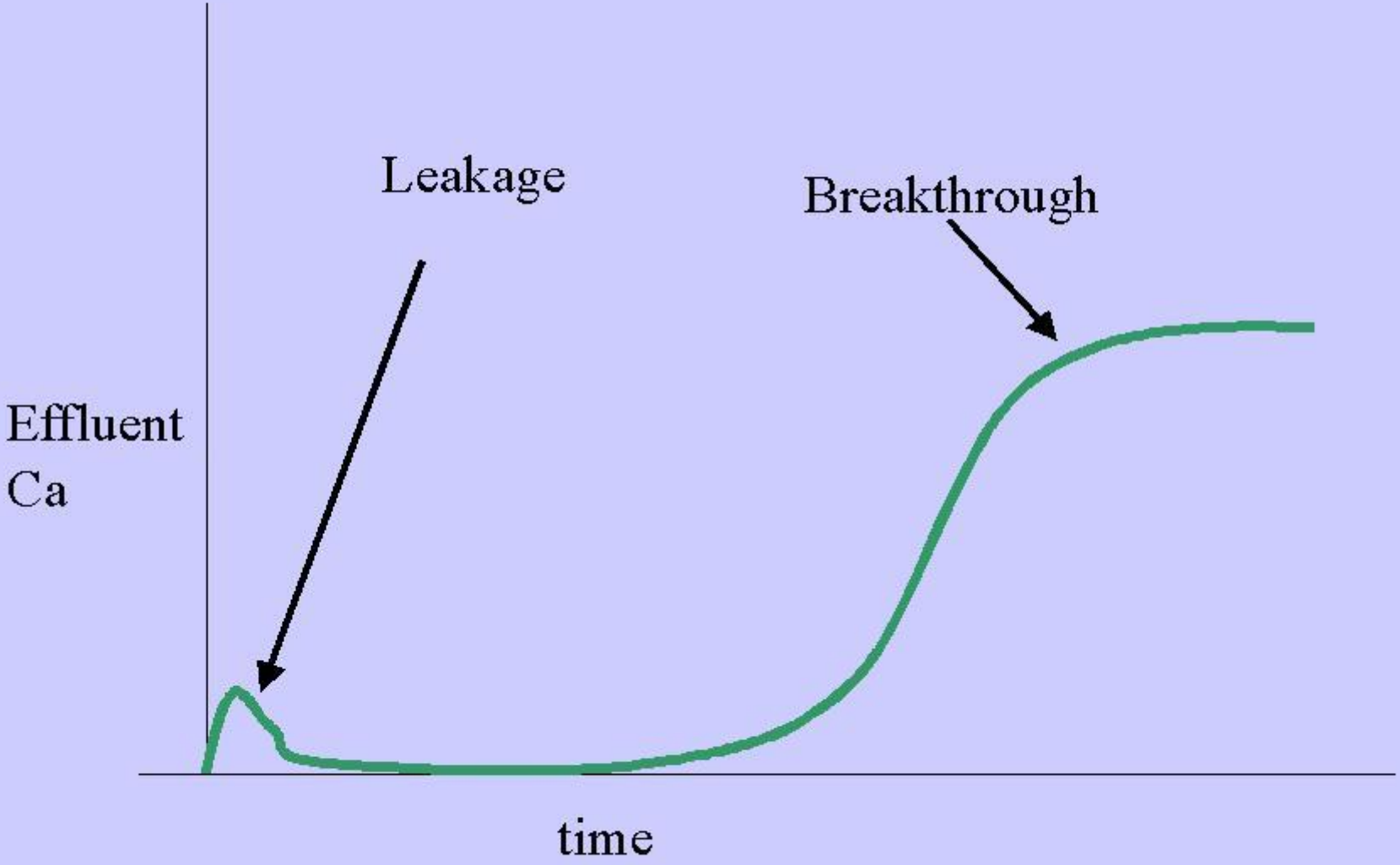
RE = (0.5(2)/3.34)x100 = 30%

Typical values for:

Column utilization: 30 – 60 %

Regeneration efficiency: = 70-45%

One of the consequences of incomplete regeneration is **leakage.** Leakage occurs at the beginning of the exhaustion cycle because there is still Ca^{2+} (continuing with the same example) on the resin. As water passes through the column, Ca^{2+} is removed at the influent end of the column so that as this water passes toward the effluent end of the column it is free of Ca^{2+} and therefore pulls Ca^{2+} off the relatively high Ca resin. This leakage is generally short-lived but can make portions of the product water unacceptable.


Leakage
Breakthrough
Effluent
Ca
time

Estimating leakage:

Assume:

$$\overline{X}_{Ca^{2+}} = 0.1$$

$$\overline{C} = 2 \text{ eq/L}$$

$$K_{Na^{+}}^{Ca^{2+}} = 3$$

Influent:

$[Ca^{2+}] = 44$ meq/L

$[Na^{+}] = 30$ meq/L

$C = 0.074$ eq/L

Note that with this influent saturation ($\overline{X}_{Ca^{2+}} = 1$) can't be attained

$$\frac{X_{Ca^{2+}}}{(1-X_{Ca^{2+}})^2} = \frac{1}{K_{Na^+}^{Ca^{2+}}} \frac{C}{\overline{C}} \frac{\overline{X}_{Ca^{2+}}}{(1-\overline{X}_{Ca^{2+}})^2}$$

$$= \frac{1}{3} \frac{(0.074)}{2} \frac{(0.1)}{(1-0.1)^2} = 1.52 \text{ x } 10^{-3}$$

$$X_{Ca^{2+}} = (1 - X_{Ca^{2+}})^2 (1.52 \text{ x } 10^{-3})$$

$$X_{Ca^{2+}} \approx 1.52 \text{ x } 10^{-3}$$

Compared to the influent concentration of Ca^{2+} this is fairly low.

Typical Design Parameters

$$\text{Total column capacity} =$$

$$(\text{column utilization}) \cdot \overline{C} \cdot (\text{bed volume})$$

$$\text{Regeneration cycle} =$$

$$(Q \cdot X_{in} \cdot C_{in})^{-1} \cdot \text{total column capacity}$$

Column Configuration

- Pressurized usually downflow

- Gravity downflow or upflow (expanded bed)

  Upflow rate restricted by size and density of resin.

  Downflow restricted by headloss and available head.

Typical design for water softening:

sulfonated polystyrene cation exchange resin with exchange capacity of about 2 equiv/l (5 meq/g dry wt).

Softening cycle:

1. soften to exhaustion
2. backwash to loosen particulate matter (not needed in upflow)
3. regeneration (downflow)
4. rinse (downflow)
5. return to forward flow

Operating parameters:

operating exchange capacity 0.6 - 1.2 eq/L

bed depth 2 - 6 ft.

head loss 1 - 2 ft.

softening flow 5 - 10 gpm/ft^2

backwash flow 5 - 6 gpm/ft^2

salt dose 3 -10 lb/ft^3 resin brine

conc. 8 - 16 % (by wt)

brine contact time 25 - 45 min.

rinse flow 1 - 5 gpm/ft^2

rinse volume 20 - 40 gal/ft^3 resin