ION EXCHANGE UNITS

Basics of Design, Operation and Troubleshooting

Ion Exchange Introduction

- **Ion exchange is a powerful technology to soften and demineralize water to extremely good quality.**
- **This technology is well proven, as it developed initially in the 1950s, and today, it is still the best to produce ultra-pure water, i.e. to remove all traces of contaminants.**
- **In addition to water treatment, ion exchange is also used in a variety of industrial and domestic applications.**

It can for instance:

- **Remove colour from cane sugar syrups to make white sugar**
- **Purify antibiotics and other pharmaceuticals**
- **Extract uranium from ores**
- **Separate metals**
- **Remove harmful substances from solutions**
- **Be used as an excipient in pharmaceutical formulations**
- **Catalyse reactions to make anti-knocking agents for petrol**
- **Produce clear and pure water for the tea or coffee you make at home**

Ion exchange resin

- Ion exchange resins are versatile materials possessing a modulable framework based on **cross-linked copolymers**
- bearing functional groups that can participate in ion exchange.
- Resins can be either cationic or anionic with different intensities of acid or base exchange abilities depending on the nature of the **functional group and ionic form!**.
- **Accordingly, they can therefore be classified into four main groups**:

(1) cationic resins with strong acid exchange ability**(SAC) (Sodium form or Hydrogen form)**

(2) with weak acid exchange ability; **(WAC)(Hydrogen form)**

(3) anionic resins with strong base exchange ability and **(SBA)(Hydroxyle form)**

(4) with weak base exchange ability. **(WBA)**

Ion exchange resin types

- **Strongly Acidic Cation Exchange Resins (SAC)**

Functional groups	**—SO3– H+ Sulphonic acid**
What they do	**- In sodium form, they remove hardness (essentially calcium and magnesium) from water and other solutions** **- In hydrogen form, they remove all cations** **- They are also used as acidic catalysts**

Ion exchange resin types

- **Weakly Acidic Cation Exchange Resins(WAC)**

Functional groups	—COOH Carboxylic acid
What they do	In hydrogen form, they remove preferentially divalent ions (e.g. calcium and magnesium) from solutions containing alkalinity

Ion exchange resin types

- **Strongly Basic Anion Exchange Resins (SBA)**

Functional groups	**$-N(CH_3)_3^+\ OH^-$ Quaternary ammonium**
What they do	**In hydroxyl form, they remove all anions** **In chloride form, they remove nitrate, sulphate and several other ions**

Ion exchange resin types

- **Weakly Basic Anion Exchange Resins (WBA)**

Functional groups	—N(CH3)2 Amines
What they do	After cation exchange, they remove chloride, sulphate, nitrate, and other anions of strong acids, but they do not remove weak acids (SiO2 and CO2)

Ion exchange resin Manufacturing

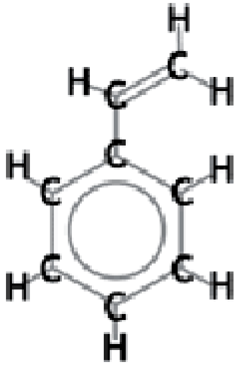
- Ion exchange resins are **polymers** onto which **functional groups** are attached.
- **The resins are produced in several steps, the two main steps being:**

a. Polymerisation of the resin matrix

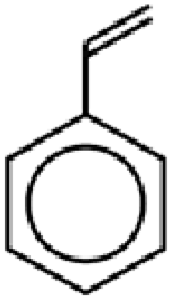
b. Functionalisation: ion exchange groups are attached to the matrix

Polymerisation

- About 90 % of all ion exchange resins are based on a **polystyrenic matrix**. The "building block" used to make this plastic skeleton is **styrene monomer**, an aromatic compound also called **vinylbenzene**.
- The **vinyl double bond** of this molecule enables polymerisation.

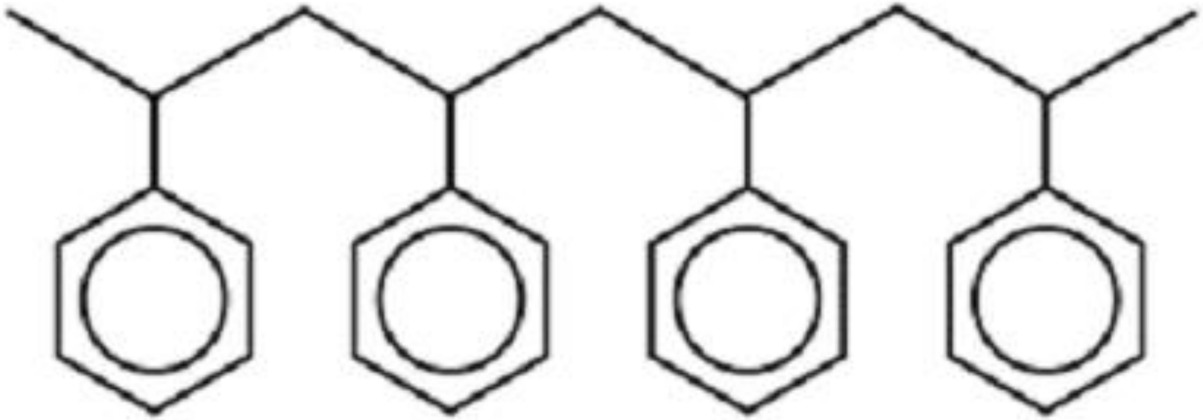


Chemical formula of styrene



Simplified representation of styrene

Polymerisation



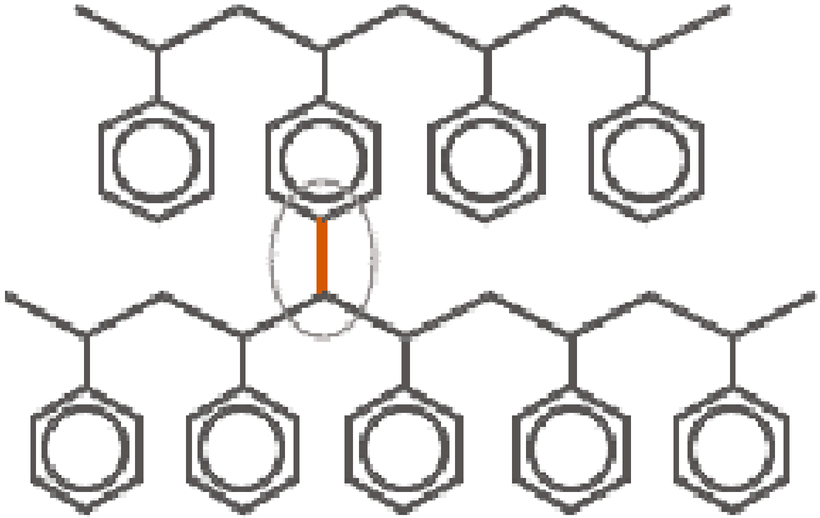
A small fraction of a polystyrene chain

Crosslinking

- The resulting linear polymer chains are entangled together, **but have little physical strength**
- they are relatively soft, and after activation **they would probably dissolve in water**.
- To give the polymer a **more stable tri-dimentional structure**, ***the polystyrene chains are cross-linked*** with another molecule at the time of polymerisation.
- The cross-linking molecule must be able to polymerise at two or three ends.
- **The most common cross-linker is divinylbenzene (abbreviated as DVB).**

Crosslinking

Divinylbenzene (DVB)



Ion Exchange Resin Structure

Cross-linked polystyrene

Crosslinking

- The second bond of the DVB molecule is shown in red and attaches to the next chain of linear polystyrene.
- The more DVB is added to the initial reaction mixture, the more rigid is the polymer.
- Most ion exchange resins are polymerised in such a way that spherical beads are obtained.
- This can occur either in a stirred reactor or with a jetting process.
- In the latter case, the bead size is very uniform.

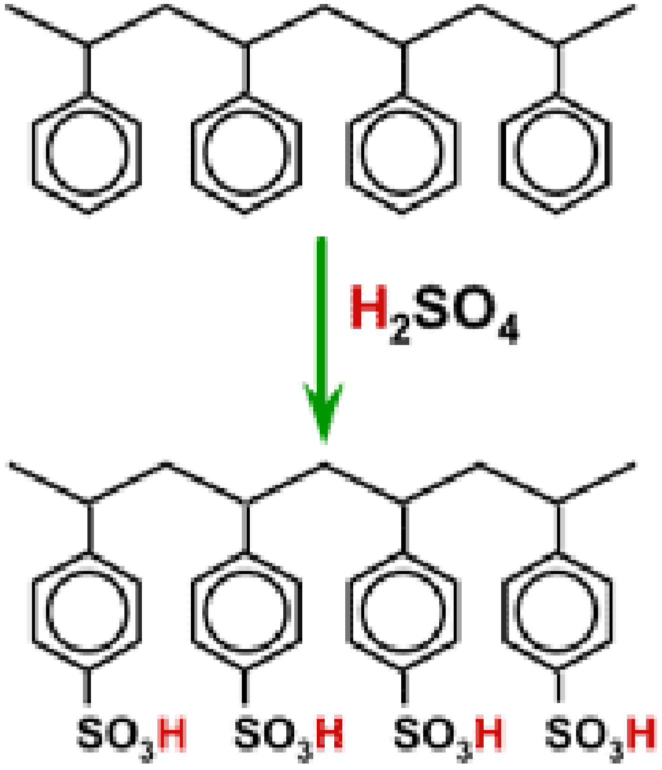
Functionalization of the polymer

- The polymer described above must be activated to convert the plastic beads into ion exchange resins.

Example: Functionalization of Strongly acidic cation exchange resins

- The activation is chemically simple: it is a sulphonation reaction. the polystyrene beads are contacted at high temperature with concentrated sulphuric acid.
- The product is a polystyrene sulphonate, which is a strong acid.
- After sulphonation, the resin is washed to remove excess sulphuric acid.
- After washing the resin is ready to use in the H+ form.

Sulphonation Reaction



Sulphonation

Ion exchange resin properties

- Particle size
- Capacity
- Moisture
- Dry matter
- Specific gravity
- Bulk density
- Effect of bed compression
- Optical aspect
- Resin volume and swelling
- Stability

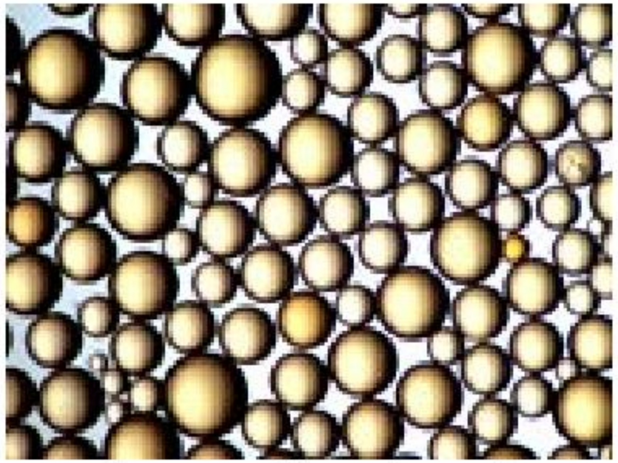
Particle size distribution

- Traditionally, the particle size distribution of a resin was **measured using a set of sieves.**
- The volume on the resin fraction remaining on each sieve is measured in a glass cylinder.
- It was found practical to express the results in cumulative percentage through a given sieve opening.

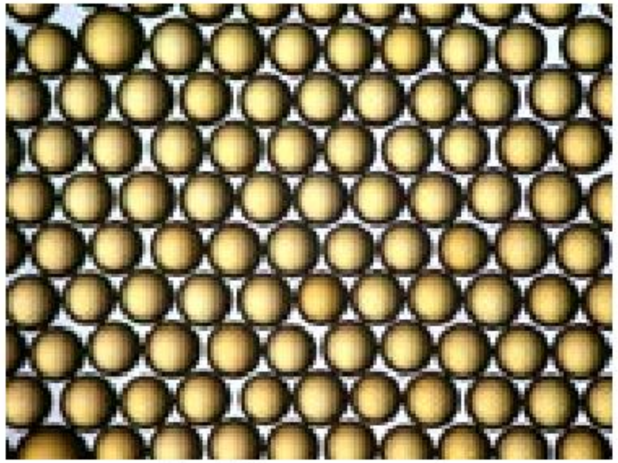
Particle size distribution

The components of a particle size distribution are:

- Mean diameter
- Uniformity coefficient
- Effective size
- Harmonic mean size
- Quantity of fined beads
- Quantity of big beads



Conventional resin
UC = 1.60



Uniform resin
UC = 1.07

What particle size means

The choice of particle size is a compromise:

finer resins deliver a higher capacity, but cause high head loss, and excess fines may produce nozzle clogging.

Coarser beads on the other hand are frequently more sensitive to osmotic stress and have slower kinetics, thus giving a lower operating capacity.

For all applications requiring separation of different resins in the same column, such as stratified or mixed bed units, selection of the right particle size is of critical importance.

Ion exchange capacity

- **Total capacity :** This is the number of active groups i.e. the number of exchangeable monovalent ions
- **Operating capacity** : This is the number of sites where exchange actually takes place during one cycle(ie, active groups shall be utilized till a break point of regeneration)
- Total capacities of new resins are measured for quality control.
- Capacities are expressed in equivalents per litre of wet resin or in equivalents per kilogramme of dried resin.
- The dry weight capacity indicates if a resin has been properly functionalised, irrespective of its water content.
- **Whilst a high total capacity is generally desirable, not all exchange sites are used in a complete ion exchange cycle**

Moisture holding capacity

- Moisture (water retention, or water content) is related to **porosity and ionic form.**
- The water content is expressed as a percentage of the moist resin weight in a given ionic form.

Moisture Effect

High moisture

- Fast Ion exchange
- good adsorption properties
- low total capacity

Low moisture

- high total capacity
- difficult to regenerate
- no removal of big ions
- tendency to fouling

Moisture Effect

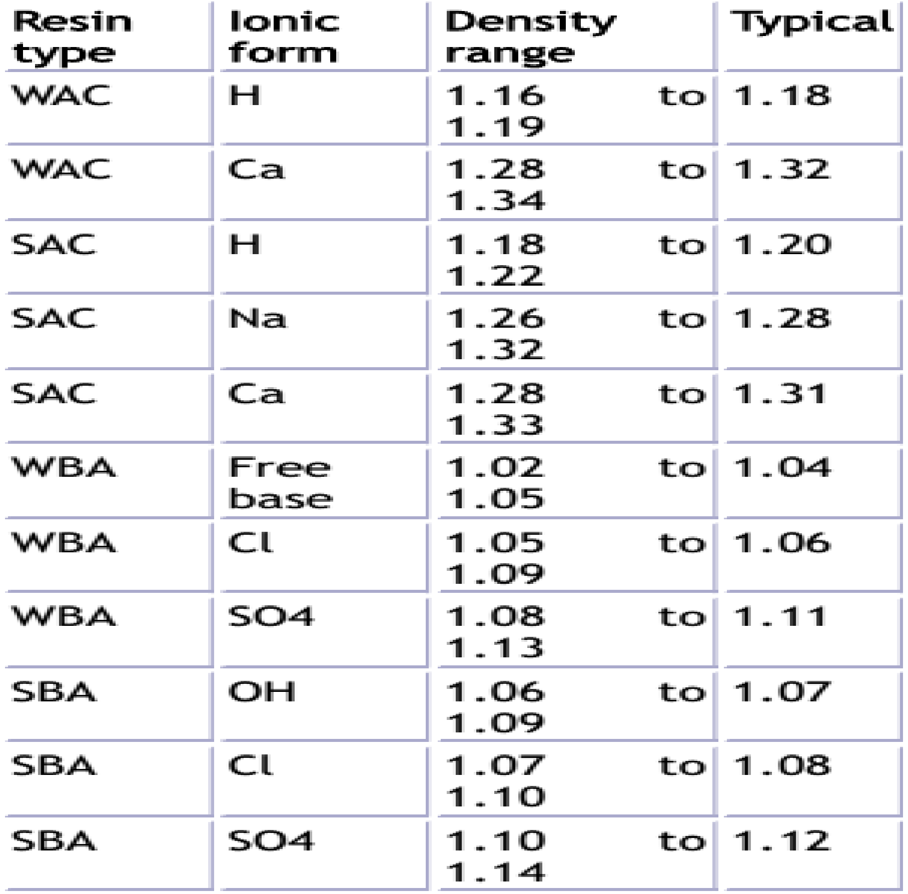
- **About half the weight of all ion exchange resins is water**, unless they have been dried or the water has been replaced with an organic solvent.
- **The water surrounds the active groups** (hydration water) **<u>and fills the voids in the resin matrix.(Stability)</u>**
- Obviously, a resin with **high moisture has less dry matter**, therefore **<u>less active groups and less capacity</u>**; but on the other hand, such a **resin may provide easier access for large ions into its structure**.

Specific gravity (true bead density)

Density is important for:

- **Mixed bed separation**
- **Backwashing**
- **Specific gravity is an important parameter for successful plant operation.**
- It is critical for all processes involving mixing or separation of 2 or 3 resins in the same column, and for adjustment of resin **backwash flow rate**
- specific gravity varies with the ionic form of the resin.
- **The ionic composition of a resin varies all the time during a cycle**, so **it is difficult to predict the exact specific gravity**. This is important to understand when backwashing a resin bed.

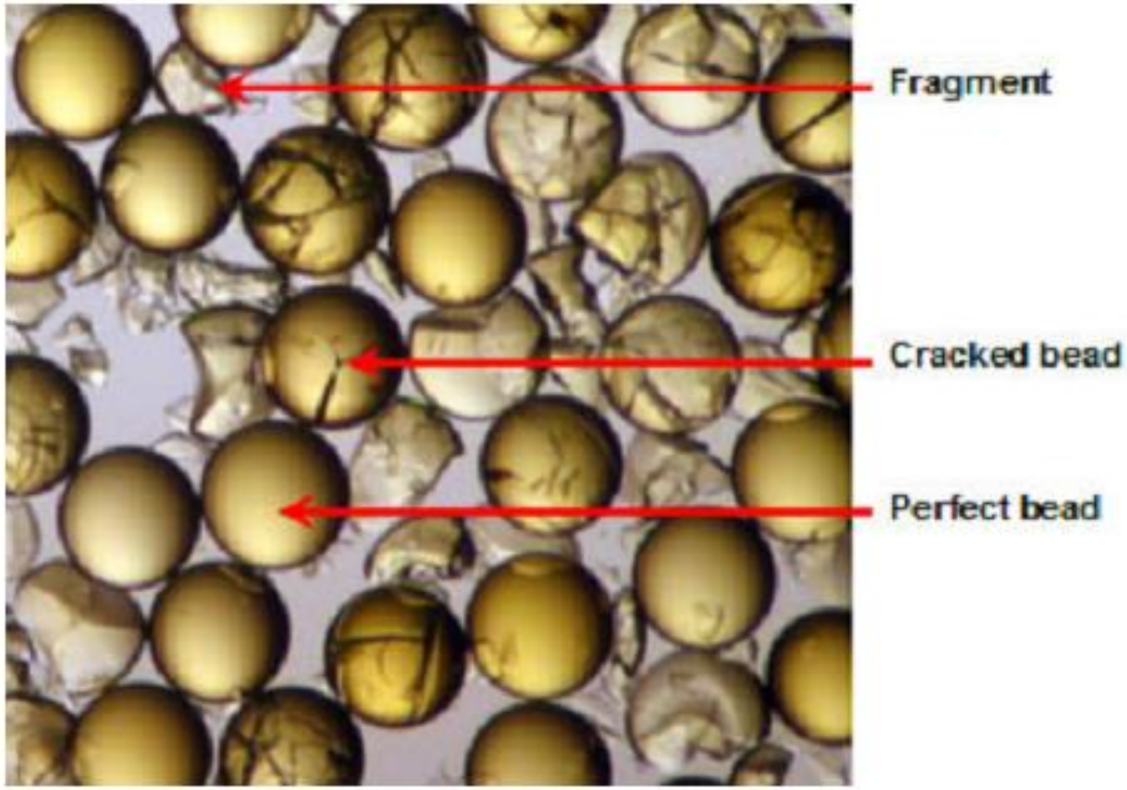
Specific gravity (true bead density)



Resin type	Ionic form	Density range	Typical
WAC	H	1.16 to 1.19	1.18
WAC	Ca	1.28 to 1.34	1.32
SAC	H	1.18 to 1.22	1.20
SAC	Na	1.26 to 1.32	1.28
SAC	Ca	1.28 to 1.33	1.31
WBA	Free base	1.02 to 1.05	1.04
WBA	Cl	1.05 to 1.09	1.06
WBA	SO4	1.08 to 1.13	1.11
SBA	OH	1.06 to 1.09	1.07
SBA	Cl	1.07 to 1.10	1.08
SBA	SO4	1.10 to 1.14	1.12

Specific gravity vs ionic form

Optical aspect



Optical aspect of a used resin

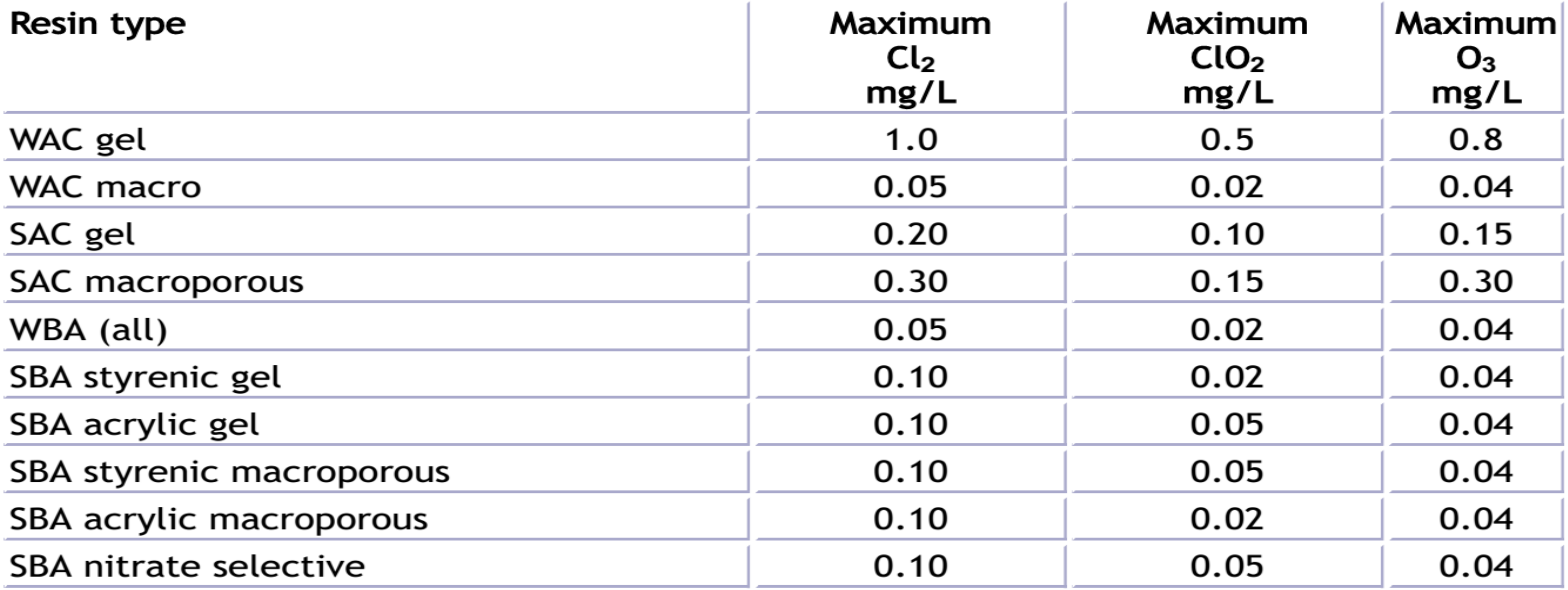
Stability

Resins must withstand various forms of stress in operation:

- Physical stress in case of resin transfer or high pressure drop
- Osmotic stress due to the change in resin volume
- Thermal stress in case high temperature or temperature variations
- Oxidants
- Organic fouling

Oxidation stability

- Excess oxidants can be neutralised with sulphite or dithionite salts or sulphur dioxide.
- Excess chlorine can be removed by an activated carbon filter.



Resin type	Maximum Cl_2 mg/L	Maximum ClO_2 mg/L	Maximum O_3 mg/L
WAC gel	1.0	0.5	0.8
WAC macro	0.05	0.02	0.04
SAC gel	0.20	0.10	0.15
SAC macroporous	0.30	0.15	0.30
WBA (all)	0.05	0.02	0.04
SBA styrenic gel	0.10	0.02	0.04
SBA acrylic gel	0.10	0.05	0.04
SBA styrenic macroporous	0.10	0.05	0.04
SBA acrylic macroporous	0.10	0.02	0.04
SBA nitrate selective	0.10	0.05	0.04

Ion Exchange Reactions

- An ion exchange resin in the ionic form A is in contact with a solution containing an ion B, an equilibrium reaction is observed.
- Here an example of cation exchange:

$$R\text{-}A^+ + B^+ \longleftrightarrow R\text{-}B^+ + A^+$$

- For the most current reaction between a strongly acidic resin in the H+ form and sodium ions (Na+) in water, equation becomes:

$$R\text{-}H^+ + Na^+ \longleftrightarrow R\text{-}Na^+ + H^+$$

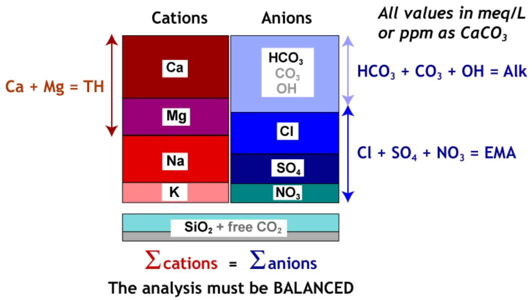
Ion Exchange Reactions

- For divalent ions, e.g. (softening reaction):

$$2\ R\text{-}Na^{+} + Ca^{++} \longleftrightarrow R_2\text{-}Ca^{++} + 2\ Na^{+}$$

Regeneration

- Regeneration consists of reversing the equilibrium in increasing the concentration of the ion displaced in the equilibrium reaction.
- For instance, a softener is regenerated by using a high concentration of [Na+] ions on the right side of reaction .
- This causes the reaction to be shifted to the left

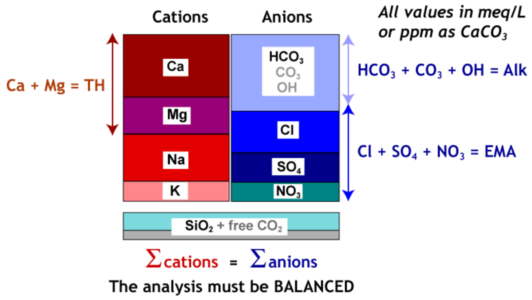


Ion Exchange Feed Water

- Ion exchange resins exchange ions. Not a surprise, but
- **The composition of the feed water affects plant performance.**
- It is therefore essential to know precisely the water composition of the feed to the ion exchange system.
- Salinity
- Suspended solids and turbidity
- Temperature
- pH value
- Organic substances in the water
- Other impurities, such as iron, manganese, aluminium, oil, polyelectrolytes…

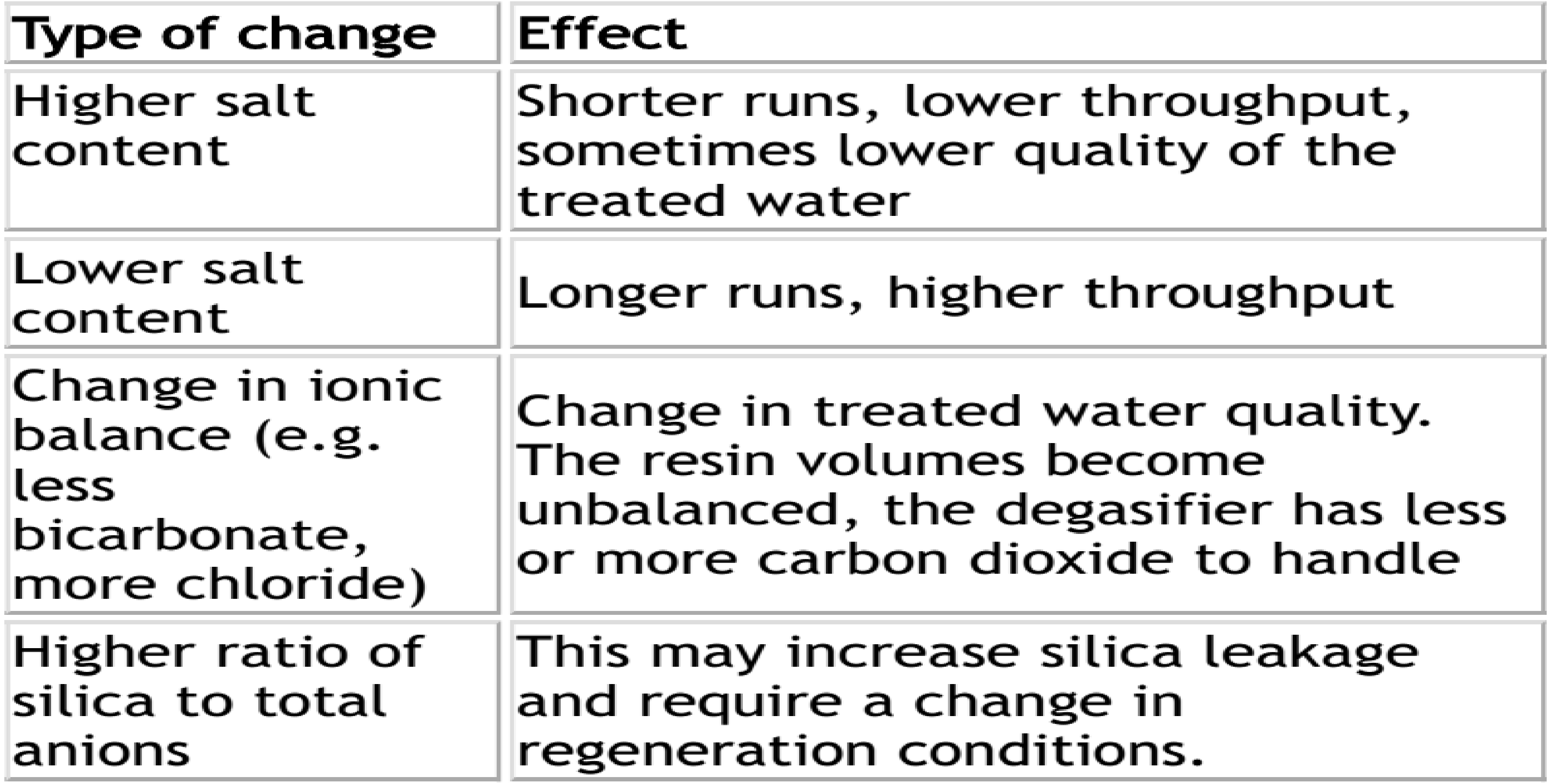
Feed Water: Salinity (water analysis)

- This is the single most important item to estimate the performance of an ion exchange system.
- It is also one of the first things to check when plant performance deteriorates.
- You cannot rely on an analysis that was made months or years ago. Some effects of a change in salinity are:



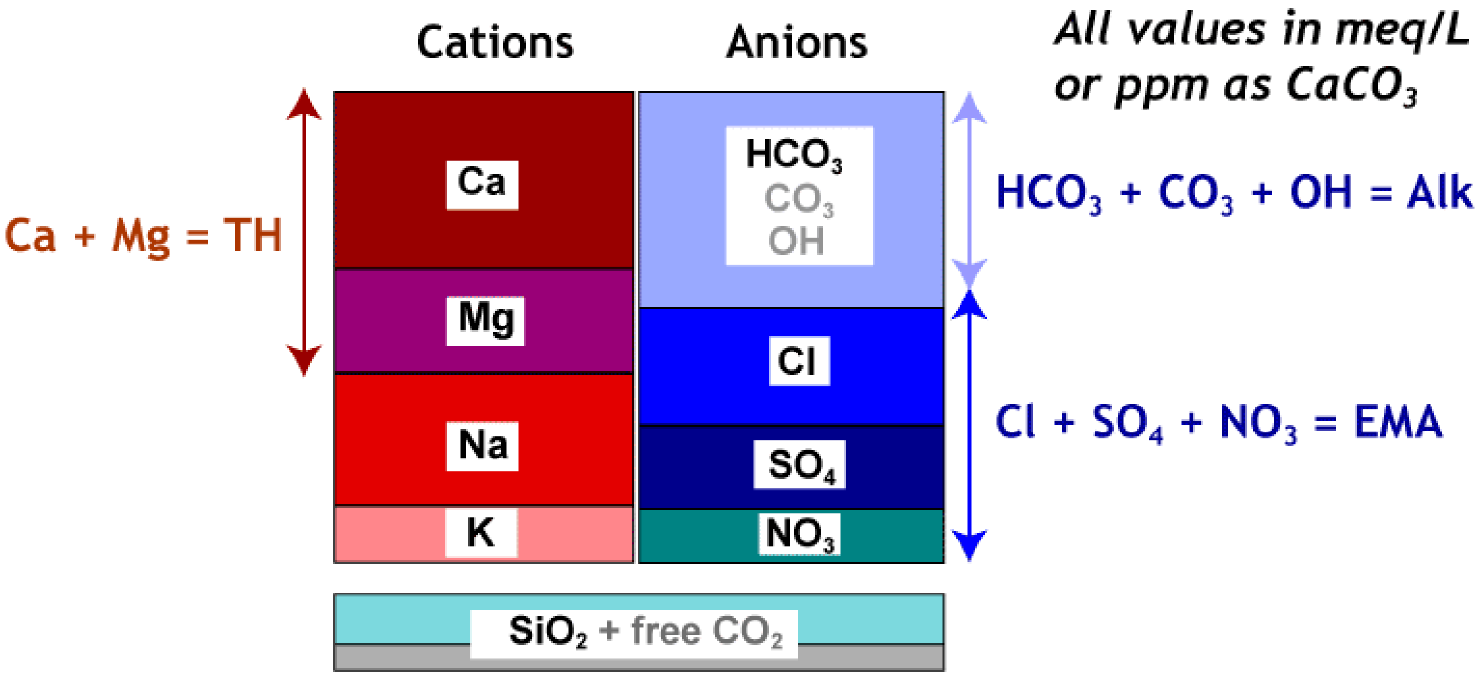
Feed Water: Salinity (water analysis)

- Some effects of a change in salinity are:



Type of change	Effect
Higher salt content	Shorter runs, lower throughput, sometimes lower quality of the treated water
Lower salt content	Longer runs, higher throughput
Change in ionic balance (e.g. less bicarbonate, more chloride)	Change in treated water quality. The resin volumes become unbalanced, the degasifier has less or more carbon dioxide to handle
Higher ratio of silica to total anions	This may increase silica leakage and require a change in regeneration conditions.

Feed Water: Salinity (water analysis)

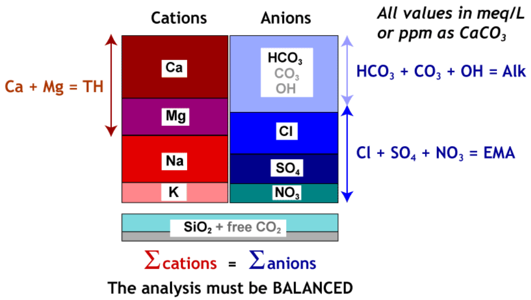


All values in meq/L or ppm as $CaCO_3$

Σcations = Σanions

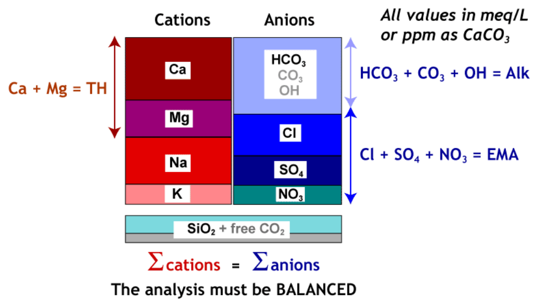
The analysis must be BALANCED

Feed Water: Salinity limits



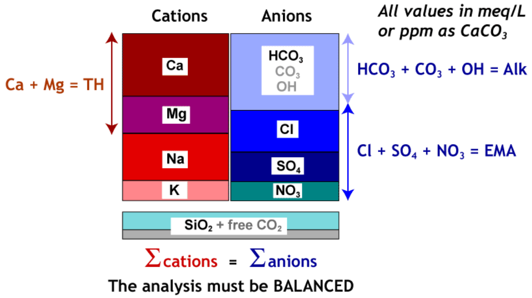
- Ion exchange is the perfect technology for low concentrations.
- At high salinity, the cycles become very short, regenerant consumption increases and in extreme cases the water required for regeneration may exceed the volume of treated water.
- As a guideline, a salinity of 20 meq/L (1000 ppm as CaCO3) seems to be the high limit, with some exceptions.
- Higher salinity water is probably best treated with RO.
- Sea water cannot be demineralised by ion exchange, as the resins would be exhausted in less than 3 bed volumes.

Feed Water: Suspended solids



- Ideally, the feed water to an ion exchange vessel should be perfectly clear and free of suspended solids.
- It is essential to ensure that mechanical filters installed ahead of an ion exchange system operate properly.
- Insufficient filtration resulting in excessive suspended solids may cause:
  - **Channeling of the resin bed**, resulting in high leakage and short runs.
  - **High pressure drop values**, sometimes resulting in flow reduction, and requiring frequent backwash of the unit.
- If the resins can be easily backwashed and cleaned, a higher quantity of suspended solids is acceptable.

Feed Water: Suspended solids

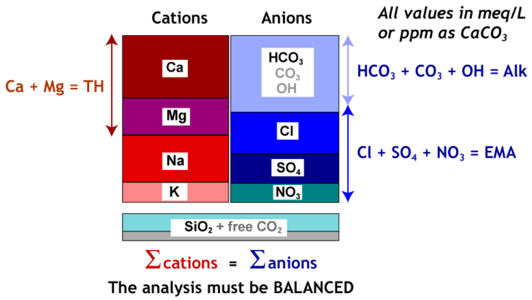


All values in meq/L or ppm as $CaCO_3$

Σcations = Σanions

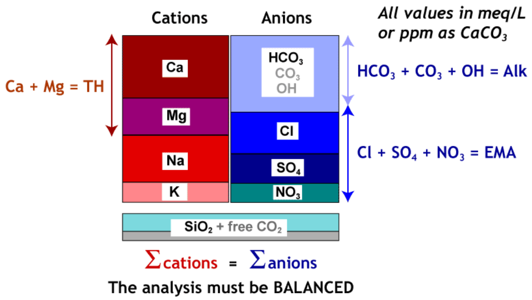
The analysis must be BALANCED

- In all cases, if the system has long cycles, the accumulated suspended solids may cause pressure drop problems even if the amount of suspended solids in the feed is relatively low
- Reverse flow regenerated vessels are not backwashed at the end of every cycle, and the pressure drop should be monitored closely to determine when a resin backwash is necessary.
- co-flow regenerated vessels can be backwashed before each regeneration, they are not very sensitive to suspended solids, and several mg/L (ppm) are usually acceptable.



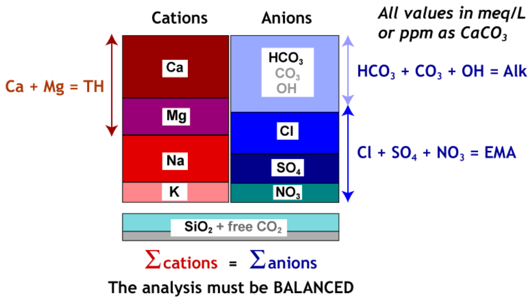
Feed Water: Turbidity

- (cloudiness or haziness) is measured in NTU (Nephelometric Turbidity Units). There is no fixed relation between turbidity and suspended solids.
- Turbidity limits Turbidity is not used much in conjunction with ion exchange systems. ***It was found that 1 NTU is more than what the columns can tolerate.***



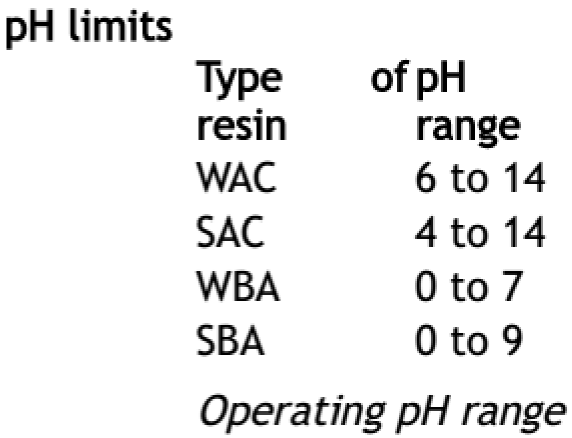
Feed Water: Temperature

- The temperature of the feed water (and of the regenerants) can affect plant performance.
- At low temperature, the operating capacity of all resins decreases.
- There is an exception to the above rule: at high temperature, the silica removal capacity of a SBA resin decreases, to become virtually zero if the temperature exceeds about 60°C.
- SBA resins and acrylic SBA resins should not be operated or regenerated at a temperature higher than 40°C. High temperatures may result in problems of rinse and a loss of strong base capacity, which will cause a higher silica leakage and shorter runs
- Cation resins can operate at high temperature, sometimes in excess of 100°C.



Feed Water: pH value

- Ion exchange resins can tolerate any pH value (0 to 14) **without suffering damage**
- In service however, resins operate only within pH limits: cation resins cannot operate at very low pH, or anion resins at very high pH, because they would be permanently regenerated and unable to exchange other ions.
- the resins are normally not used in very concentrated solutions.

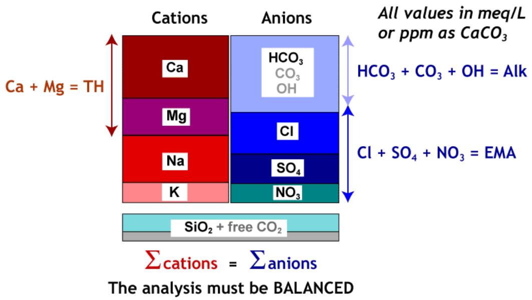


pH limits

Type resin	of pH range
WAC	6 to 14
SAC	4 to 14
WBA	0 to 7
SBA	0 to 9

Operating pH range

Feed Water: Organics



All values in meq/L or ppm as $CaCO_3$

Ca + Mg = TH

$HCO_3 + CO_3 + OH = Alk$

$Cl + SO_4 + NO_3 = EMA$

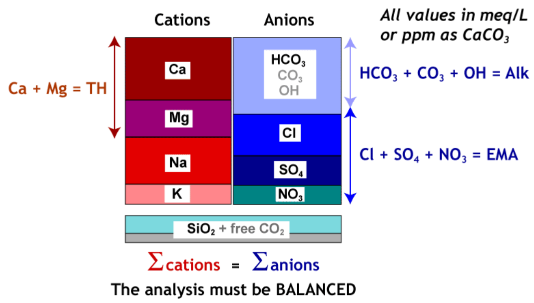
Σcations = Σanions

The analysis must be BALANCED

- Organic matter in water can interfere with ion exchange.
- The main effect of organics is **irreversible fouling** of anion exchange resins.

Some problems caused by organics are:

- Low pH (< 6) of the treated water when organic acids slip through the plant.
- High conductivity of the treated water.
- Increased silica leakage.
- Increased time for rinsing and high volume of waste water.
- Shorter runs.

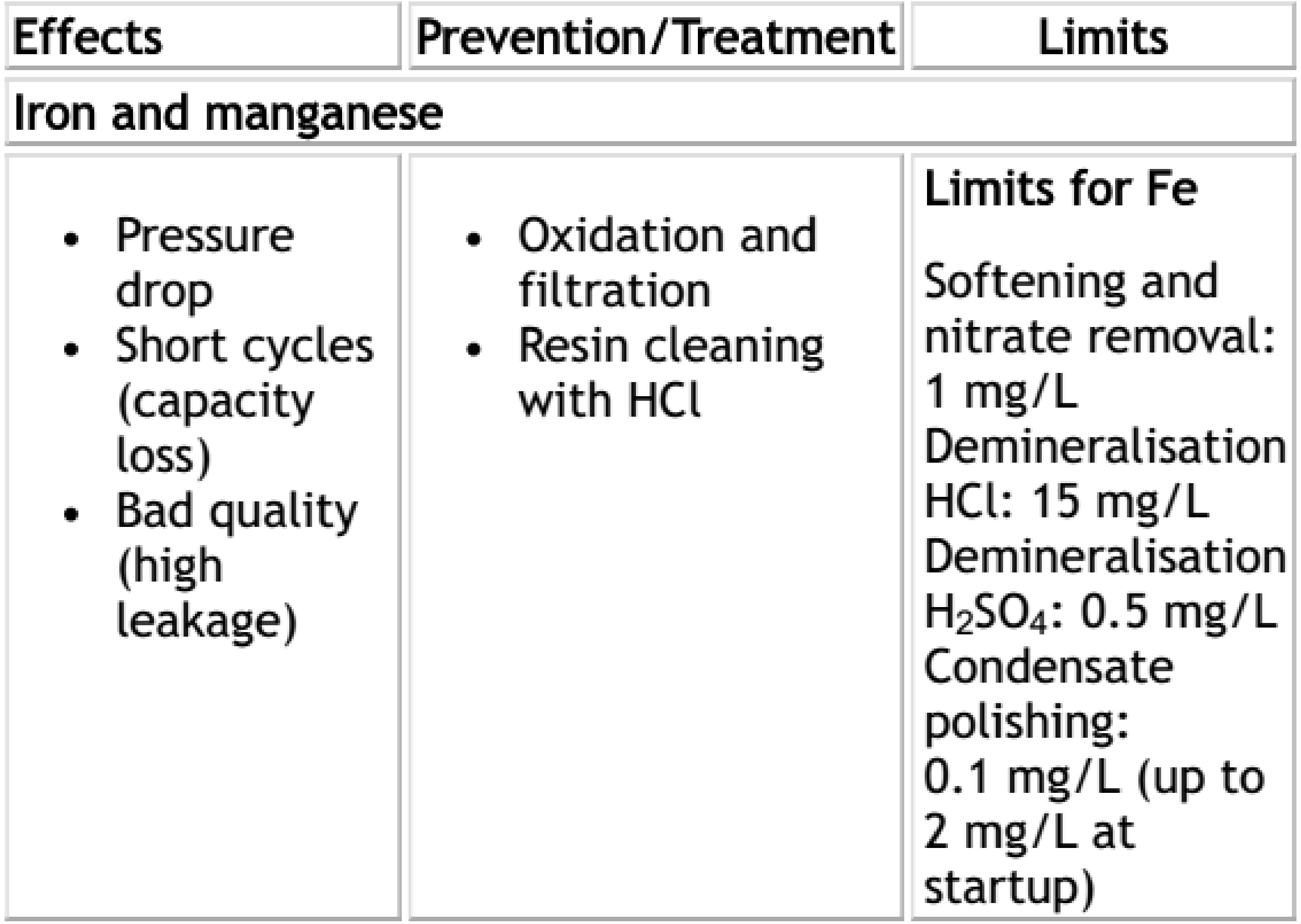


Feed Water: Organics

- The traditional measurement of organics (COD) in natural water uses the potassium permanganate oxidation method, and its result is expressed in mg/L as $KMnO4$
- Unfortunately, there is no direct correlation between this method and the more modern analysis of TOC (Total Organic Carbon).
- experience has shown that as a rule of thumb, 1 mg/L TOC (1 ppm as Carbon) can be roughly translated into 5.5 mg/L (5.5 ppm) as $KMnO4$.

Resin Type	Maximum Temperature (˚C)	Maximum Organic Load g as $KMnO_4$ per L resin
SBA styrenic type 1, gel	60	2
SBA styrenic type 2, gel	35	3
SBA styrenic type 1, macroporous	60	4
SBA styrenic type 2, macroporous	35	5
SBA acrylic	35	8
SBA Acrylic, macroporous	60	15
SBA nitrate selective, macroporous	35	2
Bifunctional acrylic	25	10
WBA styrenic, macroporous	60	12
WBA acrylic, gel	60	25
WBA boron selective	40	5

Other impurities



Effects	Prevention/Treatment	Limits
Iron and manganese		
• Pressure drop • Short cycles (capacity loss) • Bad quality (high leakage)	• Oxidation and filtration • Resin cleaning with HCl	**Limits for Fe** Softening and nitrate removal: 1 mg/L Demineralisation HCl: 15 mg/L Demineralisation H_2SO_4: 0.5 mg/L Condensate polishing: 0.1 mg/L (up to 2 mg/L at startup)

Basic ion exchange processes in water treatment

- Softening (removal of hardness)
- De-alkalisation (removal of bicarbonate)
- Decationisation (removal of all cations)
- Combined dealkalisation and softening
- Demineralisation (removal of all ions)
- Mixed bed polishing
- Nitrate removal
- Selective removal of various contaminants

Softening

- Natural water contains calcium and magnesium ions which form salts that are not very soluble.
- These cations, together with the less common and even less soluble strontium and barium cations, are called together **hardness ions**.
- When the water evaporates even a little, these cations precipitate.
- This is what you see when you let water evaporate in a boiling kettle on the kitchen stove.

Softening

- Hard water also forms scale in water pipes and in boilers, both domestic and industrial.
- It may create cloudiness in beer and soft drinks.
- Calcium salts deposit on the glasses in your dishwasher if the city water is hard and you have forgotten to add salt.
- Strongly acidic cation exchange resins (SAC, see resin types) used in the sodium form remove these hardness cations from water.
- Softening units, when loaded with these cations, are then regenerated with sodium chloride (NaCl, table salt).

Softening

- **Reactions**

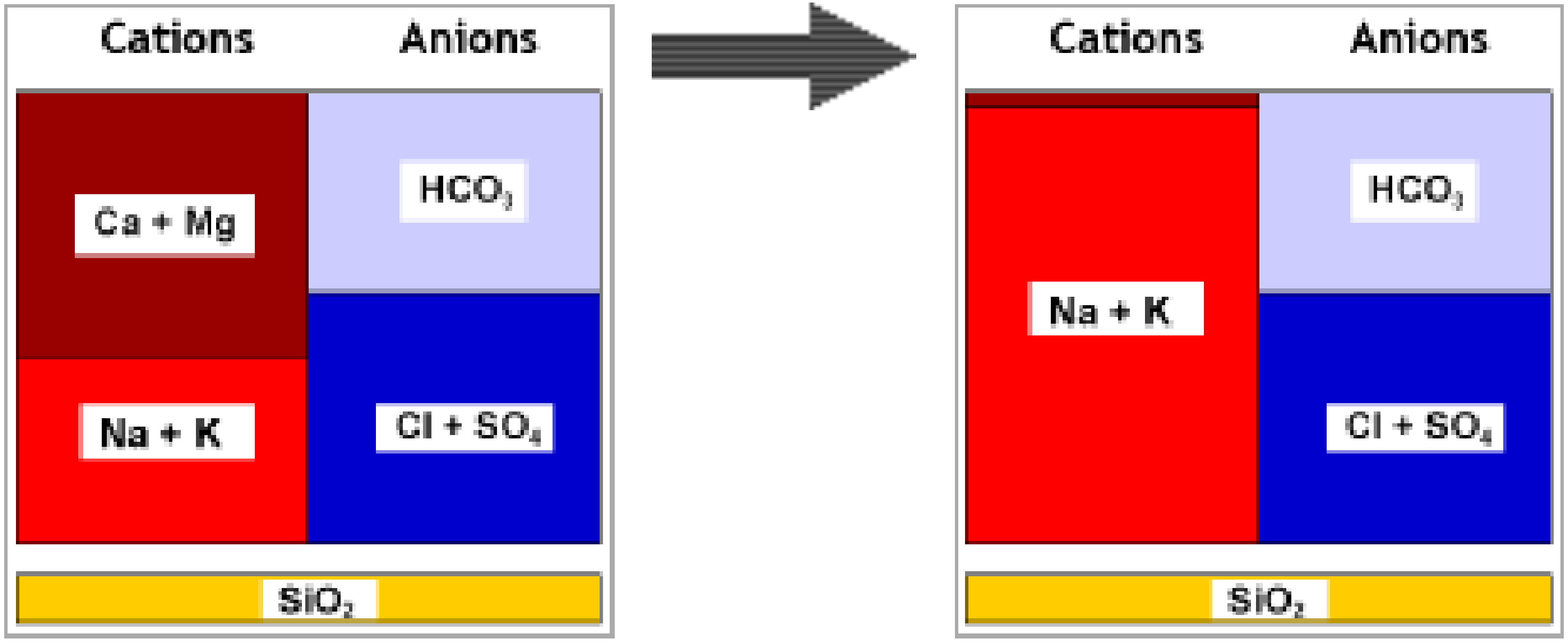
  Here the example of calcium

$$2\ R\text{-}Na + Ca^{++} \rightleftharpoons R_2\text{-}Ca + 2\ Na^{+}$$

- R represents the resin, which is initially in the sodium form. The reaction formagnesium is identical.
- The above reaction is an equilibrium.
- It can be reversed by increasing the sodium concentration on the right side. This is done with NaCl, and the regeneration reaction is

$$R_2\text{-}Ca + 2\ Na^{+} \rightleftharpoons 2\ R\text{-}Na + Ca^{++}$$

Softening

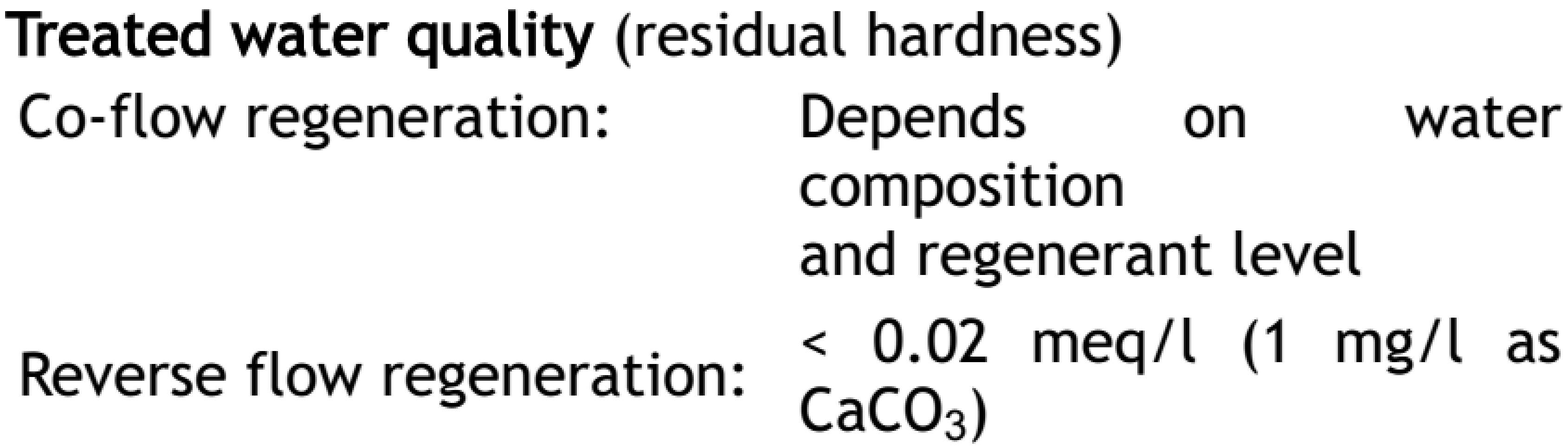


Raw water

Softened water

Softening

- What happens to the water
- The water salinity is unchanged, only the hardness has been replaced by sodium.
- A small residual hardness is still there, its value depending on regeneration conditions.



Treated water quality (residual hardness)

Co-flow regeneration:	Depends on water composition and regenerant level
Reverse flow regeneration:	< 0.02 meq/l (1 mg/l as $CaCO_3$)

Softening

- Examples for the use of softeners:
- Treatment of water for low pressure boilers
- dishwashers have a softening cartridge at the bottom of the machine
- Breweries and soft drink factories treat the water for their products with food grade resins

Softening the water does not reduce its salinity: it merely removes the hardness ions and replaces them with sodium, the salts of which have a much higher solubility, so they don't form scale or deposits.

De-alkalisation

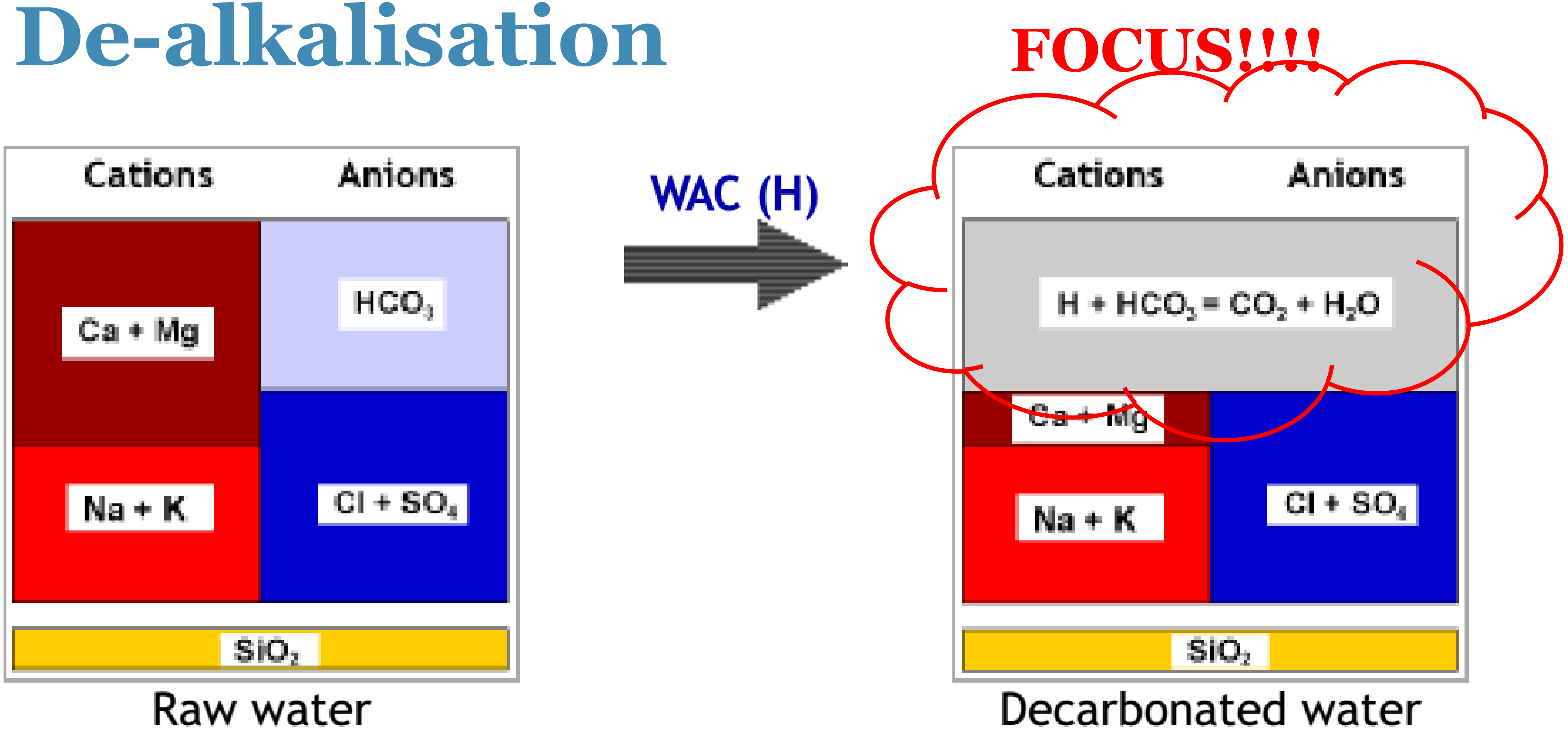
- This particular process uses a weakly acidic cation resin.
- This resin type is capable of removing hardness from water when it also contains alkalinity.
- After treatment, the water contains carbon dioxide, that can be eliminated with a degasifier tower.
- The cation resin is very efficiently regenerated with an acid, usually hydrochloric acid

$$2\ R\text{-}H + Ca^{++}(HCO_3^-)_2 \longrightarrow R_2\text{-}Ca + 2\ H^+ + 2\ HCO_3^-$$

- and the hydrogen cations combine with the birarbonate anions to produce carbon dioxide and water:

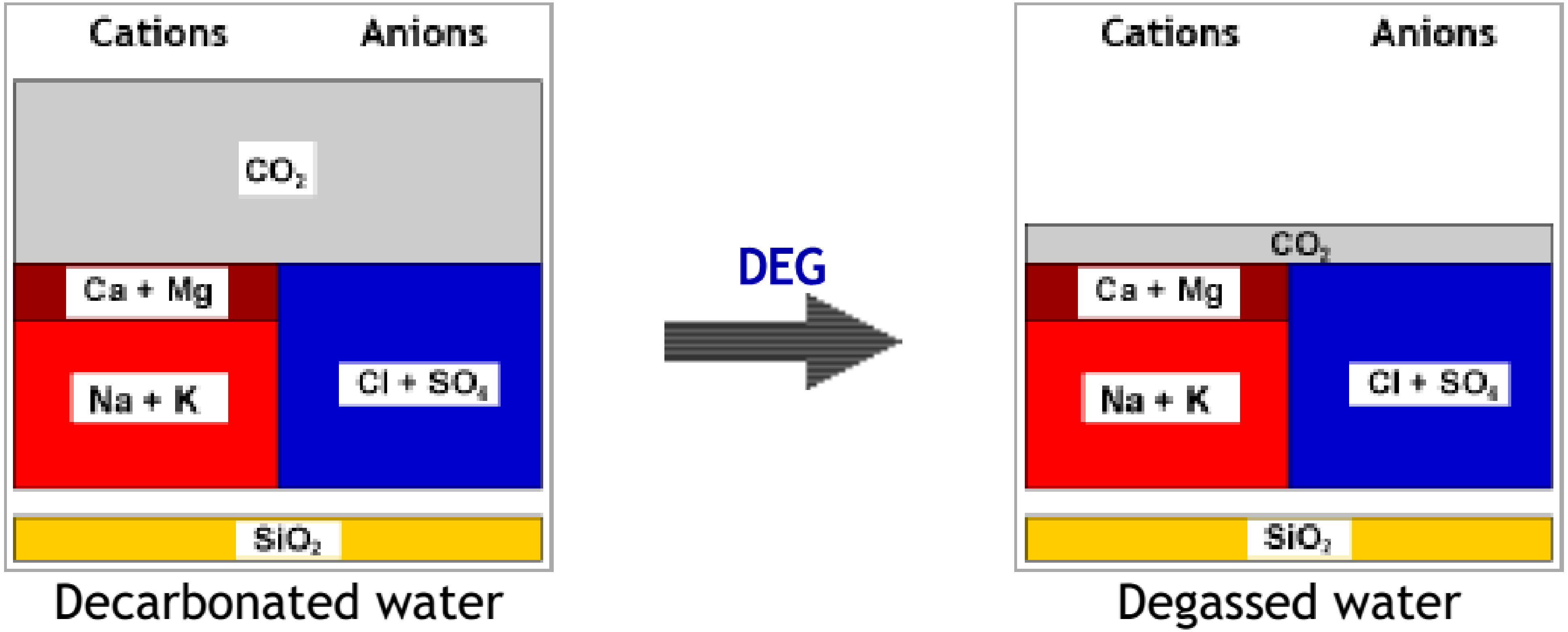
$$H^+ + HCO_3^- \longrightarrow CO_2 + H_2O$$

De-alkalisation



De-alkalisation

- Recombination of hydrogen and bicarbonate and removal of carbon dioxidewith the degasifier:



De-alkalisation

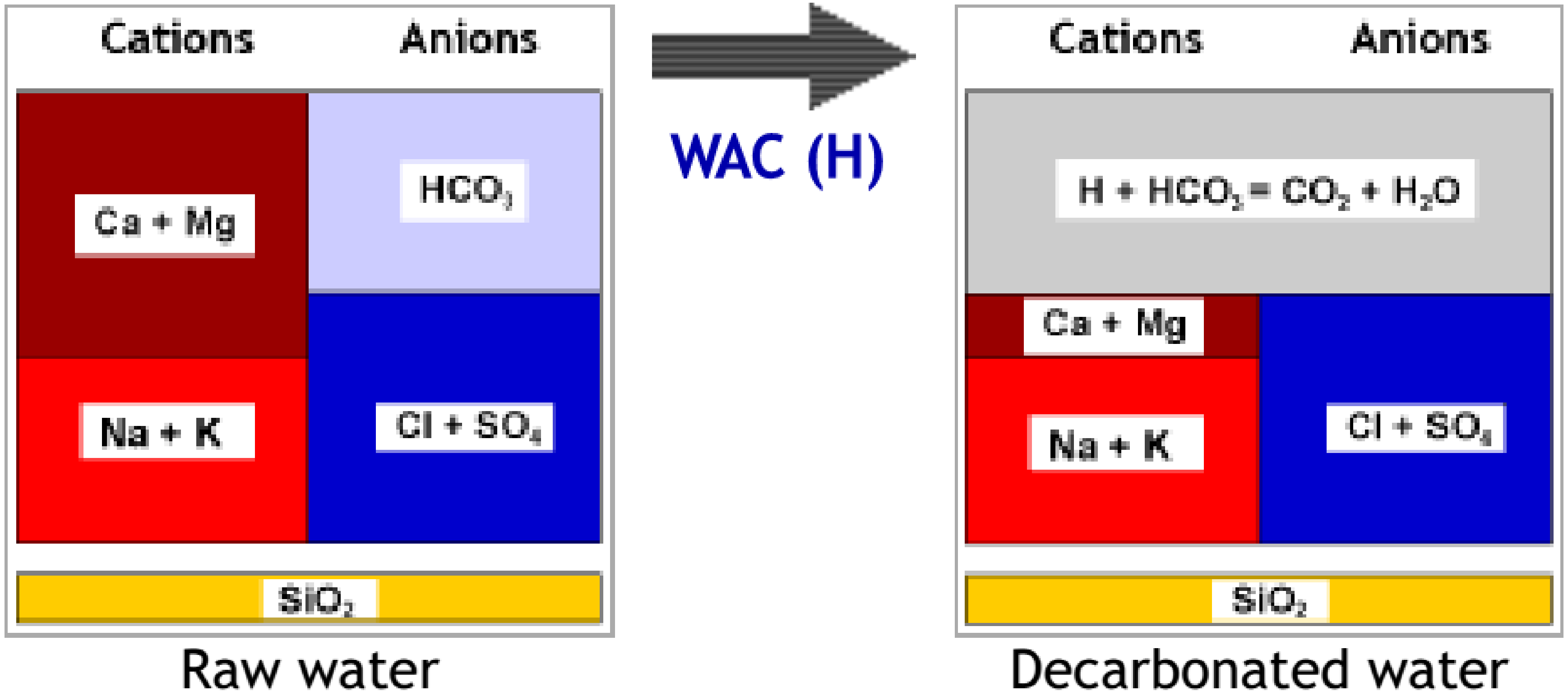
- The salinity has decreased. Temporary hardness is gone.
- De-alkalisation is used:
- In breweries
- In household drinking water filters
- For low pressure boilers
- As a first step before the SAC exchange in demineralization
- ***De-alkalisation reduces the salinity of water, by removing hardness cations and bicarbonate anions.***

Combined dealkalisation + softening

- This process is sometimes called **Carbomix**, although the resins are not mixed.
- It uses two resins in series, a WAC in the H+ form followed by a SAC in the Na+ form.
- Both resins can be put as a Stratabed in a single colum, or in two separate units.
- This is useful only when the hardness is greater than alkalinity (in meq/L) otherwise the WAC resin will do the job alone.
- **For the process to be efficient, dealkalisation must take place first.**

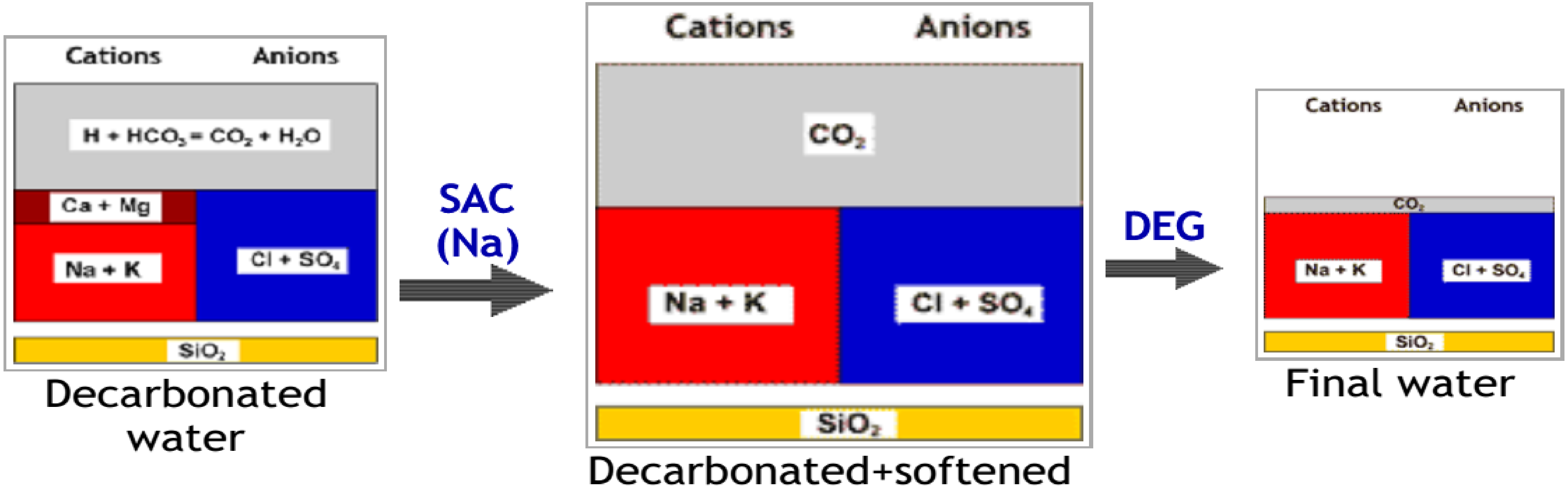
Combined dealkalisation + softening

- The first step is dealkalisation:



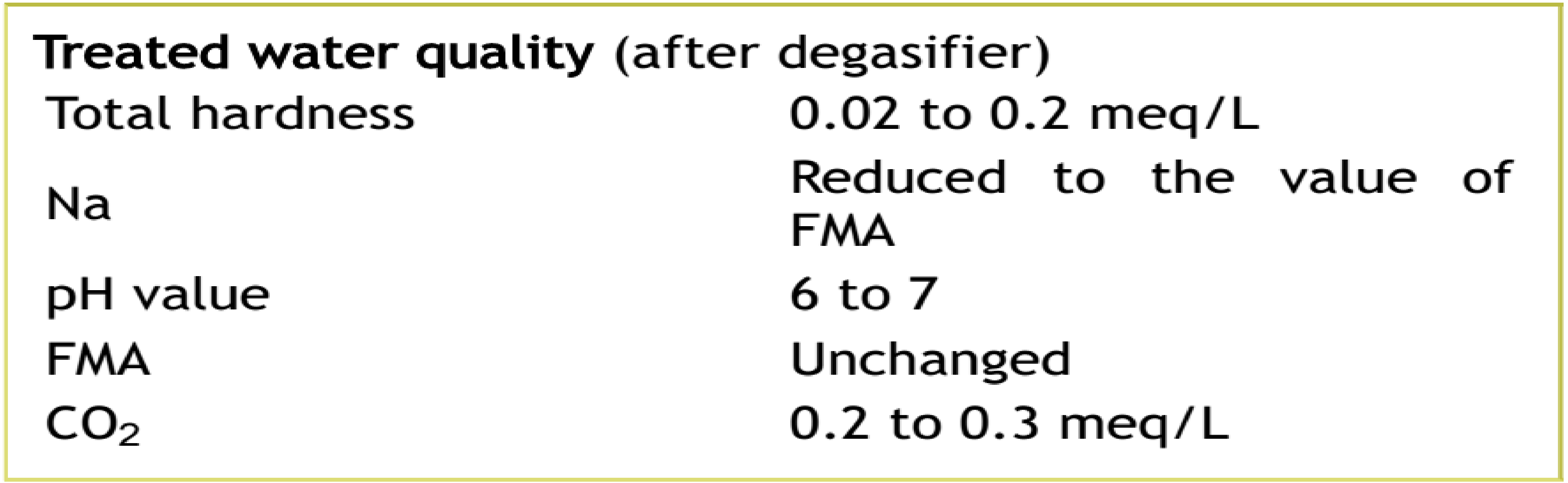
Combined dealkalisation + softening

- The second step is softening of the residual (permanent) hardness. The produced CO2 can be degassed:



Combined dealkalisation + softening

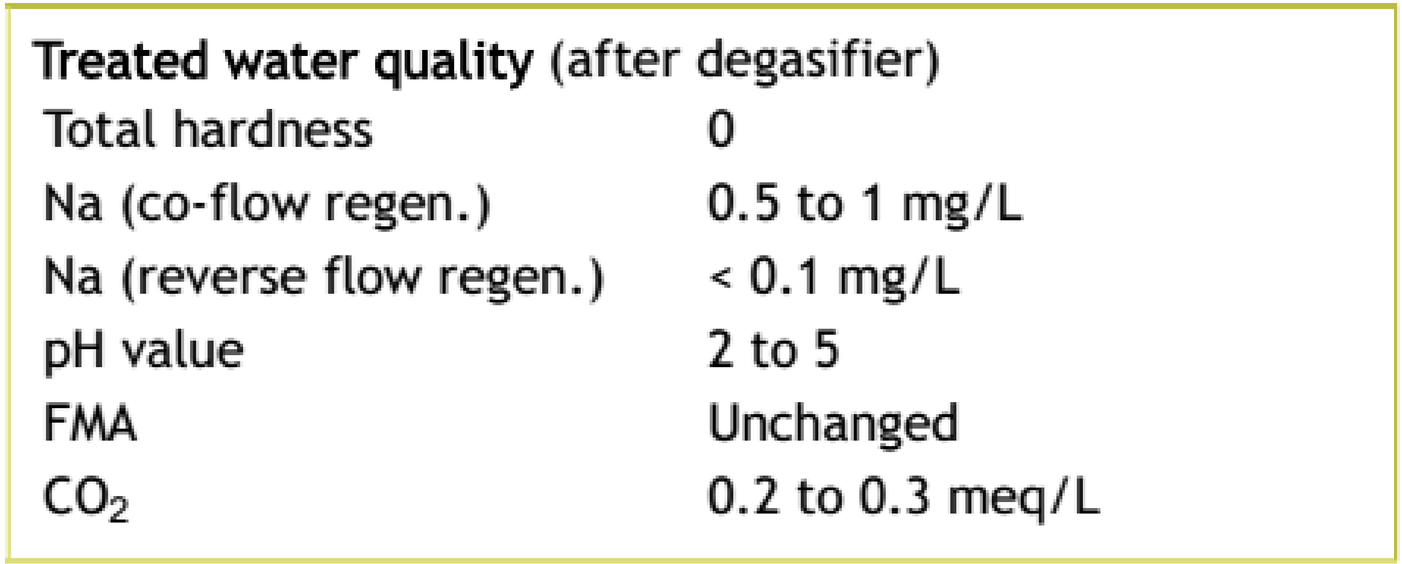
- All hardness is gone, and the salinity has been reduced.
- Regeneration is done in two steps, first with acid (preferably HCl) then with brine.



Treated water quality (after degasifier)	
Total hardness	0.02 to 0.2 meq/L
Na	Reduced to the value of FMA
pH value	6 to 7
FMA	Unchanged
CO_2	0.2 to 0.3 meq/L

Decationisation

- The removal of all cations is seldom practiced, except as a first stage of the demineralisation process, or sometimes in condensate polishing where the decationiser precedes a mixed bed unit. A strongly acidic cation exchange resin (SAC) is used in the H+ form.



Treated water quality (after degasifier)	
Total hardness	0
Na (co-flow regen.)	0.5 to 1 mg/L
Na (reverse flow regen.)	< 0.1 mg/L
pH value	2 to 5
FMA	Unchanged
CO_2	0.2 to 0.3 meq/L

Demineralisation

- For many applications, all ions in the water must be removed.
- In particular, when water is heated to produce steam, any impurity can precipitate and cause damage.
- As there are cations and anions in the water, we must use two different types of resins: a cation exchanger and an anion exchanger.
- This combined arrangement produces pure water
- Demineralisation is also called deionisation.
- The cation resin is used in the hydrogen form (H^+) and the anion resin in the hydroxyl form (OH^-), so that the cation resin must be regenerated with an acid and the anion resin with an alkali

Demineralisation

- A degasifier is used to remove the carbon dioxide created after cation exchange when the water contains a significant concentration of bicarbonate.
- The cation resin is usually located before the anion resin:
- Otherwise if the water contains any hardness, it would precipitate in the alkaline environment created by the OH- form anion resin as Ca(OH)2 or CaCO3, which have low solubility.

Demineralisation Reactions

- Let us first consider a simple demineralisation system comprising a strong acid cation exchange resin in the H+ form, a degasifier (optional) and a strong base anion exchange resin in the OH– form.
- The first step is decationisation:

$$R_{SAC}\text{-H} + Na^{+} \rightleftharpoons R_{SAC}\text{-Na} + H^{+}$$

- With calcium insead of sodium (also valid for magnesium and other divalent cations)

$$2\ R_{SAC}\text{-H} + Ca^{++} \rightleftharpoons (R_{SAC})_2\text{-Ca} + 2\ H^{+}$$

Demineralisation Reactions

- In the second step, all anions are removed with the strong base resin:

$$R_{SBA}\text{-}OH + Cl^- \rightleftharpoons R_{SBA}\text{-}Cl + OH^-$$

- The weak acids created after cation exchange, which are carbonic acid and silicic acid (H2CO3 and H2SiO3) are removed in the same way:

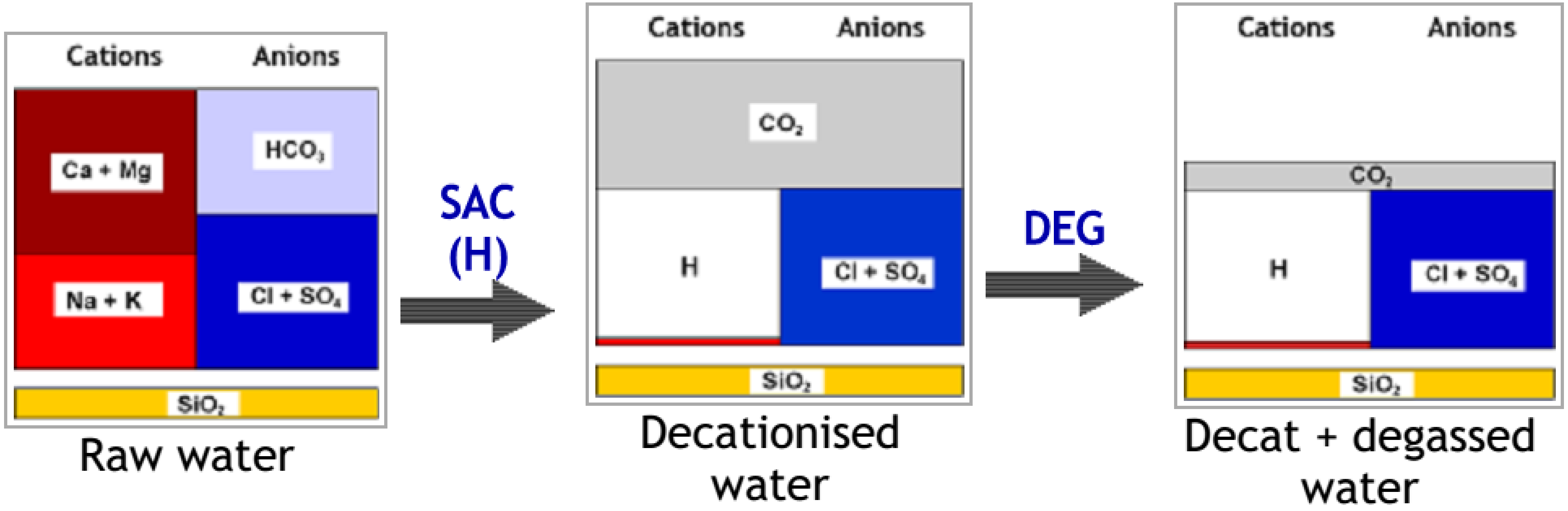
$$R_{SBA}\text{-}OH + HCO_3^- \rightleftharpoons R_{SBA}\text{-}HCO_3^- + OH^-$$

- And finally, the H+ ions created in the first step react with the OH ions of the second step to produce new molecules of water. This reaction is irreversible:

$$H^+ + OH^- \longrightarrow H_2O$$

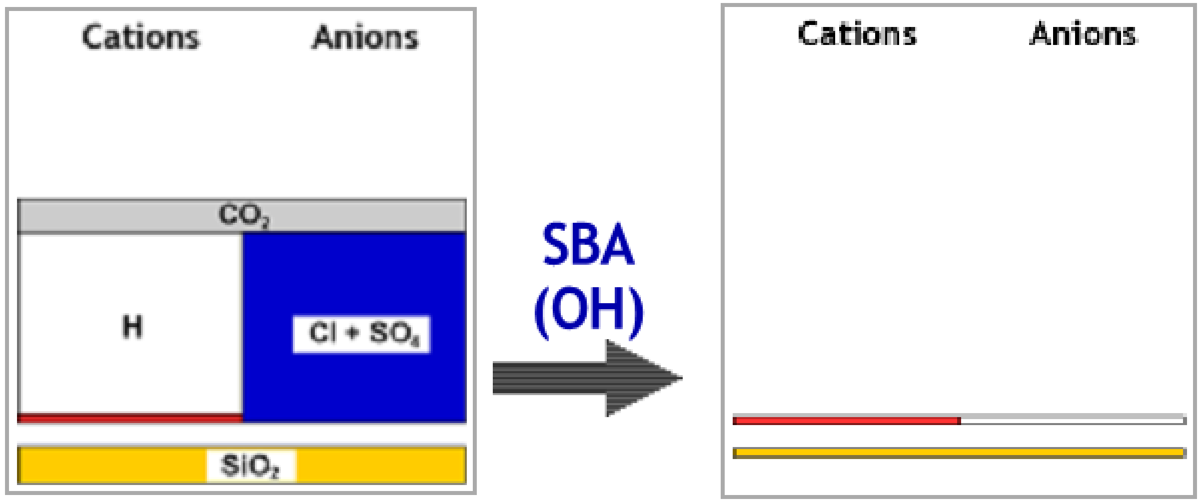
Demineralisation

1: Cation exchange removing all cations (as in decationisation) followed by degassing:



Demineralisation

2: Anion exchange removing all anions (strong and weak acids):



Decat + degassed water

Demineralised water

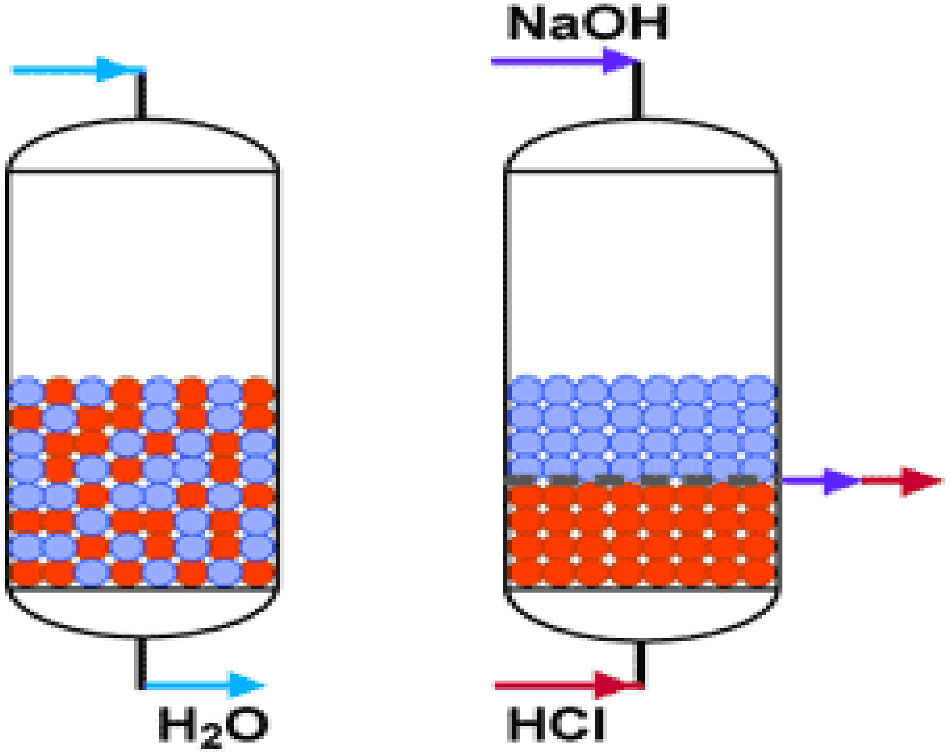
Demineralisation: Treated water quality

Conductivity (co-flow regen.)	**5 to 25 µS/cm**
Conductivity (reverse flow regen.)	**< 1 µS/cm**
Silica residual (co-flow)	**50 to 200 µg/L**
Silica residual (reverse flow)	**5 to 40 µg/L**
Sodium residual (co-flow regen.)	**0.5 to 1 mg/L**
Sodium residual (reverse flow regen.)	**< 0.1 mg/L**
CO2	**0.2 to 0.3 meq/L**
pH value	**In principle > 7 Don't use pH as a control parameter**

Mixed bed polishing

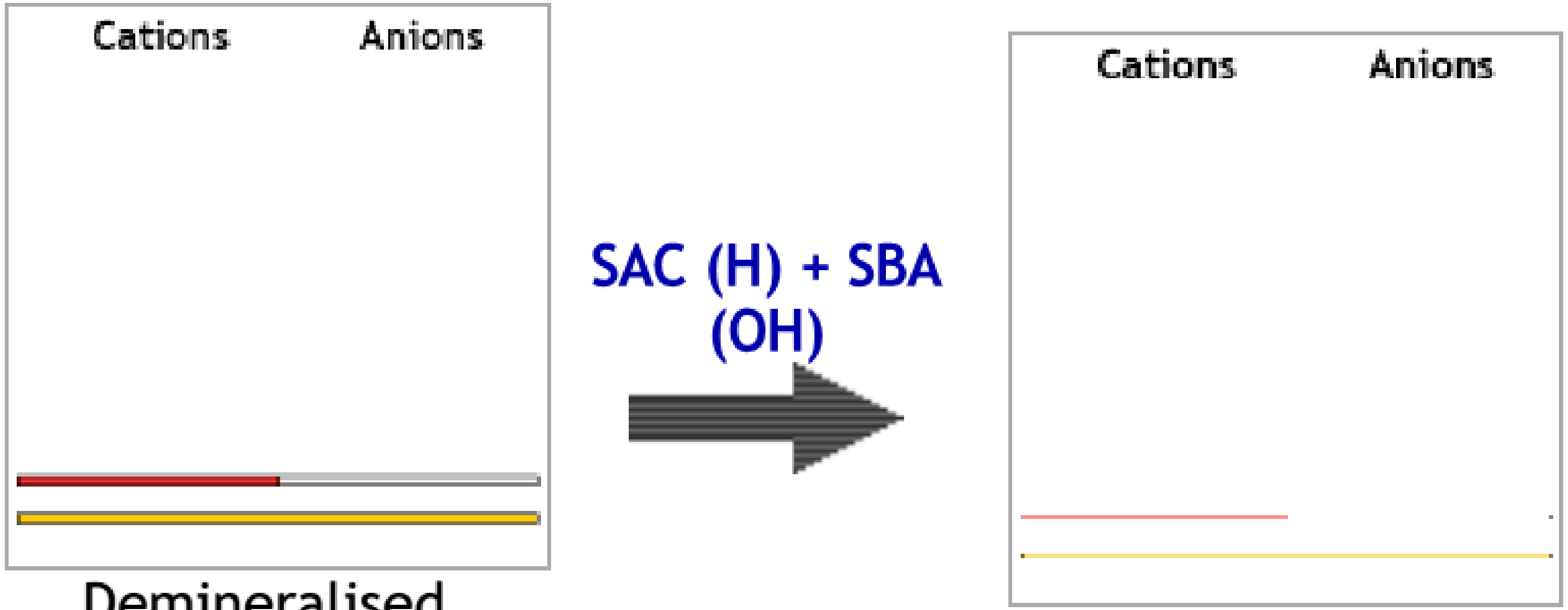
- The last traces of salinity and silica can be removed on a resin bed where highly regenerated strong acid cation and strong base anion resins are mixed.
- Mixed bed units deliver an excellent treated water quality, but are complcated to regenerate,
- as the resins must first be separated by backwashing before regeneration.
- Additionally, they require large amounts of chemicals, and the hydraulic conditions for regeneration are not optimal.
- Therefore, mixed beds are usually only used to treat pre-demineralized water, when the service run is long.

Mixed bed polishing



Mixed bed unit in service and in regeneration

Mixed bed polishing



Demineralised water

Nothing is left

Mixed bed polishing

- Mixed bed polishing produces a water with less than 0.1 µS/cm conductivity.
- With sophisticated design and appropriate resins, the conductivity of pure water (0.055 µS/cm) can be achieved.
- Residual silica values can be as low as 1 µg/L.
- The pH value should not be used as a process control, as pH meters are unable to operate at 1 µS/cm conductivity or below.

Mixed bed polishing Capacity and throughput

- The schema and treated water quality shown above apply to polishers installed downstream of an ion exchange primary demineralization system.
- The feed water to the polishing unit, in this case, contains only traces of sodium and silica.
- The operating capacity is usually limited by the anion resin, and is very low.
- However, the running time for a feed water having a conductivity of 1 µS/cm is usually 2 to 4 weeks.

Mixed bed polishing Capacity and throughput

- When the polisher is fed with water containing other ions, such as after a reverse osmosis plant, the situation is completely different.
- RO permeates often contain a relatively high proportion of carbon dioxide, and this is then the limiting factor.
- The treated water quality here may have a conductivity higher than 0.1 µS/cm (but not more than 1 µS/cm) and the throughput is only one or a few days.

Mixed bed polishing Uses

- Treatment of water pre-demineralised with ion exchange resins
- Polishing of reverse osmosis permeate
- Polishing of sea water distillate
- Treatment of turbine condensate in power stations
- Treatment of process steam condensate in various industries
- Production of ultra-pure water for the semiconductors industry

Ion exchange plant design

The aim of the plant design is to
- determine the appropriate resin stages,
- determine the appropriate resin volumes,
- calculate the required quantities of regenerant,
- calculate the pressure losses and possible flows as well as to
- determine the column geometry.

There is almost always a certain degree of flexibility and not just one "correct" design.

Ion exchange plant design

Recommendations

Basic parameters to consider when designing an ion exchange plant:

- Feed water analysis
- Production flow rate
- Cycle length
- Required quality of the treated water
- Regeneration technology
- Dimensions of the vessels
- Selection of resin types

IX Design: **Analysis of the feed water**

- All ion exchange systems are designed for a given feed water.
- Some variations of the feed water analysis are acceptable, and should be taken into account, but an ion exchange system cannot be designed efficiently for vastly different water types.
- For instance, a demineralisation system designed for the treatment of deep well water is completely different from a system designed to treat reverse osmosis permeate.
- ***The first thing to do is thus obtain a reliable water analysis.***

IX Design: **Analysis of the feed water**

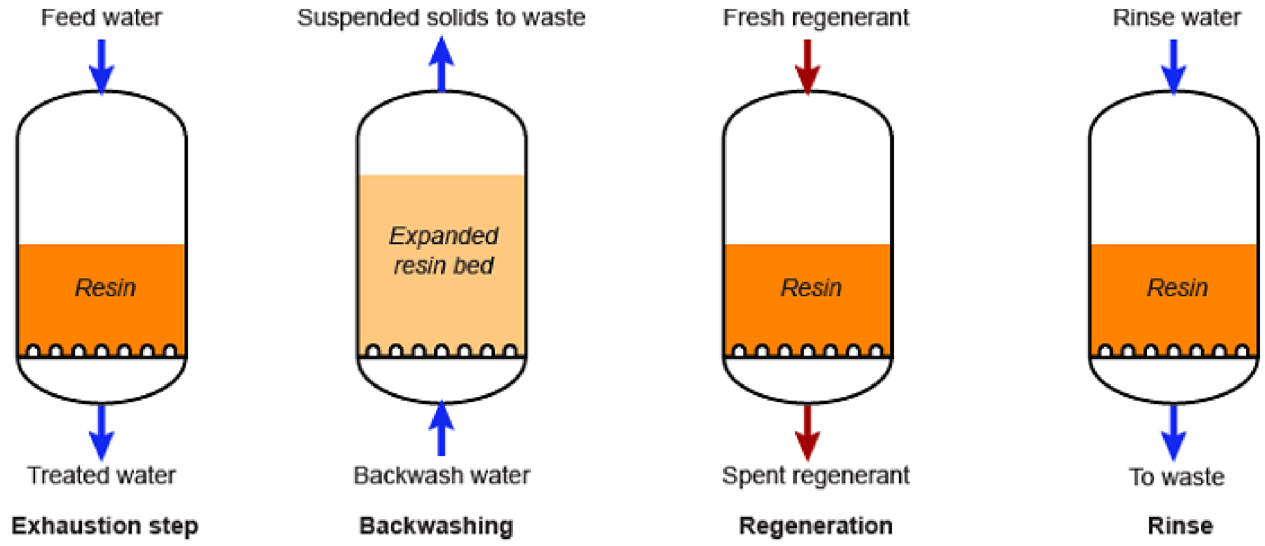
- When the water analysis is not constant, e.g. due to seasonal variations, do not take an "average composition" as the basis of your design.
- Instead, use the "most probable" case, design with this water, and check as a second step what will happen with the "minimum" and "maximum"“ waters.
- All water analyses must be perfectly balanced in terms of ions.
- The water analysis will determine what resin combination is required, and if a degasifier should be considered.(HCO3-)

IX Design: **Production flow rate**

- It is important to know whether the system will operate at constant or variable flow rate.
- Some system designs require a minimum flow rate
- Obviously, the system should be able to operate at both limits.
- In general, it is not advisable to operate intermittently, i.e. to stop production in the middle of the run and re-start it.
- ***Treated water quality may be affected after a stop not followed by regeneration.***

IX Design: **Cycle length**

- **Complete cycle of an ion exchange unit**
  The cycle of an ion exchange column used for water treatment consists of the following steps:
  1 . Exhaustion (production) step
  2. Backwash
  3. Regeneration
  4. Rinse



IX Design: **Cycle length**

Exhaustion step

- The solution to be treated (feed water) passes through the ion exchange resin bed, exhausting the resin progressively. At the breakthrough point, i.e. at the point where the ion leakage reaches a pre-determined value, the exhaustion step is stopped.

IX Design: **Cycle length**

Backwash

- Before regeneration, the resin bed is backwashed

a) to loosen it and prevent excessive compaction
b) to remove accumulated suspended solid and possible broke resin particles from the bed surface

- The bed expansion should be 50 to 100 % and the time of backwash is a few minutes.
- Backwashing the resin bed is not performed in case of reverse flow regeneration so as not to disturb the distribution of resin layers, except when the pressure drop increases excessively, or every 30 cycles or so.

IX Design: **Cycle length**

Regeneration

- The regenerant solution is then slowly introduced into the column.
- The regeneration time is usually 20 to 60 minutes.

Rinse

Rinsing the resin after regeneration is done in two steps:
1 . Slow rinse or displacement. The regenerant must be displaced with water from the resin bed until only traces of the chemical are left.

This displacement rinse is done at a low flow rate, the same as the regeneration flow rate.
2. Final fast rinse. Finally, the resin bed is submitted to a fast rinse at service flow rate to remove the last traces of regenerant. The end of this final rinse is reached when the outlet water quality meets the treated water quality specification.

With clean resins, the final rinsing time is around 20 minutes.

IX Design: **Cycle length**

In practice the Cycle time must be selected as a function of the following parameters:

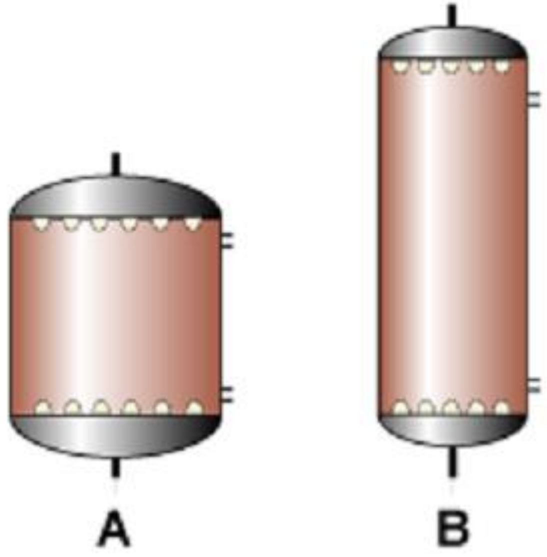
- Specific flow rate between 5 and 50 bed volumes per hour (BV/h). Mixed bed units should be designed to operate at a minimum of 12 to 15 BV/h.
- Make the system as small as possible for economical reasons (lower investment in hardware and resins).
- For packed bed systems, ensure that bed compaction is good both in the production phase and during regeneration
- With low salinity waters, e.g. when the feed water is good RO permeate, the running time can be several days.
- Mixed bed polishers after a primary demineralisation will run for several weeks before regeneration is required.

IX Design: **Treated water quality**

- In ion exchange the quality of the treated water does not depend much on the feed water analysis.
- Factors affecting the treated water quality are essentially related to the regeneration process.
- To a minor extend, temperature may affect the residual silica leakage in the treated water: at temperatures higher than about 50 °C, silica is hardly removed by strongly basic anion exchange resins (SBA).
- Other than that, you can expect the treated water quality of a regeneration system regenerated in reverse flow to be:
  Conductivity: ~ 1 µS/cm
  Silica: 10 to 25 µg/L

IX Design: **Vessel sizing**

- For a given resin volume, it is generally cheaper to make a tall and narrow column rather than a wide and short unit: in the illustration, both columns contain the same resin volume.
- Column B is cheaper, because the major cost components of the column are the dished ends and nozzle plates.
- There is no limit in height, except that the pressure drop at maximum flow rate should not exceed 100 to 150 kPa (1 to 1.5 bar) at maximum flow rate with clean resins.

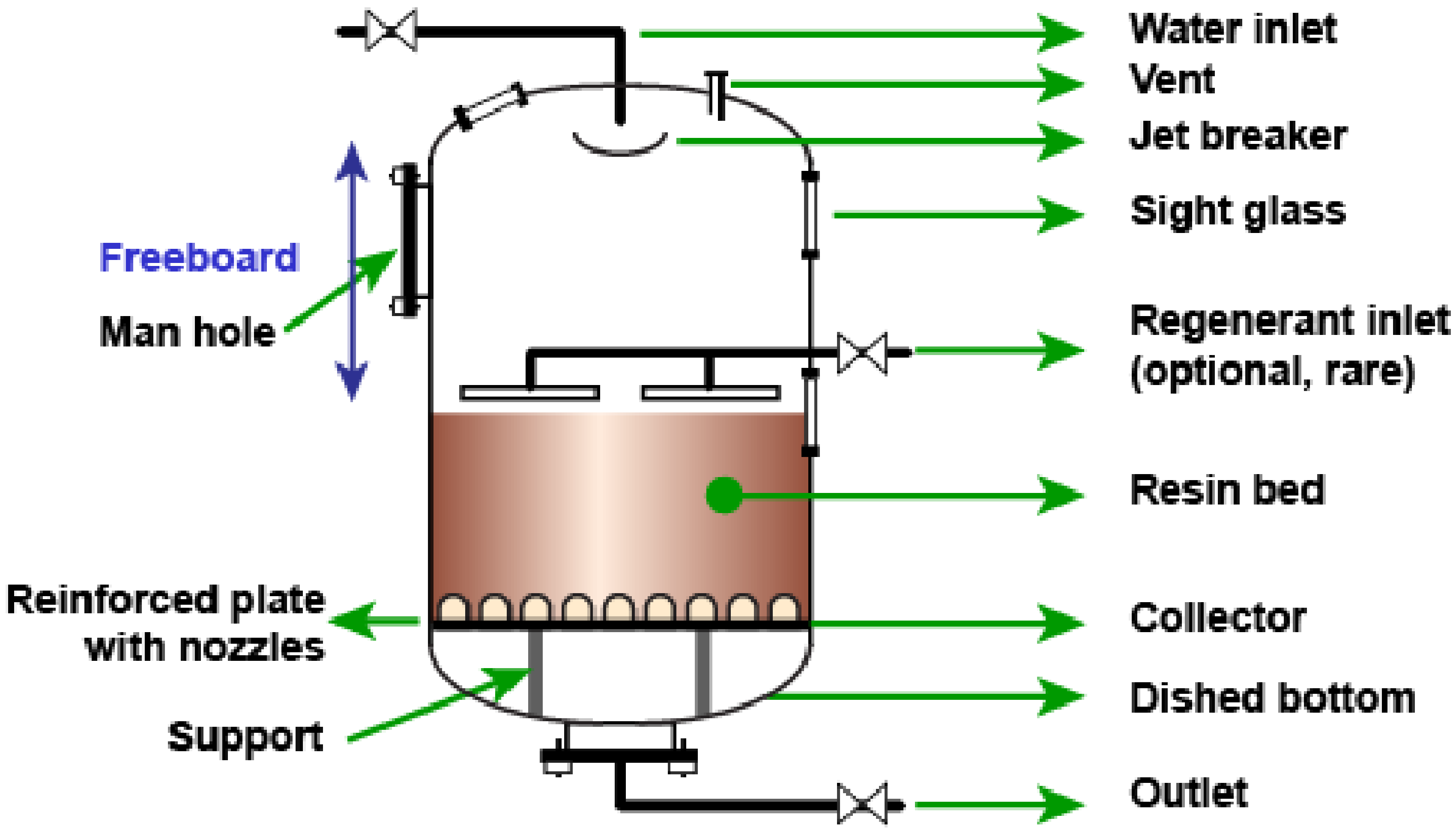


IX Design: **Resin choice**

- You will have to refer to the resin manufacturer. However, a few general recommendations can be made:
- Macroporous resins are normally not required for demineralisation or softening
- When the feed water contains high organics, acrylic anion resins are a good choice

Ion Exchange Columns

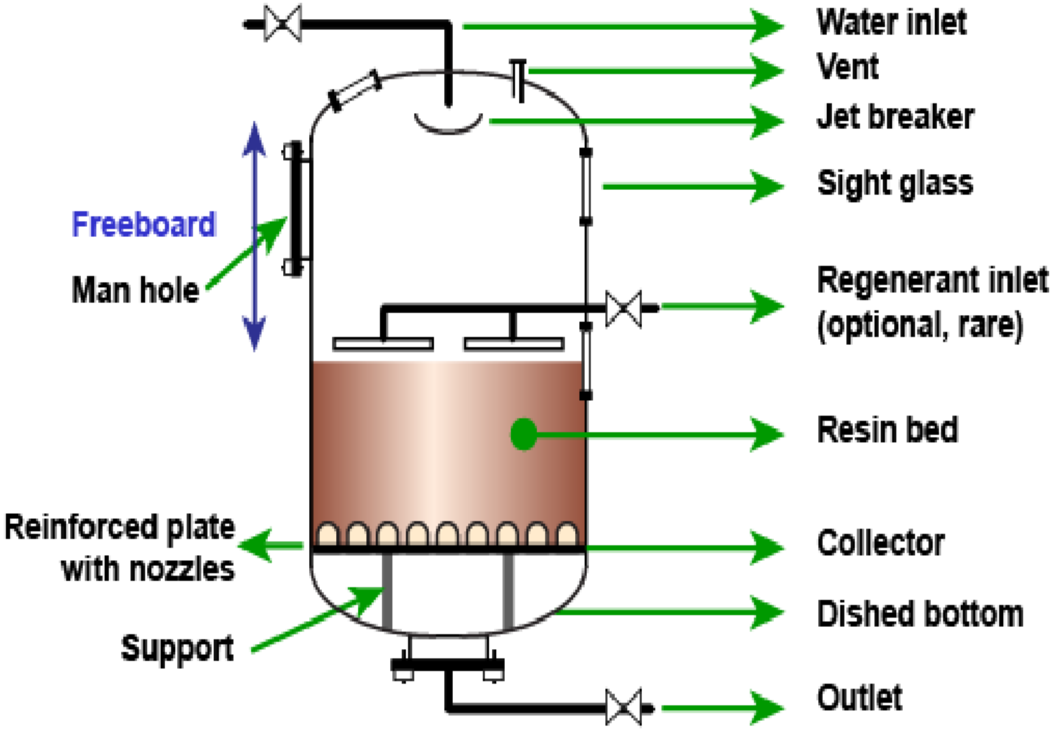
- Ion exchange resins are used in columns, in principle similar to those used for activated carbon.
- These are pressure vessels, usually made of rubber-lined steel.
- Small units are made of fiberglass reinforced plastic, and units used in the food industry are often made of stainless steel.
- A typical ion exchange column with co-flow regeneration is represented :



Co-flow regenerated column

Ion Exchange Columns

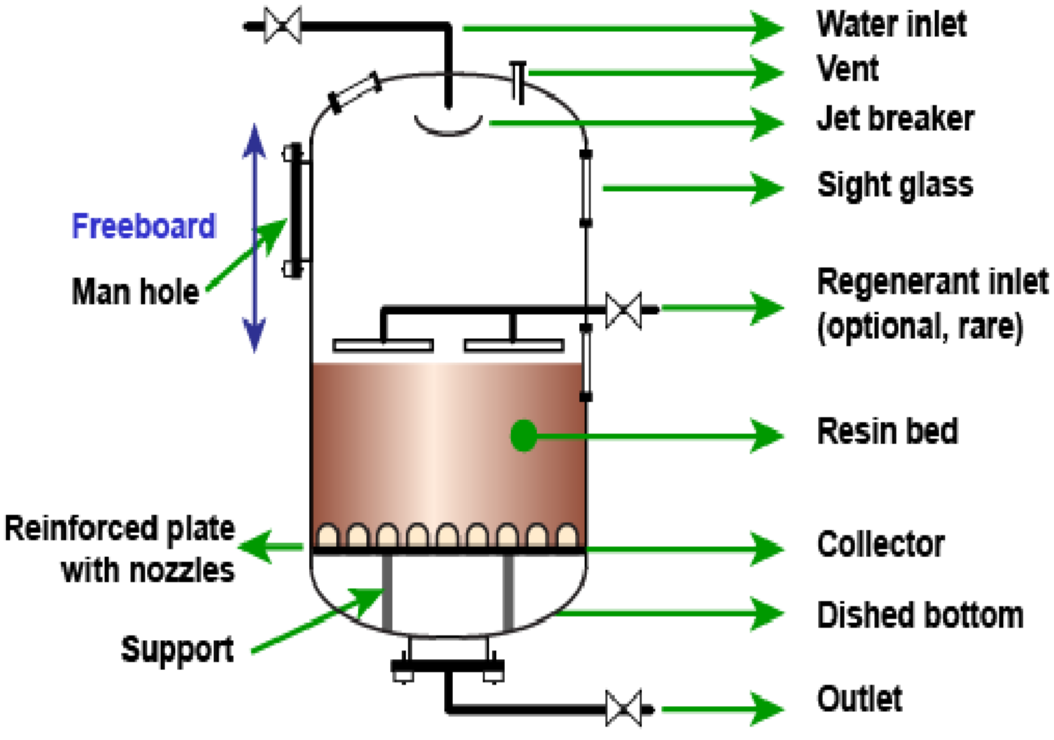
- The water enters from the top of the column So as not to disturb the surface of the resin bed, the incoming water stream is stopped b a simple jet breaker.
- The column has a large freeboard, usually about the same height as the resin bed, so th the resin can be backwashed inside the column to remove suspended solids accumulated on the bed surface.
- A manhole (shown on the left side) is necessary to inspect and possibly repair the column inside.
- Two **sight glasses** are also shown, one at the top, one at the level of the resin bed surface.



Co-flow regenerated column

Ion Exchange Columns

- An air vent is also necessary at the top, to empty the column by draining the water out for inspection or a resin change.
- One of the most important features of the vessel is the collector at the bottom: nowadays, one of the most popular types of collector is a plate with densely distributed nozzles
- A regenerant distributor is sometimes — but not always — mounted in the middle of the vessel to ensure a uniform distribution of the regenerant. In absence of such a collector, the regenerant is introduced from the top of the column, which results in some dilution of the chemicals.

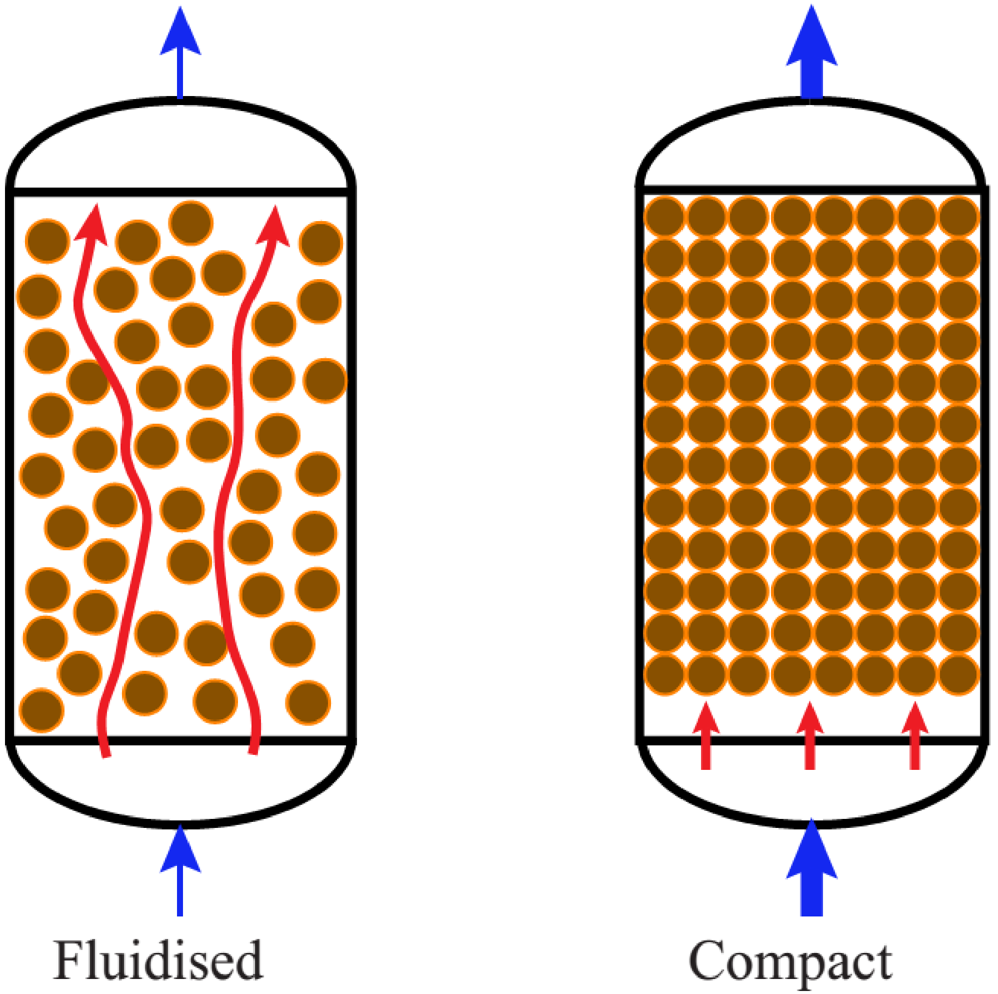


Co-flow regenerated column

Resin Bed Compactness

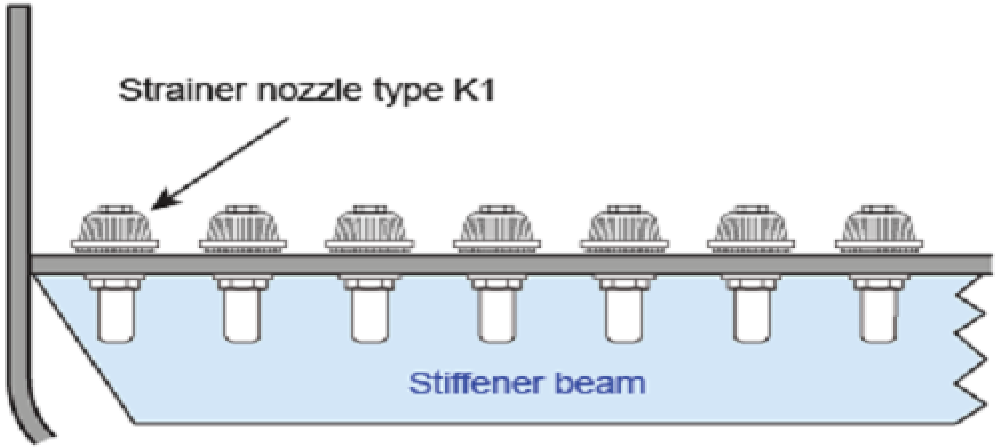
- **The bed must be compacted**
- A resin bed is only fluidised, by backwashing, for two purposes:
- To remove resin and foreign particles from the bed surface and decompact the bed after a long period of operation.
- To separate resins before regeneration in a mixed bed or separate strong from weak resin in a Stratabed.
- At all other times, the bed should not be fluidised. Just look at the picture: if the resin bed is fluidised, ions can find their way between the resin beads without being close enough for exchange.
- In a compact bed, the ions are forced to touch the beads.

Resin Bed Compactness



Nozzles

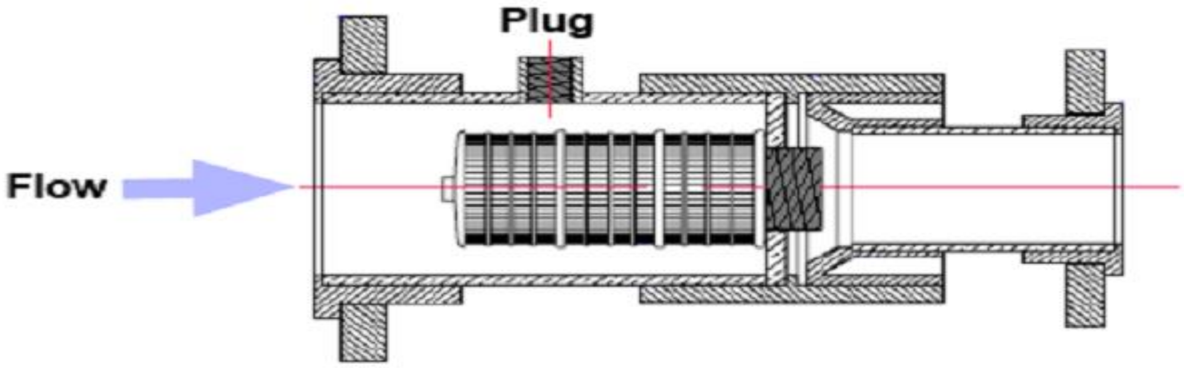
- The various column pictures on this page show different types of distribution and collection systems.
- Plates fitted at the bottom — and sometimes at the top — of the vessels with good quality nozzles are efficient distributors and collectors.



A nozzle plate with stiffening beam

Resin traps

- Resin traps should be installed at the outlet of each vessel to prevent resin from escaping in the treated water, and to prevent cation resin to enter the anion resin vessel, in case of damaged or broken nozzles or collectors.
- The drawing below shows a simple trap made from a large KSH nozzle.

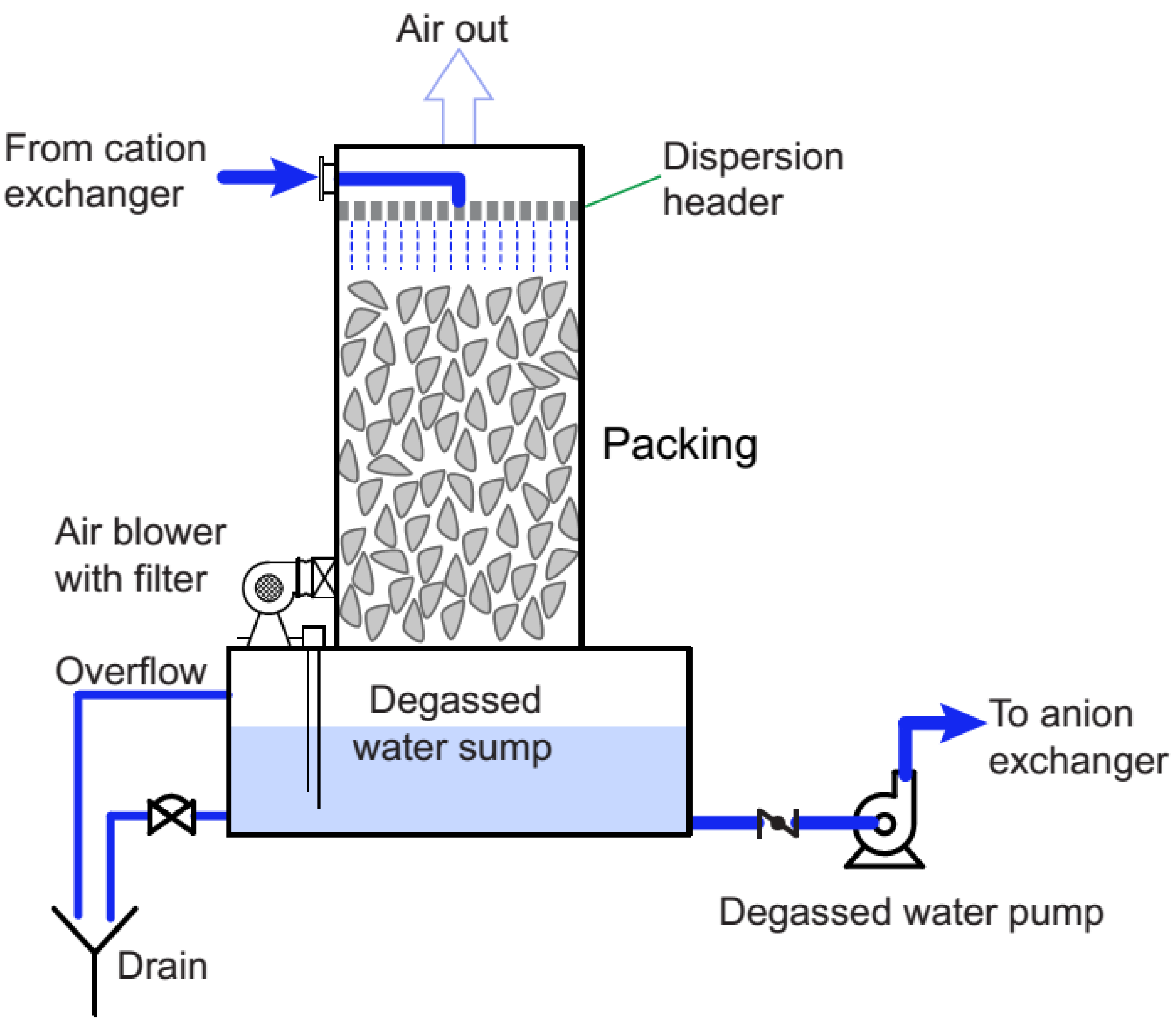


A resin trap for 25 m³/h

Degasifier

- In water demineralisation, a degasifier, or degasser, is often used to remove dissolved carbon dioxide after cation exchange.
- The most common degassers are of the so-called forced draft or atmospheric type
- The water "rains" unto a bed of packing material, and the carbon dioxide is forced to escape to the top of the column by an ascending flow of clean filtered air.

Ceramic saddle shaped and plastic packing examples


Air out
From cation exchanger
Dispersion header
Packing
Air blower with filter
Overflow
Degassed water sump
To anion exchanger
Drain
Degassed water pump

Degasifier: Principle and details

- After cation exchange, the bicarbonate and carbonate (if any) ions are converted to carbonic acid, or carbon dioxide.
- CO2 is soluble in water (seegraph below), but it tends to escape into the air, much as it does in a glass of Coca-Cola when you stir it.
- Using a degasser to remove CO2 reduces the ionic load on the strong base anion resin, and the consumption of caustic soda is thus lower.
- To be effective, the degasifier must be placed after the cation exchange column.

Degasifier: Principle and details

- Before cation exchange, the water is containing bicarbonate.
- After it, the cations in water (Ca^{++}, Mg^{++} and Na^{+} principally) are converted to H^{+} ions, which combine with the HCO_3^{-} bicarbonate anions to produce carbonic acid ($H_2CO_3 = CO_2 + H_2O$).
- Carbon Dioxide concentration increases after cation column.
- In practice, the water coming out of the cation exchange unit is introduced into a column where it is sprinkled over a bed of filling material, often polypropylene shaped as saddles to leave a maximum volume of voids in the bed.
- Air is introduced at the bottom of the column by a blower, and escapes at the top, loaded with carbon dioxide from the water.

Degasifier: Principle and details

- The solubility of CO2 in pure water is high: about 1500 mg/L at 25°C and atmospheric pressure .
- When you stir the water and divide it into small droplets in an atmospheric degasifier and blow air through the "rain", the CO2 gas tends to move into the air because the partial pressure of CO2 in air is much below the equilibrium pressure.
- The residual CO2 after an atmospheric degasifier is typically 10 mg/L as CO2.

Regeneration

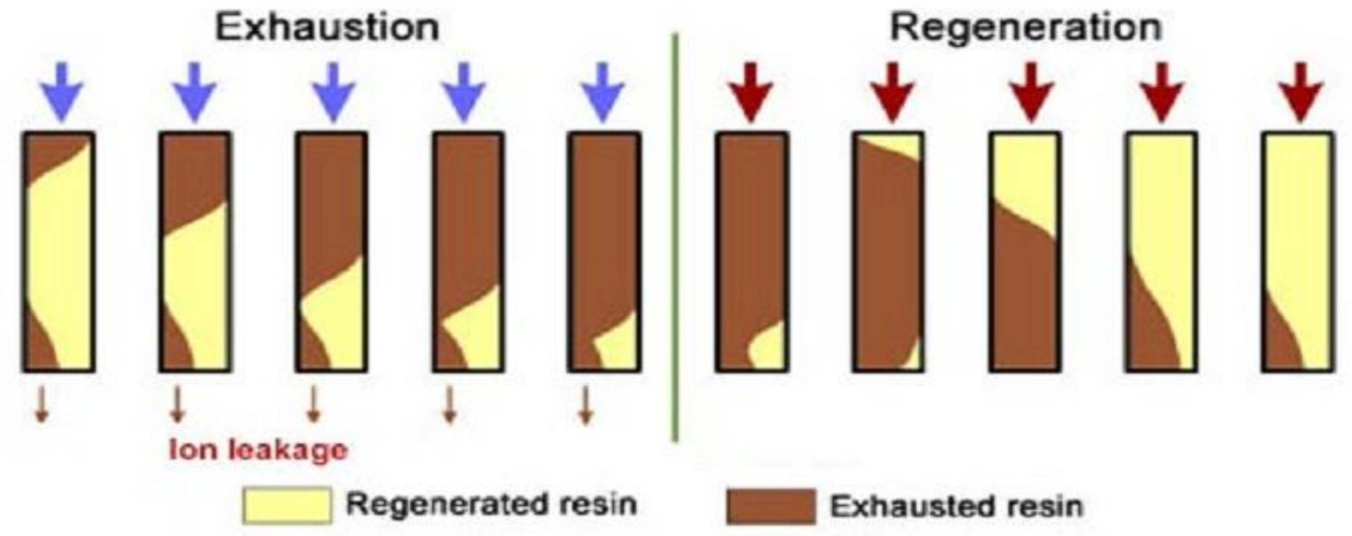
- Most ion exchange resins are used in columns.
- Ion exchange operation is basically discontinuous: a loading phase, called service run, is followed by regeneration of the exhausted resins.
- There are two main methods for the regeneration process:
- Co-flow regeneration(CFR), where the fluids are flowing from the top to the bottom of the column both during the service run as well as during regeneration.
- Reverse flow regeneration(RFR), where the fluids are flowing alternatively upwards and downwards during service and regeneration.

Regeneration: **Co-flow regeneration (CFR)**

- The Water to treat flows from the top to the bottom of the column, and the regenerant uses the same path.
- Due to excessive compactness, strongly acidic and strongly basic resins are not completely converted to the H or OH form at the end of the regeneration.
- As a result, the bottom layers of the resin bed are more contaminated than the top layers at the end of regeneration, so that when the next loading run begins the leakage is high due to the displacement of the contaminating ions by the H+ (or OH—) ions produced in the exchange.
- Possible solution for such problem is to frequently backwash the resin to avoid channelimg.

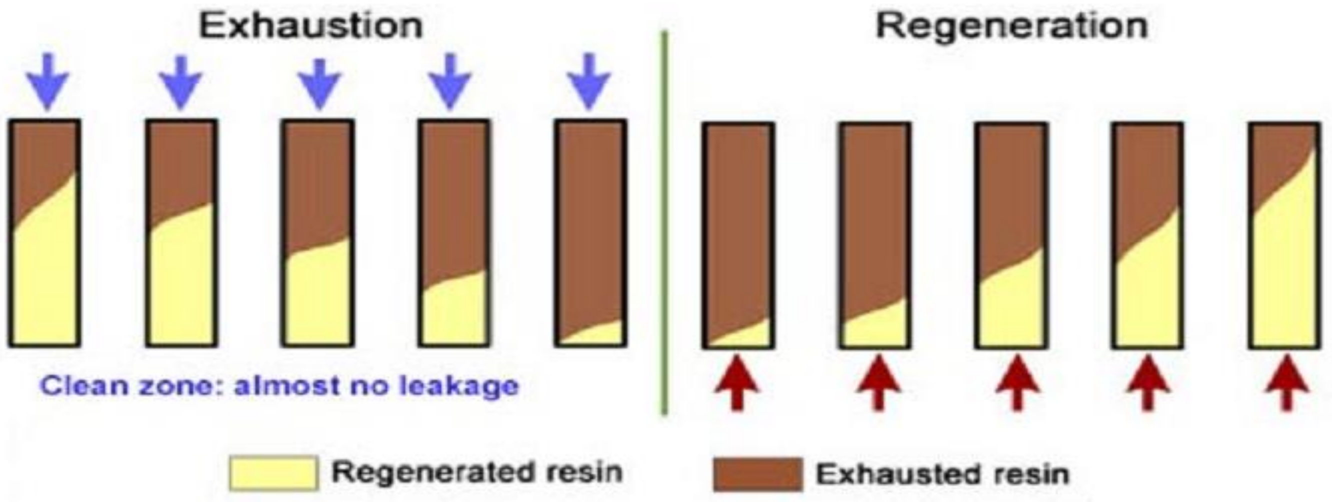
Regeneration: **Co-flow regeneration (CFR)**

- In this case, the regenerant doesn't have to push the contaminating ions through the whole resin bed.



Reverse flow regeneration (RFR)

- In this case, the regenerant doesn't have to push the contaminating ions through the whole resin bed.
- The layers which are less exhausted will be regenerated first and will be the cleanest when the next loading run (exhaustion) starts.



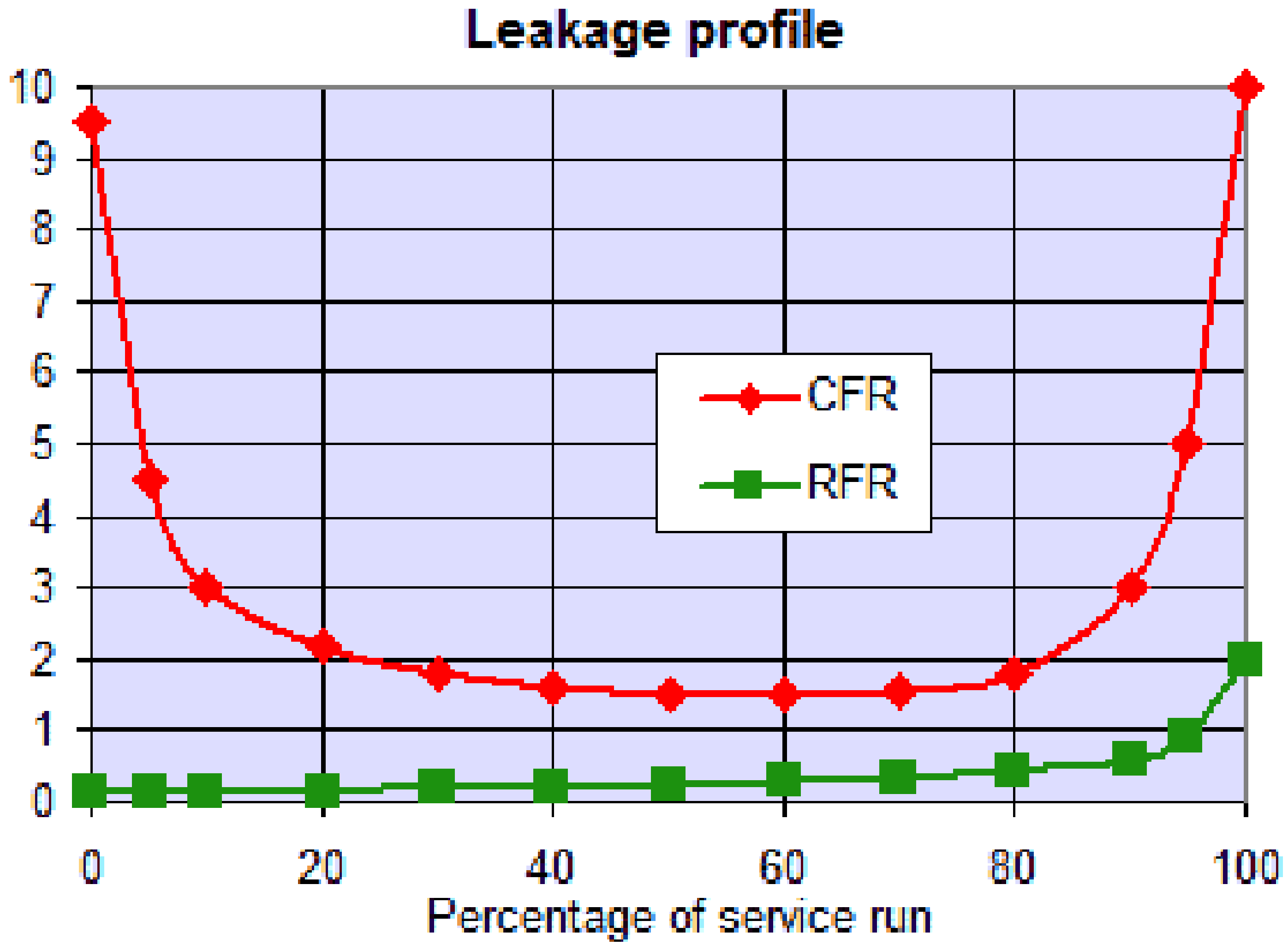
Reverse flow regeneration (RFR)

- Reverse flow regeneration offers two significant advantages:
- The treated water has a much higher purity than with co-flow, due to a very low leakage.
- Less regenerant is required, as the contaminating ions don't have to be pushed through the whole bed, and the leakage is almost independent of the regenerant dosage

CFR vs RFR

- At the end of regeneration, the exit layer of the column regenerated in CFR has the highest concentration of impurities, whereas in RFR the exit layer contains the most highly regenerated resin.
- This is why in CFR the contaminants at the bottom find their way into the treated water, more at the beginning than in the middle of the run, due to a "self regeneration“ effect, whereas in RFR any displaced contaminant from the inlet layer gets immediately removed from a layer underneath.

CFR vs RFR

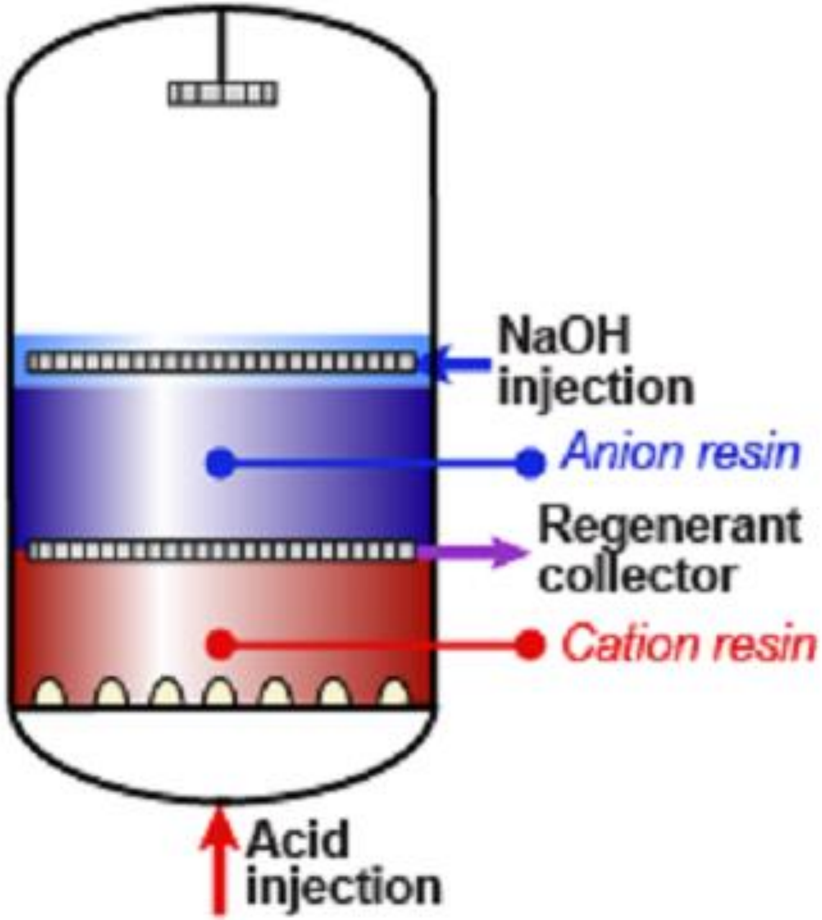

Leakage profile
10
9
8
7
6
5
4
3
2
1
0
0
20
40
60
80
100
Percentage of service run
CFR
RFR

Regeneration steps

The general regeneration procedure for ion exhange vessels is as follows:
1. Backwash resin bed (co-flow regeneration only) to remove suspended solids and de compact the bed.

(Note: in case RFR, backwash only subjected after 10-20 regenerations)
2. Inject regenerant diluted in appropriate water quality. The injection is at a low flow rate, so that the contact time is 20 to 40 minutes.
3. Displace the regenerant with dilution water at the same flow rate.
4. Rinse the bed at service flow rate with feed water until the desired treated water quality is obtained.

Mixed bed regeneration



Mixed bed regeneration

Internal regeneration of a mixed bed unit is more complicated. The steps are:

1 . Backwash resin bed to separate the cation from the anion resin.
2. Let the resins settle.
3. Optionally: drain the water down to the resin bed surface.
4. Inject caustic soda diluted in demineralised water.
5. Displace the caustic with dilution water.

Mixed bed regeneration

6. Inject acid diluted in demineralised water.
7. Displace the acid with dilution water.
8. Drain the water down to the resin bed surface.
9. Mix the resins with clean compressed air or nitrogen.
10. Refill the unit slowly with water.
11 . Do the final rinse with feed water at service flow rate until the desired treated water quality is obtained.

Mixed bed regeneration

Note 1: If no NaOH distributor is available, caustic "rains" from the top of the column down to the water level. This creates some dilution and the distribution is not as even as with a dedicated distributor.

Note 2: Cation and anion resin can be regenerated simultaneously to save time. Otherwise, always start with the anion resin.

Note 3: In condensate polishing, mixed bed units are usually regenerated externally.

Note 4: The regenerant level for mixed bed units is higher than that of separate columns, because regeneration efficiency is lower.

Recommended values:
HCl: 80 - 120 g (@ 100 %) per litre of cation exchange resin
H2SO4: 100 - 160 g (@ 100 %) per litre of cation exchange resin
NaOH: 80 - 140 g (@ 100 %) per litre of anion exchange resin

Types of regenerants

- Sodium chloride (NaCl) is normally used to regenerate SAC resins in the softening process
- For softening, potassium chloride (KCl) can also be used when the presence of sodium in the treated solution is undesirable.
- In some hot condensate softening processes, ammonium chloride (NH_4Cl) can be used
- For nitrate removal, the SBA resin can be regenerated with other compounds providing chloride ions, such as hydrochloric acid (HCl).

Types of regenerants

- For decationisation -the first step of a demineralisation process- SAC resins must be regenerated with a strong acid.
- The most common acids are hydrochloric and sulphuric acids:
- Hydrochloric acid (HCl) is very efficient and does not cause precipitations in the resin bed.
- Sulphuric acid (H2SO4) is sometimes cheaper and easier to store and to handle in general, but less efficient than hydrochloric acid: the operating capacity of the SAC resin is lower.
- Additionally, its concentration must be carefully adjusted to prevent calcium sulphate precipitation (see below). Once a CaSO4 precipitate is formed, it is very difficult to remove from the resin bed.

Types of regenerants

- For dealkalisation, the WAC resin is best regenerated with hydrochloric acid (HCl).
- When using sulphuric acid, the concentration must be kept under 0.8 % to avoid calcium sulphate precipitation. Other, weaker acids can also regenerate WAC resins, such as acetic acid (CH3COOH) or citric acid.

Types of regenerants

- SBA resins are always regenerated with caustic soda (NaOH) in the demineralisation process.
- Caustic potash (potassium hydroxide KOH) is in principle also applicable, but usually more expensive.
- WBA resins are usually also regenerated with caustic soda, but other regenerants— weaker alkalis — can also be used, such as:
- Ammonia (NH3)
- Sodium carbonate (soda ash, Na2CO3)
- A lime suspension (calcium hydroxide, Ca(OH)2)

Regenerants Concentrations

- NaCl (softening and nitrate removal): 10 %
- HCl (decationisation, de-alkalisation and demineralisation):2- 5 %
- NaOH (demineralisation): 4-10 %

Regenerants Concentrations(Sulphuric Acid)

- H_2SO_4: for SAC resins, the acid concentration must be carefully selected between 0.7 and 6 % as a **function of the proportion of calcium in the feed water** .
- For WAC resins, the concentration is usually 0.7 %.
- Too high a concentration may cause calcium sulphate precipitation.
- For SAC resins, stepwise concentrations are often used: after a first step at a low concentration, a second step is carried out at a higher concentration once a great part of the calcium on the resin has been eluted. In rare cases, three steps are used.
- The steps at higher concentrations reduce the quantity of dilution water and increase the sulphuric acid efficiency

Regenerants Temperature

- NaCl and HCl are used at ambient temperature.
- The temperature of H_2SO_4 should not exceed **25°C** so as to reduce the risk of $CaSO_4$ precipitation.
- NaOH: with co-current regeneration, a temperature of 40°C is recommended to ensure good elution of silica; with reverse flow regeneration, caustic can be applied at ambient temperature except in case of a high silica load.

Water quality for regeneration

- Water is used in different regeneration steps.
- Water quality may differ from step to other and from technology to other.
- Reasons for limiting water quality for regeneration steps as following:
- **Backwash**: backwashing anion resins in the OH form with feed water may cause calcium carbonate precipitation.
- For cation resins in the H form, raw water brings some risk, as bicarbonate may convert co carbon dioxide, create bubbles and force some resin to float. Resins regenerated in reverse flow are not backwashed every cycle.

Water quality for regeneration

- **Compaction**: this step is only required in Upcore (Amberpack Reverse) and Stratapack systems and is considered in IXCalc as a very short backwash; it requires the type of water used for regenerant dilution.
- **NaOH dilution (CFR):**if the raw water contains any hardness, you can't use raw water to dilute NaOH otherwise precipitation may occur (bicarbonate in raw water is converted to carbonate and CaCO3 has a very low solubility)
- **Acid dilution (RFR):** if the dilution water contains any cations, you spoil the highly regenerated part of the resin and the treated water quality drops.

Water quality for regeneration

- **Brine dilution (RFR):** for softening units, the same reasoning applies as for acid dilution of demineralisers.
- **NaOH Dilution (RFR):** the same reasoning applies as for acid dilution. Therefore demineralised water must be used.
- **Displacement rinse (CFR & RFR):** the water used there is always the same water as that used for regenerant dilution. In general, the flow rate used for dilution water during regenerant injection is maintained, and the dosing pump of the concentrated regenerant is merely stopped.

Water quality for regeneration

- Softening: Quality of water required for each regeneration step

Step	Reverse flow regeneration	Co-flow regeneration
Backwashing	Feed water	Feed water
Compaction	Soft water	Feed water
Dilution	Soft water	Feed water
Displacement	Soft water	Feed water
Final rinse	Feed water	Feed water

Water quality for regeneration

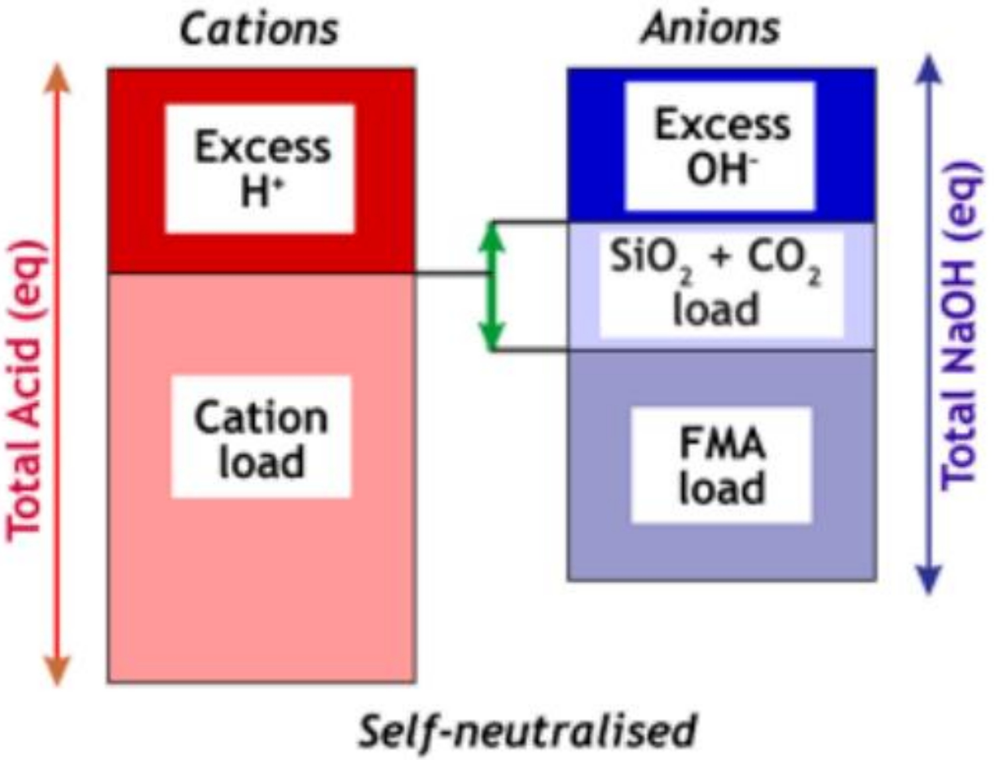
- Demineralisation: Quality of water required for each regeneration step

Step	Reverse flow regeneration		Co-flow regeneration	
	Cation	Anion	Cation	Anion
Backwashing	Feed water	Decationised	Feed w.	Decationised
Compaction	Demin. or decat.	Demineralised		
Dilution	Demin. or decat.	Demineralised	Feed w.	Decat. or demin.
Displacement	Demin. or decat.	Demineralised	Feed w.	Decat. or demin.
Final rinse	Feed water	Decationised	Feed w.	Decationised

Neutralisation

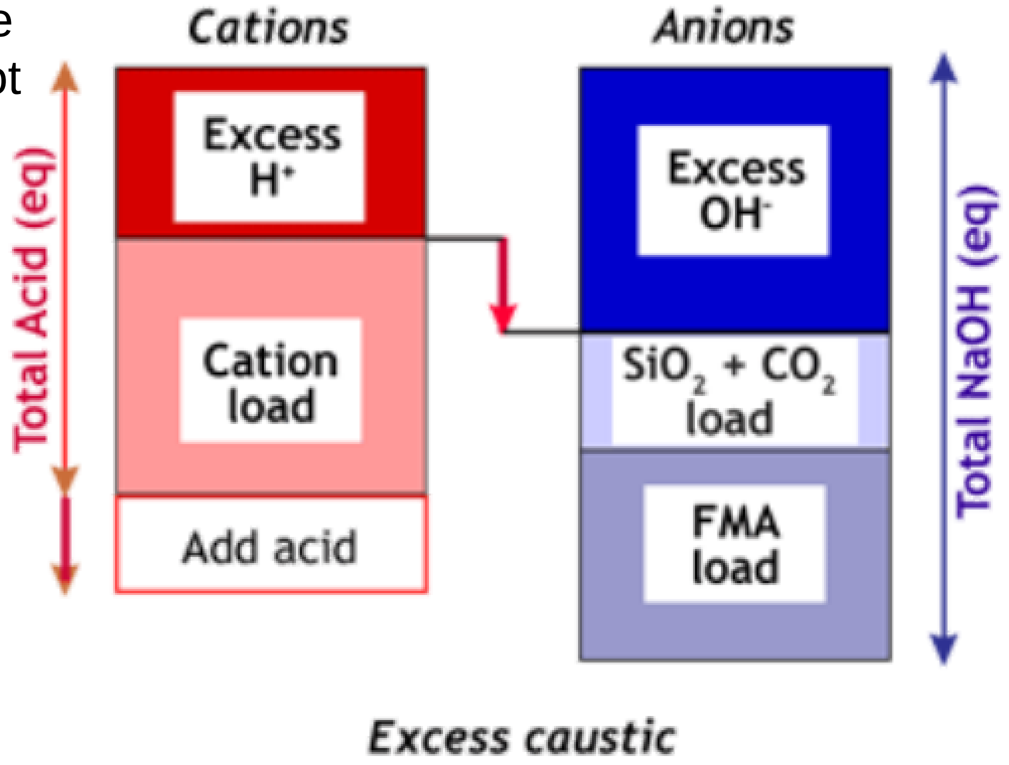
- In many plants, regulations require that the waste produced by regeneration of ion exchangers is neutral.
- Mixed regeneration waste is considered neutral when the pH value of the waste is between 6 and 9.
- By adjusting the quantity of each regenerant, a neutral regeneration waste can often be obtained.
- The way to calculate **excess acid** and **excess alkalinity** is not straightforward, because Na_2CO_3 and Na_2SiO_3 obtained in the spent caustic are also effective to neutralise excess acid.
- They cause a buffering effect, which eventually provides some flexibility in the adjustment of neutralisation.

Neutralisation: Self-neutralised waste



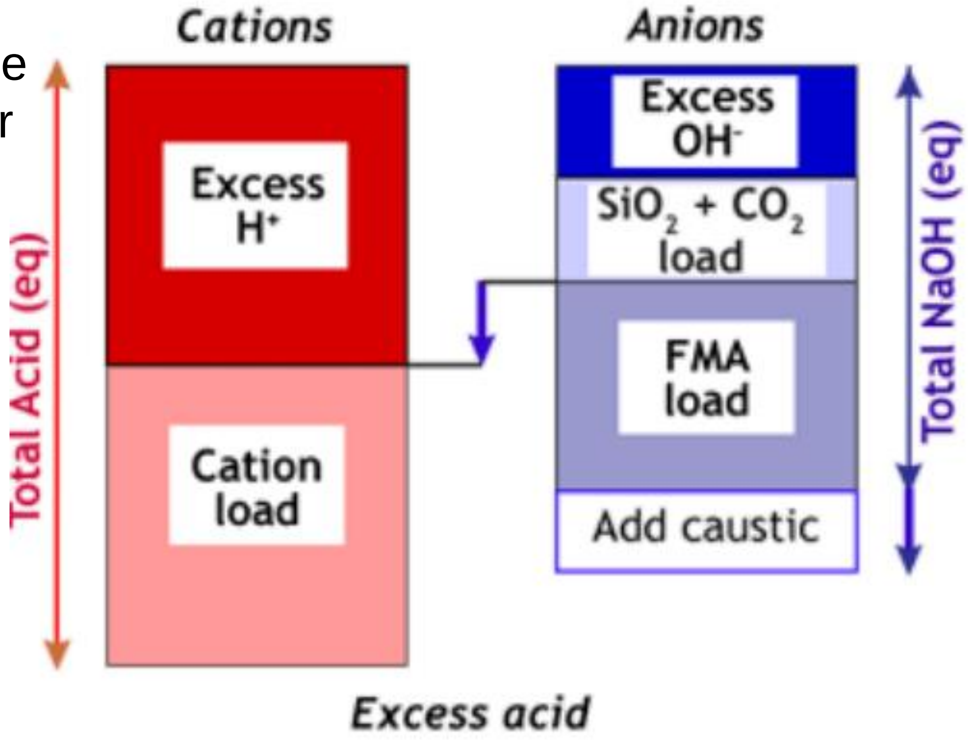
Neutralisation: Excess alkalinity

This case occurs often when the water treatment system does not include a degasifier.



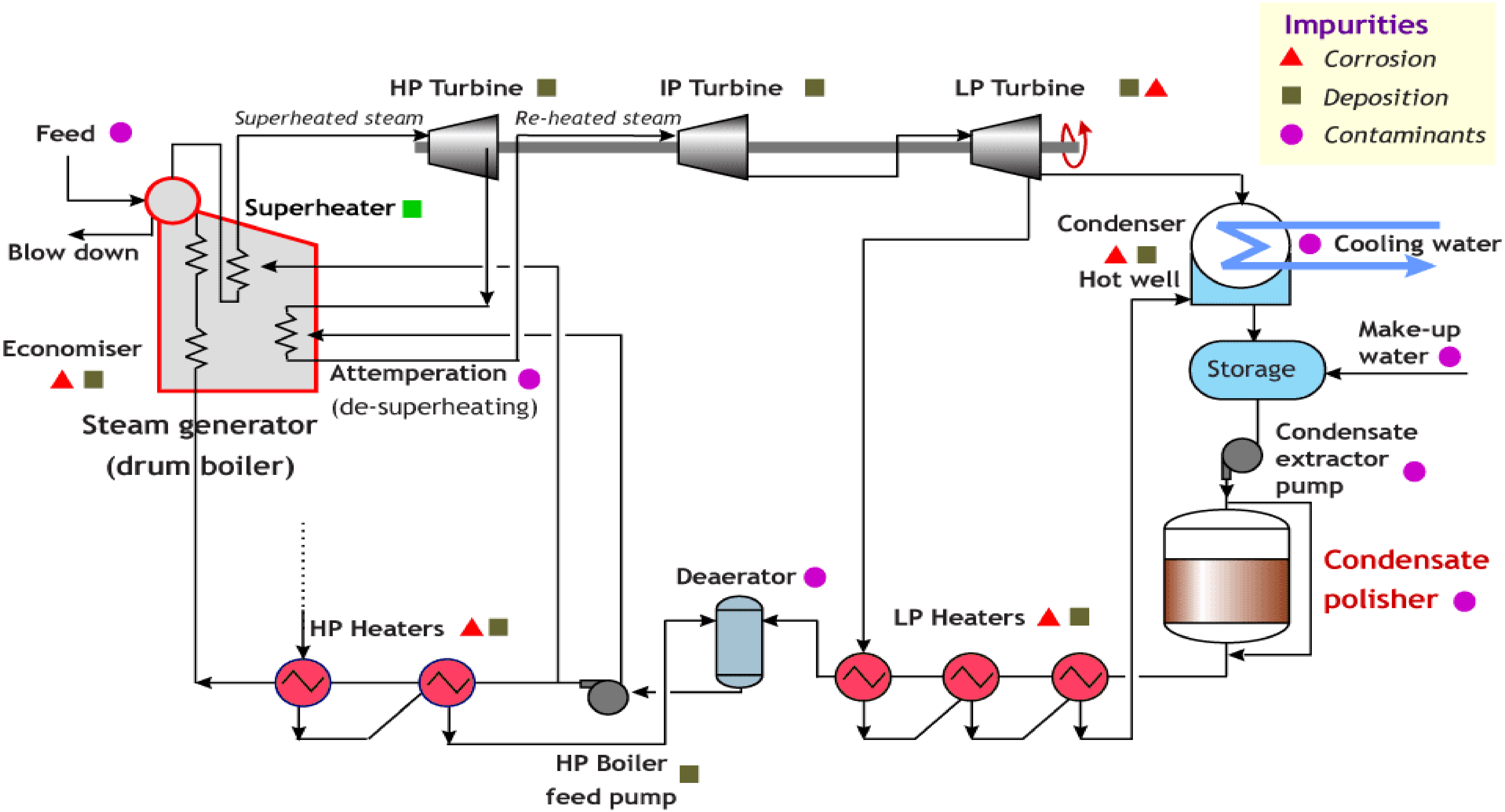
Neutralisation: Excess acidity

This case occurs often when the water is degassed, and when there is a double stage anion exchanger (WBA + SBA)



Condensate polishing

- Fossil-fuelled (coal, oil, gas) and nuclear power stations produce electricity with turbines powered with high pressure steam
- After going through the turbine, the steam is condensed and recycled.
- To avoid deposits on the turbine blades and corrosion in the steam circuit, the steam must be extremely pure.
- However, being permanently recycled, the condensate collects corrosion and erosion products from the boiler and pipework
- The contaminants in the condensate must have a concentration of a few µg/L (ppb) or less.


Impurities
▲ Corrosion
■ Deposition
● Contaminants
HP Turbine ■
IP Turbine ■
LP Turbine ■ ▲
Superheated steam
Re-heated steam
Feed ●
Blow down
Superheater ■
Economiser ▲ ■
Attemperation ●
(de-superheating)
Steam generator
(drum boiler)
Condenser ▲ ■
Hot well
Cooling water ●
Make-up
water ●
Storage
Condensate
extractor
pump ●
Condensate
polisher ●
Deaerator ●
LP Heaters ▲ ■
HP Heaters ▲ ■
HP Boiler
feed pump ■

Condensate polishing

- Therefore, the condensate, in many (but not all) power stations, is treated with ion exchange resins, ion exchange being the only process capable of achieving these low residual values.
- Many new power stations are being built, particularly in emerging countries such as India and China, so that the number of condensate polishing project has increased tremendously since the beginning of the 21st Century.
- Whilst ion exchange processes for water demineralisation were mainly developed in Europe, the champions of condensate polishing design are largely American.

Condensate polishing

Duties of a condensate polisher

The condensate polisher must fulfill two simultaneous duties:

1 . it must remove the "crud", wich is suspended solids (mostly metal oxides) resulting from corrosion and erosion;

2. it must also remove any dissolved solids originating from the make-up water, possible leaks of the condenser, or from regeneration of the ion exchange resins.

This means that the polisher must perform filtration and demineralisation at the same time.

Usually Mixed bed columns are used for condensate polishing.

Operation Cases Monitoring

- Plant in service Normal Conditions
- Service Real time Monitoring Parameters
- Service Flow-Level Controls
- Service Conductivity Real time Monitoring
- Service pH Real time Monitoring
- Regeneration Phases operation