Ion Exchange Process Design

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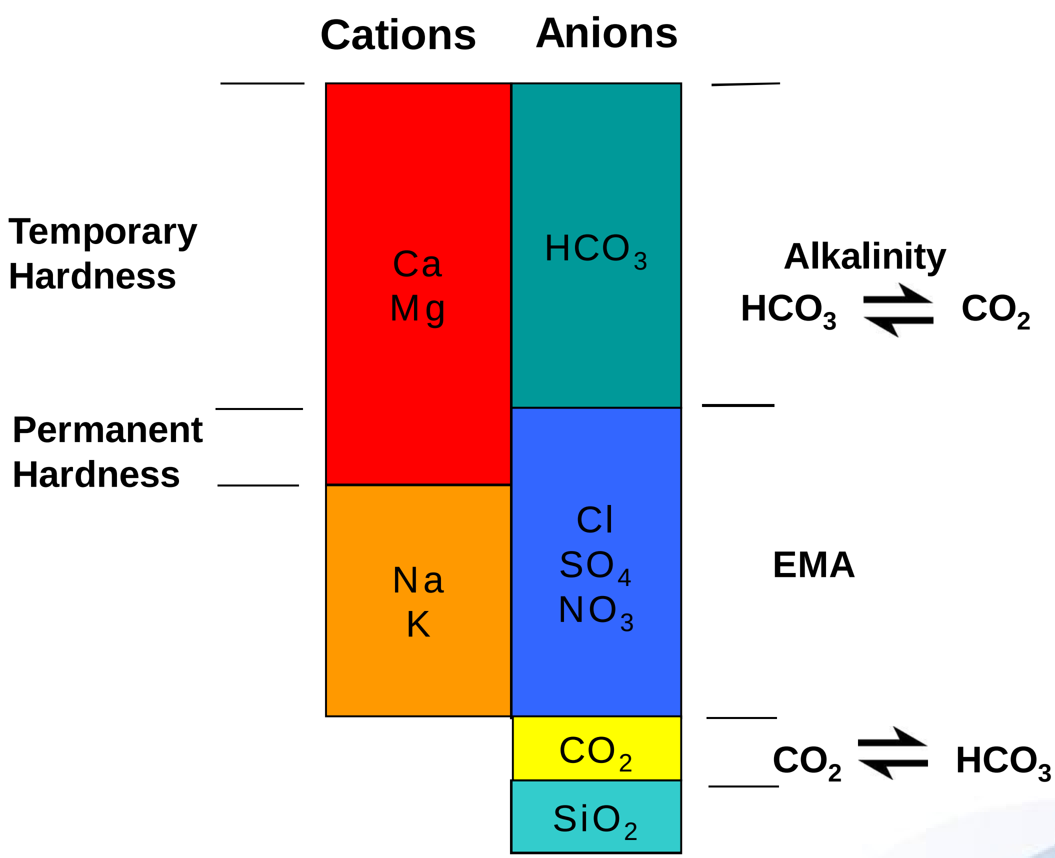
Aim of ion exchange process

To reduce the Total Dissolved Solids (TDS) of the water to that specified for subsequent use.

Water Composition - TDS



Organics (humates, fulvates etc) are generally attracted to anion resin

The Ion Exchange Demineralisation Process (Strongly functional Resins)

- Strong acid cation resins (SAC) exchange H^+ ions with cation portion of TDS and are regenerated by dilute acid solution (H^+)
  - Water becomes decationised resulting in a solution of weak and strong acids
- Strong base anion resins (SBA) exchange OH^- ions with anion portion of TDS and are regenerated by dilute sodium hydroxide (OH^-)
  - Weak and strong acids removed
- Feed Water → Cation (H^+ form) → Anion (OH^- form) →Demin Water
  - Prevents precipitation of insoluble cation hydroxides
  - Anion exchange better from acid solutions

The Demineralisation Ion Exchange Operating Cycle

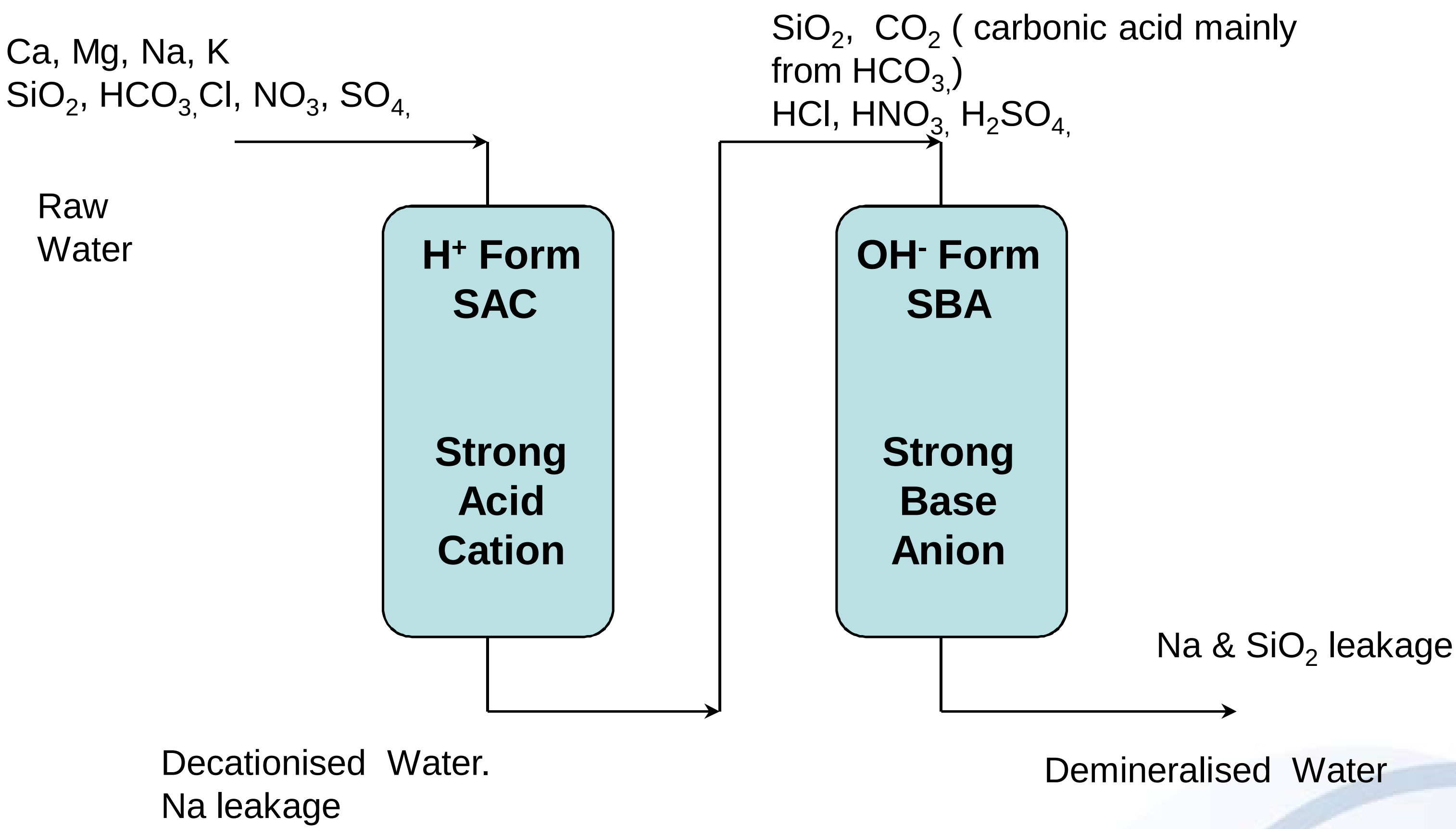
The demineralisation plant with down flow service and downflow regeneration (Co-flow regeneration) operating cycle is as follows:

- Demineralisation service flow/resin exhaustion
- Resin bed backwashing
- Resin regeneration
- Resin rinsing

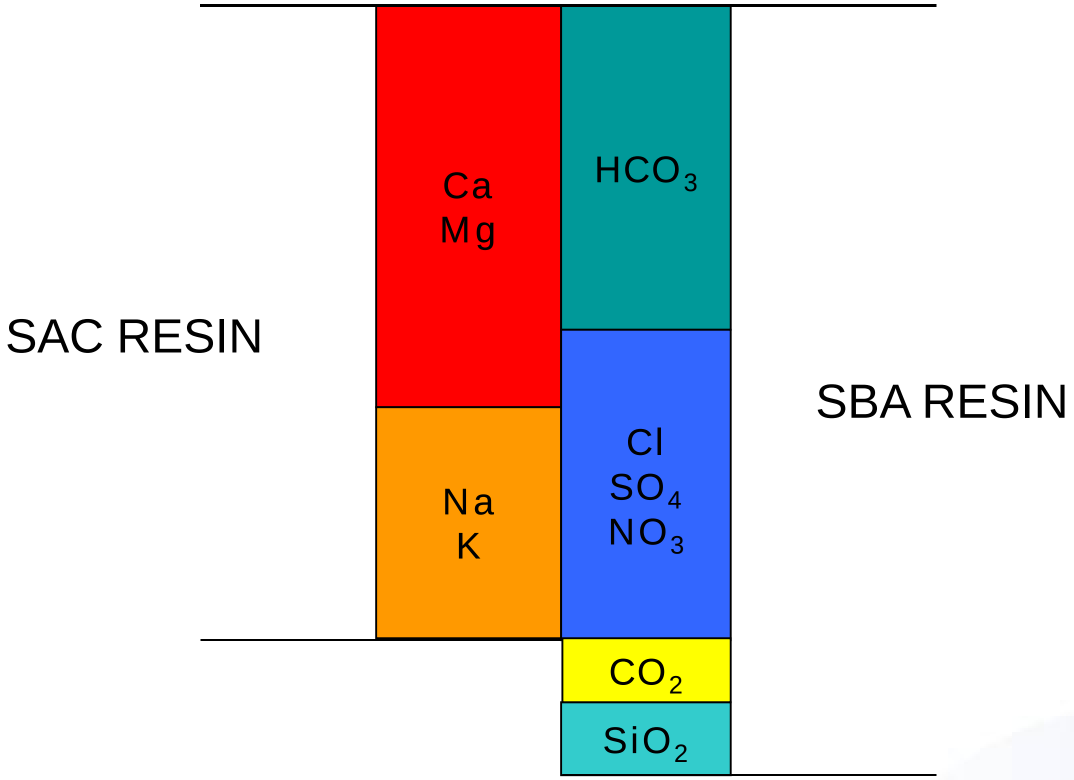
Regeneration cycle

- Ion exchange process is a batch process

The Simplest Demineralisation Process is SAC→SBA



SAC + SBA



Cation Resin Exhaustion

- Cation exchange

$$(R^-H^+) + (M^+A^-) \leftrightarrow (R^-M^+) + (H^+A^-)$$

- where
  - (R^-H^+) is the regenerated cation exchange resin
  - (M^+A^-) is the dissolved salt in the raw water
  - (R^-M^+) is the exhausted cation resin

Anion Resin Exhaustion

- Anion exchange

$$(R^{+}OH^{-}) + (H^{+}A^{-}) \leftrightarrow (R^{+}A^{-}) + (H^{+}OH^{-})$$

– where
  - $(R^{+}OH^{-})$ is the regenerated anion exchange resin
  - $(H^{+}A^{-})$ is the acid produced from the anions in the raw water and the H^{+} ions produced in the cation exchange process above
  - $(R^{+}A^{-})$ is the exhausted anion resin

Resin Selectivity – SAC & SBA

- Strong acid cation (SAC) exchanger
  - Na most weakly held by cation resin
  - Na first to breakthrough the resin bed
- Strong base anion (SBA) exchanger
  - SiO_2 / HCO_3 most weakly held by anion resin
  - SiO_2 / HCO_3 therefore the first to break through the resin bed
  - SiO_2 / HCO_3 breakthrough often occurs when a SAC/SBA plant exhausts

Cations	Anions	Affinity
Ca^{2+}	SO_4^{2-}	Higher
Mg^{2+}	NO_3^-	↓
K^+	Cl^-	↓
Na^+	HCO_3^-	↓
H^+	$HSiO_3^-$	↓
-	OH^-	Lower

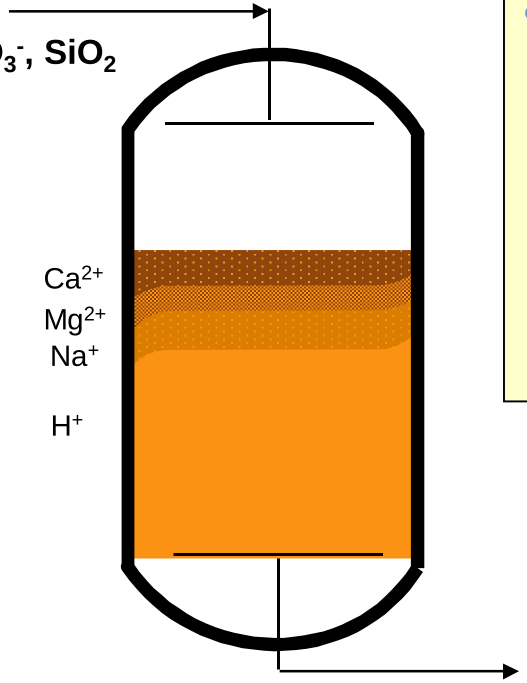
The Chromatography Effect

- Partly used cation resin

Ca^{2+} , Mg^{2+}, Na^{+}

Raw water

SO_4^{2-}, Cl^-, NO_3^- , HCO_3^-, SiO_2



- **CHROMATOGRAPHIC ABSORPTION OF IONS**
  - **more attractive ions get adsorbed first and remain at top of bed**
  - **adsorption process is extremely efficient, reliable and reproducible**

H^+ , (Equilibrium leakage Na^+)

Decationised water

SO_4^{2-} , NO_3^-, Cl^- , CO_2, SiO_2

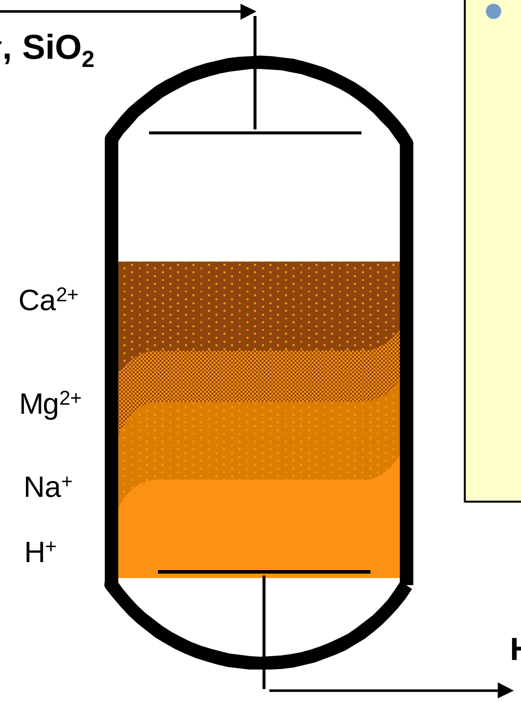
The Chromatography Effect

- Partly used cation resin

Ca^{2+} , Mg^{2+} , Na^{+}

Raw water

SO_4^{2-}, NO_3^{-}, Cl^{-}, HCO_3^{-}, SiO_2



H^{+} , (Equilibrium leakage Na^{+})
Decationised water
SO_4^{2-} , NO_3^{-}, Cl^{-} , CO_2 , SiO_2

- **CHROMATOGRAPHIC ABSORPTION OF IONS**
  - as more ions pass through the bed, less attractive ions are displaced and gradually move down through the bed
  - shape of "front" depends on good distribution of water flow

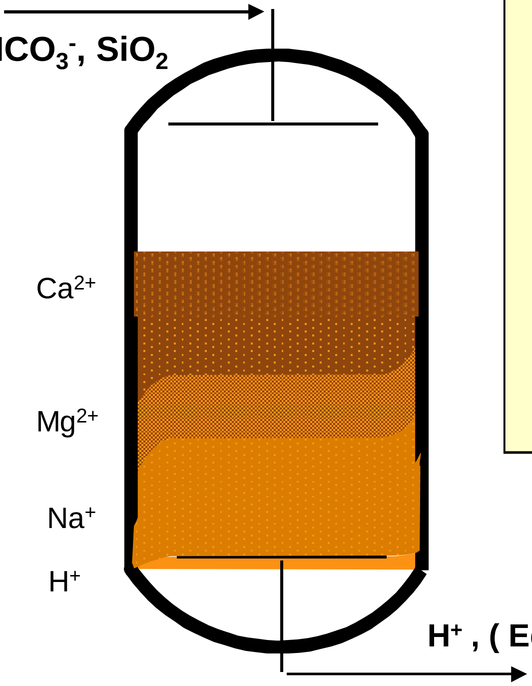
The Chromatography Effect

- Exhausted cation resin

Ca^{2+} , Mg^{2+} , Na^{+}

Raw water

SO_4^{2-}, NO_3^{-}, Cl^{-}, HCO_3^{-}, SiO_2



H^{+} , (Equilibrium leakage Na^{+} plus Na^{+} slip))

Decationised water

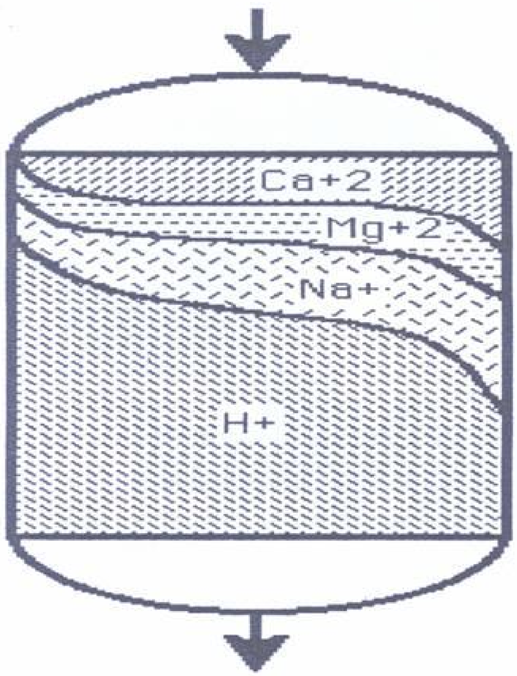
SO_4^{2-} , NO_3^{-}, Cl^{-} , CO_2, SiO_2

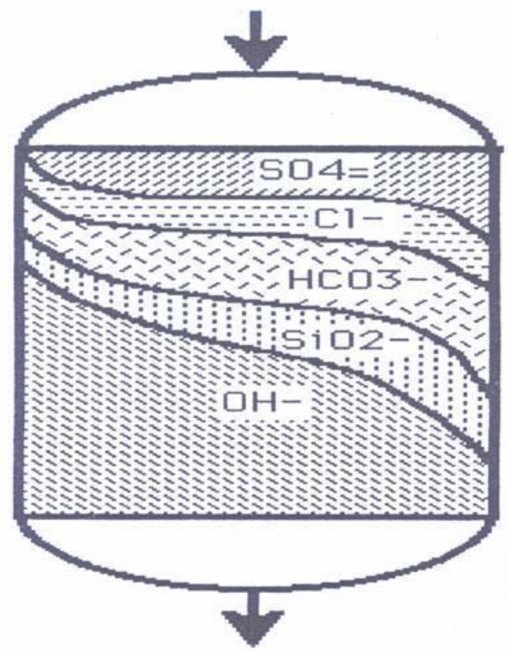
SAC and SBA resins cannot be fully regenerated and will always contain some contaminant ions

- **CHROMATOGRAPHIC ABSORPTION OF IONS**
  - **breakthrough of ions occurs when first front reaches the distributor**
  - **first ion to break through is sodium**
  - **unless the unit is grossly over-run, the risk of calcium breakthrough is minimal**

Service Flow

Summary SAC and SBA Selectivity Profiles





Resin Capacity

- Total capacity:
  - Represents the total ion exchange sites on the resin
  - Quoted in equivalents/litre of resin and equivalents/kg of resin

- Operating capacity
  - Proportion of the total capacity used in the ion exchange process
  - Quoted in equivalents/litre of resin and equivalents/kg of resin

- Many use units of grams of $CaCO_3$ / litre of resin – g_{CaCO3} / l_{Resin}

- Operating capacity is substantially lower than Total capacity

Operating Capacity

- Operating capacity is a design feature and depends on:
  - TDS and composition of raw water
  - Feed water flowrate
  - Service flow time
  - Resin total capacity and resin “health”
  - Product water specification (end point)
  - Regenerant type and concentration
  - Chemical regeneration level
  - Contact time
  - Economic constraints of the design

Typical Service Flow Operating Conditions

- Flowrate: 8 - 40BV/h
  - Very low flowrate can give poor flow distribution (<20 % full service flow)
    - Special distribution system
  - Higher flowrate can lead to a deeper reaction zone. Early breakthrough and lower resin bed capacity (>60 m/h)
  - For a given flowrate, lower dP and higher capacity can be achieved with narrow bead size distribution and smaller beads.

- Operated to predetermined breakthrough point
  - Batch set-point (common)
  - Cation breakthrough based on conductivity
  - Anion breakthrough based on silica – variable feed water

The Demineralisation Ion Exchange Process – Co-Flow

- Demineralisation service flow/resin exhaustion
- Resin bed backwashing
- Resin regeneration
- Resin rinsing

Resin bed backwashing

- Flow to expand resin bed typically 40 - 60%
- Required to:
  - De-compact resin bed
  - Remove suspended solids and resin fines
  - Reclassify the resin bed
- Prevents:
  - High bed pressure drop
    - Resin bead breakage
    - Reduced service flow
- Assists:
  - Efficiency of demineralisation & regeneration process

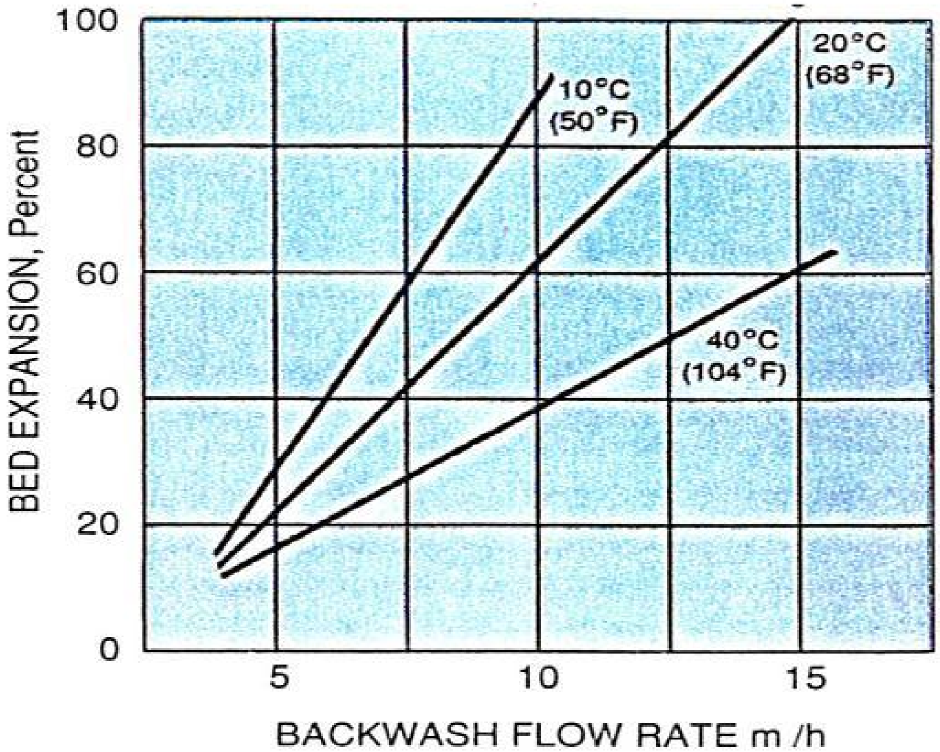
Typical Operating Conditions

- Use raw water (co flow cation)
- Use de-cationised water (co-flow anion)
- 2 to 4 BV backwash volume
  - can depend on feed water solids content and can be extended as necessary

- Backwash flowrate depends on:
  - Resin mean bead size
  - Resin bead size distribution
  - **Water temperature**

Note: Consult resin supplier's Technical Data Sheet for precise operating conditions for specific resin types

Effect of Temperature on Backwash



At equilibrium

The Demineralisation Ion Exchange Cycle

- Demineralisation service flow/resin exhaustion
- Resin bed backwashing
- Resin regeneration
- Resin rinsing

Which Cation Regenerant?

- HCl – Hydrochloric Acid
  - Can be used at high concentration (e.g. 5% w/v) during regeneration even on hard water
  - Offers higher resin capacity for given regen level (g_{acid}/l_{Resin})
  - Good for iron removal
  - Needs fume control
  - Greater storage volume required
  - More expensive OPEX and CAPEX

- H_2SO_4 – Sulphuric Acid
  - Difficult regeneration with high TH / TC ratio
  - Heat of dilution with high bulk concentration
  - Lower efficiency
  - Cheaper OPEX and CAPEX

Regeneration Regimes

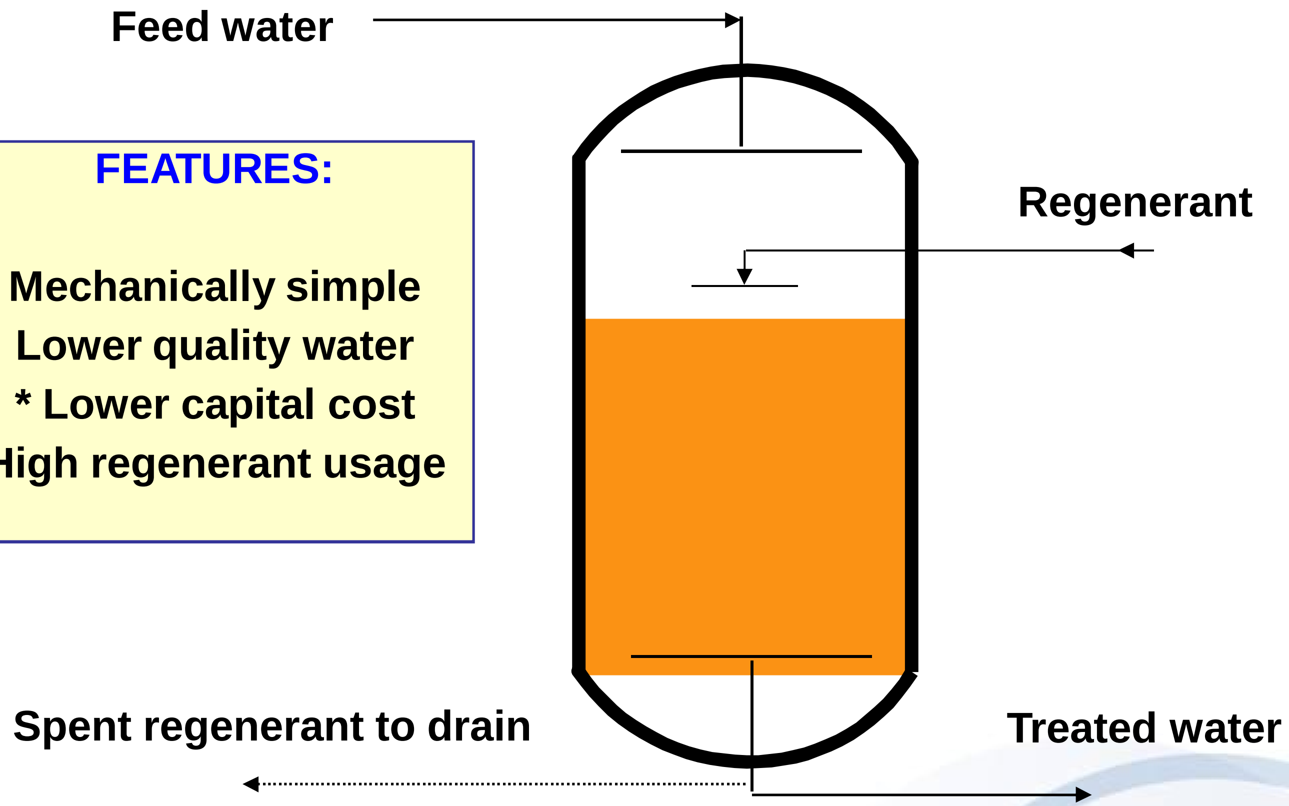
- Co-flow regeneration
  - Regenerant flow in the same direction as the service flow
  - Larger quantity of regenerant required to displace the strongest held ion on the longest path to the bed exit
  - Leads to:
    - Higher leakage on resumption of service flow
    - Higher regenerant use/cost to achieve very low TDS water
  - Process is:
    - Lower cost / simplest equipment
    - More forgiving of poor feed water quality
    - Used when treated water spec is not stringent

Note: A large excess of regenerant over stoichiometric requirement is always used to achieve an economic working capacity in both SAC and SBA resins.

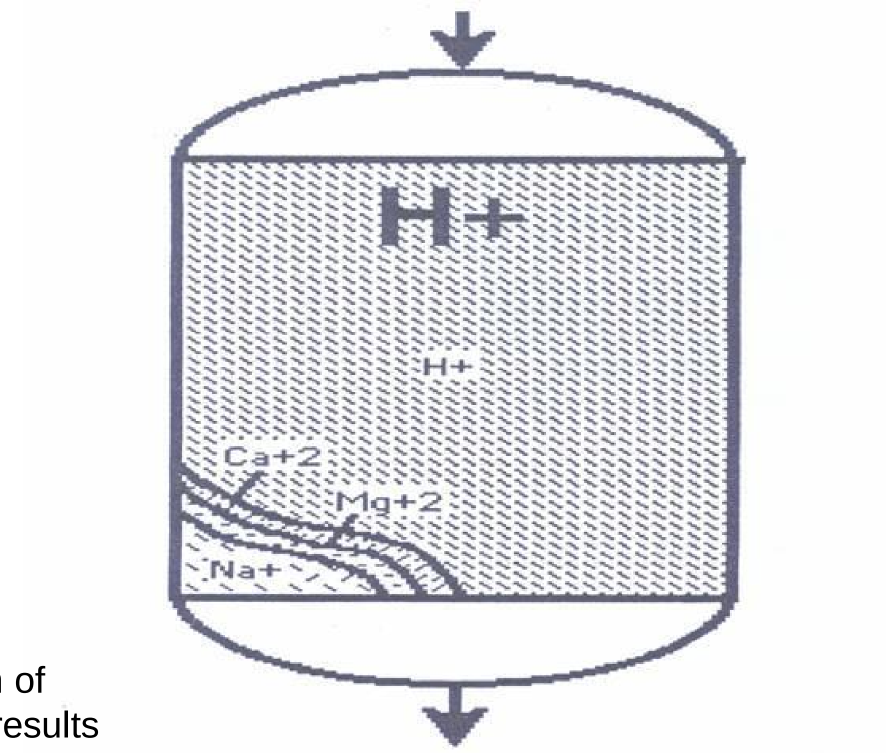
Co-Flow Regeneration

FEATURES:

Mechanically simple
Lower quality water
*** Lower capital cost**
High regenerant usage



SAC Co-flow Regeneration Profile



Trace cations at bottom of regenerated resin bed results in leakage

Counter-Flow Regeneration

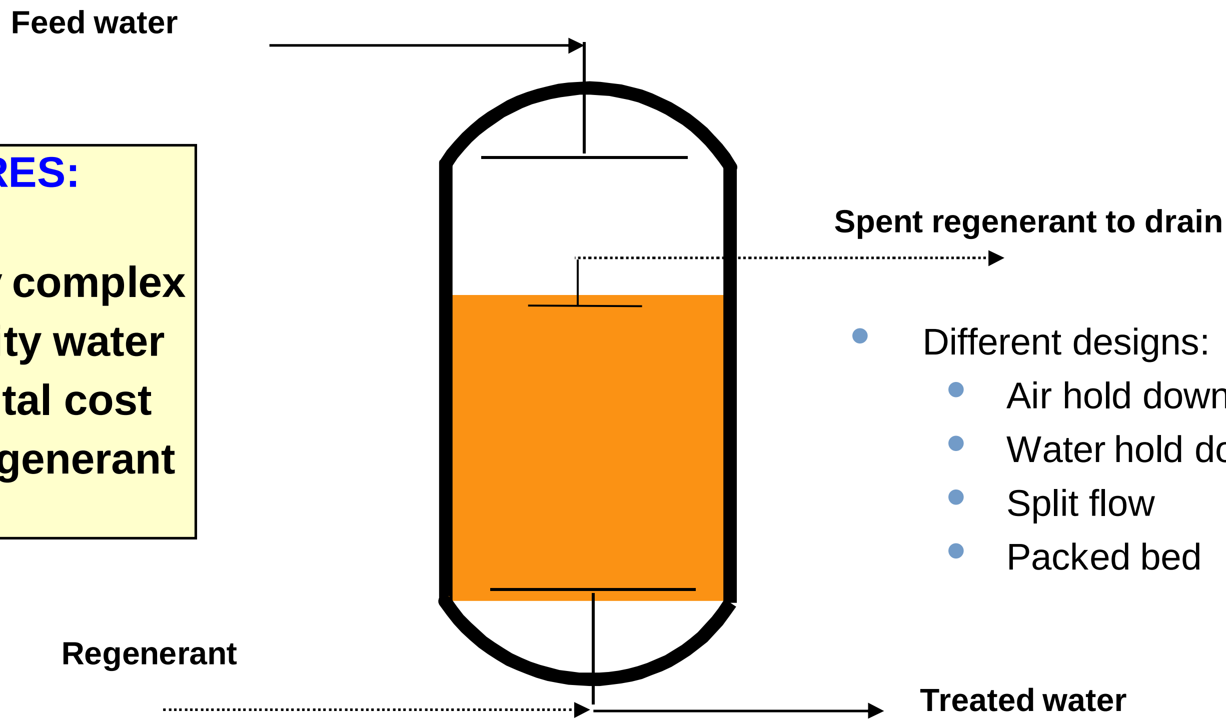
- Counter-flow regeneration
  - Regenerant flow in the opposite direction to the service flow
  - Highest quality regen chemical on least exhausted resin means higher quality in service
    - Highest regenerated resin at service outlet
  - Compared to co-flow regeneration leads to:
    - Lower leakage on resumption of service flow
    - Lower regenerant use or higher capacity
  - Process is:
    - Historically higher cost/more complex equipment than co-flow regeneration
    - Used when treated water with a higher specification is required

Note: A large excess of regenerant over stoichiometric requirement is always used to achieve an economic working capacity in both SAC and SBA resins.

Counter-Flow Regeneration

FEATURES:

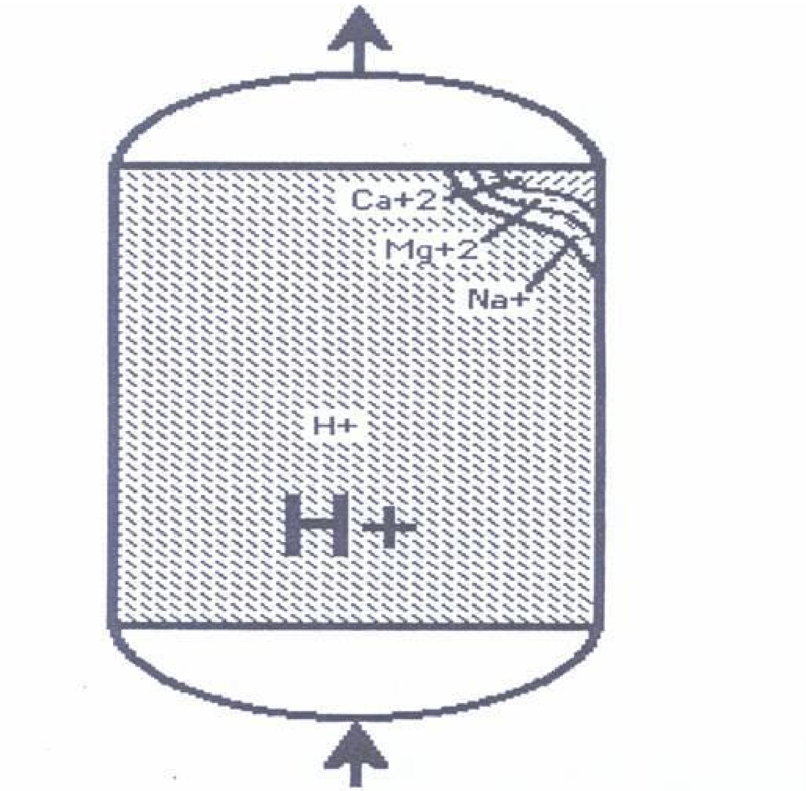
Mechanically complex
Higher quality water
Higher capital cost
Uses less regenerant



- Different designs:
  - Air hold down,
  - Water hold down
  - Split flow
  - Packed bed

NOTE: Counter-flow regeneration may be difficult when water has elevated suspended solids

SAC Counter-flow Regeneration Profile

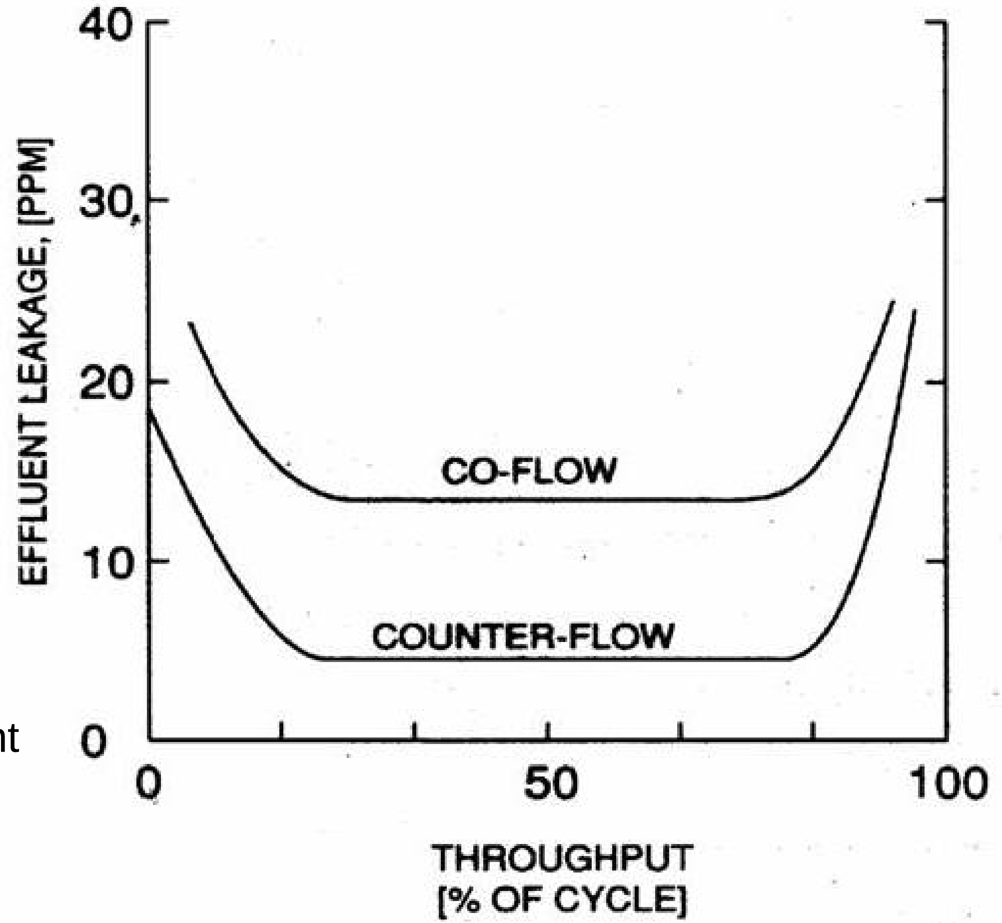


Resin at service outlet is very highly regenerated, creating polishing zone

Maintaining Compact Beds in Counter-flow Regeneration Plants

- Effective counterflow regeneration requires that the resin bed is not disturbed during regeneration.
- Upflow of regenerants would tend to fluidise and mix the bed
- The answer is to hold the bed in place by:
  - **Air hold down**
  - **Water hold down**
  - **Split flow (Co-Counter flow regeneration)**
  - **Packed Bed**

Leakage from Co-flow and Counterflow Regenerated SAC Resin



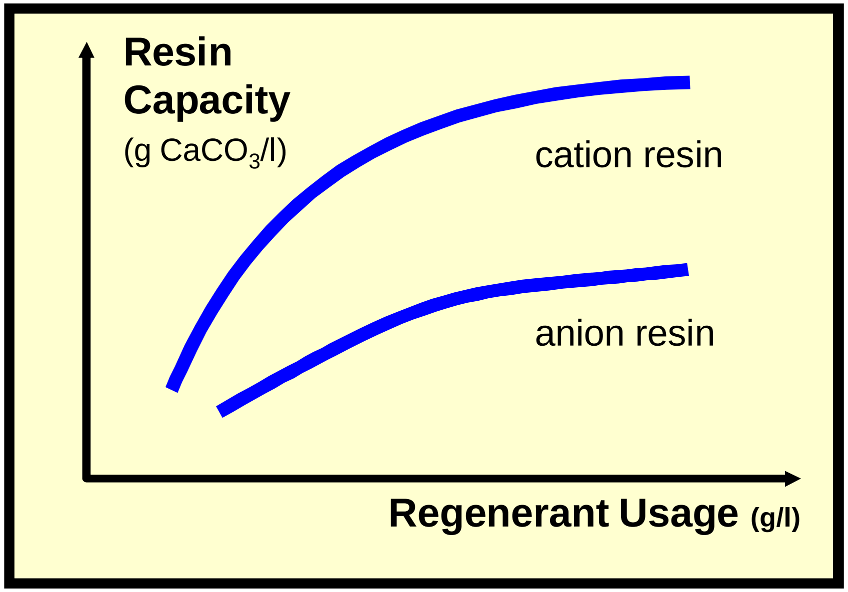
Co -flow regen plant outlet quality is dependent on feed quality

Treated Water Quality Obtained

- SAC – $SBA_{(Type\ 1)}$
  - Co-flow Regeneration (25°C)
    - Conductivity 5 - 30 μS/cm
    - Silica 0.1 - 0.5 mg/l as SiO_2
  - Counter-flow Regeneration (25°C)
    - Conductivity 0.5 - 2 μS/cm
    - Silica 0.002 - 0.05 mg/l as SiO_2
    - Sodium 0.05 - 0.2 mg/l as Na

Typical Resin Regeneration Operating Conditions

- SAC resin
  - 2 to 8 BV/h dilute acid flow
    - H_2SO_4 tends to use high rate
  - 3 to 6% HCl or 0.7 to 3% H_2SO_4
  - Dosage 60 to 160g acid/litre of resin
    - (often to suit neutral effluent)



- SBA resin
  - 2 to 4 BV/h
  - 3 to 6% NaOH
  - Dosage 60 to 160g NaOH/litre of resin

Note: Consult resin supplier's Technical Data Sheet for precise operating conditions for specific resin types

The Demineralisation Ion Exchange Cycle

- Demineralisation service flow/resin exhaustion
- Resin bed backwashing
- Resin regeneration
- Resin rinsing

Resin Rinsing

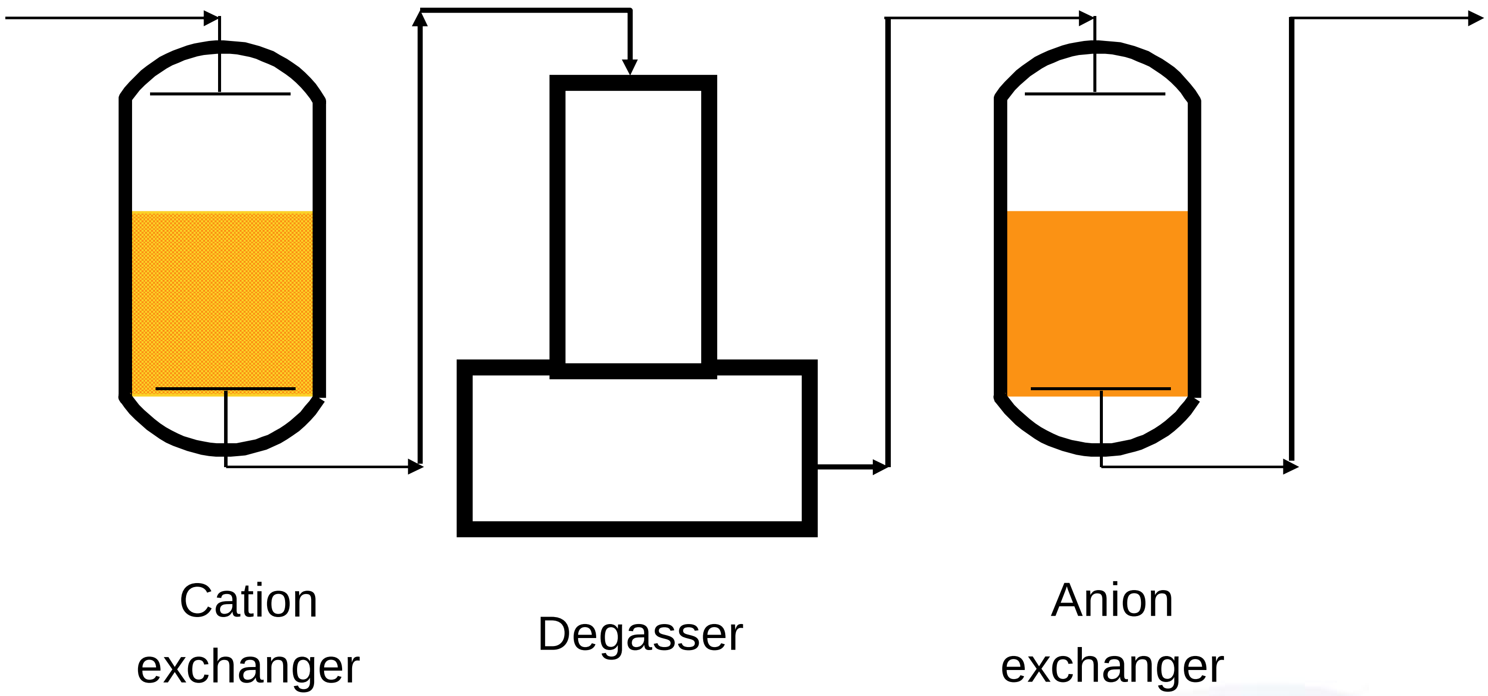
- Required to remove regenerant & eluted contaminants from the resin beds.
- Slow/Displacement rinse
  - Downflow of 3BV water at 5BV/h (typical) or dilution water flow.
  - Continuation of the chemical regeneration
- Fast Rinse
  - Ideally rinse to drain (min 1-2 BV)
  - Recirculation of water round cation and anion resins to save water
    - Co flow plant will recycle to below achievable outlet quality
  - Flowrate as feed water flowrate until treated water quality achieved

Note: Consult resin supplier's Technical Data Sheet for precise operating conditions for specific resin types

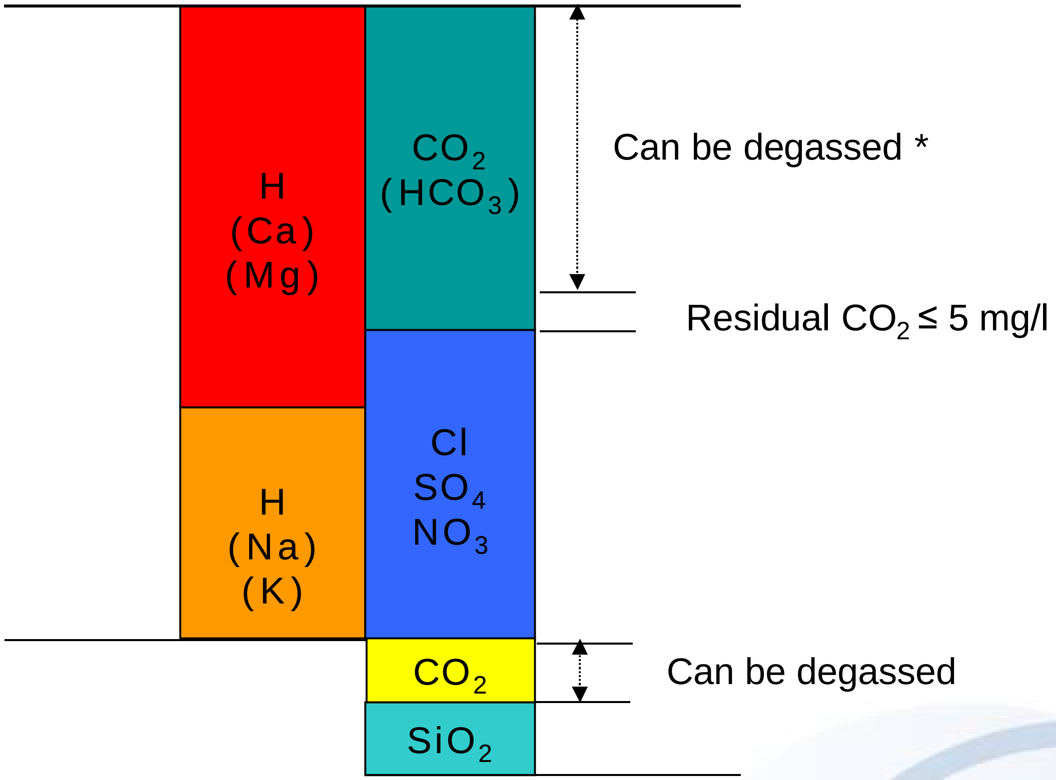
Alternatives to SAC → SBA

- Alternative plant layouts and alternative resins for improved economics of treating a range of feed water compositions.
- Examples are:
  - Add a Degasser before the SBA unit
  - Use Weak Acid Cation resin (WAC) before SAC resin
  - Use Weak Base Anion (WBA) resin before SBA resin

Role of the Degasser



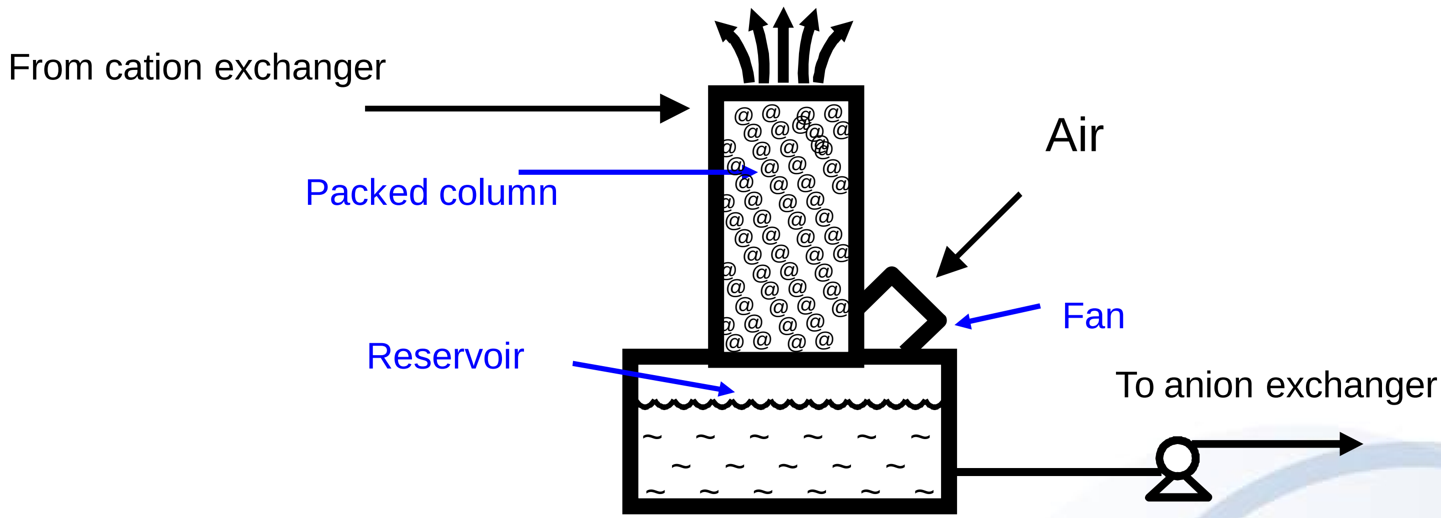
Degassing



*After SAC Resin

The Degasser

- Relies on equilibrium between CO_2, HCO_3, and pH
- Used to reduce alkalinity in **decationised** water by stripping carbon dioxide using air
- Takes load off Anion column. Lower operating cost
- Does little work if the raw water alkalinity is low



Summary

- SAC - DG – SBA
  - Degasser considered when alkalinity is >1 meq/l (>50 g $CaCO_3$)
  - Degasser reduces the CO_2 to <5mg/l
  - Bicarbonate anion load on the SBA unit reduced, therefore less resin is required.
  - Capital costs savings on larger plants
  - Operating cost savings due to reduced NaOH regenerant requirement for SBA resin.
  - Requires re-pumping from degasser sump
  - Treated water quality as SAC - SBA

Role of Weak Acid Cation (WAC) Resin

- Used for cation removal (usually Ca and Mg) associated with bicarbonate
  - "temporary hardness"
- Higher capacity than SAC resins (4 eq/l total capacity)
- Regenerated with low quantities of acid
  - 105% of theory
- Regenerated in series with SAC ("thoroughfare") utilises the large excess of acid required to regenerate the SAC resin
  - Acid → SAC → WAC
- Can be used in SAC vessel as layered bed or separate WAC vessel
  - Feed water → WAC → SAC

Role of Weak Base Anion (WBA) Resin

- Weak base anion resin
  - Polystyrenic or polyacrylic
  - Does not remove CO_2 or SiO_2
  - Used to remove strong acids (FMA) after SAC resin, taking the load off the SBA resin
  - Can be effective on water with high organic load (helps protect the SBA resin) and is easily regenerated
  - Regenerated with low quantities of alkali (130% of theory)
  - Can be regenerated in series with SBA resin using the excess alkali from SBA ("thoroughfare")
    - Alkali → SBA → WBA

Layered Bed Option

- Weak functionality resin bed can be located above strong resin in same compartment
  - Stratified bed – downflow service – upflow regen
- Weak resin can go below strong in separate compartments
  - Schwebebett – upflow service – downflow regen
- Resin bed design and operating criteria must still be met by individual resin beds.
- Resin bed separation (stratified bed) maintained on resin backwash by:
  - Density difference of the resins
  - Minimum bead size overlap or very narrow bead size distribution of the two resins (special grades required)
- Main advantage is in savings in capital cost
- Not always suitable when there is a large volume difference between weak and strong functionality resins
- Can be difficult to operate.

Choice of Resin and Process

- Choice dependent on:
  - Raw water composition
    - Chemical composition of TDS
    - Resin foulants
    - Resin degradation chemicals
    - Silica content
    - Temperature
  - Treated water specification
  - Flowrate of water to be treated
  - Plant mechanical design
  - Economic constraints (CAPEX & OPEX)
  - Environmental Obligations or constraints

High Organics Water

- A high level of organics may be a seasonal feature or a permanent feature
- Organics foul anion resins, particularly SBA styrenic gels
- A WBA (styrenic or acrylic) before a SBA can often help.
- Alternatively, use acrylic SBA
- Organic fouling can be minimised by good design
  - Long Caustic contact time
  - Raise regen temperature above feed water temperature
  - Regular resin maintenance

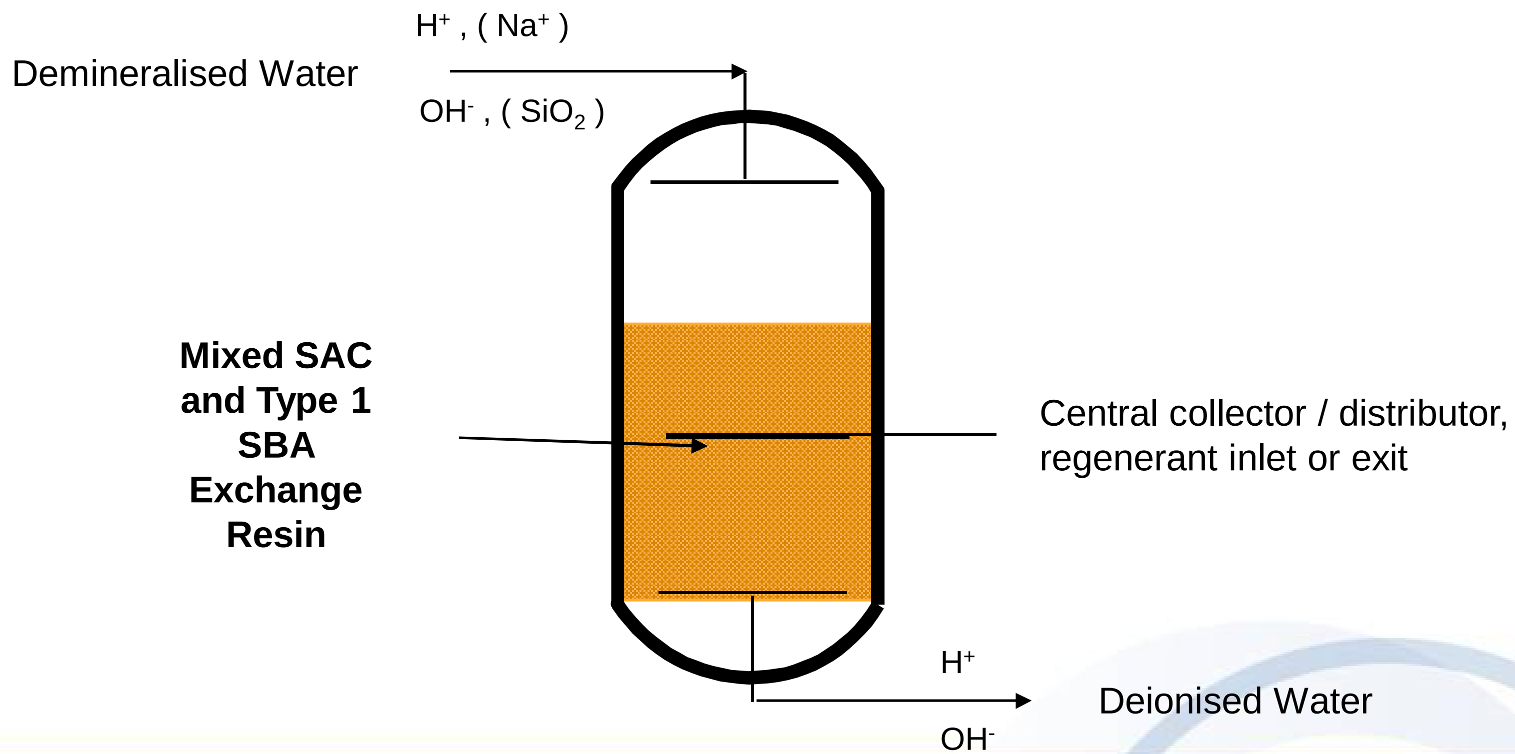
When Higher Treated Water Quality Required

Producing Higher Quality Water

- Residual conductivity, sodium and silica in treated, water is due to the equilibrium leakage from the SAC and SBA resins
  - Counterflow regen system offers better quality than co flow regen system
- When higher treated water quality is required this leakage must be reduced
- Install a polishing system. Options are:
  - Polishing mixed bed
  - SAC Polishing bed (Catpol, Hipol)

Mixed Bed Ion Exchanger

- Reduces residual ions leaked from cation and anion resins



Mixed Bed Ion Exchange Polishing

- Design
  - SAC and Type 1 SBA resins used
  - SAC resin volume selected to be just above central collector, or beds separated by inert layer which surrounds the central collector
- Operating sequence
  - Service Flow
    - Feed in down-flow through the mixed bed of SAC and Type1 SBA resin.
    - Resins never run to exhaustion.
    - Runs at high linear rate (45-65 m/h)
    - Each component requires minimum resin depth of 500mm
    - Higher chemical concentrations used
    - High regeneration levels

Treated Water Quality Obtained

– SAC → SBA → Polishing MB

– Co-flow or Counter-flow regeneration (25˚C) of the main SAC and SBA resin beds – no quality advantage

– Treated water quality from **polishing** mixed beds:
  - Conductivity <0.1 μS/cm
  - Silica <0.02 mg/l as SiO_2
  - Sodium 0.01 - 0.1 mg/l as Na

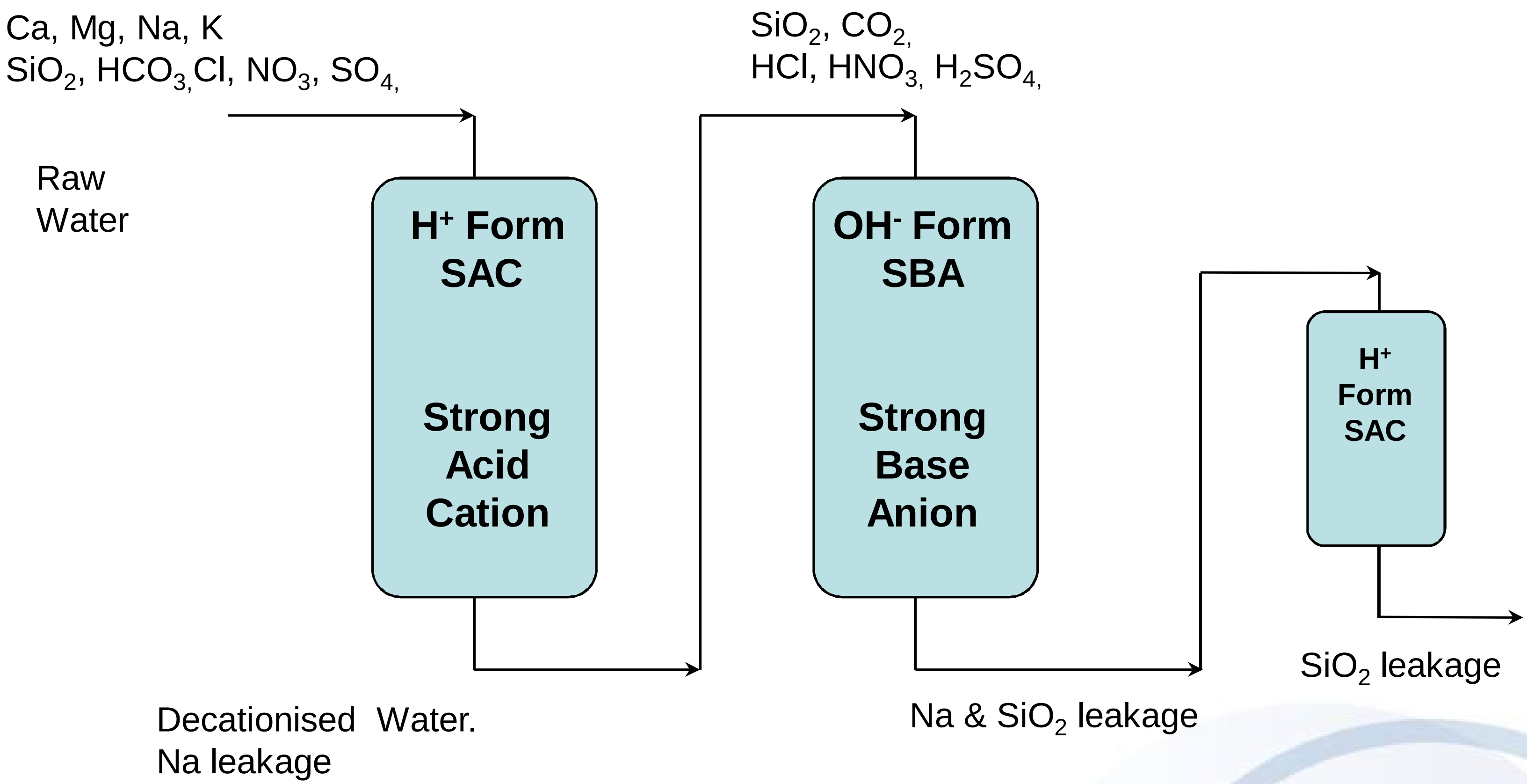
Note: All the design and operating specifications must be strictly adhered to if the design quality treated water is to be achieved.

Cation Polisher

- Usually used with counterflow regenerated SAC and SBA
- Used to remove NaOH leakage from SBA bed
- Na is dominant contaminant at SBA outlet (mainly from caustic regenerant)
- Small resin volume, highly regenerated, high BV/H
  - Operate at typically 500 BV/H or 150 m/h
- No silica removal – not as robust as mixed bed
  - Can be used as a silica inferential endpoint device (HCO_3 breakthrough on anion)
- Very cost effective
- No additional regeneration cost
  - Acid thoroughfared with SAC unit.
- Can normally achieve < 0.1 µS/cm & < 0.01 ppm Na

Service Flow

Process is SAC→SBA→SAC



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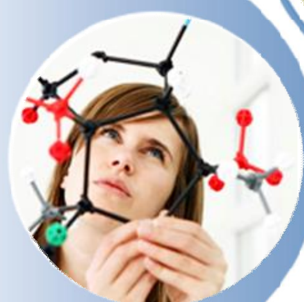

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