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.
Organics (humates, fulvates etc) are generally attracted to anion resin
The Ion Exchange Demineralisation Process (Strongly functional Resins)

- Strong acid cation resins (SAC) exchange $\text{H}^+$ ions with cation portion of TDS and are regenerated by dilute acid solution ($\text{H}^+$)
  - Water becomes decationised resulting in a solution of weak and strong acids

- Strong base anion resins (SBA) exchange $\text{OH}^-$ ions with anion portion of TDS and are regenerated by dilute sodium hydroxide ($\text{OH}^-$)
  - Weak and strong acids removed

- Feed Water $\rightarrow$ Cation ($\text{H}^+$ form) $\rightarrow$ Anion ($\text{OH}^-$ form) $\rightarrow$ 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

- Ion exchange process is a batch process
The Simplest Demineralisation Process is SAC→SBA

Raw Water

Ca, Mg, Na, K
SiO₂, HCO₃, Cl, NO₃, SO₄,

H⁺ Form SAC
Strong Acid Cation

Decationised Water. Na leakage

SiO₂, CO₂ (carbonic acid mainly from HCO₃)
HCl, HNO₃, H₂SO₄,

OH⁻ Form SBA
Strong Base Anion

Na & SiO₂ leakage

Demineralised Water
SAC + SBA

SAC RESIN

Ca Mg

HCO$_3$

Na K

Cl SO$_4$ NO$_3$

CO$_2$

SiO$_2$

SBA RESIN
Cation Resin Exhaustion

- Cation exchange

\[(R\cdot H^+) + (M^+A^-) \leftrightarrow (R\cdot M^+) + (H^+A^-)\]

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

<table>
<thead>
<tr>
<th>Cations</th>
<th>Anions</th>
<th>Affinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>SO$_4^{2-}$</td>
<td>Higher</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>NO$_3^-$</td>
<td></td>
</tr>
<tr>
<td>K$^+$</td>
<td>Cl$^-$</td>
<td></td>
</tr>
<tr>
<td>Na$^+$</td>
<td>HCO$_3^-$</td>
<td></td>
</tr>
<tr>
<td>H$^+$</td>
<td>HSiO$_3^-$</td>
<td></td>
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<tr>
<td>-</td>
<td>OH$^-$</td>
<td>Lower</td>
</tr>
</tbody>
</table>
The Chromatography Effect

- Partly used cation resin
  \( \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+ \)

Raw water

\( \text{SO}_4^{2-}, \text{Cl}^-, \text{NO}_3^-, \text{HCO}_3^-, \text{SiO}_2 \)

- 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

\( \text{SO}_4^{2-}, \text{NO}_3^-, \text{Cl}^-, \text{CO}_2, \text{SiO}_2 \)
The Chromatography Effect

- Partly used cation resin
  \[ \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+ \]

Raw water
  \[ \text{SO}_4^{2-}, \text{NO}_3^-, \text{Cl}^-, \text{HCO}_3^-, \text{SiO}_2 \]

- 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

Service Flow

\[ \text{H}^+, (\text{Equilibrium leakage } \text{Na}^+) \]

Decationised water
  \[ \text{SO}_4^{2-}, \text{NO}_3^-, \text{Cl}^-, \text{CO}_2, \text{SiO}_2 \]
The Chromatography Effect

- Exhausted cation resin
  \[ \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+ \]
  
  Raw water
  \[ \text{SO}_4^{2-}, \text{NO}_3^-, \text{Cl}^-, \text{HCO}_3^-, \text{SiO}_2 \]

  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

  Decationised water
  \[ \text{H}^+, (\text{Equilibrium leakage Na}^+ \text{ plus Na}^+ \text{ slip}) \]
  \[ \text{SO}_4^{2-}, \text{NO}_3^-, \text{Cl}^-, \text{CO}_2, \text{SiO}_2 \]
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 – $g_{CaCO_3}/l_{Resin}$

• 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 ($g_{\text{acid}}/l_{\text{Resin}}$)
  - Good for iron removal
  - Needs fume control
  - Greater storage volume required
  - More expensive OPEX and CAPEX

- **H$_2$SO$_4$ – 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

Feed water

Regenerant

Spent regenerant to drain

Treated water

Resin regeneration
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

FEA TURES:
Mechanically complex
Higher quality water
Higher capital cost
Uses less regenerant

Spent regenerant to drain

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

Feed water
Regenerant
Treated water
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\textsubscript{(Type 1)}

  - Co-flow Regeneration (25\textdegree C)
    - Conductivity 5 - 30 $\mu$S/cm
    - Silica 0.1 - 0.5 mg/l as SiO\textsubscript{2}

  - Counter-flow Regeneration (25\textdegree C)
    - Conductivity 0.5 - 2 $\mu$S/cm
    - Silica 0.002 - 0.05 mg/l as SiO\textsubscript{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
    - $\text{H}_2\text{SO}_4$ tends to use high rate
  - 3 to 6% HCl or 0.7 to 3% $\text{H}_2\text{SO}_4$
  - 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

Cation exchanger → Degasser → Anion exchanger
Degassing

*After SAC Resin

Can be degassed

Residual CO\(_2\) ≤ 5 mg/l

Can be degassed *
The Degasser

- Relies on equilibrium between \( \text{CO}_2 \), \( \text{HCO}_3^- \), 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 CaCO₃)
  - Degasser reduces the CO₂ 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 $\to$ SAC $\to$ WAC

- Can be used in SAC vessel as layered bed or separate WAC vessel
  - Feed water $\to$ WAC $\to$ 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 $\rightarrow$ SBA $\rightarrow$ 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

Demineralised Water

Mixed SAC and Type 1 SBA Exchange Resin

Central collector / distributor, regenerant inlet or exit

Deionised Water

$H^+ , (Na^+)$

$OH^- , (SiO_2)$
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 SiO₂
  - 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
Process is SAC → SBA → SAC

Ca, Mg, Na, K
SiO₂, HCO₃, Cl, NO₃, SO₄,

Raw Water

H⁺ Form SAC
Strong Acid Cation

SiO₂, CO₂,
HCl, HNO₃, H₂SO₄,

OH⁻ Form SBA
Strong Base Anion

Na & SiO₂ leakage

Decationised Water.
Na leakage

SiO₂ leakage

H⁺ Form SAC

Service Flow