Ion Exchange
RESIN SELECTION

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I WILL BRING YOU HAPPINESS!!

Resin selection = HAPPINESS
When it comes to resin selection the magic number is:

Why happiness......
Content

• General considerations

• Let’s count to 5
  – 1: WAC
  – 2: SAC
  – 3: WBA
  – 4: SBA
  – 5: ?

• Mixed bed
Basic choice: beadsize distribution

- **Uniform particle size resins**
  - Uniformity coefficient in a range of 1.1 – 1.2
  - High performance applications
  - For packed bed systems
  - Mixed bed applications

- **Special graded resins**
  - Uniformity coefficient in a range of 1.1 – 1.5
  - For layered bed applications
  - For packed bed systems

- **Standard Gaussian**
  - Uniformity coefficient in a range of 1.3 – 1.8
  - For standard applications (co-flow)

\[
\text{Uniformity Coefficient (UC)} = \frac{\text{screen size retaining 40\% (d60)}}{\text{screen size retaining 90\% (d10)}}
\]
Basic choice: Matrix

• Gel matrix
  – High capacity
  – High chemical efficiency
  – Good mechanical stability
  – Translucent pseudo cristaline structure

• Macroporous matrix
  – Lower capacity than gel
  – Higher mechanical stability than gel
  – SAC for better resistance to oxidation / high temperature
  – SBA for high load of organic components
  – Opaque proreus structure
Basic choice : Functionality

- Cation exchangers
  - Weak
  - Strong

- Anion exchangers
  - Weak
  - Strong
  - Type 1 / Type 2
  - Bi-functional
  - Acrylic / Styrenic
Choice #1: Weak acid cation resin (WAC)

WAC specifics
- Functional group: carboxylic acid (hydrogen form)
- Standard & graded bead size distribution
- Chemical form: H
- Macroporous / gel matrix
- High mechanical and chemical stability
- Volume increase
  - (H to Na) 60 - 100% @ complete exhaustion
- High Total Volume Capacity
- High regeneration efficiency
- High operating capacity
  (depending on water specification)
Weak Acid Cation Resins – How do they work?

- It is the H\(^+\) ion connected to the COO\(^-\) which exchanges with the cations associated with the temporary hardness to release H\(^+\) ions into the water in **service operation**

\[
\text{H}^+ + \text{Ca(HCO}_3\text{)}_2 \rightarrow \text{(CO}_2\text{H}^+\text{)}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O}
\]

- On **regeneration** the acid replaces the H\(^+\) ions and removes the captured cation which passes to drain with the excess acid.

\[
\text{(CO}_2\text{Ca}^{++})_2 + 2\text{HCl} \rightarrow \text{(CO}_2\text{H}^+\text{)}_2 + \text{CaCl}_2
\]

- Operating capacity is largely set by the water specification and not with the regeneration level.
Weak Acid Cation Resins – Performance

- Regeneration can be with sulphuric / hydrochloric acid
- HCl is the safest acid regenerant
  - Using sulphuric acid could cause calcium sulphate precipitation as all the loading is hardness.
  - Regenerant volume is smaller with HCl
- In terms of capacity, sulphuric acid and hydrochloric work equally as well
- Depending on the operating conditions chemical efficiencies of 105 -110 % are commonly achieved on well designed systems
- WAC resin performance is set by:
  - Hardness to Alkalinity Ratio (Preferably > 1.0 → economic evaluation!)
  - Flow rate (Preferably < 40 BV/h)
  - Water Temperature (Preferably above 10 °C)
  - pH > 4,2
Your selection #1:

When to select a WAC:
- based on economical evaluation
- when hardness to alkalinity ratio > 1

Criteria:
- Good resistance to oxidants
- Good mechanical stability

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Choice #2 Strong acid cation resin (SAC)

- **SAC specifics:**
  - Functional group: Sulphonic acid
  - Takes all cations
  - Operating capacity depending on regeneration level
  - Chemical form: H or Na
  - Standard gaussian & UPS bead size distribution
  - Differentiation by % DVB
  - MP and gel matrix
  - Gel is more sensitive to oxidation
  - Oxidation attacks the structure
  - Selectivity order

Cation Resin selectivity: Fe > Ca > Mg > K > Na > H
Sodium leaks first!
Strong Acid Cation Resins – How do they work?

- In **service** operation it is the H+ ion connected to the SO$_3^-$ group which exchanges with **all** cations to release H+ ions into the water.

  $\text{SO}_3\text{H} + \text{NaCl} \rightarrow \text{SO}_3\text{Na} + \text{HCl}$

- On **regeneration** the acid replaces the H+ ions and removes the captured cation which passes to drain with the excess acid.

  $\text{SO}_3\text{Na} + \text{HCl} \rightarrow \text{SO}_3\text{H} + \text{NaCl}$

- Remember – pH exit SAC unit should be typically between 2 - 3
Strong Acid Cation Resins –
Factors affecting resin life / resin choice

- Two main factors affect resin life:

A. Oxidative Attack

- Resin matrix de-crosslinks / beads go soft (can turn to jelly) / resin water content will rise → increased swell → decreasing TVC / high pressure drop irreversible problem.
- Options:
  1. Reduce dosing levels of chlorine / chlorine dioxide etc.
  2. Choose resin with higher DVB cross linking (gel= higher total capacity, or macroporous cation resin)– lasts longer.

B. Iron / Manganese Fouling

- Reduced capacity due to irreversible fouling - periodic HCl acid soak / reducing agent will extend resin life
Effect of % DVB on SAC resin

- Total capacity
- Selectivity
- Physical stability
- Chemical stability

- Water retention
- Swelling
- Kinetics
- Regenerability
- Organic desorption ability

IF % DVB
Strong Acid Cation Resins – Different Acids for Regeneration

- Regeneration can be with sulphuric / hydrochloric or nitric acid
  - (Potential risks of using Nitric Acid – safety issues)

- HCl is the best acid regenerant – it gives a higher working capacity than sulphuric acid
  - typically 50 g/l as CaCO₃ (1 eq/l) at moderate regeneration levels, while sulphuric acid capacity would be nearer to 30 g/l as CaCO₃ (0.6 eq/l).

- HCl can be applied at higher concentrations – typically 4 to 5% strength giving lower waste water volumes than sulphuric acid.
- Sulphuric acid concentrations are determined by the amount of calcium present in the water and loaded on to the resin.
  - Often H₂SO₄ can only be applied at 2% or less on high hardness waters to stop calcium sulphate precipitation.

- HCl is better at controlling iron fouling

- Depending on acid and regeneration level, chosen chemical efficiencies of 130 - 250 % of stoichiometry are commonly employed.
Your selection #2:

When to select a SAC: - For full demineralization / softening

Criteria: - % DVB (standard 8%)
- Beadsize distribution
- gel / MP matrix

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Choice #3: weak base anion resin WBA

- **WBA specifics**
  - Functional group: tertiary amine (most cases)
  - UPS & graded & standard gaussian bead size distribution
  - Chemical form: free base
  - MP matrix
  - Styrenic and Acrylic matrix
  - Acrylic matrix at high organic load
  - Good TOC barrier for SBA
  - Takes up strong acids
  - High regeneration efficiency
  - High operating capacity depending on water specification
  - Selectivity order

Anion Resin selectivity: $\text{SO}_4 > \text{NO}_3 > \text{Cl} > \text{OH}$
Silica / bicarbonate passes through!
Anion Resins (WBA / SBA) – How do they work?

- During production cycle, the tertiary amine is capable of adsorbing the strong acid to the free electron pair of the amine

\[
\text{CH}_2\text{N}:(\text{CH}_3)_2 + \text{HCl} \rightarrow \text{CH}_2\text{HN}(\text{CH}_3)_2\text{Cl}
\]

- On regeneration the sodium hydroxide (caustic soda) pushed out the HCl and neutralize captured anion which passes to drain with the excess

\[
\text{CH}_2\text{HN}(\text{CH}_3)_2\text{Cl} + \text{NaOH} \rightarrow \text{CH}_2\text{N}:(\text{CH}_3)_2 + \text{NaCl} + \text{H}_2\text{O}
\]
Weak Base Anion Resins

- In IWT Demineralisation normally only encounter the polystyrenic macroporous (most of the cases) and polyacrylic gel on specific circumstances like high organic load.

- Advantages
  - Higher working capacity than SBA typically 40-55 g/l as CaCO$_3$. (0.8 – 1.1 eq/l)
  - Regeneration efficiency very high – typically 120-145% of stoichiometry (depending on organic load)
  - Polystyrenic versions are highly porous and this combined with their lack of strong base functionality means that all WBA resins offer good resistance to organic fouling.
  - Acrylic versions have a high reversibility due to the hydrophilic nature of the structure and because of less entanglement (no aromatic rings)
  - Acrylic weak base resins will take bi-carbonate

- Disadvantages
  - Only removes free mineral acids species (FMA) after the cation bed (H$_2$SO$_4$ / HNO$_3$ / HCl).
  - Will not remove significant loadings of Silica / Bicarbonate / CO$_2$ (Some SB content)
Your selection #3:

When to select a WBA:
- Presence of FMA
- For partial demineralization
- Enhanced efficiency in pair with SBA
- For TOC barrier

Criteria:
- Matrix: Styrenic or Acrylic → normally stryrenic

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Choice #4: strong base anion resin SBA → more complex!

- **SBA specifics**
  - Functional group: quaternary amine (most cases)
  - UPS & graded & standard gaussian bead size distribution
  - Chemical form: Cl, SO$_4$ or OH
  - MP and gel matrix
  - **Type 1 and Type 2 functionality**
  - **Styrenic and Acrylic matrix**
  - **Bi-functional**
  - Acrylic matrix for high organic load
  - Takes up all anions
  - Selectivity order

Anion Resin selectivity:

SO$_4$ > NO$_3$ > Cl > HCO$_3$ > Silica > OH
Silica leaks first!
Polystyrenic Strong Base
Anion – Type 1

• Gel Type
  – Advantages:
    • Widely applied for standard applications
    • Low Silica Leakage
    • Good Thermal Stability & lifetime (60 °C max. in OH⁻ form)
    • Outstanding osmotic and mechanical stability
    • Low rinse water demands (3-4 bed volumes)
    • specially suitable for demineralisation of industrial water in combination with WBA (Most used resin combination worldwide)
  – Disadvantages:
    • Relatively low working capacity (25 - 35 g/l as CaCO₃ ~0,5 eq/l)
    • Good lifetime in absence of irreversible organics loading (6-8 years)
    • More prone to organic fouling

• Macroporous Type
  – Lower working capacity (18-20 g/l as CaCO₃ ~ 0,36 – 0,4 eq/l) than gel version
  – Good resistance to organic fouling due to larger surface area
  – Better kinetics
  – High resistance to osmotic shock.
Polystyrenic Strong Base Anion – Type 2

- **Gel Type**
  - **Advantages**
    - Highest SBA Working Capacity of 30-36 g/l as CaCO$_3$ (0.6 – 0.72 eq/l) For small filter construction.
  - **Disadvantages**
    - Higher Silica Leakage compared to Type 1 (important on co-flow regenerated plant where there is no polishing mixed bed)
    - Lower Thermal Stability (35 °C max. in OH⁻ form)
    - Prone to organic fouling

- **Macroporous Type**
  - Lower working capacity of 25-29 g/l as CaCO$_3$ (0.5 – 0.58 eq/l) than gel version but offers much better resistance to organic fouling due to larger surface area.
  - Also offers better kinetics and resistance to osmotic shock
Polyacrylic Strong Base Anion –
Type 1 only

- Gel Type
  - Advantages
    - Good Working Capacity (similar to Polystyrenic Type 2, 25-33 g/l as CaCO$_3$ (0,5 – 0,65 eq/l)
    - Very good resistance to organic fouling
    - Good silica leakage (similar to Polystyrenic Type 1 resin)
  - Disadvantages
    - Inferior Thermal Stability (35 °C max. In OH- form)
    - Due to higher bead elasticity – does not like operating at high m/h rates (high pressure drop)
    - Acrylic resin in general have a higher rinse water consumption and will increase in time

- Macroporous Type
  - The macroporous version is not used in anion demineralisation but is mainly employed as an organic scavenger resin due to excellent reversible removal of organics, high surface area. Good resistance to osmotic shock.
Polystyrenic Bifunctional Gel Anion
– (Weak & Strong Base Combined)

• Advantages
  – High Working Capacity calculated as overall 28-40 g/l as CaCO$_3$ (0,56 – 0,8 eq/l)*
  – Regeneration efficiency very high – typically 120-130% of stoichiometry
  – Polystyrenic versions are highly porous with an acceptable resistance to organic fouling

Disadvantages
  – Single filter only suitable for waters with low weak acid loading (usually less than 20% recommended)
  – High silica / bicarbonate / CO$_2$ waters unsuited
  – Due to lower dissociation – does not like operating at high BV/h rates (max. 35 BV/h)

* Note: different ratios in the market available with approx. 25% SBA and 75% WBA or 10% SBA and 75% WBA
Polyacrylic Bifunctional Gel Anion
– (Weak & Strong Base Combined)

• Advantages
  – High overall operating capacity 30-43 g/l as CaCO$_3$ (0.6 – 0.85 eq/l)
  – Good resistance to organic fouling (better than styrenic bifunctional)

• Disadvantages
  – Only suitable for waters with low weak acid loading (usually less than 20% recommended) High silica / bicarbonate / CO$_2$ waters unsuited.
    • On UK waters plants without degassing towers, or tight silica spec exit anion, are unlikely to use this resin.
  – Thermal Stability (35 °C max. In free base/OH$^-$ form)
  – Due to higher bead elasticity – does not like operating at high m/h rates (high pressure drop)

* Note: These are only found based on Polyacrylic Structure with approx. 50% SBA and 50% WBA sites
Anion Resins - Swelling

- Volume changes on SBA and WBA resins are different:
  - SBA shrink as they exhaust / swell on regeneration.
  - WBA swell as the exhaust / shrink on regeneration.

- A SBA resins swell by 10-25% from the fully exhausted to the fully regenerated form.

- A WBA resins shrink by 20-25% from the fully exhausted to the fully regenerated form.

- Acrylic resins also undergo irreversible expansion when first used.
  - Typically this is of the order of 3 - 8% - (very important when designing plants)
The Problems of Organic fouling
– Correct Resin Selection

• Consequences:
  – Increased Rinse Times
  – Reduced Capacity
  – Increased TOC leakage
  – Reduced resin lifetime
  – Increased chemical consumption
  – Increased operational downtime
  – It will have influence down stream applications like boilers / turbines (conductivity in first condensate)

• The increased rinse time and reduced capacity due to organic fouling is one of the biggest reasons why anion resins are changed.

• Uptake or organics is easy, to remove is the challenge. Correct resin selection will help.

• The problem is bigger on “thin waters” as the organic load per liter resin will be higher.

• Each resin has a maximum tolerance to organic load
Organic Scavenger Resins

- There are five types of organic scavenger resins:
  - Polyacrylic Macroporous SB Anion
  - Polyacrylic gel WB anion
  - Polystyrenic Highly Macroporous Type 1 SB Anion
  - Polystyrenic Highly Macroporous WB Anion
  - Polystyrenic (high moisture) Gel Type 1 SB Anion

- All resins specially designed as resins to act as pretreatment to a demineralisation plant / anion exchanger. Their total capacity is too low to act as a conventional anion resin, the existing functional groups change the water quality (HCO₃ capacity - Chloride leakage (attention with existing plants with degassifiers).

- Some sites do not like to deal with the caustic in the effluent and hence you also see brine only organic scavengers usually employing 250-300 g/l NaCl regen levels.
  - When not using caustic soda in the regenerant then this favours using the Polyacrylic Macroporous Strong Base Anion Resin.

- Scavengers are normally regenerated with a mixture of brine (NaCl) and Caustic Soda (NaOH). Typical regen conditions 150 g/l NaCl with 30-35 g/l NaOH applied as a 10% brine.
Comparison of SBA Resins:

- **Operating Capacity**
  Bifunc Acry > Type 2 Styr Gel > Type 2 Styr Macro = Type 1 Acry Gel > Type 1 Styr Gel > Type 1 Styr Macro

- **Thermal Stability**
  Type 1 Styr > Type 2 Styr > Type 1 Acry > Bifunc

- **Silica Leakage – (Co-flow regenerated)**
  Type 1 (Styr & Acry) < Type 2 < Bifunc

- **Organic Fouling (depends on organic matter)**
  Type 1 Acry Gel < Bifun Acry < Type 1 Styr Macro < Type 2 Styr Macro < Type 1 Styr Gel < Type 2 Styr Gel.

- **Rinse water consumption**
  Styr (5 BV) < Acryl (8-10 BV)

- **Price**
  Bifun Acry > Type 1 Acry Gel > Macro Styr Types 1&2 > Gel Styr Types 1&2
Simplefied selection guide

Styrenic type 1 gel

SiO$_2$ or Temp?

- High
- Low

Type 2 gel

Organics?

- High
- Low

SiO$_2$ or Temp?

- High
- Low

Styrenic type 1 gel

Hot NaOH or feed temp?

- Yes
- No

SiO$_2$?

- Low <5%
- High >30%
- Medium

Acrylic bi-functional

Acrylic type 1 gel

Type 2 macro

Styrenic type 1 macro

Medium
Your selection #4:

When to select a SBA:
- Presence of weak acids
- For TOC removal

Criteria:
- see selection guide, but generally: styrenic type 1 gel

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When it comes to resin selection the magic number is:

???

You only need 4 resins + 1 to cover 80 – 90 % of your cases

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<td>5 your specific circumstances: Acrylic / type 2</td>
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Exceptions

• Based on preferences
  – Most people like to stick to what they know
• Based on specific system requirements
  – Floating inert resins are developed based on specific system requirements
  – For internal regenerable mixed bed application resins need good separation.
  – High velocity systems; need for high kinetic resins
• Based on specific water composition
  – Low TDS with high organics and or silica
Polishing Mixed Bed Units

Resin selection for make up polishing mixed bed with internal regeneration

- Combination of SAC / SBA resins
- The SBA is always a Type 1 to obtain low Silica values.
- The SAC sodium leakage can be minimized by using a higher %DVB as selectivity for sodium increases with increasing DVB.

- The readily encountered options are:
  a. All gel resin combination (mostly used)
  b. All macroporous resin combination.
  c. Gel cation with macroporous anion combination.

- Never use macroporous cation with gel anion - THEY WILL NOT SEPARATE WELL

- Trio beds use buffer beads as intermediate interface to minimize cross contamination of the SAC / SBA resins during regeneration
Summary

- Resin selection is critical in getting the best performance from your ion exchange plant!

- Select resins on technical grounds and considerations.

- Get to know your plant, existing resin types and specific circumstances so you can make an educated assessment!

- The resin manufacturer is there to help. So if you have doubts, consult us.

- Although the background of resin selection contains a lot of chemistry, remember the number 5. Just select the standard 4+1 and you can cover 80-90% of your cases.