where science meets business

Ion Exchange
RESIN SELECTION

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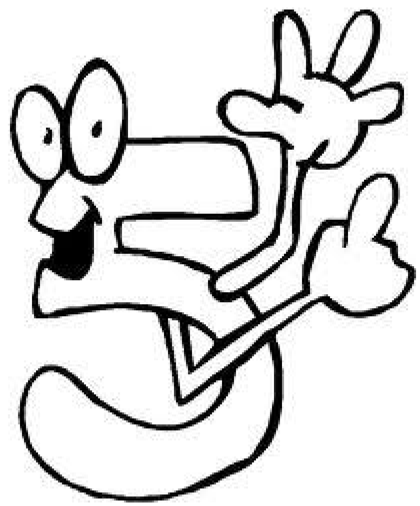
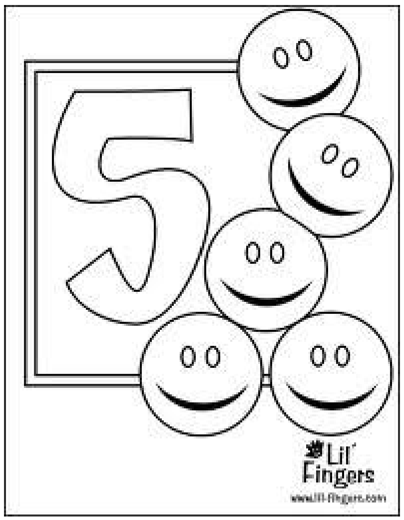
I WILL BRING YOU HAPPINESS!!

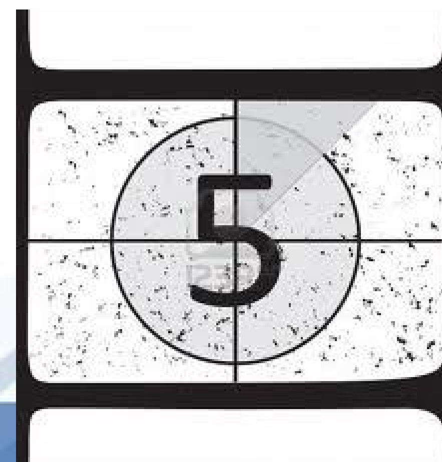
Resin selection = HAPPINESS

Why happiness......

When it comes to resin selection the magic number is:







Content

- General considerations
- Let's count to 5
  - 1: WAC
  - 2: SAC
  - 3: WBA
  - 4: SBA
  - 5: ?
- Mixed bed

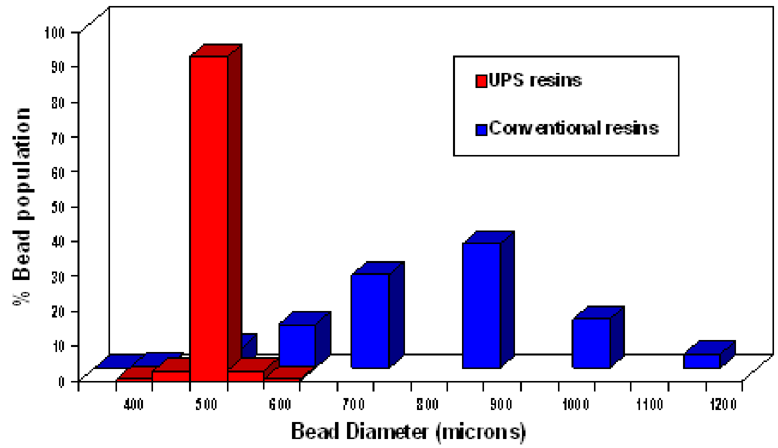
Basic choice : beadsize distribution

- Uniform particle size resins
  - Uniformity coefficient in a range of 1,1 – 1,2
  - High performance applications
  - For packed bed systems
  - Mixed bed applications

Uniformity Coefficient (UC) = screen size retaining 40% (d60) / screen size retaining 90% (d10)

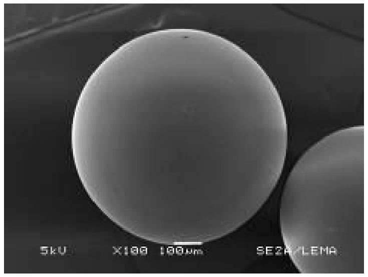
- Special graded resins
  - Uniformity coefficient in a range of 1,1 – 1,5
  - For layered bed applications
  - For packed bed systems

- Standard Gaussian
  - Uniformity coefficient in a range of 1,3 – 1,8
  - For standard applications (co-flow)

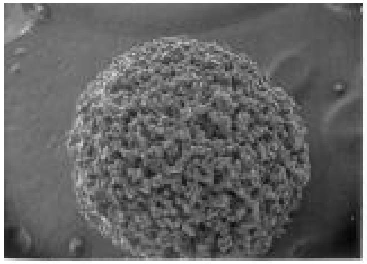


Basic choice : Matrix

- 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

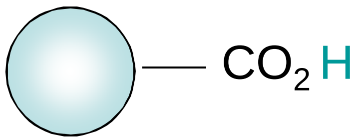


Basic choice : Functionality

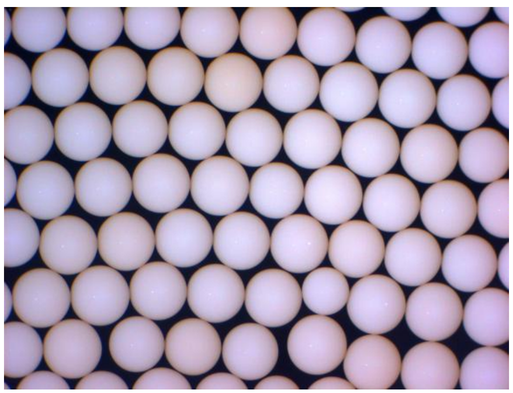
- Cation exchangers
  - Weak
  - Strong

- Anion exchangers
  - Weak
  - Strong
  - Type 1 / Type 2
  - Bi-functional
  - Acrylic / Styrenic

Choice #1 :Weak acid cation resin (WAC)



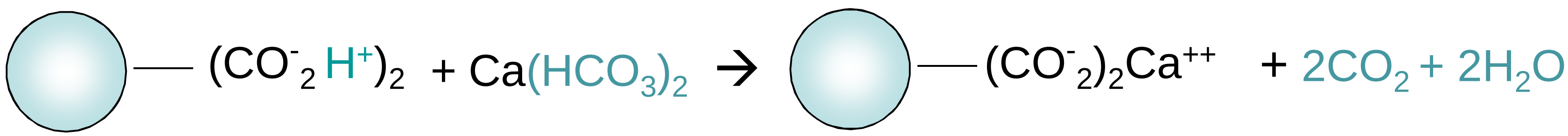
weak-acid-cation (WAC)



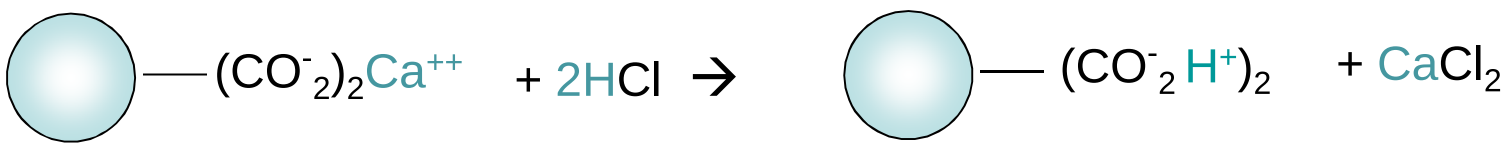
- **WAC specifics**
  - Functional group: carboxylic acid (hydrogen form)
  - Standard &graded bead size distribution
  - Chemical form : H
  - Macroporous / gel matrix
  - High mechanical and chemical stability
  - volume increase
    - (H to Na) 60 - 100% @ complete exhaustion
  - High Total Volume 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**

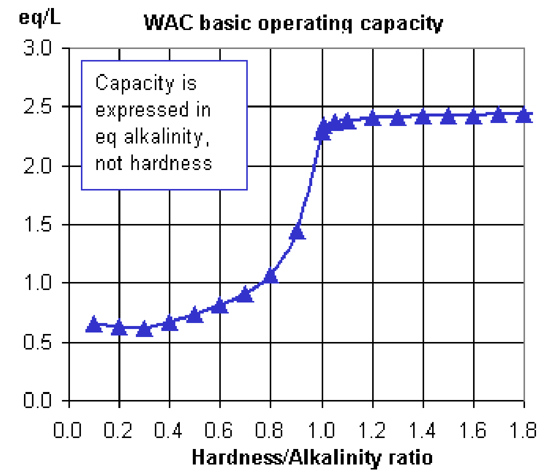


- On **regeneration** the acid replaces the H+ ions and removes the captured cation which passes to drain with the excess acid.



- 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

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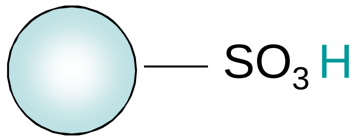
Your selection #1:

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

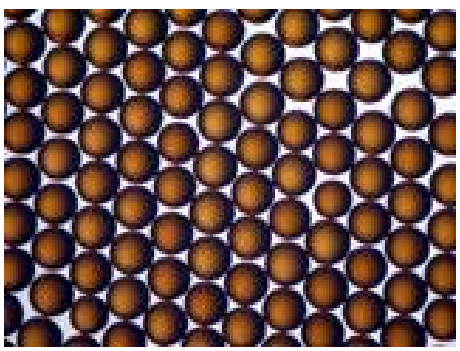
Criteria: - Good resistance to oxidants
- Good mechanical stability

	standard industrial grade				
		structure	matrix	functionality	DVB
1	WAC	acrylic	gel	carboxylic	--

Choice #2 Strong acid cation resin (SAC)



strong-acid-cation (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.

$$\text{(resin)}-SO_3H + NaCl \rightarrow \text{(resin)}-SO_3Na + HCl$$

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

$$\text{(resin)}-SO_3Na + HCl \rightarrow \text{(resin)}-SO_3H + NaCl$$

- 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

IF % DVB

- Total capacity
- Selectivity
- Physical stability
- Chemical stability

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

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 $CaCO_3$ (1 eq/l) at moderate regeneration levels, while sulphuric acid capacity would be nearer to 30 g/l as $CaCO_3$ (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 H_2SO_4 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.

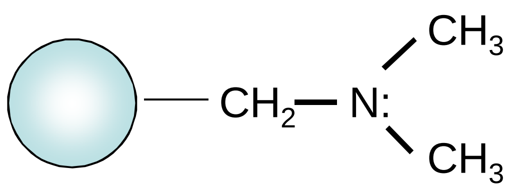
Your selection #2:

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

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

	standard industrial grade				
		structure	matrix	functionality	DVB
1	WAC	acrylic	gel	carboxylic	--
2	SAC	styrenic	gel	sulphonic	8%

Choice #3: weak base anion resin WBA



weak-base-anion (WBA)

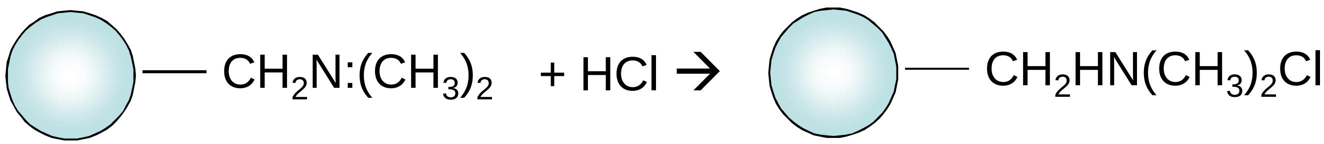
- **WBA specifics**
  - Functional group: tertiary amine (most cases)
  - UPS & graded & standard gaussian bead size distribution
  - Chemical form : free base
  - MP matrix
  - Styrenic and Acrylic matrix
  - Acrylic matrix at high organic load
  - Good TOC barrier for SBA
  - Takes up strong acids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

Anion Resin selectivity: $SO_4 > NO_3 > Cl > OH$

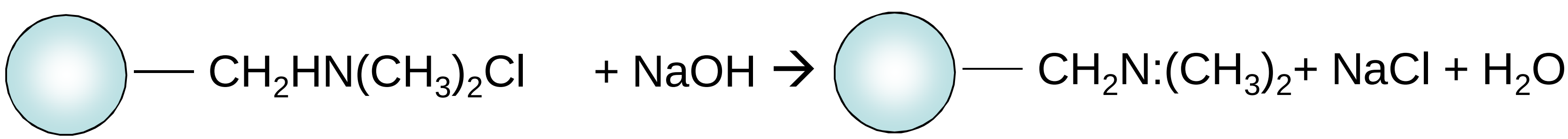
Silica / bicarbonate passes through!

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



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



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_2S0_4 / HNO_3 / HCl).
  - Will not remove significant loadings of Silica / Bicarbonate / CO_2. (Some SB content)

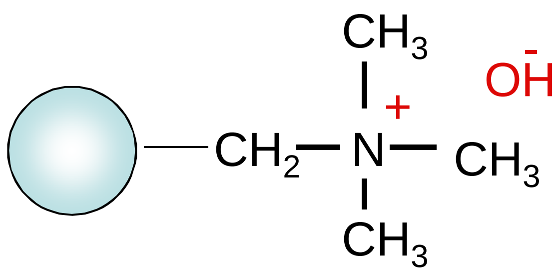
Your selection #3:

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

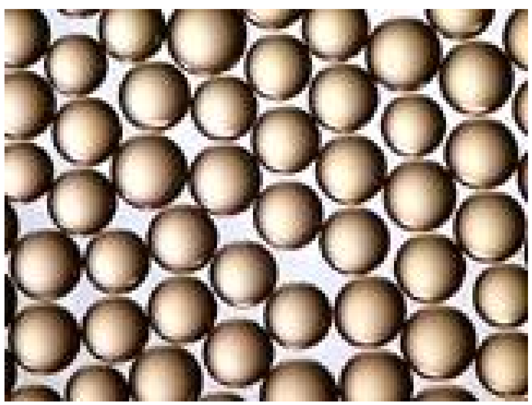
Criteria:
- Matrix: Styrenic or Acrylic → normally stryrenic

	standard industrial grade				
		structure	matrix	functionality	DVB
1	WAC	acrylic	gel	carboxylic	--
2	SAC	styrenic	gel	sulphonic	8%
3	WBA	styrenic	MP	tert amine	--

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



strong-base-anion (SBA)



- **SBA specifics**
  - Functional group: quaternary amine (most cases0
  - UPS & graded & standard gaussian bead size distribution
  - Chemical form : Cl, SO4 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

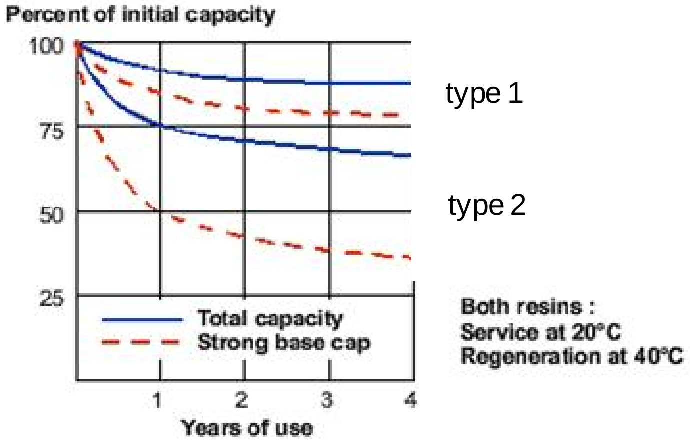
Silica leaks first!

Polystyrenic Strong Base Anion – Type 1

- Gel Type
  - Advantages:
    - Widely applied for standard applications
    - Low Silica Leakage
    - Good Thermal Stability & lifetime (60 ^{o}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 combinagtion with WBA (Most used resin combination worldwide)
  - Disadvantages:
    - Relatively low working capacity (25 - 35 g/l as $CaCO_3$ ~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 $CaCO_3$ ~ 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 ^{o}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 ^oC 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

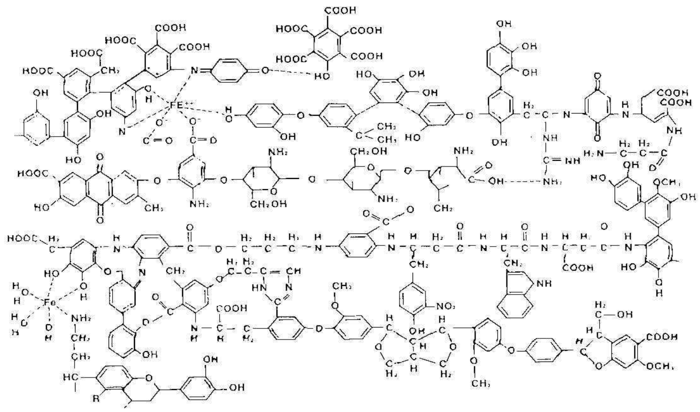
- Volume changes on SBA and WBA resins are different:
  - SBA shrink as they exhaust / swell on regeneration.
  - WBA swell as the exhaust / shrink on regeneration.

- 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

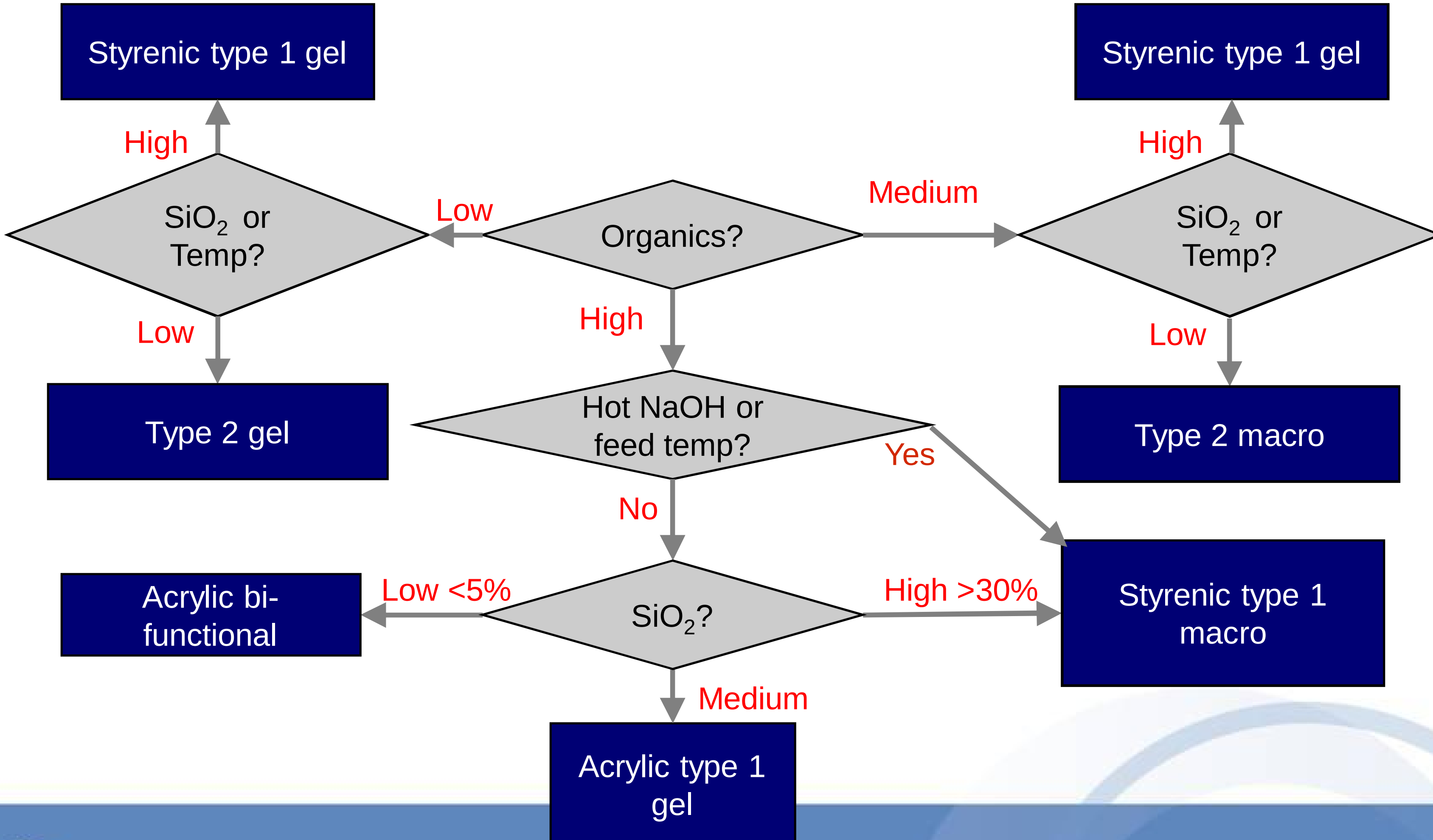
- **Silica Leakage – (Co-flow regenerated)**
  Type 1 (Styr & Acry) < Type 2 < Bifunc

- **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



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

	standard industrial grade				
		structure	matrix	functionality	DVB
1	WAC	acrylic	gel	carboxylic	--
2	SAC	styrenic	gel	sulphonic	8%
3	WBA	styrenic	MP	tert amine	--
4	SBA T1	styrenic	gel	quart amine	--

When it comes to resin selection the magic number is:

???

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

	standard industrial grade				
		structure	matrix	functionality	DVB
1	WAC	acrylic	gel	carboxylic	--
2	SAC	styrenic	gel	sulphonic	8%
3	WBA	styrenic	MP	tert amine	--
4	SBA T1	styrenic	gel	quart amine	--
5	your specific circumstances: Acrylic / type 2				

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 seperability.
  - 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

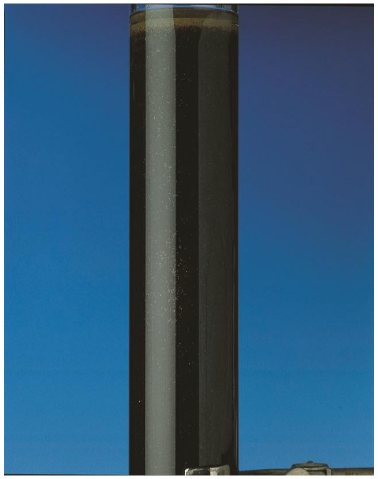
Resin selection for make up polishing mixed bed with internal regeneration

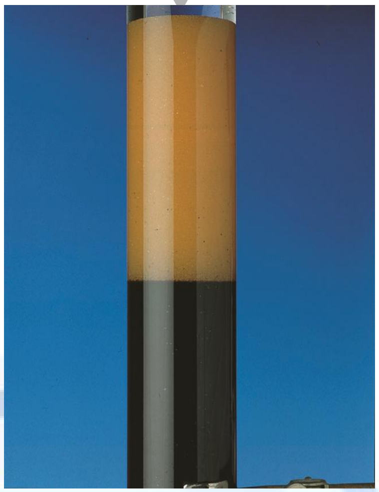
- Combination of SAC / SBA resins
- The SBA is always a Type 1 to obtain low Silica values.
- The SAC sodium leakage can be minimized by using a higher %DVB as selectivity for sodium increases with increasing DVB.

- 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.

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