Resin Types and Production

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Properties of an Ion Exchanger

Synthetic Ion Exchangers require certain properties to perform demineralisation. The three main properties required are:

a. Insoluble in, but permeable by water.
b. An ability to exchange ions, with the different types of ions commonly encountered in water supplies.
c. To allow the passage of water through the resin bed at optimum rates without undue pressure drop.

Hopefully during this presentation it will become clear how this is achieved and why some resin manufacturers produce over 400 different products!

A major resin producer will have 100's of products in their range.

When you purchase any ION EXCHANGE RESIN

THE BEST RESIN IS NOT USUALLY THE CHEAPEST

THE BEST RESIN IS:

THE RESIN WHICH IS BEST SUITED TO YOUR PLANT DESIGN AND OPERATING CONDITIONS

Synthetic Resin Production – Major production costs

- **Styrene Monomers**
- **Divinyl benzene**
- **Acrylic Monomers**
- **Sulphuric acid**
- **Caustic soda**
- **Amines   i.e. Trimethylamine, etc...........**

These raw materials, together with **energy, water and waste water** costs are the main drivers concerning the price of ion exchange prices.

It is not a labour intensive process

Most derived from Oil – Oil price rising – resin prices rise!

Synthetic Resin Types

There are many different types of synthetic ion exchangers.

Two principle polymer backbones which are used in producing resins in IWT:

1. **Polystyrenic**
2. **Polyacrylic**

90% of sales Polystyrenic resins

10% of sales Acrylic – but play an essential part on many sites in IWT, treating waters with high either **high temporary hardness** or with **significant organic loading**.

Synthetic Resin Production

There are many aspects involved in producing ion exchange resins, but it can be split into main parts.

These are:

PART 1. Formation of the polymer bead.

PART 2. Converting the bead to an active an ion exchanger by attaching a suitable functional group.

Polymer Bead Production

Historically polymer bead production is by **suspension polymerisation in a stirred reactor**.

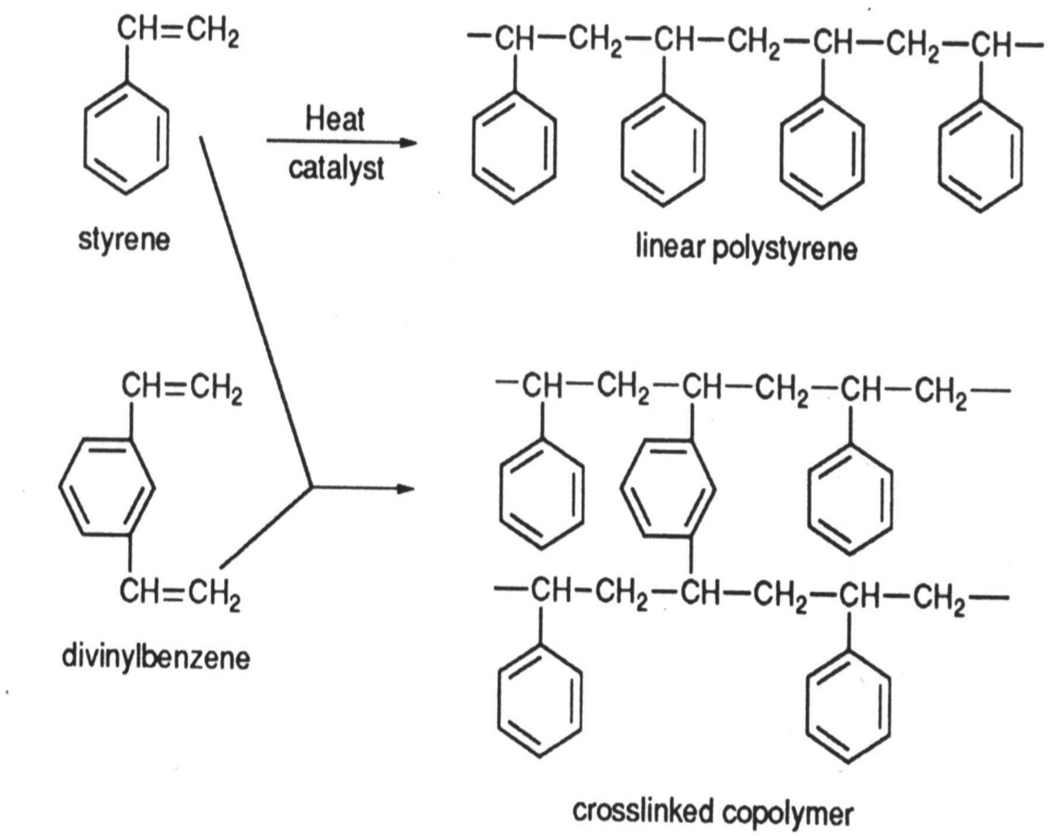
However**, new polymer production techniques** have been introduced by all the leading ion exchange producers for many of the "new generation of narrow grade resins.

In all cases a **cross linking agent** is introduced.

- Bead Formation
- Makes the resin insoluble in water even when the hydrophilic active groups are added.

Main X linking agent: **DVB**

Polystyrenic Resin Production



There are other chemicals:
Catalyst
Polymer aids
Protective Colloids
Etc.
However, they do not appear in the bead structure

Resin Structure

Common terms: Gel or Macroporous

Gel Resins

These are solid single phase **gel beads** and are **translucent (light will pass through them).**

Macroporous (Macroreticular) Resins

These resin beads are best described as like a **"Swiss Cheese".**

The holes / pores are produced by introducing a **porogen** which give the resin other improved characteristics for certain applications.

Beads are **opaque (light will not pass through them**)

Summary Slide 1 – You should have noted!

1. Synthetic resins used in IWT and oil is a major factor in production cost.
2. IWT Resins are made with Polystyrenic or Polyacrylic backbones.
3. Resins are cross linked with DVB and varying the DVB content affects performance.
4. Structure can be gel or macroporous.
5. Gel resins translucent (single gel phase).

   Macroporous resins, opaque (light scatters due to internal surfaces on pores)

Adjusting Resin Cross Linking

As you increase the DVB (X linking), the following characteristics are changed:

1. Bead becomes **stronger (crush strength).**
2. It allows more active sites to be introduced. **(Higher total capacity)**
3. It makes the **structure tighter** – less water content in the beads (**moisture content reduces**).
4. The beads become heavier **– higher S.G**.

We will return to this again later to see how this affects performance and range of products offered.

Introducing and Increasing Porosity

When you introduce and as you increase the porosity:

1. Increase the **elasticity** of the resin.

2. Increase in **surface area**.

3. **Improved the access** into the beads to the active sites.

4. **Reduced** breaking weight **strength** of beads.

5. Where there are holes there are no ion exchange sites **(less capacity unless you increase the DVB**).

Resin Grading – Standard grades

For standard batch production, when the beads are produced they are hard, inert, polymer beads which can be handled easily and we can now dry them and sieve them so that we can make standard or special grades for different applications.

All manufacturers produce **standard grade** resins.

300 – 1200 microns (i.e. 0.3 – 1.2 mm).
(Nominal <1% fines "outside of range" at the fine end and up to maximum of 5% at the coarse end.)

The inert polymer beads are much smaller but **swell when activated (as the active groups are hydrophilic)** water will then readily enter the beads.

Special Grading - Examples

High flow rates – less fine beads

Mixed Beds and Stratified Beds – good separation

Special Engineered Systems – trimmed at fine and coarse end.

NEW TREND – INCREASING USE OF:

Narrow /Uniform Beads

Increased use of packed bed designs in IWT for counter flow regeneration etc.

Product Rationalisation

Narrow Uniform Grade Resins

Now produced by all the leading suppliers to the UK:

Monosphere / Marathon / (Amberjet)	Dow (R&H)
Monoplus	Lanxess
Purofine / Puropack etc.	Purolite

Each company has there own special manufacturing techniques for producing these resins, minimising the waste copolymer produced.

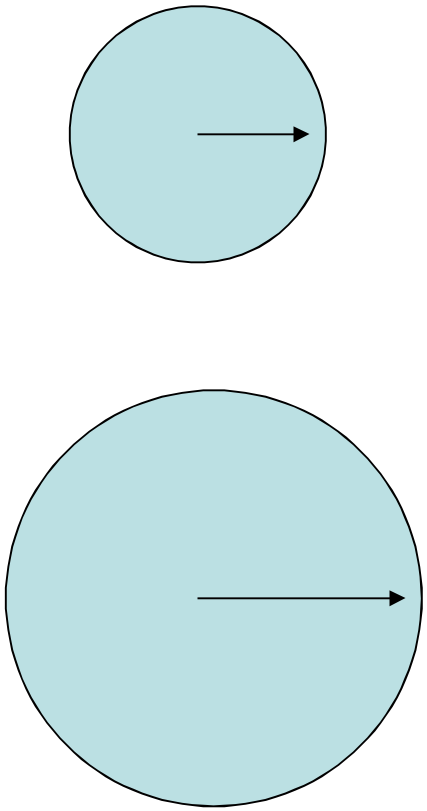
Other less well knwn UK suppliers also have a range of narrow grade uniform resin beads for IWT.

Narrow Uniform Grade Resins

Because of their more uniform size these resins offer certain advantages. The five principle advantages are as listed below:

1. Stronger beads.
2. Lower pressure.
3. Improved capacity or lower regenerant usage.
4. Reduced rinse volumes due to reduced diffusion paths.
5. Increased surface area – slower surface fouling.

Narrow Uniform Grade Resins



IWT narrow grade resins are typically found in the range of 400 – 800 microns

Some have a very low **uniformity coefficient i.e. 1.1**)

Standard grade resins 300 – 1200 microns.

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Narrow Uniform Grade Resins

The advantages in performance are dependent on:

1. The application.

2. The size of the ion (rate of diffusion on regeneration) being removed.

3. Regeneration Level (contact time).

HOWEVER, PLEASE REMEMBER – Improving cation resin performance by changing to narrow grade resins can give rise to other operating problems – your plant can become anion limiting.

Summary Slide 2 – You should have noted!

1. Resins made from Polystyrene or Acrylic
2. Resins can use varying % DVB (cross liking agent)
3. Structure can be gel or macroporous
4. Changing the X linking agent – affects performance.
5. Introducing or changing the porosity – affects performance.
6. Inert polymer beads can be graded for different applications of the final products to give “special cuts”.
7. Trend towards Narrow Grade Resins produced by special techniques and offering some improvement in performance.

REMEMBER – We still have not activated the resin into an ion exchanger. That is what we will look at next!

PART 2

Polymer Activation – Producing an Ion Exchanger

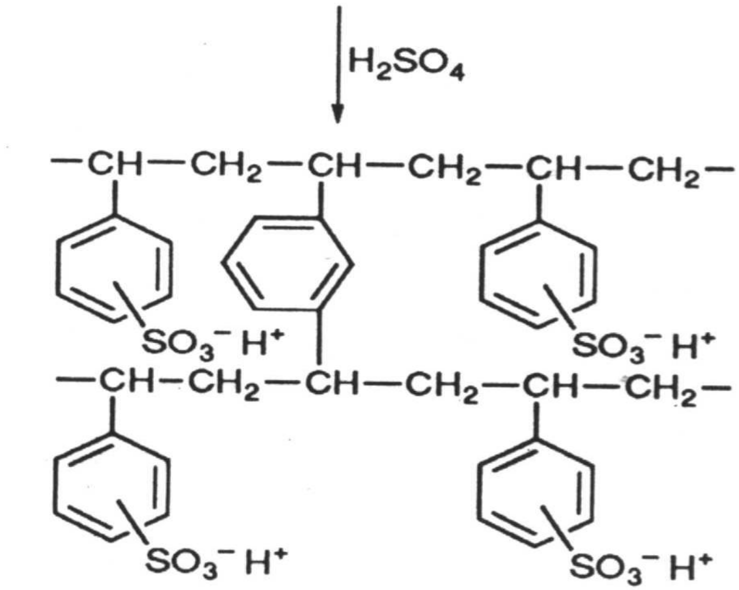
When activated their are four main types of ion exchangers in IWT Demineralisation:

1. Strong Acid Cation Resins
2. Strong Base Anion Resins
3. Weak Acid Cation Resins
4. Weak Base Anion Resins

Strong Acid Cation Resins – **All polystyrenic based**

Adding $SO_3^-H^+$ to allow H+ to exchange with cations in the water.

Colour of the resin determined by how you sulphonate the resin.



styrenic sulfonic acid resin

Na^+

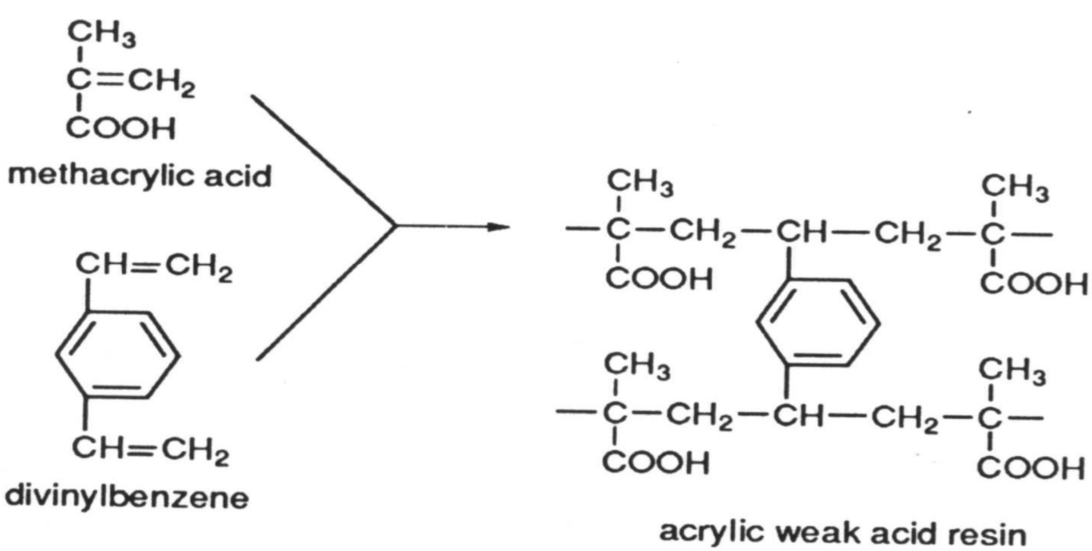
Cation Resin - **SO_3H^+**

Cation Resin - **SO_3Na^+ + H^+**

Weak Acid Cation Resins – **All polyacrylic based.**

Adding COO$^-$H$^+$ to allow H+ to exchange with cations in the water

Process: Carboxylic functionality (usually by hydrolysis of acrylate, methacrylate or arcylonitrile copolymers)



Ca^{2+}

$RCOOH^+$

$COOH^+$

2 x RCOOCa + 2H$^+$

Summary Slide 3 – You should have noted!

Strong Acid Cation Resins:

Relatively simple production technique from one relatively cheap type of polymer (polystyrenic) – hence SAC resins are relatively cheap. Active group **$SO_3^-H^+$**

Weak Acid Cation Resins:

More complicated production technique from one more expensive type of polymer (polyacrylic) – hence WAC resins are much more expensive. Active group **COO^-H^+**

Next: Anion activation – far more options / more complicated and hence anion resins are much more expensive.

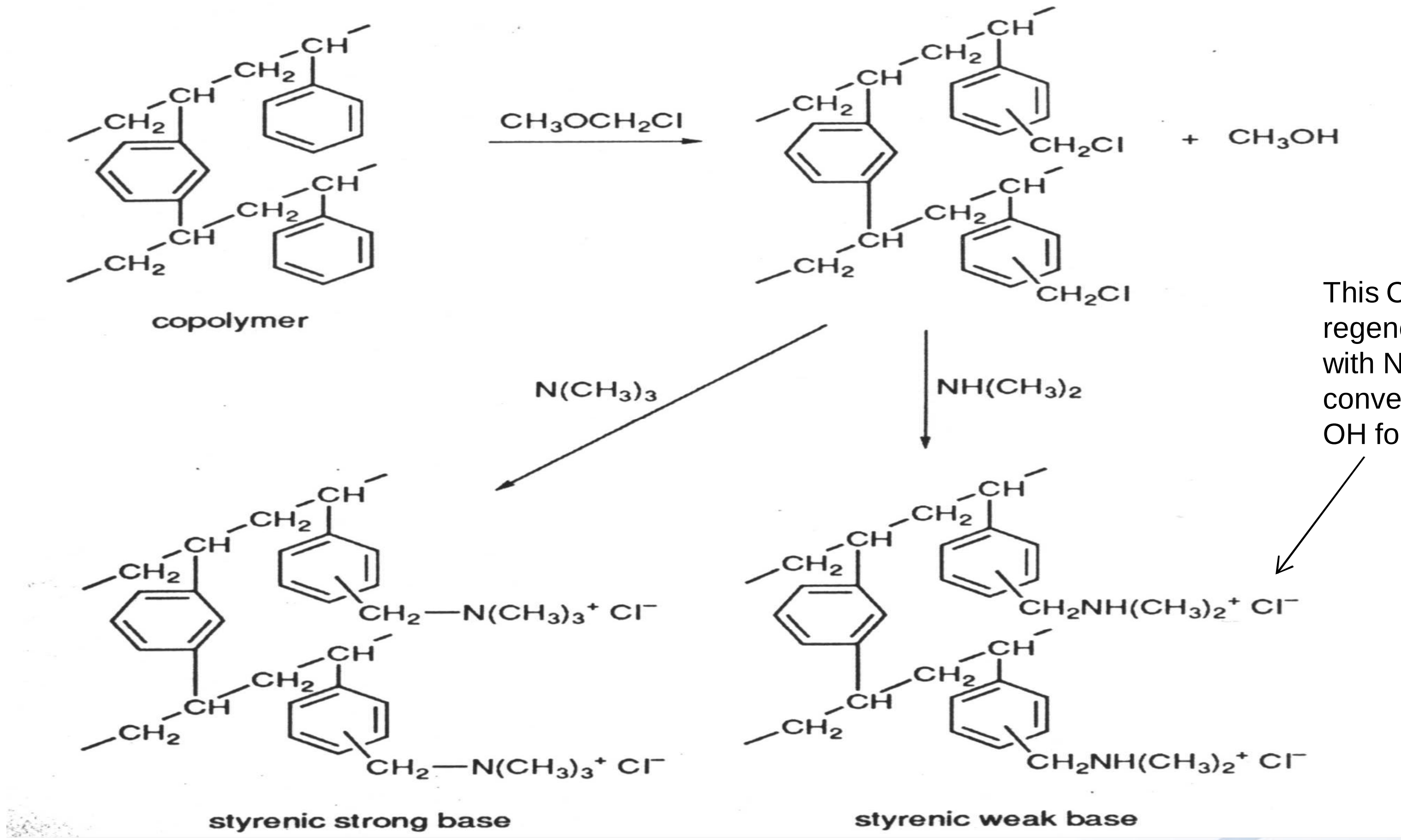
Anion Resins (Weak and Strong)

Anion resins can be **polystyrenic or polyacrylic.**

Process: Much more complicated. A **two stage process** comprising of chloromethylation and then amination.

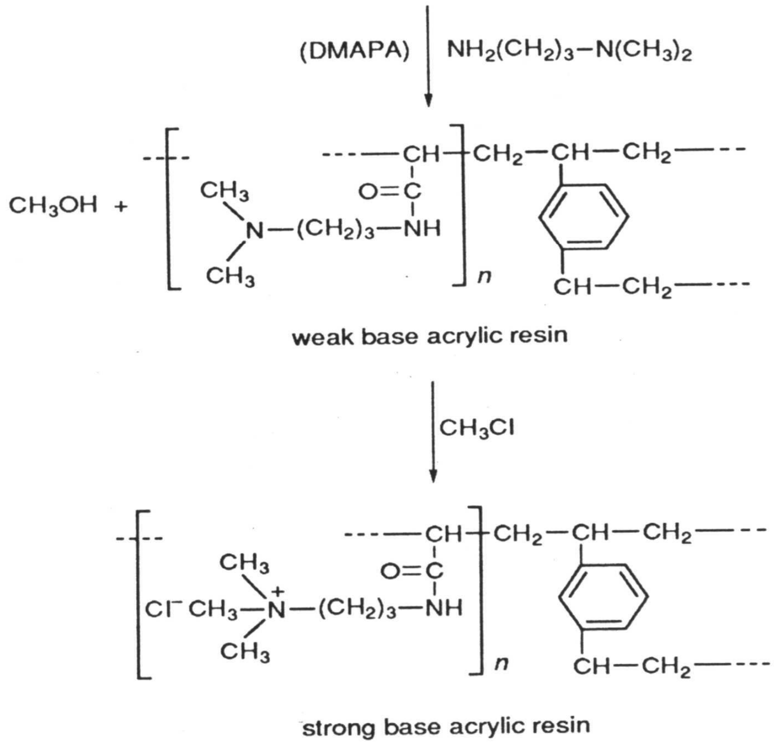
Chloromethylation	Putting a **handle on to the resin matrix** to attach the amine active group. Some secondary cross linking occurs.
Amination	**Anion active group** added. The resin can be weak base or strong base depending on the amine applied.

Example: Chloromethylation and Amination of polystyrenic anion resin to SBA & WBA



This Cl site is regenerated with NaOH and converted to OH form.

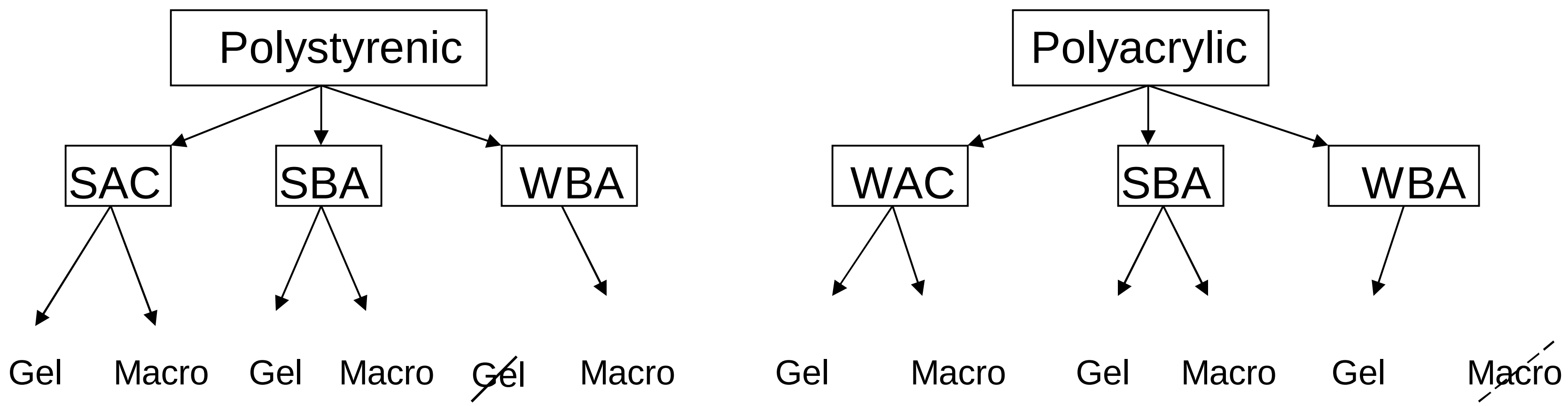
Example: Amination of polyacrylic anion to WBA then SBA



Summary Slide 4 – Synthetic Ion Exchange Resin Options (IWT – Demineralisation)

Note* 1. The gel polystyrenic weak base resin is not manufactured.

2. The macroporous weak base acrylic is made but not normally encountered in IWT – Demineralisation.



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Strong Acid Cation Resins – How do they vary?

Resin manufacturers brochure have long list of SAC resins.

Main characteristics are:

1. Total capacity
2. Moisture content
3. Structure
4. Specific Gravity

You will notice as the total capacity increases the moisture content decreases and specific gravity increases. This is brought about by changes in the DVB content.

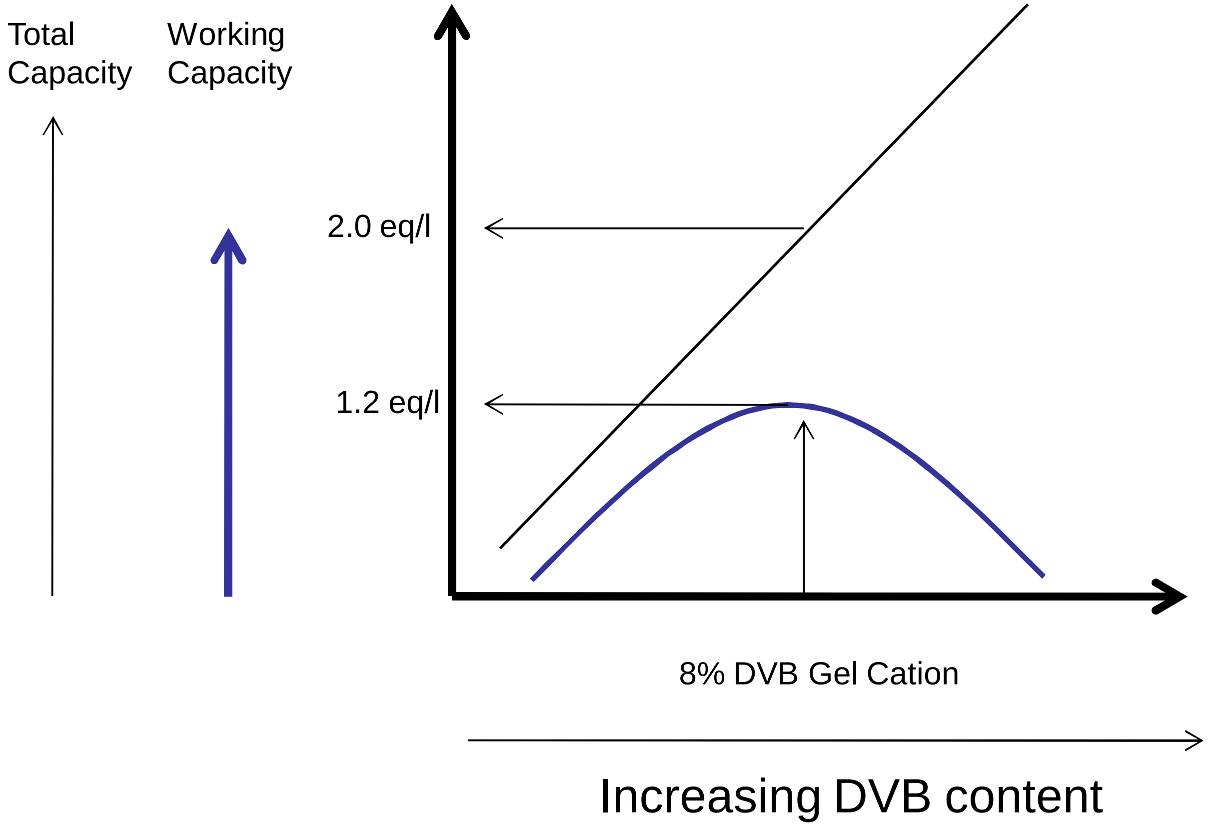
- Do you remember an earlier slide (slide 17) – well done!

Strong Acid Cation Resins – How do they vary?

So as the DVB X linking increases:

1. More total capacity – higher activity
2. Physically stronger bead
3. Lower moisture content (tighter structure)
4. Beads are heavier (more dense)

So to make a strong resin with the highest activity and to get the resin with the best performance for your plant you should install a high DVB, high total capacity resin - **WRONG**



<u>Graph showing variation in DVB content with Total Capacity / Working Capacity for a given HCl regen level</u>

Strong Acid Cation Resins – How do they vary?

In addition to having gel and macroporous versions, as you increase the DVB / Total Capacity of the resin the structure becomes so tight you affect the kinetic performance and the regenerability of the resins.

8% DVB gel cation resin gives you the optimum performance in cation unit IWT demineralisation

1. Highest Working Capacity
2. Best Kinetic Performance
3. Good Regenerability

<u>Weak Acid Cation Resins</u> – How do they vary

The weak acid cation resins vary much less. In real terms in today's modern demineralisation plants you tend to come across the same types of WAC resin from all the manufacturers.

They are all acrylic WAC and are either gel or macroporous and because WAC resins are used widely in the soft drinks / brewing / drinking water filter markets food grade versions are more common.

The trend to mainly producing macroporous WAC resins is due to volume changes encountered between regenerated and exhausted forms.

Anion Resins – How do they vary?

You can change the DVB content, you can have gel or macroporous versions, but the main difference in anion resins is determined by the amine used to activate the resin.

A quaternary amine will give strong base activity, but you can vary the temperature resistance, silica leakage and working capacity of the resin depending on the quaternary amine used.

A tertiary amine will give weak base activity and other amines both primary and secondary amines are found on certain weak base resins.

Anion Resins – How do they vary?

The main anion active group options:

Strong base resins employ a quaternary ammonium groups.

Polystyrenic Strong base type 1 resins use (TMA)

Polystyrenic Strong base type 2 resins use (DMEA)

Polyacrylic Strong base resins uses a more complicated route by forming the weak base anion first which is then converted to the strong base to give a type 1 functionality.

Weak base employ a tertiary amino groups

Weak base polystyrenic resins predominantly use (DMA)

Weak base polyacrylic resins employ (DMPA)

Summary Slide 5 – Synthetic Ion Exchange Resin Options (IWT – Demineralisation)

Note* 1. The gel polystyrenic weak base resin is not manufactured.

2. The macroporous weak base acrylic is made but not normally encountered in IWT – Demineralisation.

3. This slide does not show all grading options.