

Introduction

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1.1 Demineralization of Water Using Ion Exchange Resins – Ion Exchange Phenomena

Natural water contains dissolved salts, which dissociate in water to form charged particles called ions. These ions are usually present in relatively low concentrations. The presence of some of these ions leads to problems for applications such as in heating systems, steam generation etc. and hence are termed as ionic impurities. The commonly encountered ions in water include the positively charged Cations, namely Calcium, Magnesium and Sodium. The negatively charged anions include the alkalinity, sulfates, chlorides and Silica.

Ion Exchange resins are well suited for removal of these impurities for the following reasons:

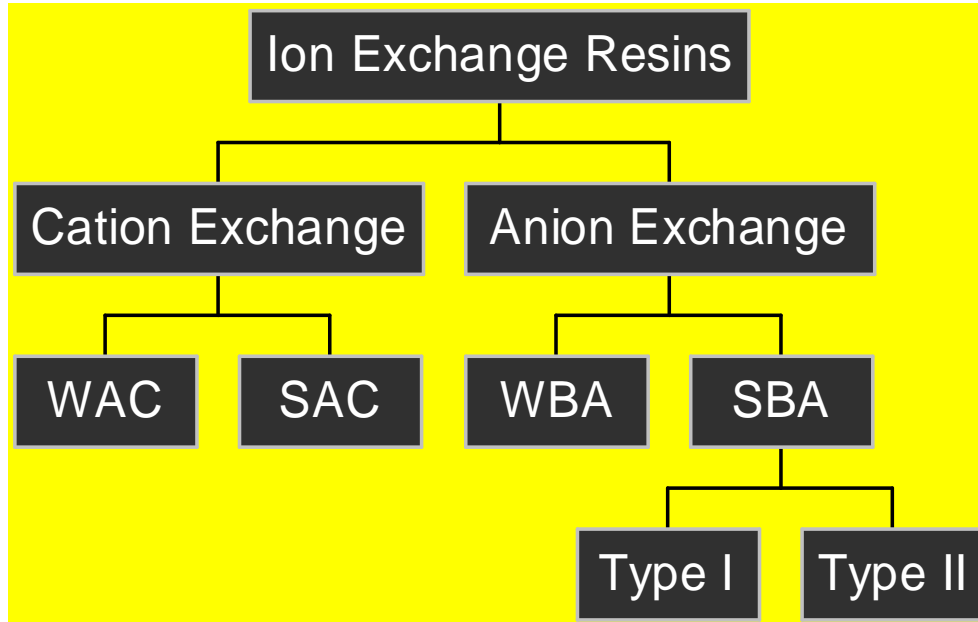
1. Resins have a very high capacity to remove ions in low concentrations.
2. Resins are most stable and can be readily regenerated.
3. Resins are stable over a wide range of temperatures.
4. The process is suitable for both large and small installations.
5. The process is reversible.

Ion Exchange Resins are generally insoluble polymeric materials manufactured using suspension polymerisation using Styrene and Divinylbenzene (DVB) that carry ion exchangeable functional groups.

These ions can be exchanged with stoichiometrically equivalent amount of ions of the same sign. Carriers of exchangeable Cations are called **Cation exchangers** and that for anions are called **Anion exchangers**.



1.2 Types of ion Exchange resins



Different types of Ion Exchange Resins

Cation Exchange Resin

◆ Strong Acid Cation (SAC)

- ◆ Poly styrene based resins with sulfonic Acid Group ($-\text{SO}_3\text{H}$) as functional group
- ◆ Can exchange all the cations.
(Eg. SAC in H form can remove Na ion from a solution containing NaCl as well as NaHCO_3)

◆ Weak Acid Cation (WAC)

- ◆ Acrylic Base Resins with carboxylic acid group ($-\text{COOH}$) as functional group.
- ◆ Regeneration very efficient, almost stoichiometric.
- ◆ These resins can be used effectively in conjunction with SAC.
- ◆ Can remove hardness associated with alkalinity only.

(E.g. WAC in H form can remove Na ions associated with bicarbonate ions but not with Cl ions from a solution that contains both NaCl as well as NaHCO_3)



Anion Exchange Resin:

◆ Strong Base anions

- ◆ Will remove All Anions from water
- ◆ Strong Base Anion Exchange Resins can be categorized as Type I or Type II depending on the nature of the functional groups / type of amine used during the chemical activation process.

◆ Type I

- Quaternary Ammonium Functional Group. Chemically it has three methyl groups.
- Functional group with the highest basicity amongst commonly used anion resins.
- Used when very low silica levels are desired (< 0.2 ppm)
- Requires excess of regenerant than type II SBA resins

◆ Type II

- ◆ Quaternary Ammonium Functional Group. Chemically one of the methyl groups of type-I is replaced with ethanol group.
- ◆ Less Basic Functional Group as compared to Type I
- ◆ Higher Silica Leakage Compared to Type I (< 0.5 ppm) Easier to Regenerate.

◆ Weak Base

- ◆ Tertiary Amine Functional Group.
- ◆ Much Lower basicity compared to SBA
- ◆ Will remove anions associated with free mineral acidity (e.g. Cl, sulfate from solution of respective mineral acids).
- ◆ Cannot remove anions associated with weak acids (carbonic, silicic acids).
- ◆ Can be regenerated with stoichiometric quantities of regenerant.



- ◆ The regeneration process is essentially a neutralization of the strong acids that are collected on the resin and hence the waste caustic from the SBA can be utilized for enhance economics.
- ◆ Will not remove silica from water

1.3 Applications of Ion Exchange Reins

Based on the desired quality of water required, the resins are selected. The selected resins based on the selected scheme are then filled in vessels. The broad applications are described as follows:

- a. Water Softening
- b. Dealkalization or Partial Demineralization
- c. Demineralization (with or without silica removal)
- d. Mixed Bed
- e. Other Application in water
 - ◆ Nitrate, Fluoride Removal
 - ◆ Heavy Metal Removal
 - ◆ Organic/Tannin/color Removal
 - ◆ Process applications.
 - ◆ Pharmaceuticals
 - ◆ Food & Beverages
 - ◆ Textile recycling colour removal.
 - ◆ Power plants.
 - ◆ Nuclear power plants
 - ◆ Catalyst in certain processes.
 - ◆ Precious metal recovery.

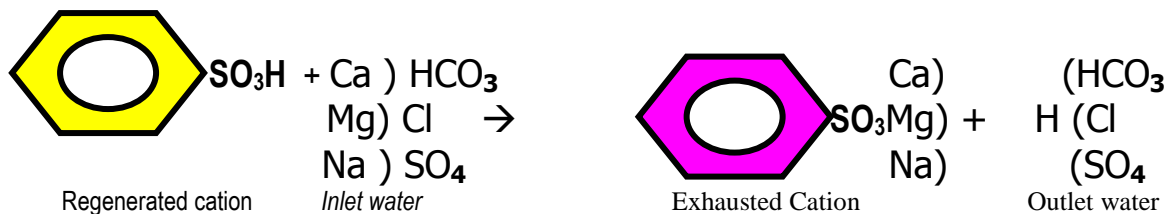


1.4 Reactions involved in the demineralization of water using ion exchange resins

Water Demineralization:

- ◆ Strong Acid Cation Exchanger to remove Cation

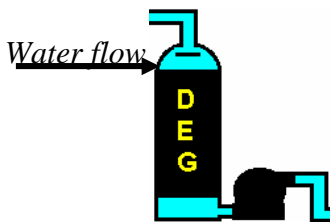
CATION SERVICE CYCLE



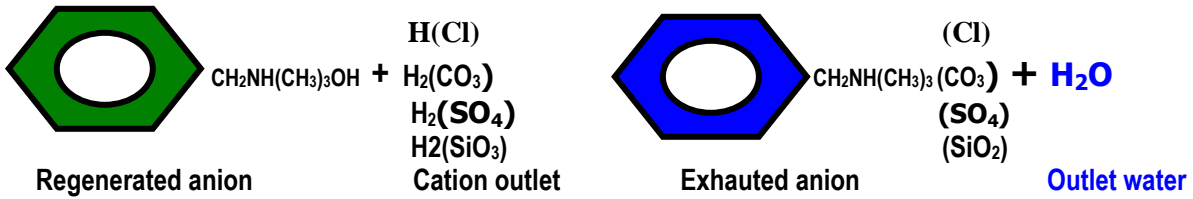
REGENERATION



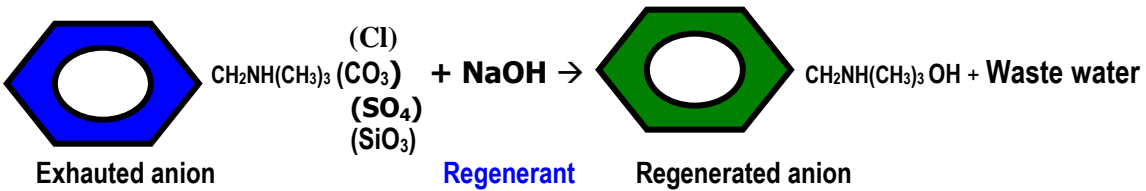
- ◆ Degasser to Remove Carbonic Acid



ANION SERVICE CYCLE



REGENERATION



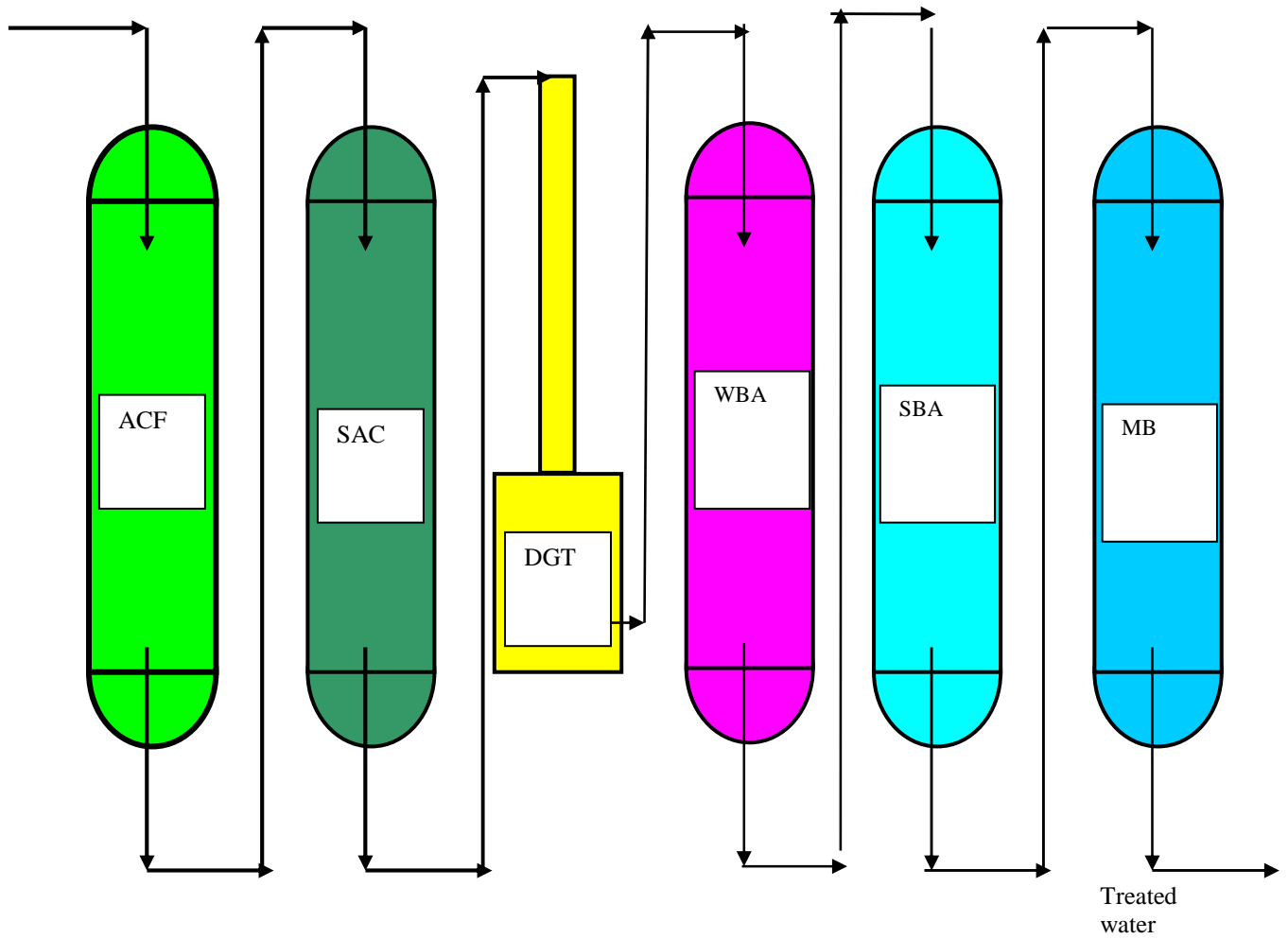
Mixed bed Polishing



- ◆ Employed when very high water quality is desired
- ◆ Intimate mixture of SAC in H form and SBA in OH form is used
- ◆ Typically SBA outlet is passed through Mixed Bed to further improve the water Quality
- ◆ Treated water quantity
 - conductivity less than 1 micro seimens/cm²
 - pH – 6.8 to 7.2
 - Silica Leakage <0.02 ppm.
- ◆ For the purpose of regeneration resin is separated by backwash, regenerated separately with 5% HCL and 5% NaOH and mixed after washing.



1.5 Typical Scheme of DM plant.



1.6 Methodology used for Ion Exchange resin analysis:

1) Total Exchange capacity (TEC): TEC Is the Quantitative indication of how many ions can be exchanged by the resin. Total Exchange Capacity is expressed as meq/ml or equivalents/liters.e.g. For TulsionT-42 Na, exchange capacity of 1.8 meq/ml means that for every 1 ml of resin there are 1.8 milli equivalents of exchange sites available. TEC is expressed per unit volume of the resin.

2) Moisture: Moisture content of the resin is of two types; namely surface moisture and bound moisture. While surface moisture can be removed by centrifuge, bound moisture is a specific property of the resin and can be removed only by drying at higher temperature. Generally the moisture specified in resin products refers to this bound moisture. The moisture content of the resin depends on the degree of cross-linking of the resins. Moisture content is measured as percentage of water per unit weight of wet resin. For a given resin moisture content will vary as the ionic form of the resin changes. (E.g. Na and H form of Tulsion T-42 have different moisture content). Increase in Moisture content of a used resin will be an indicator of de-cross linking of the matrix.

3) Bead Strength (BS): This is an important property from application point of view as it is directly related to the life of the Resin. It mainly depends on crosslinking structure (Gel /Macroporous) of resin. BS gives stability and gets affected by temperature – different resins have different temperature stability – shown in our Literatures. BS gives resistance to osmotic shock and this happens when resin changes its ionic form as it undergoes shrinking and swelling. This can cause physical degradation of the polymer matrix. BS also gives an indication of the De-cross linking of the resin. Due to temperature and presence of strong Oxidizing agents which leads to Loss of ionic Groups that is Chemical Degradation of ionic groups.

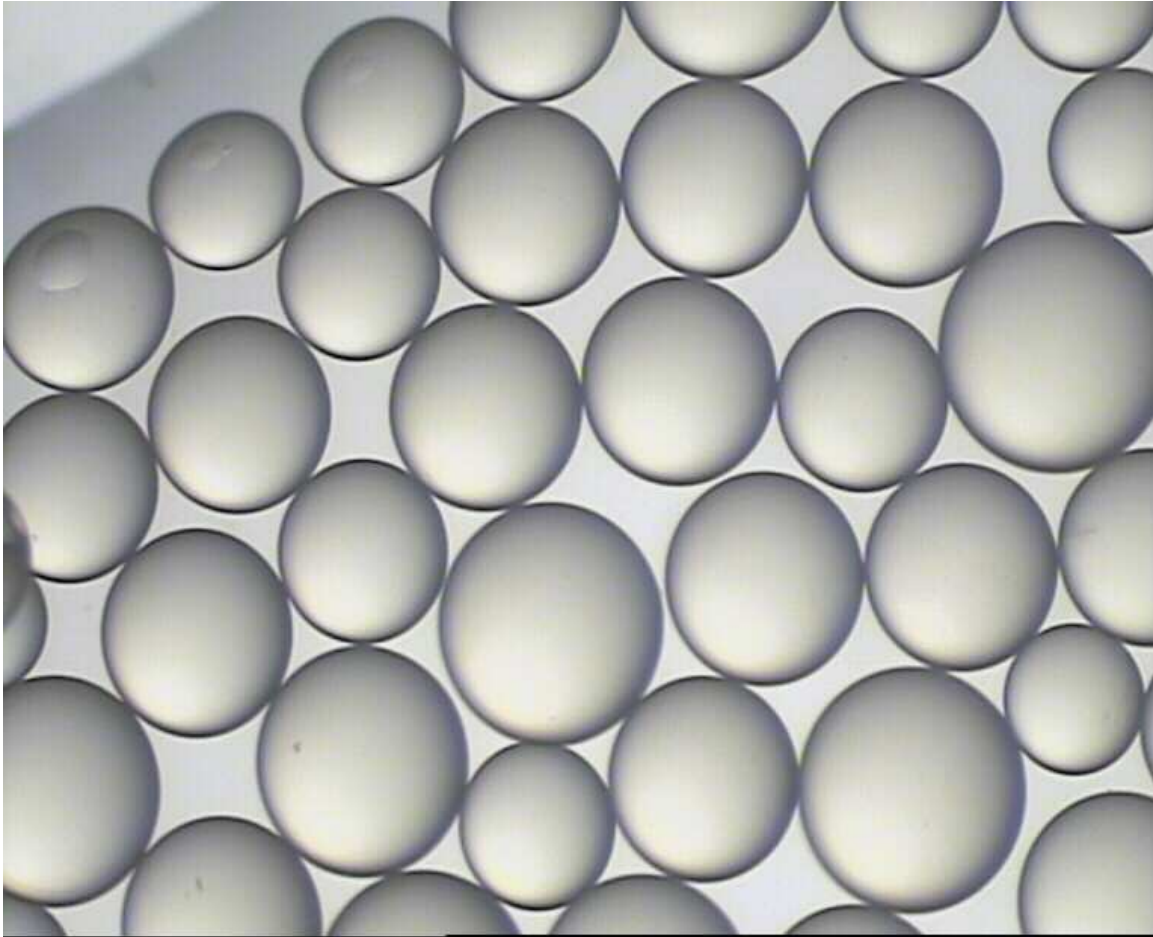


4) Fine contents: Particle Size of the Ion Exchange Beads determines the kinetics (speed of exchange) as well as pressure drop. Finer the particle size, faster is the kinetics, but higher is the pressure drop. Industrially Relevant Particle Size is a compromise between these two factors. It is not practical to have all the beads of exactly the same size. Particle size distribution is measured by sieving the materials through sieves of different openings. In water treatment, resins with a normal distribution from 0.3 mm (50 US mesh) to 1.2 mm (16 US Mesh) size beads are used. Effective Size of beads is sieve opening in mm on which 90% of the beads are retained. Uniformity Coefficient is the ratio of sieve opening in mm on which 40% of the sample is retained to the sieve opening in mm on which 90% of the sample is retained. Range refers to majority of the material and not 100%. (E.g. a particle size range of 0.3 to 1.2 mm denotes to majority of material (say >95%) in this range)

Fines content refers to percentage of material passing through the smallest of the specified sieve, namely 0.3 mm in above case. Excess fines creates problem in resin operation. The oversize resins than the specified range are termed as coarser resins.



An Example of Ion Exchange Resin Microscopic Image:-



*Reference Image : Cation in good condition when observed under high resolution
Microscope*

