ROLE OF WEAK ACID CATION RESIN IN WATER TREATMENT

by
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Weak acid cation (WAC) resin plays an important role in water treatment. It is usually manufactured from acrylic acid and divinyl benzene (DVB) as a crosslinking agent, although some manufacturers make it from methacrylic acid or its derivatives. It is widely used unit in a demineralisation plants for dealkalisation of water. The total capacity of WAC resin at 210 g/l as $CaCO_3$ is higher than other ion exchange resins. The resin is regenerated with dilute acid using near stoichiometric quantity. Hence, the waste water generated during regeneration is almost neutral. WAC resin operates in a alkaline pH range and exhibits large volume change when converted to different forms. Hence, it is called the workhorse of water treatment processes.

Introduction

Ion exchange processes (softening, dealkalisation or demineralisation of water) involve the use of synthetics ion exchange resins – co-polymers of divinyl benzene and styrene with functional groups attached to them. The process itself is reversible and the ion exchange resins can be used over and over again, making the process most economical.

Ion exchange resins are classified into strong and weak acid cation or strong and weak base anion exchange resins depending on the functional groups present in the resin. The functional group present in a strong acid cation(SAC) resin, for example, carboxylic acid (COOH) group.

Water contains both alkaline salts (carbonates, bicarbonates of calcium, magnesium and sodium) and neutral salts (chlorides, sulphates and nitrates of calcium and magnesium and sodium). Demineralisation of water, therefore, involves the use of at least two types of resin - SAC resin that exchanges cations present in the water with the hydrogen ions, and a weak or strong base resin that exchanges the anions with hydroxyl ions. In ion exchange parlance we say that the SAC resin *splits* both the alkaline and neutral salts into acids which are then absorbed by the anion resin.

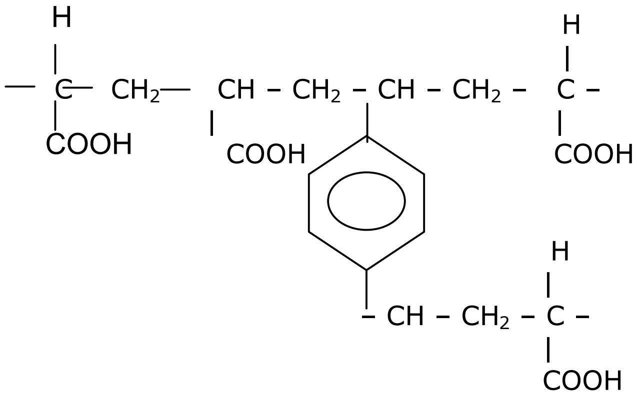
Weak acid (or weak base) resins are relatively more efficiently regenerated than their strong acid or strong base counterparts. It is possible to improve the efficiency of the process by using a combination of resins - a weak acid cation resin followed by a strong acid resin and a weak base resin followed by a strong base resin. The net result is reduced cost of producing demineralised water.

This article attempts to bring out the role played by a WAC resin in water treatment.

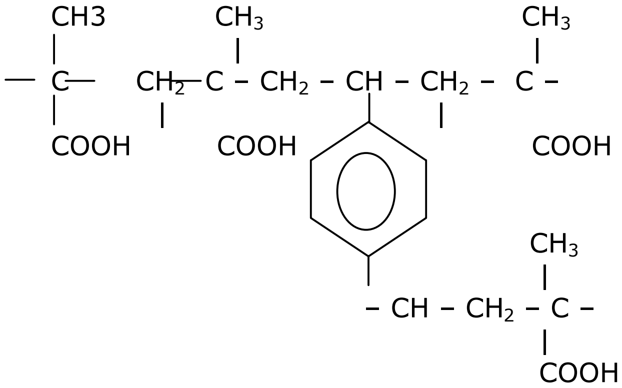
Manufacture of WAC resin

WAC resins are manufactured by co-polymerisation of acrylic acid with DVB as a cross linking agent. Sometimes, methacrylic acid or its derivates are used in place of acrylic acid. Hence, the acid strength of WAC resin differs depending on the raw materials used in its manufacture.

Structure of WAC resin from cross-linked acrylic acid

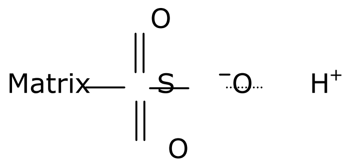


Structure of WAC resin from cross linked methacrylic acid



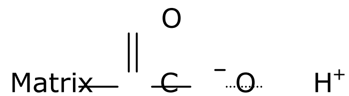
Selectivity and kinetics of WAC resin
In the ion exchange process, the exchange of ions depends on the functional groups. The functional group of SAC and WAC resins are as below:

Strong Acid Cation (SAC)



(Sulphonic acid group)

Weak Acid Cation (WAC)



(Carboxylic acid group)

In the case of SAC resin, the sulphur atom is highly electro-negative and therefore attracts the electrons from the oxygen atom, which in turn attracts electrons from the hydrogen atom making it more electro-positive. This property enables the resin to behave like a strong acid. It is therefore capable of splitting both types of salts - alkaline as well as neutral. Kinetics of the resin is film diffusion controlled. In other words, its ion exchange capacity is independent of exhaustion time.

In the case of a WAC resin, however, the carbon atom is relatively less electro negative and hence there is relatively less flow of electrons from the hydrogen atom, making it behave like a weak acid. While it is capable of splitting alkaline salts, it has no action on neutral salts.

$$2RCOOH + Ca(HCO_3)_2 \rightarrow (RCOO)_2Ca + 2CO_2 + 2H_2O$$

The resin , however, when converted into sodium form can remove Ca, Mg and heavy metals as shown below:

$2RCOONa + CaSO_4 \rightarrow (RCOO)_2Ca + Na_2SO_4$
$2RCOONa + PbSO_4 \rightarrow (RCOO)_2Pb + Na_2SO_4$
Where R is Resin Matrix

The WAC resin has the highest affinity for hydrogen than trivalent, divalent and monovalent ions. Therefore, the regeneration of WAC resin can be completed by using slight excess quantity of acid. Low concentration can be used for the regeneration. In other words, even spent acid from downstream SAC unit can also be used to regenerate the resin.

SAC resin has higher affinity for trivalent, bivalent and monovalent ions. The affinity for hydrogen is lower than other monovalent ions. Hence, a large quantity of acid is required to regenerate the resin. In order to elute trivalent cations from SAC resin, a higher concentration of acid is required. These are the major differences between WAC and SAC resin.

While resins made from acrylic acid take up sodium from sodium bicarbonate solution, those made from methacrylic acid will not be able to do so. Hence, in water containing a mixture of bicarbonates, resin made from acrylic acid will remove calcium and magnesium initially and then remove sodium as well, while the resin made from methacrylic acid based resin will remove only calcium and magnesium bicarbonate.

WAC resins are available in gel and macroporous structures. WAC resins undergo maximum volume change from hydrogen to sodium form and vice versa for both gel and macroporous resin. This puts a lot of pressure on the macroporous structure. Gel and macroporous resins have almost equal and high capacity per unit volume.

Advantages of WAC resin

There are certain advantages of WAC resins on account of their relatively low acidity:

- WAC resin can be regenerated to its total capacity by using a slight excess of acid over the theoretical requirement. Therefore, the waste water generated at the time of regeneration is almost neutral.

- Even a weak acid such as carbonic acid may be used to regenerate a WAC resin.

- WAC resin has little utility in acid media. It exhibits high capacities (and regeneration efficiencies) for treating electrolytes of alkaline nature such as cation (Ca^{++} and Mg^{++}) and trivalent cations (Cr^{+++} and Fe^{+++}) when operated in neutral or slightly basic media. These cations can be easily eluted by using any acid for regeneration which may not be possible for SAC resins.

Disadvantages of WAC resins

The major disadvantages of the WAC resin are:

- WAC resin is effective in operating pH of neutral and basic media only.
- The kinetics of WAC resin are inferior to those of SAC resins.
- WAC resin exhibits marked degree of volume expansion when converted from hydrogen form to sodium form. The swelling is almost 100%.

$$RCOOH + NaOH \rightarrow RCOONa + H_2O$$

This volume change must be considered at the time designing the WAC unit to accommodate such volume change on exhaustion of WAZ bed/resin.

Applications

The applications of WAC resin in water treatment include:

- Removal of alkalinity from water - the process is called dealkalisation.
- Treatment of water containing a high proportion of alkaline salts in relation to neutral salts - the weak and strong acid resins can be used either in separate vessels or in the same vessel (layered bed).
- Softening of water containing high salinity (e.g. softening of sea water)
- Removal of heavy metals from water/waste water.

Dealkalisation: WAC resins can be used for removal of alkalinity from water

1. Low/medium pressure boiler feed water: High alkalinity in boiler feed waters may necessitate a high blowdown from the boilers. Dealkalisation not only removes alkalinity but also reduces dissolved solids by removing cations associated with alkalinity. This will bring down the blowdown requirement of these boilers.

2. Manufacture of beverages: Most concentrates used in the manufacture of beverages are acidic and hence water used in manufacture of the beverages must be low in alkalinity (typically less than 50 mg/l). Dealkalisation can be used to remove the excess alkalinity present in water.

3. Dealkalisation can be used in place of acid addition for removal of alkalinity from cooling tower makeup.
   $2\ R\text{-}COOH + 2Ca(HCO_3)_2 \rightarrow (RCOO)_2Ca + 2H_2O + 2CO_2$

After exhaustion, it is regenerated with acid
$2RCOOCa + 2\ HCl \rightarrow 2RCOOH + 2CaCl_2$

The alkalinity removal of WAC depends on total hardness to alkalinity ratio and flow rate. The weak acid cation exchange resins are preferably used when hardness to alkalinity ratio is >60%. When this ratio is 100%, maximum capacity is obtained. The exhaustion cycle is operated up to an end point of 30 ppm alkalinity as $CaCO_3$ in the treated water. The current practice is to terminate the unit service cycle at a hardness breakthrough of 5 ppm $CaCO_3$. Usually a degasser is installed downstream of the WAC to remove free carbon dioxide.

The regeneration of the resin is completed using hydrochloric acid or sulphuric acid. When sulphuric acid is used care should be taken to avoid the precipitation of calcium sulphate in the resin bed. This is achieved by using sulphuric acid concentration in the range of 0.8 to 1% maximum.

However, by use of stage-wise regeneration i.e using a low concentration acid such as 0.5% to 1% followed by a higher concentration of acid 2 - 3% at a relatively high flow rate, it is possible to reliably use sulphuric acid to avoid undesirable precipitation of calcium sulphate on the resin bed.

Hydrochloric acid is used routinely for the regeneration of WAC at a concentration of 4% to 5%. The waste water produced during regeneration contains calcium chloride, which is highly soluble and there is no danger of precipitation.

WAC in layered bed cation: as we have seen above, WAC removes alkalinity associated with hardness efficiently. If this is combined with SAC resin, complete decationisation can be achieved very efficiently by using WAC and SAC in a single bed termed *layered bed* cation. Due to the density difference in the two resins, WAC resin remains on the top of the SAC resin. The water is passed at the time of treatment from top to bottom and regeneration is carried out in countercurrent mode using either a water hold down system or an air hold down system. There are number of installations in India where the layer bed cation has been used successfully. The combined resins give high efficiency and generate almost neutral effluent during the regeneration. It is economical as one column is used instead of two. Additionally, a lower pump head is required to pump water through a single unit.

Softening: More recently, WAC resins are operated in the form of sodium for softening saline water. Owing to the salinity of some of the waters, sulphonic acid magnesium. For water having salinity >10000 ppm, SAC exchangers are ineffective. It has been observed that the WAC resin can be used for this application upto the salt concentration of at least 100000 ppm. However, the WAC resin cannot be regenerated with brine solution but needs to be regenerated first by acid and then sodium hydroxide. This can be illustrated by the following equation.

Service:

$$2\,RCOONa + CaSO_4 \longrightarrow (RCOO)_2Ca + Na_2SO_4$$

Regeneration

a) Conversion to hydrogen form: $(RCOO)_2Ca + 2HCl \rightarrow 2RCOOH + CaCl_2$

b) Conversion to sodium form $RCOOH + NaOH \longrightarrow RCOONa + H_2O$

Heavy metal removal from water: The WAC resin does not split the neutral salt in hydrogen form but splits the salts in sodium form. This has been used in an application for the removal of heavy metals from water and waste water. Most laboratories generating effluent containing heavy metals can benefit from the use of WAC resin for removal of the heavy metals from the effluent.

The unit containing sufficient quantity of WAC is fitted at the outlet of waste water where heavy metals need to be removed. WAC resins remove all the heavy metals without changing the waste water composition except for the contaminants removed.

Operating tips for WAC plants

1. WAC resin is effective for feed water pH upto 8.5. If feed water pH is > 8.5, then the hydroxide alkalinity reacts with calcium ions adsorbed on the resin bed and calcium hydroxide and carbonates precipitate on the resin bed. The feed water pH should not be on the acidic side as that would make exchange of ions ineffective.

2. In ion exchange treatment, the minimum bed height of resin is an important factor. If the bed depth is < 0.75 m, there is possibility of higher ionic leakage in the treated water which will affect the water quality. Since WAC has a lower reaction rate, a minimum bed depth of 0.75 m is maintained in all the water treatment units. This is also the reason why the exhaustion cycle for WAC resin is always higher, normally 10 - 20 hours. Lower flow rates and higher bed depths are preferred.

Sometimes this leads ineffective regeneration of the resin in the bottom part of the bed and to hardness slippage in the initial stage of the service cycle. To avoid this, the resin bed is soaked at the time of regeneration in acid for 10 – 20 minutes. During the soaking operation, the acid gets time to reach the bottom portion of the bed which helps to improve the ion leakage at initial stages of the run. After acid injection, the resin bed is slow rinsed and then fast rinsed to obtain the desired treated water quality.

Conclusion

The features and lesser known applications discussed in this article will help to derive the maximum benefits from the use of weak acid cation resins.

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