Enhancing the performance of Ion Exchange Resins in DM plants

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Introduction

Water needs to be treated to make it more acceptable for a desired end-use viz. human consumption, industrial processes or even to allow discharge into the environment without adverse ecological impact. The treatment processes includes physical, chemical and biological treatments. The choice of one or a combination of treatments depends on the nature of water to be treated and its end use. Industry uses water, as a raw material in boilers, in process applications, cooling water treatment, plant wash down and also for sanitary uses. All the applications needs specific water treatment protocols. Especially, the water used for steam generation needs to be treated very specifically, which includes demineralization of the water. Ion exchange method is normally practiced for demineralization The advantages of ion exchange method over other methods resulted in their wide acceptance in utilizing the ion exchange resins for water demineralization and softening. In demineralization process cations and anions are replaced by a cation and anion exchange resins respectively. Almost all industries use boilers and hence, DM plant based on ion exchange process is one of the prerequisites of the essential utilities for an industry. DM plant failure causes substantial loss as it leads to process break down, which is unacceptable.

The design and operating parameters of a DM plant are based on the quality of water to be treated and also the quality of water required for the boiler operation. Thus, the ion exchange process is carried out in a carefully designed DM plant which operates on recommended operating conditions. Any deviation in plant operation may lead to undesired results viz, less out put capacity, unwanted water quality etc. Despite the operation of the DM plant as per the design parameters, there are some other causes which may fail to the deliver the required results. One of the primary reason for such failure is the deterioration of the ion exchange resins used in the DM plant. Slow deterioration of ion exchange resin is a natural phenomena and therefore, every DM plant resin is having a definite life span. The life of a cation and anion exchange resins are normally five and three years respectively. Besides the natural deterioration, there are some other causes that deteriorate the performance of ion exchange resin. It may be a temporary or a permanent cause. When the resin performance is restored with a chemical or physical treatment, it is called as temporary cause. A permanent cause leads to an un-repairable damage to the resin. The cost of damage due to permanent failure can be calculated clearly. But the cost due to due to temporary failure can not be estimated directly. But it has got a definite impact, sometimes more than the permanent failure, on the over all process cost. The resin failure can be classified into three broad categories, viz., physical, chemical and biological. Understanding each of them is necessary to eliminate their ill effects besides prevent their recurrence.

Therefore, it is essential to operate DM plant efficiently with out any break down. The aim of the present article is to address the failures and suggestions to prevent such failures in any DM plant so that their performance can be maintained and even extended.

Physical failures

This occurs mainly due to improper pretreatment and deviation from the designed plant operating conditions. The important physical failures need to be addressed are physical loss, contamination, dehydration, attrition, depositions and oil fouling.

1. Physical loss

This is the actual loss of resin from the vessel. Such physical loss occurs due to improper back wash and/or strainer failure. During service cycle foreign materials like clay particles gets accumulate in the top layer of the resin bed. After completion of service cycle resin needs to be backwashed to remove such accumulated foreign materials. Backwash should be done at the recommended flow rate. If backwashed at high flow rates, over-fluidization of resin bed occurs. Subsequently, it results in resin loss. Therefore, always backwash the resin with the recommended flow rate. The back was flow rate is inversely proportional to the water temperature. Therefore, selection of back wash flow rate is very critical where the water temperature various significantly with respect seasons. The service provider will help in determining the backwash flow rate related to temperature.

Strainers are placed at the top and bottom of the DM vessel to arrest the loss of resin media. The strainers do fail and in such instances resin beads are carried away with the water. The resin loss occurs slowly but lead to considerable resin loss on continuous operation. Loss of resin by strainer failure creates more problem as this resin may enter in the preceding unit which results in cross contaminating the resin or any other media in that vessel. These cause direct resin loss and hence classified as permanent failure. Periodic inspection of the strainer plates is helpful in reducing such losses. Resin trap installation is also helpful to identify and reduce the resin loss.

2. Contamination

Contamination of resins in DM plant occurs during actual use due to the carry over of suspended matters. The suspended maters such as corrosion products originate from pipes or vessels, damaged rubber lining, silt or foreign materials due to failure of pre-filter etc generally contaminate the resin beds. These contaminants will ingress undesirable leachables or even ionic impurities in the treated water. This reduces the desired out put water quality and it creates a major problem especially where resins are used in highly purified form such as pharma and biotechnological application. Continuous and careful control of the inlet water quality to the resin vessel is one of primary requirements to reduce such occurrences.

Contamination of the resin bed also occurs due to improper packing and storage either at manufacturing site or at the plant site. Such contaminations due to storage occur rarely. During installation or break down maintenance, resins should be stored in a clean containers or tightly closed bags to avoid such failures. Periodic maintenance of plant hardware also limits such failures.

3. Dehydration

Ion exchange resins possess a polymeric porous structure. This porous matrix holds water in its interstitial spaces. Resin beads absorb water and swells. Water is an essential medium for the exchange processes to occur as it acts as medium for ion transport.

Dehydration occurs when resin is stored in hot condition or directly under sunlight for a long period. Beads slowly loose its water and shrinks. Upon re-hydration beads absorbs water and swells in a random manner leading to cracks and pieces. This mechanism is so severe that drying and re-wetting, if occurs several times can lead to powdering of resin. This leads to a permanent damage as a portion of resin is converted into powder. To avoid this, resins must be stored in a moist condition in a cool place, away from direct sunlight. A regular inspection and re-wetting is necessary for long time storage. Re-wetting of a dried resin must be done with a dilute solution of brine instead of plain water to reduce the damage.

Water should always present above the resin bed. In case of the failure of certain valves, the water bed above the resin bed gets dried. Subsequently, it looses its moisture. This occurs mainly in DM plants which are operated intermittently. Periodic checking of the plant and valves avoid such failures.

4. Attrition

It is a physical degradation in which resin particles breaks into fines, due to their aberration with each other or with the walls of the container. This is slow phenomena and occurs almost in all resin units. It is predominant in moving beds. Attrition leads to an increased pressure drop across the resin bed and also changes the shape of the resin beads. Lower cross-linked beads are more susceptible to attrition. Attrition loss is a permanent damage and it can not be stopped but can be controlled. A periodical inspection of resin sample drawn from an operating vessel helps in reducing attrition losses. Modern day applications in process like condensate polishing, continuous deionization, hydraulic resin transfer, mechanical bed cleaning etc needs high attrition resistant resins.

5. Depositions

Depositions in the resin bed though not common but posses a threat if not taken care immediately. Resin beds acts as a filtering media for the incoming water which contains dirt, silt, polyelectrolytes and tiny particles. This generally occurs in the first unit of the ion exchange train, which leads to channeling, excessive pressure drop and poor resin performance. Initially depositions are temporary failures but may lead to permanent failure. Deposits are removed by backwashing the resin bed with higher flow rate. An extended air-scouring is useful in removing these deposits. A proper control on pre-treatment operations will help to avoid this problem.

6. Oil fouling

Water contaminated with oil when enters the resin leads to oil fouling. This imparts the hydrophobicity on the resin beads and subsequently reduces the capacity of resin. Oil fouling enhances deposition of silt to form a thick layer on the resin beads which increases the pressure drop. This is a temporary effect and can be solved by cleaning of resin. Resins fouled by oil are cleaned off-line using an appropriate resin cleaner. Care must be taken to avoid oil contamination in the raw water to be treated. An oleophilic resin pre-filter can be installed to avoid this problem permanently.

Chemical failures

The chemical failures occur mainly due to the chemical reactions occurring between the resin and the inlet water. The important chemical failures are chemical precipitation, metallic fouling, organic fouling, osmotic shocks, oxidation, silica fouling and thermal shocks are addressed here.

1. Chemical Precipitation/fouling

Precipitation or fouling generally occurs due to reaction of ionic impurities with the exchangeable ions on the resin group. This reduces resin performance as it blocks the void spaces there by increasing the pressure drop, resin failure etc. Various type of precipitates and the reason for that are depicted in the following table.

Resin bed	Type of precipitate	Reason for precipitation
Cation	$CaSO_4$, $MgSO_4$	Sulfuric acid regeneration
	$Ca(OH)_2$, $Mg(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$	Alkali is used for cleaning before acid wash.
Anion	$Ca(OH)_2$, $Mg(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$	Raw water rinse or over exhausted cation bed.

To avoid sulphate type precipitations, it is advised to follow the recommended regeneration protocol strictly.

Fouling of cation resin due to iron and aluminum is found to be a common cause. In water pretreatment alum is used as coagulant in clarifier. Aluminum or iron from the residual alum exchanged irreversibly with the hydrogen ion of resin. It may lead to de-crosslinking and subsequent powdering of the resin. This is a permanent effect, and leads to shortening of resin life. Other metallic ions that foul the resin beds are aluminum, barium, copper, cadmium, lead, radium, and zinc.

Removal of these precipitates is done by treating the resin bed with hydrochloric acid. In severe cases a resin cleaner is used to remove the precipitates. Cleaning efficiency depends on the severity of fouling and type of cleaner used. A good pretreatment and monitoring of the water quality for these contaminants is necessary to prevent resin fouling.

2. Organic fouling

It is a chemical phenomenon more predominant in anion exchangers. Surface water contains organics of natural origin derived from decaying process of flora and fauna in its contact. These are high molecular weight, large multifunctional weakly dissociated organic acids such as humic acid and fulvic acid. During water treatment process these species adsorb on anion exchange resin through a combination of highly basic medium in resin phase and mechanism of van der Waal's forces. Aromatic sulfonated compounds and phenols are also absorb over strong base anion exchangers.

Organic species occupy the functional sites on the resin matrix during long periods of service cycle. During regeneration of the resin, which lasts for less than an hour, most of them due to their high molecular weight and slow diffusion kinetics are not eluted thus causing a built up in the resin bed. The acid groups then pick up sodium ions during regeneration. During rinsing these organic moieties hydrolyzes slowly. This requires excess rinse volume. If not rinsed properly, these moieties penetrates resin bead and blocks the exchangeable site irreversibly. After several such irreversible exchanges of organics, a cumulative effect is observed on the quality and quantity of treated water. This may induce bead cracking and bead distortion. The severity and its impact depend on the nature and properties of organics. Figure 1 depicts the typical performance characteristics of an organically fouled resin. The capacity reduction was observed gradually during operation. After regeneration, the resin restores its capacity back.

Following symptoms are observed of an organically fouled anion bed

a) Reduced output between regeneration.
b) Premature increased ionic leakages in the treated water
c) Increase requirement of rinse volume.

When an anion resin is fouled, a partial restoration of exchange sites can be achieved by desorbing them with alkaline brine. Sorbed organic species are thus converted to an ionized form, which are then displaced due to the high ionic concentration of the chloride ions and the alkalinity. When organics could not be controlled in the pretreatment, an organic scavenger resin unit is advised preceding strong base anion exchanger to protect the later from fouling.

3. Osmotic shocks

Ion exchange resins have a property of swelling and shrinking under normal course of operation. This depends on the nature and concentration of ionic species in the surrounding aqueous phase and also the amount of cross-linking agent in the matrix. An osmotically stable resin must have sufficient elasticity to avoid its breakage during intended use. During exhaustion and regeneration osmotic stresses are reversed. Successive such swelling and shrinking leads to resin failure.

A physically strong resin need not be osmotically stable. Larger beads are relatively less resistant to breakage than the smaller ones. An indicative test can be performed in the laboratory to find out osmotic stability of a resin. This is one of the most critical phenomena and decides the strength and life of resins.

4. Oxidation

Ion exchange resins under normal operating conditions are resistant to oxidation. But they do undergo oxidation, which have a definite impact on their performance. Oxidation leads to the de-crosslinking of resin matrix, which increases its water content and make resin soft. Compared to cation resins, anion resins are more vulnerable for oxidation. Unlike cation, anion resin failure is not only limited to matrix failure but also convert the strong base group to weak base group. The net effect being loss of strong base capacity of the resin to exchange weakly ionized anionic species such as bicarbonate and silica, which leads to unacceptable output water quality.

Oxidation occurs due to presence of free chlorine and oxygen. The process of oxidation is further enhanced by presence of metallic ions such as iron, copper or any other transitional metal ions. Higher feed water temperature further enhances these oxidative destruction processes. One of the pretreatment of water which enters the resin bed is disinfection using chlorine. Usually, free chlorine is neutralized with sulphites. If this operation is done improperly, the resin failure due to oxidation can be avoided considerably.

5. Silica fouling

Silica is present in the water in the soluble or in an insoluble, perhaps colloidal form. Silica is objectionable in whatever form it exists in the water to be treated for steam generating systems. Pretreatment methods like sedimentation and filtration or sometimes physical entrapment by membranes are used to remove insoluble or colloidal silica. However, soluble silica in water is removed by strong base anion resin. During regeneration it is removed as sodium silicate. NaOH dissolves most of the silica in the resin bed. However, traces of silica, left in the bed polymerizes in the resin bed.

In thoroughfare system, caustic from the strong base resin is used for the regeneration of weak base resin. This caustic contains eluted silica, which polymerizes in the .weak base resin bed as the bed pH is between 5 and 8. Silica built up in this manner leads to resin embrittlement and subsequent fracture. This problem is more prevalent in layered bed anions, where weak and strong base resins are in single vessel.

Regenerant concentration and injection flow must be maintained within the recommended limits to avoid such silica fouling. In case of thoroughfare system initial one third portion of caustic eluted from strong base resin should be discarded. The remaining elute is only to be passed through weak base resin. These preventive measures will be helpful to avoid silica fouling in regular operation. But, if the silica fouling occurs due to slow build up of silica, it can be removed by a hot caustic (at 40 – 45^{0}C) treatment. This reduces the silica fouling considerably and increase the resin life.

6. Thermal shocks

Strong acid cation exchanger is stable up to 120^{o}C, where as weak acid cation exchanger are stable up to 100^{o}C. Anion resins have lesser thermal stability and hence they are more susceptible to thermal shocks. Strong base type 1 resins with polystyrene matrix are stable up to 60^{o}C in hydroxide form. Where as, strong base type 2 resins in hydroxide form are stable only up to 40^{o}C. Weak base anion resins are stable up to 80^{o}C. Anion resins if operated above these temperatures leads to degradation. Above the specified temperature strong base functional groups are converted to weak base groups. This leads to the loss of strong base capacity.

There is no remedy for the resin deteriorated due to thermal shocks. Therefore, it is advisable to prevent the failure. To avoid such failure, it is strongly recommended to operate the plant with in the designed temperature limits. In addition, it is also advisable to inform the season temperature variations prevailing in the locality of the plant to the DM plant vendor. It is one of the important criteria in designing the DM plant.

Biological failure

Ion exchange resins in DM applications are subjected to extreme changes in pH during regeneration which normally do not favour biological growth. However, biological growth problems do occur due to extended storage of resins, unutilized or intermittently used DM plants. In such cases, resin bed accumulates microorganisms. The water surrounding the resin bed normally contains low concentrations of nutrients such as nitrates, phosphates along with the bed temperature is helpful for housing and growth of microorganism. The microbial fouling could be identified by the clumping of resin bed together. Some times, they impart rotten egg odor due to the presence of anaerobic sulfate reducing bacteria.

To prevent or reduce bio-fouling, resin should be stored in a biostatic solution. The normal biostatic solution contains sodium chloride up to 25% concentration. It is also advised to remove air from the resin unit during storage. The stored resins should be cleaned by an extended air scour followed by a double regeneration. Highly fouled systems need cleaning and disinfection. This should be considered as a last resort as this may cause oxidative attack on resin matrix. Cleaners should be used only when the resin in the exhausted form. A periodic disinfection of the resin bed then becomes essential to prevent it from fouling.

The trouble free operations of a DM plant in all industries are vital to their productivity. Therefore, knowledge on the identifying and taking remedial measures are defiantly helpful in continuous trouble free operation of a DM plant. The failures highlighted in this article should be used as guidelines. In actual operation, the remedial measures should be taken based on the severity and recurrence of the problem.

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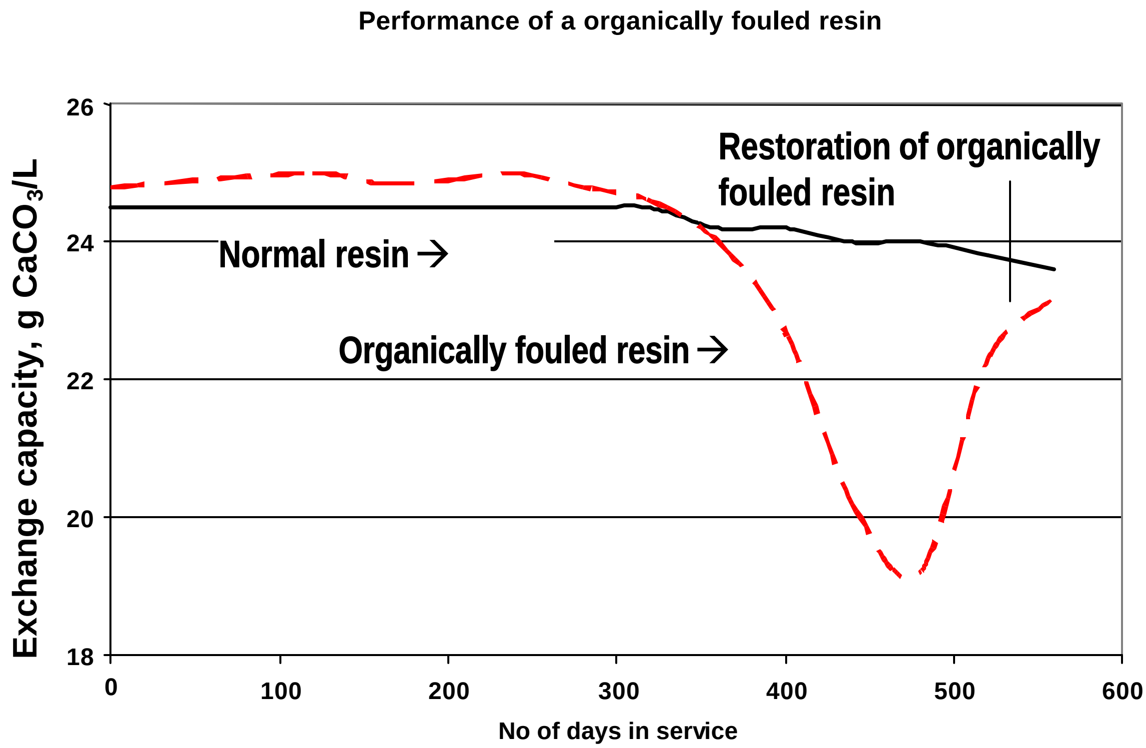

Figure 1 : **Typical graph on the degradation of resin capacity due to organic fouling.**