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The Pivotal Role of Ion Exchange Resins in Water Treatment

Introduction

Overview

Ion exchange resins, synthetic or natural polymers with ion-attracting functional groups, have become integral components of water treatment protocols worldwide. This paper explores their pivotal roles in mitigating challenges associated with water quality, emphasizing their applications in diverse sectors, including industrial processes, municipal water treatment plants, and specialized applications such as pharmaceutical production.

Water Softening

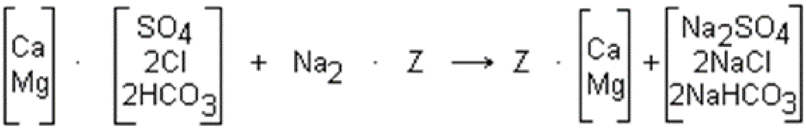
A primary function of cation exchange resins lies in water softening, a process crucial for preventing scale formation in pipes and appliances. Through selective exchange, these resins replace hardness ions like calcium and magnesium with more soluble ions like sodium, enhancing the quality of water for consumption and industrial use. The economic and operational benefits of preventing scale deposition underscore the indispensable role of ion exchange resins in maintaining infrastructure longevity and efficiency. Lets talk about types of softening.

SODIUM ZEOLITE SOFTENING

Sodium zeolite softening is the most widely applied use of ion exchange. In zeolite softening, water containing scale-forming ions, such as calcium and magnesium, passes through a resin bed containing SAC resin in the sodium form. In the resin, the hardness ions are exchanged with the sodium, and the sodium diffuses into the bulk water solution. The hardness-free water, termed soft water, can then be used for low to medium pressure boiler feedwater, reverse osmosis system makeup, some chemical processes, and commercial applications, such as laundries.

Principles of Zeolite Softening

The removal of hardness from water by a zeolite softening process is described by the following reaction:

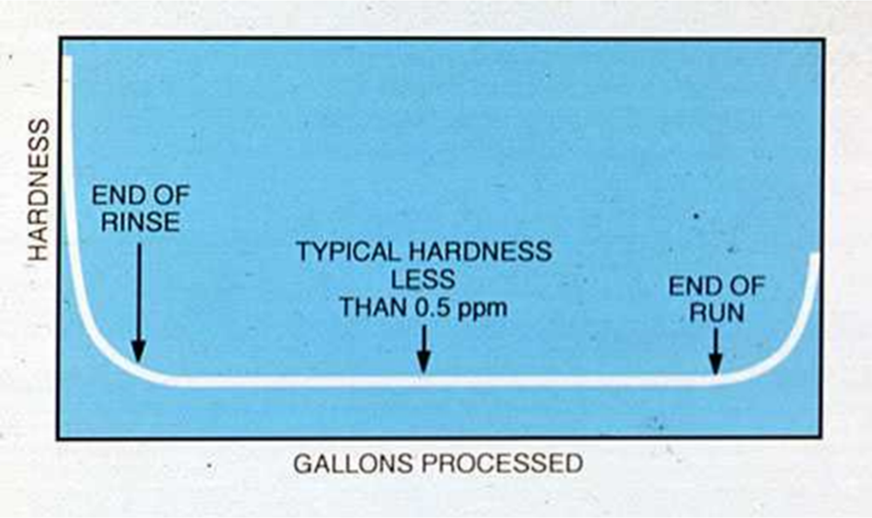


$$\begin{bmatrix}Ca\\Mg\end{bmatrix}\cdot\begin{bmatrix}SO_4\\2Cl\\2HCO_3\end{bmatrix} + Na_2\cdot Z \longrightarrow Z\cdot\begin{bmatrix}Ca\\Mg\end{bmatrix}+\begin{bmatrix}Na_2SO_4\\2NaCl\\2NaHCO_3\end{bmatrix}$$

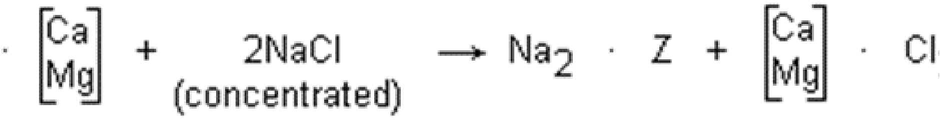
Water from a properly operated zeolite softener is nearly free from detectable hardness. How-ever, some small amounts of hardness, known as leakage, are present in the treated water. The level of hardness leakage is dependent on the hardness and sodium level in the influent water and the amount of salt used for regeneration.

After final rinse, the softener produces a low, nearly constant level of hardness until the ion exchange resin nears exhaustion. At exhaustion, the effluent hardness increases sharply, and regeneration is required (see Figure 8-a).

Figure 8-a



As illustrated by the softening reactions, SAC resin readily accepts calcium and magnesium ions in exchange for sodium ions. When exhausted resin is regenerated, a high concentration of sodium ions is applied to the resin to replace calcium and magnesium. The resin is treated with a 10% sodium chloride solution, and regeneration proceeds according to the following equation:



$$\cdot\begin{bmatrix}Ca\\Mg\end{bmatrix} + \underset{\text{(concentrated)}}{2NaCl} \longrightarrow Na_2\cdot Z + \begin{bmatrix}Ca\\Mg\end{bmatrix}\cdot Cl$$

During regeneration, a large excess of regenerant (approximately 3 times the amount of calcium and magnesium in the resin) is used. The eluted hardness is removed from the softening unit in the waste brine and by rinsing.

After regeneration, small residual amounts of hardness remain in the resin. If resin is allowed to sit in a stagnant vessel of water, some hardness will diffuse into the bulk water. Therefore, at the initiation of flow, the water effluent from a zeolite softener can contain hardness even if it has been regenerated recently. After a few minutes of flow, the hardness is rinsed from the softener, and the treated water is soft.

The duration of a service cycle depends on the rate of softener flow, the hardness level in the water, and the amount of salt used for regeneration. Table 8-1 shows the effect of regenerant level on the softening capacity of a gelular strong cation resin. Note that the capacity of the resin increases as the regenerant dosage increases, but the increase is not proportional.

The regeneration is less efficient at the higher regenerant levels. Therefore, softener operating costs increase as the regenerant level increases. As shown by the data in Table 8-a, a 150% increase in regenerant salt provides only a 67% increase in operating capacity.

Table 8-a. Effect of regenerant salt level on strong acid cation resin softening capacity.

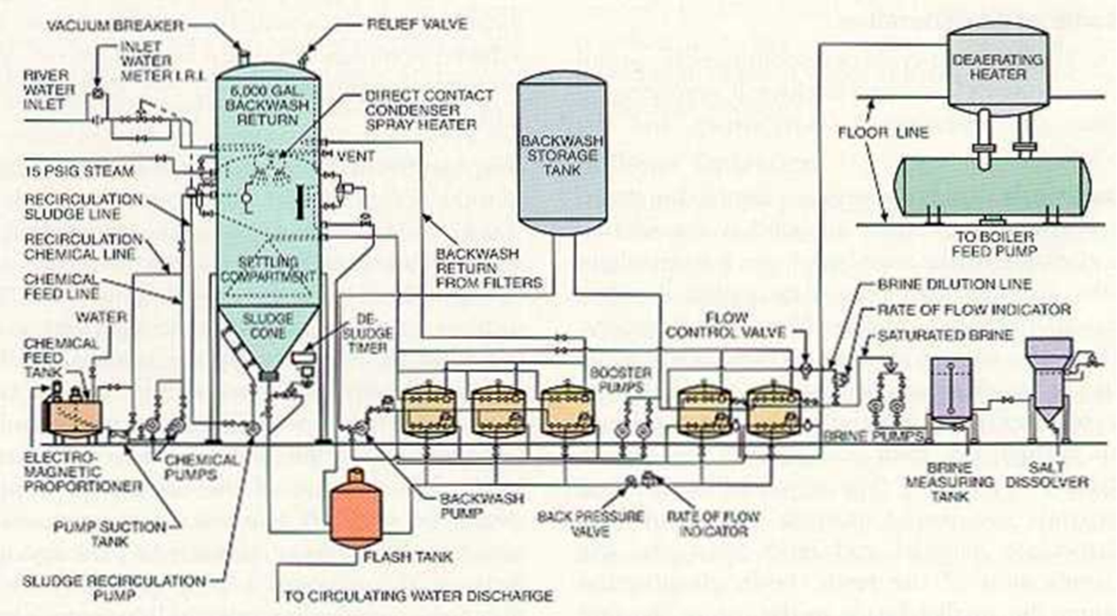
Table 8-1. Effect of regenerant salt level on strong acid cation resin softening capacity.

Salt (lb/ft$_3$)	**Capacity (gr/ft$_3$)**
6	**18,000**
8	**20,000**
10	**24,000**
15	**30,000**

HOT ZEOLITE SOFTENING

Zeolite softeners can be used to remove residual hardness in the effluent from a hot process lime or lime-soda softener. The hot process effluent flows through filters and then through a bed of strong acid cation resin in the sodium form (see Figure 8-c).

Figure 8-c



The equipment and operation of a hot zeolite softener is identical to that of an ambient temperature softener, except that the valves, piping, controllers, and instrumentation must be suitable for the high temperature (220-250°F). Standard strong cation resin can be used at temperatures of up to 270°F, but for a longer service life a premium gel or macroreticular resin is recommended. When operating a zeolite system following a hot process softener, it is important to design the system to eliminate flow surges in the hot lime unit. Common designs include the use of backwash water storage tanks in the hot lime unit and extended slow rinses for the zeolite in lieu of a standard fast rinse.

Applications and Advantages

Scale and deposit buildup in boilers and the formation of insoluble soap curds in washing operations have created a large demand for softened water. Because sodium zeolite softeners are able to satisfy this demand economically, they are widely used in the preparation of water for low and medium pressure boilers, laundries, and chemical processes. Sodium zeolite softening also offers the following advantages over other softening methods:

- treated water has a very low scaling tendency because zeolite softening reduces the hardness level of most water supplies to less than 2 ppm
- operation is simple and reliable; automatic and semiautomatic regeneration controls are available at a reasonable cost
- salt is inexpensive and easy to handle
- no waste sludge is produced; usually, waste disposal is not a problem
- within certain limits, variations in water flow rate have little effect on treated water quality
- because efficient operation can be obtained in units of almost any size, sodium zeolite softeners are suitable for both large and small installations

Limitations

Although sodium zeolite softeners efficiently re-duce the amount of dissolved hardness in a water supply, the total solids content, alkalinity, and silica in the water remain unaffected. A sodium zeolite softener is not a direct replacement for a hot lime-soda softener. Plants that have replaced their hot process softeners with only zeolite softeners have experienced problems with silica and alkalinity levels in their boilers.

Because the resin is such an efficient filter, sodium zeolite softeners do not function efficiently on turbid waters. Continued operation with an influent turbidity in excess of 1.0 JTU causes bed fouling, short service runs, and poor effluent quality. Most city and well waters are suitable, but many surface supplies must be clarified and filtered before use.

The resin can be fouled by heavy metal contaminants, such as iron and aluminum, which are not removed during the course of a normal regeneration. If excess iron or manganese is present in the water supply, the resin must be cleaned periodically. Whenever aluminum coagulants are used ahead of zeolite softeners, proper equipment operation and close control of clarifier pH are essential to good softener performance.

Strong oxidizing agents in the raw water attack and degrade the resin. Chlorine, present in most municipal supplies, is a strong oxidant and should be removed prior to zeolite softening by activated carbon filtration or reaction with sodium sulfite

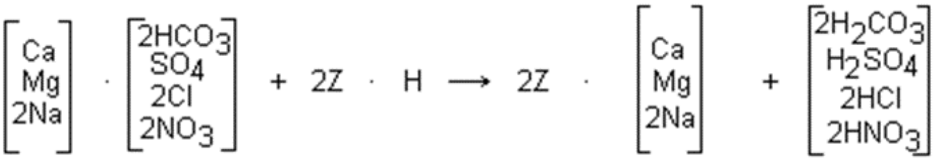
DEMINERALIZATION

Softening alone is insufficient for most high-pressure boiler feedwaters and for many process streams, especially those used in the manufacture of electronics equipment. In addition to the removal of hardness, these processes require removal of all dissolved solids, such as sodium, silica, alkalinity, and the mineral anions (Cl^{-}, $SO4^{2-}$, $NO3^{-}$).

Demineralization of water is the removal of essentially all inorganic salts by ion exchange. In this process, strong acid cation resin in the hydrogen form converts dissolved salts into their corresponding acids, and strong base anion resin in the hydroxide form removes these acids. Demineralization produces water similar in quality to distillation at a lower cost for most fresh waters.

Principles of Demineralization

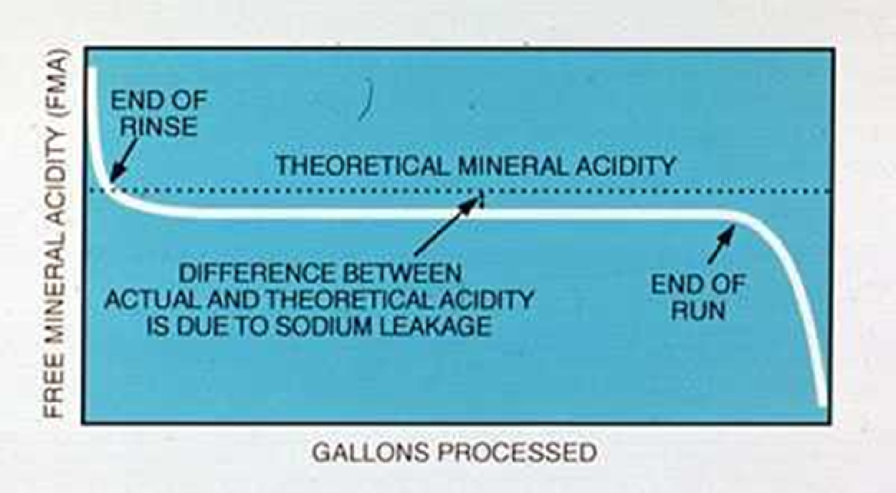
A demineralizer system consists of one or more ion exchange resin columns, which include a strong acid cation unit and a strong base anion unit. The cation resin exchanges hydrogen for the raw water cations as shown by the following reactions:



$$\begin{bmatrix}Ca\\Mg\\2Na\end{bmatrix} \cdot \begin{bmatrix}2HCO_3\\SO_4\\2Cl\\2NO_3\end{bmatrix} + 2Z \cdot H \longrightarrow 2Z \cdot \begin{bmatrix}Ca\\Mg\\2Na\end{bmatrix} + \begin{bmatrix}2H_2CO_3\\H_2SO_4\\2HCl\\2HNO_3\end{bmatrix}$$

A measure of the total concentration of the strong acids in the cation effluent is the free mineral acidity (FMA). In a typical service run, the FMA content is stable most of the time (see Figure 8-d).

Figure 8-d



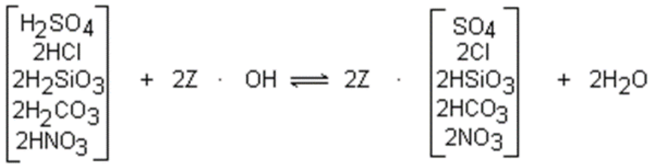
If cation exchange were 100% efficient, the FMA from the exchanger would be equal to the theoretical mineral acidity (TMA) of the water. The FMA is usually slightly lower than the TMA because a small amount of sodium leaks through the cation exchanger. The amount of sodium leakage depends on the regenerant level, the flow rate, and the proportion of sodium to the other cations in the raw water. In general, sodium leakage increases as the ratio of sodium to total cations increases.

As a cation exchange unit nears exhaustion, FMA in the effluent drops sharply, indicating that the exchanger should be removed from service. At this time the resin should be regenerated with an acid solution, which returns the exchange sites to the hydrogen form. Sulfuric acid is normally used due to its affordable cost and its availability. However, improper use of sulfuric acid can cause irreversible fouling of the resin with calcium sulfate.

To prevent this occurrence, the sulfuric acid is usually applied at a high flow rate (1 gpm per square foot of resin) and an initial concentration of 2% or less. The acid concentration is gradually increased to 6-8% to complete regeneration.

Some installations use hydrochloric acid for regeneration. This necessitates the use of special materials of construction in the regenerant system. As with a sodium zeolite unit, an excess of regenerant (sulfuric or hydrochloric acid) is required up to three times the theoretical dose.

To complete the demineralization process, water from the cation unit is passed through a strong base anion exchange resin in the hydroxide form. The resin exchanges hydrogen ions for both highly ionized mineral ions and the more weakly ionized carbonic and silicic acids, as shown below:

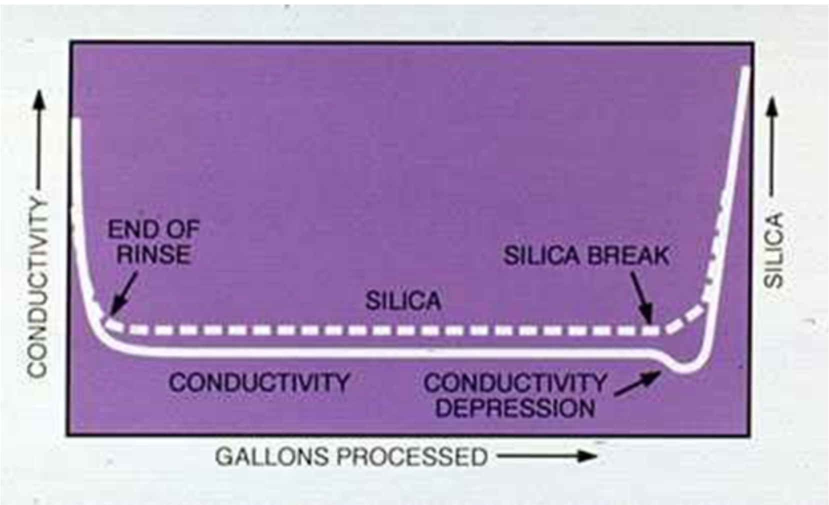


$$\begin{bmatrix} H_2SO_4 \\ 2HCl \\ 2H_2SiO_3 \\ 2H_2CO_3 \\ 2HNO_3 \end{bmatrix} + 2Z \cdot OH \rightleftharpoons 2Z \cdot \begin{bmatrix} SO_4 \\ 2Cl \\ 2HSiO_3 \\ 2HCO_3 \\ 2NO_3 \end{bmatrix} + 2H_2O$$

The above reactions indicate that demineralization completely removes the cations and anions from the water. In reality, because ion exchange reactions are equilibrium reactions, some leakage occurs. Most leakage from cation units is sodium. This sodium leakage is converted to sodium hydroxide in the anion units. There-fore, the effluent pH of a two bed cation-anion demineralizer system is slightly alkaline. The caustic produced in the anions causes a small amount of silica leakage. The extent of leakage from the anions depends on the chemistry of the water being processed and the regenerant dosage being used.

Demineralization using strong anion resins removes silica as well as other dissolved solids. Effluent silica and conductivity are important parameters to monitor during a demineralizer service run. Both silica and conductivity are low at the end of the fast rinse (see Figure 8-e).

Figure 8-e



When silica breakthrough occurs at the end of a service run, the treated water silica level increases sharply. Often, the conductivity of the water decreases momentarily, then rises rapidly. This temporary drop in conductivity is easily explained.

During the normal service run, most of the effluent conductivity is attributed to the small level of sodium hydroxide produced in the anion exchanger.

When silica breakthrough occurs, the hydroxide is no longer available, and the sodium from the cation exchanger is converted to sodium silicate, which is much less conductive than sodium hydroxide. As anion resin exhaustion progresses, the more conductive mineral ions break through, causing a subsequent increase in conductivity.

When the end of a demineralizer run is detected, the unit must be removed from service immediately. If the demineralizer is allowed to remain in service past the breakpoint, the level of silica in the treated water can rise above that of the influent water, due to the concentrating of silica that takes place in the anion resin during the service run.

Strong base anion exchangers are regenerated with a 4% sodium hydroxide solution. As with cation regeneration, the relatively high concentration of hydroxide drives the regeneration reaction. To improve the removal of silica from the resin bed, the regenerant caustic is usually heated to 120°F or to the temperature specified by the resin manufacturer. Silica removal is also enhanced by a resin bed preheat step before the introduction of warm caustic.

Demineralization Equipment and Operation

The equipment used for cation-anion demineralization is similar to that used in zeolite softening. The primary difference is that the vessels, valves, and piping must be made of (or lined with) corrosion-resistant materials. Rubber and polyvinyl chloride (PVC) are commonly used for ion exchange vessel linings. The controls and regenerant systems for demineralizers are more complex, to allow for such enhancements as stepwise acid and warm caustic regenerations.

Demineralizers are similar in operation to zeolite softeners. The service flow rate guidelines for a demineralizer range from 6 to 10 gpm per square foot of resin. Flow rates of over 10 gpm per square foot of resin cause increased sodium and silica leakage with certain waters. Anion resin is much lighter than cation resin. Therefore, the backwash flow rates for anion exchange resins are much lower than those for cation resins, and anion resin expansion is affected by the temperature of the water more than cation resin expansion. The water used for each step of anion resin regeneration should be free from hardness, to prevent precipitation of hardness salts in the alkaline anion resin bed.

Continuous conductivity instruments and silica analyzers are commonly used to monitor anion effluent water quality and detect the need for regeneration. In some instances, conductivity probes are placed in the resin bed above the underdrain collectors to detect resin exhaustion before silica breakthrough into the treated water occurs.

Advantages and Limitations

Demineralizers can produce high-purity water for nearly every use. Demineralized water is widely used for high pressure boiler feedwater and for many process waters. The quality of water produced is comparable to distilled water, usually at a fraction of the cost. Demineralizers come in a wide variety of sizes. Systems range from laboratory columns that produce only a few gallons per hour to systems that produce thousands of gallons per minute.

Like other ion exchange systems, demineralizers require filtered water in order to function efficiently. Resin foulants and degrading agents, such as iron and chlorine, should be avoided or removed prior to demineralization. Anion resins are very susceptible to fouling and attack from the organic materials present in many surface water supplies. Some forms of silica, known as colloidal, or non-reactive, are not removed by a demineralizer. Hot, alkaline boiler water dissolves the colloidal material, forming simple silicates that are similar to those that enter the boiler in a soluble form. As such, they can form deposits on tube surfaces and volatilize into the steam.

DEALKALIZATION

Often, boiler or process operating conditions require the removal of hardness and the reduction of alkalinity but not the removal of the other solids. Zeolite softening does not reduce alkalinity, and demineralization is too costly. For these situations, a dealkalization process is used. Sodium zeolite/hydrogen zeolite (split stream) dealkalization, chloride-anion dealkalization, and weak acid cation dealkalization are the most frequently used processes.

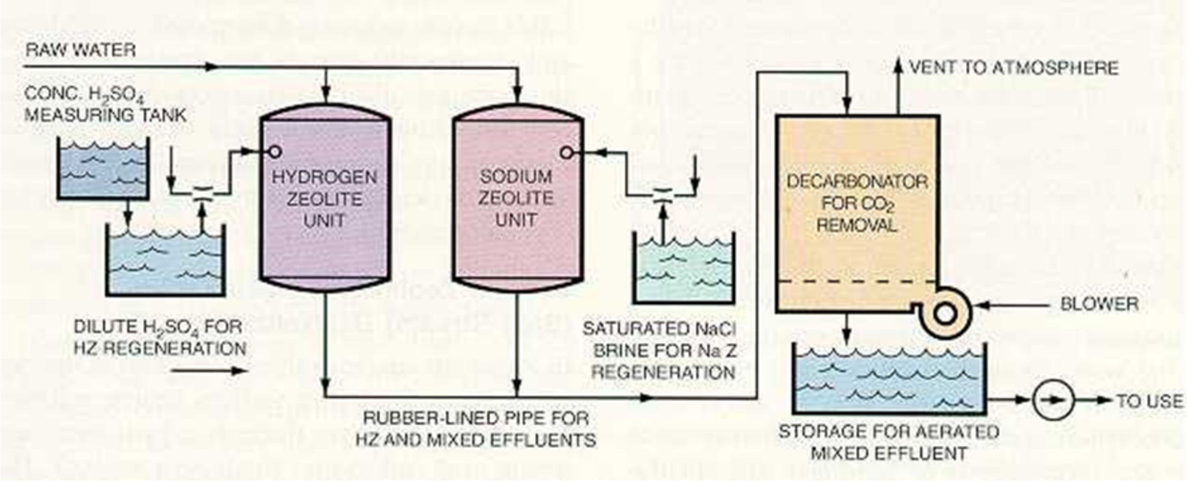
Sodium Zeolite/Hydrogen Zeolite (Split Stream) Dealkalization

In a split stream dealkalizer, a portion of the raw water flows through a sodium zeolite softener. The remainder flows through a hydrogen-form strong acid cation unit (hydrogen zeolite). The effluent from the sodium zeolite is combined with the hydrogen zeolite effluent. The effluent from the hydrogen zeolite unit contains carbonic acid, produced from the raw water alkalinity, and free mineral acids. When the two streams are combined, free mineral acidity in the hydrogen zeolite effluent converts sodium carbonate and bicarbonate alkalinity in the sodium zeolite effluent to carbonic acid as shown below:

$$2NaHCO_3 + \begin{bmatrix} 2HCl \\ H_2SO_4 \\ 2HNO_3 \end{bmatrix} \longrightarrow \begin{bmatrix} 2NaCl \\ Na_2SO_4 \\ 2NaNO_3 \end{bmatrix} + 2H_2CO_3$$

Carbonic acid is unstable in water. It forms carbon dioxide gas and water. The blended effluents are sent to a decarbonator or degasser, where the carbon dioxide is stripped from the water by a countercurrent stream of air. Figure 8-f shows a typical split stream dealkalization system.

Figure 8-f

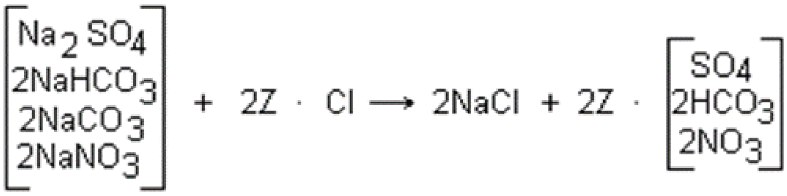


The desired level of blended water alkalinity can be maintained through control of the percentage of sodium zeolite and hydrogen zeolite water in the mixture. A higher percentage of sodium zeolite water results in higher alkalinity, and an increased percentage of hydrogen zeolite water reduces alkalinity.

In addition to reducing alkalinity, a split stream dealkalizer reduces the total dissolved solids of the water. This is important in high alkalinity waters, because the conductivity of these waters affects the process and can limit boiler cycles of concentration.

Sodium Zeolite/Chloride Anion Dealkalization

Strong base anion resin in the chloride form can be used to reduce the alkalinity of a water. Water flows through a zeolite softener and then an anion unit, which replaces the carbonate, bicarbonate, sulfate, and nitrate ions with chloride ions as shown in these reactions:



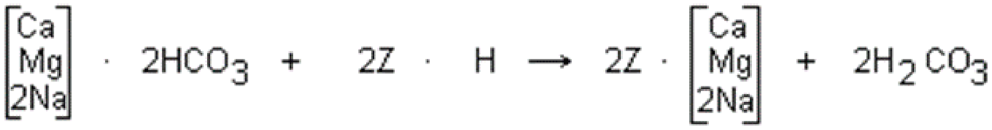
$$\begin{bmatrix} Na_2SO_4 \\ 2NaHCO_3 \\ 2NaCO_3 \\ 2NaNO_3 \end{bmatrix} + 2Z \cdot Cl \longrightarrow 2NaCl + 2Z \cdot \begin{bmatrix} SO_4 \\ 2HCO_3 \\ 2NO_3 \end{bmatrix}$$

The chloride anion dealkalizer reduces alkalinity by approximately 90% but does not reduce total solids. When the resin nears exhaustion, treated water alkalinity increases rapidly, signaling the need for regeneration.

The zeolite softener is regenerated as previously described. In addition, the anion resin is also regenerated with a sodium chloride brine that returns the resin to the chloride form. Frequently, a small amount of caustic soda is added to the regenerant brine to enhance alkalinity removal.

Weak Acid Cation Dealkalization

Another method of dealkalization uses weak acid cation resins. Weak acid resins are similar in operation to strong acid cation resins, but only exchange for cations that are associated with alkalinity, as shown by these reactions:



$$\begin{bmatrix} Ca \\ Mg \\ 2Na \end{bmatrix} \cdot 2HCO_3 + 2Z \cdot H \longrightarrow 2Z \cdot \begin{bmatrix} Ca \\ Mg \\ 2Na \end{bmatrix} + 2H_2CO_3$$

where Z represents the resin. The carbonic acid (H_2CO_3) formed is removed by a decarbonator or degasser as in a split stream system.

The ideal influent for a weak acid cation system has a hardness level equal to the alkalinity (both expressed in ppm as $CaCO_3$). In waters that are higher in alkalinity than hardness, the alkalinity is not removed to its lowest level. In waters containing more hardness than alkalinity, some hardness remains after treatment. Usually, these waters must be polished by a sodium zeolite softener to remove hardness.

During the initial portion of a weak acid cation service run (the first 40-60%) some cations associated with mineral anions exchange, producing small amounts of mineral acids in the effluent. As the service cycle progresses, alkalinity appears in the effluent. When the alkalinity in the effluent exceeds 10% of the influent alkalinity, the unit is removed from service and regenerated with a 0.5% sulfuric acid solution. The concentration of regenerant acid should be kept below 0.5-0.7%, to prevent calcium sulfate precipitation in the resin. Weak acid cation resin exchange is very efficient. Therefore, the amount of acid required is virtually equal (chemically) to the amount of cations removed during the service cycle.

If the materials of construction for the down-stream equipment or overall process cannot tolerate the mineral acidity present during the initial portions of the service cycle, a brine solution is passed through the regenerated weak acid resin prior to the final rinse. This solution removes the mineral acidity without a significant impact on the quality or length of the subsequent run.

Equipment used for a weak acid cation dealkalizer is similar to that used for a strong acid cation exchanger, with the exception of the resin. One variation of the standard design uses a layer of weak acid resin on top of strong acid cation resin. Because it is lighter, the weak acid resin remains on top. The layered resin system is regenerated with sulfuric acid and then with sodium chloride brine. The brine solution converts the strong acid resin to the sodium form. This resin then acts as a polishing softener.

Direct Acid Injection

In the process of direct acid injection and decarbonation, acid is used to convert alkalinity to carbonic acid. The carbonic acid dissociates to form carbon dioxide and water and the carbon dioxide is removed in a decarbonator. The use of an acid injection system should be approached with caution, because an acid overfeed or a breakdown in the pH control system can produce acidic feedwater, which corrodes the iron surfaces of feedwater systems and boilers. Proper pH monitoring and controlled caustic feed after decarbonation are required.

Advantages and Limitations of Dealkalization Systems

Ion exchange dealkalization systems produce hardness-free, low-alkalinity water at a reasonable cost, and with a high degree of reliability. They are well suited for processing feedwater for medium-pressure boilers, and for process water for the beverage industry. Split stream and weak acid cation systems also reduce the total dissolved solids. In addition to these advantages, the following disadvantages must be considered:

- dealkalizers do not remove all of the alkalinity and do not affect the silica content of a water
- dealkalizers require the same influent purity as other ion exchange processes; filtered water that is low in potential foulants must be used
- the water produced by a dealkalization system using a forced draft decarbonator becomes saturated with oxygen, so it is potentially corrosive