SODIUM CATION EXCHANGE (ZEOLITE) WATER SOFTENING PROCESS

A. History

The name zeolite comes from the two Greek words "zein" and "lithos" which mean "boiling stone". It was first applied by Granstedt, a Swedish geologist, in 1756 to describe a certain class of natural minerals which when heated, swelled and gave off their water of hydration. These zeolites are hydrated double silicates consisting of an alkali or alkali earth oxide, alumina, silica and water.

In 1818 Fuchs, a German chemist, produced the first synthetic zeolite by mixing solutions of sodium aluminate and sodium silicate.

In 1845 Thompson, and Englishman, passed a solution of manure through a filter made of ordinary garden soil and found that the ammonia was removed from solution. Way, an English chemist, concluded in 1852 that this exchange property of soils was due to their content of small amounts of zeolites. In 1858 Eichhorn, a German chemist, proved that the exchange properties of zeolites were reversible.

In 1905 Gans, a German chemist, discovered that zeolites could be used to soften hard waters. He also invented processes for synthesizing zeolites and designed the equipment – the zeolite water softener – in which they were used. The amount of salt required for regeneration was about 1 lb per kilograin of calcium and magnesium hardness in the raw water (64.8 mg = 1 grain).

Then stabilized greensand, consisting of potash, magnesia, ferrous and ferric iron, alumina, silica, and water of hydration, came into use and, while its capacity was less than that of synthetic zeolites (5 kgrns/ft^3 for greensand vs. 8-10 kgrns/ft^3 for synthetic zeolite), it was a very rugged material, rapid in its reactions, could be used on iron and/or manganese bearing waters, had the same capacity for magnesium hardness as for calcium hardness, and was quite efficient on salt consumption (i.e. 0.5 lb/kgrn of calcium and magnesium hardness).

In 1934 and 1935, entirely new types of cation exchangers were developed. Not only could they be used in the sodium cycle when regenerated with salt, but also in the hydrogen cycle when regenerated with an acid. One group of these cation exchangers was the carbonaceous type which was made by the sulfonation of coal. They gave capacities of 6-7 kgrn/ft^3 and required 0.4 lb salt per kgrn of calcium and magnesium hardness.

Later work led to the development of a number of other cation exchangers among which were the sulfonated styrene types. They were made by the sulfonation of a resin produced in a bead form by copolymerization of styrene and divinylbenzene. Because of their physical appearance, they became known as gel resins. Normal capacities and salt consumptions of these exchangers are 20-27 kgrns/ft^3 and .3 - .5 lb/kgrn respectively.
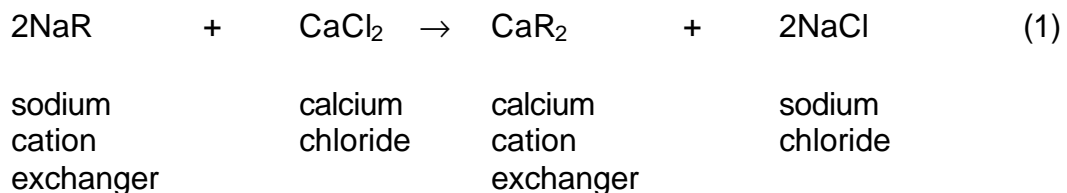
B.   Chemistry Related to Ion Exchange

An ion is an electrically charged component of a substance which has been dissolved in water. For example, if sodium chloride is put into water, it dissolves and then dissociates into two separate ions – a positive sodium ion and a negative chloride ion. Sodium chloride no longer exists in such a solution unless its solubility product is exceeded, at which point it precipitates as sodium chloride.

Ions are split into two groups. The cations such as calcium, magnesium, sodium, hydrogen, iron, etc. have a net positive charge; the anions such as bicarbonate, carbonate, hydroxide, chloride, sulphate, etc. have a net negative charge.
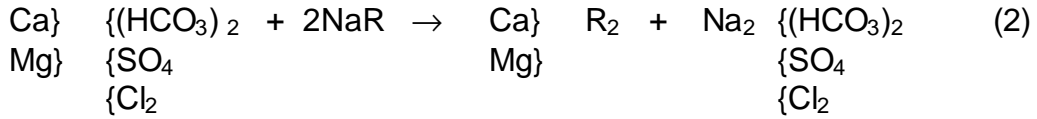
In all water supplies, the total amount of cations must be equal to the total amount of anions after both are mathematically converted to a common base such as "ppm CaCO$_3$".

An ion exchanger is an insoluble substance that has the property of exchanging an ion which has been hung onto its structure with another ion in the water. A representative ion exchange reaction is as follows:

$$2NaR \quad + \quad CaCl_2 \quad \rightarrow \quad CaR_2 \quad + \quad 2NaCl \qquad (1)$$

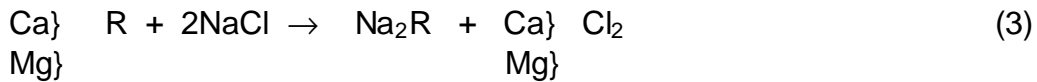| sodium
cation
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The raw water contains the ion that is to be removed by ion exchange. When this unwanted ion comes into contact with the regenerated exchanger during its service run, it displaces the ion that was attached to the resin and takes its place on the resin. When a hard water is passed through a bed of sodium cation exchanger, the calcium and magnesium are taken up and held by the cation exchanger which simultaneously gives

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up an equivalent amount of sodium in exchange for them. This reaction may be represented by the following equation:

$$Ca\} \quad \{(HCO_3)_2 + 2NaR \rightarrow \quad Ca\} \quad R_2 + Na_2 \{(HCO_3)_2 \qquad (2)$$
$$Mg\} \quad \{SO_4 \qquad \qquad Mg\} \qquad \qquad \{SO_4$$
$$\{Cl_2 \qquad \qquad \qquad \{Cl_2$$

Iron, ammonium, barium, potassium, etc. are similarly exchanged for sodium from the ion exchanger. In any event, since an equivalent amount of sodium is given up for the unwanted ion, the amount of dissolved solids in the raw water is the same as in the effluent of a sodium cycle exchanger.

When the ability of a sodium cycle exchanger to produce completely softened water is exhausted, the softener unit is taken out of service and regenerated with a solution of common salt. This reaction may be represented by the following:

$$Ca\} \quad R + 2NaCl \rightarrow \quad Na_2R + Ca\} \ Cl_2 \qquad \qquad (3)$$
$$Mg\} \qquad \qquad \qquad Mg\}$$

Calcium and magnesium are removed from the resin in the form of their chlorides and the resin is simultaneously restored to the sodium form.

The typical performance of a sodium cycle softener is tabulated in Table 1 below.

Table 1:   **Typical Performance of a Sodium Cycle Softener**

Parameter	Concentration In Raw Water	Concentration in Softener Effluent
Calcium, ppm $CaCO_3$	66	0-1.5
Magnesium, ppm $CaCO_3$	18	0-1.5
Total Hardness, ppm $CaCO_3$	84	0-3
Sodium, ppm $CaCO_3$	24	105-108
Alkalinity, ppm $CaCO_3$	62	62
Sulphate, ppm $CaCO_3$	30	30
Chloride, ppm $CaCO_3$	16	16
Silica, ppm SiO_2	9	9
Total Dissolved Solids, ppm	166	166

C.   Steps of Softener Operation

The normal operation of a sodium cycle exchanger consists of a regeneration cycle, which includes backwashing, brining, slow rinsing, and fast rinsing, as well as a service cycle.

Backwashing, as the name implies, involves the passage of water upward through the resin bed for the following reasons:

1.   bed expansion releases any accumulation within the resin bed and fluffs the bed to allow more efficient contact between brine and resin during the brining step;

2.   particle and resin fines removal prevents channeling, high pressure drop, and poor kinetics during the service step;

3.   regrading or classification of the resin bed contributes to the uniform distribution of regenerant during the brining step.

Backwashing should be carried out for a minimum of 10 minutes or until the backwash effluent is clear. The backwash flow rate should be sufficient to expand the bed a minimum of 50%, yet not so excessive as to cause a loss of resin. At a set flow rate, bed expansion depends on the backwash water temperature – the lower the temperature, the greater the expansion due to the higher viscosity of water at the lower temperature. Therefore, backwash flow rate should be adjusted as the water temperature varies. Curves are available from resin suppliers which relate bed expansion to the backwash flow rate and the temperature of the water.

The second step in the regeneration cycle is the brining operation. Brine, prepared from rock salt or evaporated salt containing a minimum of 98% NaCl, is injected into the water space above the resin bed at a concentration of 10 wt.% and allowed to flow through the resin bed. The 10% brine concentration may be arrived at either by preparing a 10% solution directly or by diluting the saturation strength of 26%. Usually, the latter method is employed. The brine regenerate flow rate must be slow enough to provide sufficient contact time between the brine and resin, yet fast enough to prevent channeling of the brine. Usually, this flow rate is in the order of 1 USGPM/ft^3 resin. The total amount of salt required per regeneration depends on the volume of the resin and the desired capacity rating of the resin, but is within the range of 5 to 25 lbs./ft^3 of resin. Curves are available from resin suppliers, which relate the capacity rating of the resin to the pounds of salt required per cubic feet of resin. Once the regenerate concentration and flow rate, resin volume, and the required amount of salt are all established, the duration of the brining operation

may be calculated directly. However, a brine curve should be established and checked periodically. This involves hydrometer resting of the softener effluent during the brining stage. If the curve is too narrow, the brine flow rate should be reduced or brine strength increased.

The third step in the regeneration cycle is the slow rinse. This water flow rate should be approximately 1 USGPM/ft^3 resin. If an eduction system is used for regeneration, the proper slow rinse flow rate may be obtained by discontinuing the eduction of saturated brine. The quantity of slow rinse water required is approximately ½ of the resin bed volume plus the volume of space between the resin and the distribution laterals. This provides a "plug" of slow rinse water which forces the remaining brine completely through the bed. The duration of the slow rinse may be calculated directly once the rinse water flow rate, the volume of resin, and the dimensions of the vessel are established.

The fourth and final step in the regeneration cycle is the fast rinse. This water flow rate should be performed at approximately 1.5 USGPM/ft^3 resin to completely remove waste brine containing the exchanged cations. The duration of the rinse is determined by the total hardness in the rinse water effluent.   When the hardness has decreased to less than 1 ppm as $CaCO_3$, rinsing may be considered complete.

The service cycle is conducted most efficiently at a flow rate of approximately 6-8 USGPM/ft^2 resin bed. Continuous operation at or above the maximum flow rate of 15 USGPM/ft^2 may result in channeling, bed compaction, leakage, or premature hardness breakthrough. Continuous operation at or below 3 USGPM/ft^2 resin bed can result in decreased capacity and leakage because at these flow rates, water is not forced through the bed. The result is that water travels the path of least resistance, so that contact between water and resin is poor and complete exchange does not take place. Service flow rates may be too low when softened water needs are minimal, or when the softening units are overdesigned.

D. Design of Softeners

When designing a softener, the parameters which must be identified include the volume of resin, the size of the vessel, and the construction features of the vessel.

The volume of resin may be calculated from the following formula:

$$V = \frac{Vw \quad L}{1000K} \qquad (4)$$

where V = volume of resin, ft^3
      Vw = volume of water treated, USG
      L = ionic load, grains $CaCO_3$/USG
      K = resin exchange capacity[3], kgrns/ft^3

With a resin exchange capacity of 20 kgrns/ft^3, an ionic loading of 100 ppm $CaCO_3$ (i.e. 5.8 grns/USG) and a requirement to treat 100,000 USG between regenerations, the resin volume would be 29 ft^3.

With a flow rate of 100 USGPM at 10 USGPM/ft^2, the diameter of the vessel would be 3.5 feet and the depth of the resin bed would be 3 feet. In order to provide 100% freeboard (i.e. the height of the space above the resin compared to the height of the resin bed), the vessel height would be 6 feet.

The shell of the softener vessel consists of a steel cylinder with heads dished to correspond with the vessel diameter and a metal thickness to withstand the operating pressure.

The functions of the underdrain system at the bottom of the softener shell are as follows:

1. uniform collection of the softened water during the service run;
2. uniform distribution of the backwash water during the backwash step prevents channeling and loss of resin;
3. uniform withdrawal of the brine and rinse water prevents pocketing of either to occur.

The most common underdrain configuration consists of a header – lateral system with strainer heads.

Layers of graded gravel (coarsest at the bottom and finest at the top), surmounted by a layer of coarse sand are located above the strainer system in order to support the resin bed and to assist in the even distribution of water during all steps of the regeneration cycle as well as the service cycle.

Slightly below the top of the straight side of the shell is the wash water collector which serves, during softening and rinsing, to introduce and deflect the incoming water and, during backwashing, to collect the backwash water and deliver it to the outgoing piping. Deflection of the incoming water is necessary, otherwise it may hollow out a portion of the resin bed and cause a greater flow through this portion than the rest of the resin bed.

A short distance above the surface of the resin bed is the brine distribution system which serves to introduce and uniformly distribute the diluted brine over the resin bed so that all parts of the bed will come into even contact with it.

D.   **Troubleshooting Softener Malfunctions**

Softener effluent may periodically indicate hardness leakage or decreased exchange capacity. Normally, difficulties can be attributed to one of four causes, i.e. mechanical failures, resin degradation, improper operational controls, and changes in feedwater chemistry.

Mechanical failures take the form of plugged or broken distribution laterals, improperly functioning multiport valves, or clogged underdrain screens and support media.

To determine whether the resin is performing poorly because of chemical or physical degradation, core resin samples should be checked for exchange capacity, physical stability, and foulants. Core samples should be collected and analyzed annually.

Improper operational controls involve service flow rate; backwash flow rate and water temperature; regenerant concentration, dosage and flow rate; slow rinse flow rate and water volume; fast rinse flow rate and volume; and total hardness levels in the softened water and fast rinse effluent. To ensure that these controls are properly set, each one should be checked periodically.

Softeners are normally designed for an average feed composition. Key considerations are total hardness, metallic compounds, suspended solids, and oxidizing agents. A permanent change from the original characteristics may result in low quality water, decreased capacity, and resin degradation. Operational and mechanical modifications can minimize these problems.

E. Resin Degradation

The various forms of softener resin degradation include osmotic shock, mechanical strain, thermal shock and iron, aluminum, calcium carbonate or magnesium hydroxide fouling.

Osmotic shock is caused by excessive bead expansion during the service cycle, and contraction during regeneration.

Mechanical strain results in broken beads which lowers capacity due to channeling and higher pressure drop.

Thermal shock is caused either by extreme temperature variations (i.e., when a hot service cycle is followed by a cold backwash) or by continuous operation above the maximum allowable temperature for the resin in service.

Iron foulants may originate from such sources as contaminated water supply, corroded water distribution piping, surface water supply containing organically sequestered iron, or contaminated regenerant. Most frequently, iron enters as the insoluble ferric form, coating the surface of the beads, thus prohibiting efficient contact between water and resin. Washing with a reducing agent such as sodium hydrosulfite will reduce the iron to the soluble ferrous form. Alternately, a hydrochloric acid solution may be used to dissolve the ferric form iron directly.

Aluminum, calcium carbonate, and magnesium hydroxide fouling are caused by carry over of coagulants or hardness from the pretreatment system. These precipitates coat the surfaces of the resin beads thus reducing its capacity.