Zeolites

What are zeolites?

Zeolites are naturally occurring hydrated sodium alumino silicate minerals capable of exchanging reversibly its sodium ions (Na^+) for hardness causing ions (e.g., Ca^{2+}, Mg^{2+}, etc.) in water. The chemical representation of zeolites are $Na_2O.Al_2O_3.xSiO_2.yH_2O$, where x = 2-10 & y = 2-6. In short, we can mentioned it as Na_2Ze.

Zeolite is derived from the *Greek* word *Zein + Lithos*, meaning "*boiling Stone"*. If heated strongly, zeolite melts with bubbling moisture, which look like as if a stone is boiling. *The term zeolite was coined by Swedish Geologist Axel Cronsted in 1756.* Zeolite has open structure with many cavities or pores. This porous structure permits free movement of water molecules and ions.

Types of Zeolites:

Zeolites are of two types: (1) **Natural zeolites:** They are relatively less porous in nature. Example: $Na_2O.Al_2O_3.4SiO_2.2H_2O$; (2) **Synthetic/artificial zeolites:** They are made in the laboratories of industries. Such zeolites are relatively more porous and less durable, but *having large ion exchange capability per unit weight*. They are prepared by heating together sodium carbonate Na_2CO_3, alumina Al_2O_3 and silica SiO_2 in a muffle furnace maintained at about 1000 ^{0}C. Artificial zeolites are also called as **Permutit**.

Q. Give reason that artificial zeolites are preferred over natural one for the softening of hard water.

Answer: As the artificial is more porous *it has large ion exchange capability per unit weight* than natural one.

Zeolite Softening Process

Principle: It is based on ion-exchange process.

Working: *Softening of Hard water* is done in a **Zeolite softener (see Fig.)**. The hard water is passed/percolated at a specified rate through a bed of zeolites fixed in a cylindrical stainless steel softener so that hardness causing ions (Ca^{+2}, Mg^{+2}, etc.) are retained by the zeolite bed and outgoing water contains sodium ions (Na^+). The reaction taking place during the softening process is mentioned as below:

$$Na_2Ze + CaCl_2 \rightarrow CaZe + 2NaCl$$

$$Na_2Ze + Ca(HCO_3)_2 \rightarrow CaZe + 2\ NaHCO_3$$

$$Na_2Ze + Mg(HCO_3)_2 \rightarrow MgZe + 2\ NaHCO_3$$

From the above reaction we learnt that with the progress of softening process more and more Na_2Ze are converting into CaZe/MgZe and the sodium salt concentration is increasing in the outgoing water. In other words, the Na^+ ion content responsible for ion exchange is decreasing with time. So, after some time the zeolite (Na_2Ze) is completely converted into calcium and magnesium zeolite of no ion exchange capability. It means after some time it ceases to soften water and zeolite is said to be gets exhausted. At this stage, the feeding of hard water to the softener is temporarily stopped and regeneration is done for the exhausted zeolite.

Regeneration of exhausted zeolite is done by treating with a concentrated (10%) NaCl solution (known as *Brine solution*). The reaction taking places during the regeneration process are:

$$CaZe + 2NaCl \rightarrow Na_2Ze \text{ (reclaimed zeolite)} + CaCl_2 \quad \text{(washings)}$$

$$MgZe + 2\ NaCl \rightarrow Na_2Ze + MgCl_2$$

The washings are led to the drain and the regenerated zeolite bed is used for softening process.

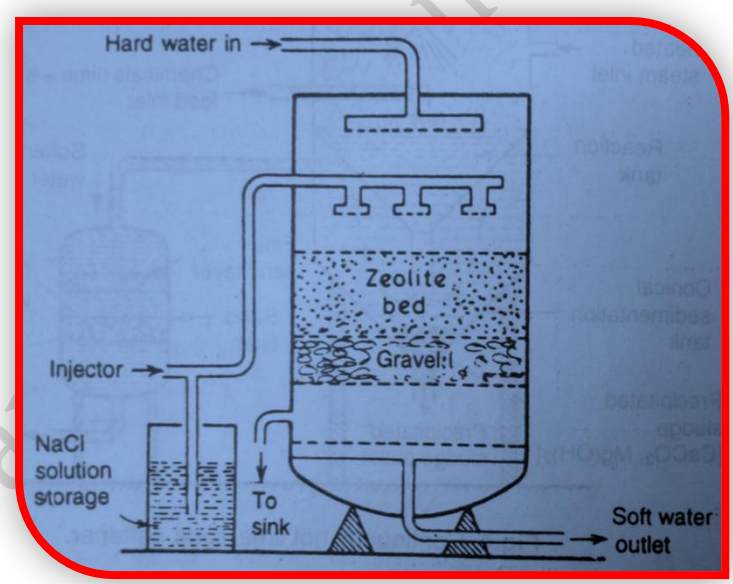

Fig. Zeolite softener

Limitations of zeolite process:

1. Turbid water clogs the pores of the zeolite and thereby making it inactive.
2. Water containing ions like Mn^{2+} and Fe^{2+} are firmly stick to the zeolite bed so very difficult to be regenerated.
3. Acidic water destroys the zeolite bed.
4. Hot water tends to dissolve the zeolite bed.
5. Water softened by this process contains salts like $NaHCO_3$ causes boiler corrosion.
6. Higher cost of the plant is also a limiting factor.
7. Not free from dissolved gases and bacteria

Q. Give reason that sodium chloride is preferred for regeneration exhausted zeolite.

Answer: It is of low cost and the products of regeneration (washings) are highly soluble so that can be easily rinsed out from the zeolite bed.

Q. Turbid water should not be softened by zeolite process. Give reason

Ans. Turbid water clogs the pores of the zeolite and thereby making it inactive

Q. How to soften turbid hard water using a zeolite softener?

Ans. At first suspended matter must be removed by coagulation before it is fed into the softener.

Q. **Acidic water should not be softened by zeolite process. Give reason**

Ans. Acidic water destroys the zeolite bed.

Q. How to soften acidic hard water using a zeolite softener?

Ans. Acidic water must be neutralized with soda in advance before feeding into zeolite bed.

Q. How to regenerate an exhausted zeolite bed?

Ans. It is done by treating with a concentrated (10%) NaCl solution (known as *Brine solution*). The reaction taking places during the regeneration process are:

$$CaZe + 2NaCl \rightarrow Na_2Ze \text{ (reclaimed zeolite)} + CaCl_2 \quad \text{(washings)}$$

$$MgZe + 2\ NaCl \rightarrow Na_2Ze + MgCl_2$$

Q. Water softened by zeolite softener is not fit for boiler. Give one reason.

Ans. It contains salt like $NaHCO_3$ which undergoes decomposition under boiler condition to form NaOH, a caustic mass.

$$NaHCO_3 \rightarrow NaOH + CO_2$$

The caustic mass makes the water alkaline and leads to alkaline boiler corrosion called as ***Caustic Embrittlement*****.**

Q. Water should be free from ions like Mn^{2+} and Fe^{2+} before fed into the boiler. Give reason.

Ans. Water containing ions like Mn^{2+} and Fe^{2+} are firmly stick to the zeolite bed so very difficult to be regenerated.

Advantages of Zeolite process:

1. The residual hardness is about 10 ppm whereas in L-S process it lays between 15-60 ppm.
2. Equipment used is compact and occupies less space.
3. It is clean in use. No sludge formation occurs during the process.
4. Less skilled people can operate as well as maintain easily.
5. Less time is needed for softening as compared to L-S process.

Comparison between Zeolite and L-S process

Sl. No.	Zeolite process	L-S process
1.	Produces water of residual hardness of 10-15 ppm	Produces water of residual hardness lays between 15-60 ppm
2.	Based on ion exchange principle	Based on precipitation principle
3.	Softened water contain large amount of sodium salts	Treated water contains lesser % of Na-salts
4	Capital cost is high	Capital cost is low
5	Not suitable for treating acidic and turbid water	No such limitation
6	Equipment occupies less space	Occupies more space
7	No sludge formation	Sludge formation occurs
8	Dissolved gases are not removed	They are removed in hot L-S process
9	No bacteria are killed	They are killed in hot L-S process
10	Treated water contains large amount of $NaHCO_3$	Free from $NaHCO_3$
11	Less skill is required to operate it	Skilled operate can operate it successfully

Q1. A water sample contains the following constituents: 100 ppm $Ca(HCO_3)_2$, 75 ppm HCl, 300 ppm $FeSO_4$ and 90 ppm $MgSO_4$. What precautions the operator will take before softening by Zeolite process?

Ans. The sample contains acid and iron salts. Acid can damage the zeolite bed, while Fe2+ ions adhere strongly to the bed, preventing effective regeneration. Therefore, the operator must first remove the acids and Fe2+ ions before proceeding with the softening process.

Solved Numerical

Example-1 The hardness of 10,000 liters of a sample of water was reduced by passing it through a zeolite softener. If the Exhausted zeolite needed 200 liters of NaCl solution containing 150 g/L of NaCl for regeneration then find the hardness of water.

Solution:

NaCl as $CaCO_3$ eq = $(150 \times 10^3) \times (100/2 \times 58.5)$, for NaCl, n-factor = 1

$= (150 \times 10^3) \times 100/117 = 128205.128$ mg/L

We know that S_1V_1 (for NaCl) = S_2V_2 (for water)

That is S_{NaCl} x V_{NaCl} = S_{water} x V_{water}, Here S = strength and V = Volume

So, 128205.128 x 200 = S_{water} x 10,000

⇨ S_{water} = (128205.128 x 200) /10,000 = 2564.1 ppm

Example-2 An exhausted zeolite softener was regenerated by passing 150 L of NaCl solution having a strength of 150 g/L of NaCl. Find the total volume of water that can be softened by this zeolite softener, if the hardness of water is 500 ppm.

Solution:

NaCl as $CaCO_3$ eq = (150×10^3) x (100/2 x 58.5), for NaCl, n-factor = 1

= (150×10^3) x 100/117 = 128205.128

Now,

S_{NaCl} x V_{NaCl} = S_{water} x V_{water}, Here S = strength and V = Volume

⇨ 128205.128 x **150 = 500 x** V_{water}

⇨ V_{water} = (128205.128 x **150)/500 = 38461.53** L

Assignment

1. **The hardness of 10,000 liters of a sample of water was reduced by passing it through a zeolite softener. The Exhausted zeolite needed 100 liters of NaCl solution containing 200 g/L of NaCl for regeneration. Find the hardness of water.**

2. **An exhausted zeolite softener was regenerated by passing 350 L of NaCl solution having strength of 100 g/L of NaCl. Find the total volume of water that can be softened by this zeolite softener, if the hardness of water is 750 ppm.**