بسم الله الرحمن الرحيم

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WATER & WASTEWATER TREATMENT LAB.

EXPERMENT (4)

HARDNESS REMOVAL

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- **Abstract:**

- HARDNESS mainly is The amount of metallic salts, such as calcium, magnesium or iron ions dissolved in water.
- The source is naturally dissolved calcium and magnesium from soil and lime. The symptoms are soap deposits; scaly deposits in plumbing and appliances; and decreased cleaning action of soaps and detergents.
- The term hardness was originally applied to waters that were hard to wash in, referring to the soap wasting properties of hard water.

- **Introduction:**

- Apart from taste, hardness is not considered as harmful parameter of water because these multivalent cations do not cause any problems to human health, but there existence may lead to reaction that leave insoluble mineral deposits that may not be appropriate for a various uses.
- Cations have +3 or bigger charges will not be harmful, because in normal conditions like pH=6~8, these cations will be settled down.
- Hard water is water contaminated with compounds of calcium and magnesium. Dissolved iron, manganese, and strontium compounds can also contribute to the "Total hardness" of the water, which is usually expressed as ppm $CaCO_3$. Water with a hardness over 80 ppm $CaCO_3$ is often treated with water softeners, since hard water produces scale in hot water pipes and boilers and lowers the effectiveness of detergents.
- The main sources of hardness of water is from groundwater stones and rocks such as dolomite and limestone which provide magnesium and calcium respectively.
- Hardness is divided into two types, and the removal method will vary according to it:
  1. Carbonate hardness: that is combined with types of alkalinity like CaCO3, MgCO3, Ca(HCO3)2, Mg(HCO3)2, Ca(OH)2, Mg(OH)2. This type is called temporary due to the ability of removal by boiling. This type can form calcium carbonate scales and carbon dioxide that can react with water to give carbonic acid which causes corrosion of iron or steel equipment.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

  2. Non-Carbonate hardness like CaSO4, MgSO4, CaCl2, MgCl2. This type is called permanent hardness. This type can form soap scum .

$$CaSO4 + NaCO3 \rightarrow CaCO3 + Na2SO4$$

- A water softener reduces the dissolved calcium, magnesium, and some degree manganese and ferrous iron ion concentrations in hard water. A common water softener is sodium carbonate (Na2CO3). These "hardness ions" cause three major kinds of undesired effects. Most visibly, metal ions react with soaps and calcium-sensitive detergents, hindering their ability to lather and forming a precipitate—the familiar "bathtub ring". Presence of "hardness ions" also inhibits the cleaning effect of detergent formulations.

- Lime-soda ash treatment for the reduction of hardness involves the addition of slake lime ($Ca(OH)_2$) to a hard water supply to remove the carbonate hardness by precipitation with the precipitation being removed by filtration. Non-carbonate hardness is in turn reduced by the addition of soda ash (Na2C03) to form insoluble precipitate which is also removed by filtration.
- This particular method of removing hardness a sometimes used by municipal water plants to reduce the amount of calcium and magnesium in a water supply. While it is quite effective in reducing hardness, it is not a complete removal treatment.
- Lime-soda ash treatment is especially effective if a water contains bicarbonate (temporary) hardness. Where calcium and magnesium are primarily in chloride or sulfate compounds, this treatment is noticeably less effective.
- Slaked lime is used to remove calcium bicarbonate from water. In the water to be treated, the slaked lime ions react with the calcium bicarbonate to form the very slightly soluble calcium carbonate. This precipitated material is usually removed by first settling and then filtering.

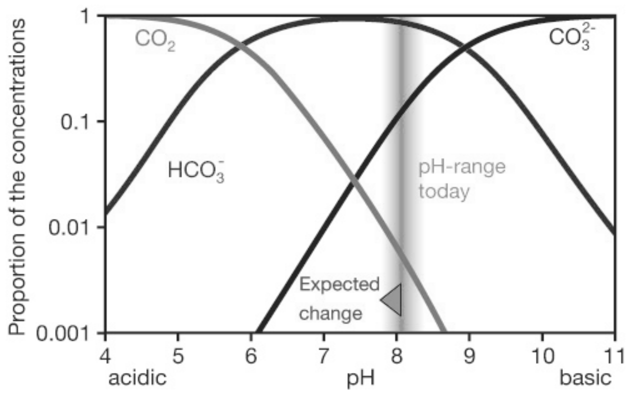
$$Ca(OH)_2 + Ca(HC0_3)_2 \rightarrow 2\ CaCO_3 \text{ [insoluble compound]} + 2\ H_20$$

- **Theory:**

- Hardness removal is divided into two types:
  1. Lime soda ash treatment: which is the most widely used type due low cost of lime and soda ash. The lime $Ca(OH)_2$ simply is added to the water of known dose that is adequate to make the carbonate hardness settle down, and soda ash (Na_2CO_3) to remove the non-carbonate hardness.

     This type also is divided into two types:

     A. Optimum dose: which is the minimum dose giving the specified concentration for end-use. That means the lowest concentration is not always the best. For example, the optimum hardness for residential uses is 150~400 mg/l as $CaCO_3$, therefore, the dose of lime gives us that hardness is the optimum dose.
        - The advantages of this method are lower the costs of lime and reduce the quantities of sludge formed by the precipitates of lime and soda ash.
        - The principle idea of this method that we have to find the optimum dose of lime ignoring the effect of soda ash, then at that dose of lime, we repeat the experiment one more time to find the optimum dose of soda ash.
        - The soda ash is not really participating in removal of hardness, but it gives a high pH to water so that we can remove non-carbonate hardness. Look to the next figure.



B. Excess lime treatment [Calculated dose] :

$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + H_2O$

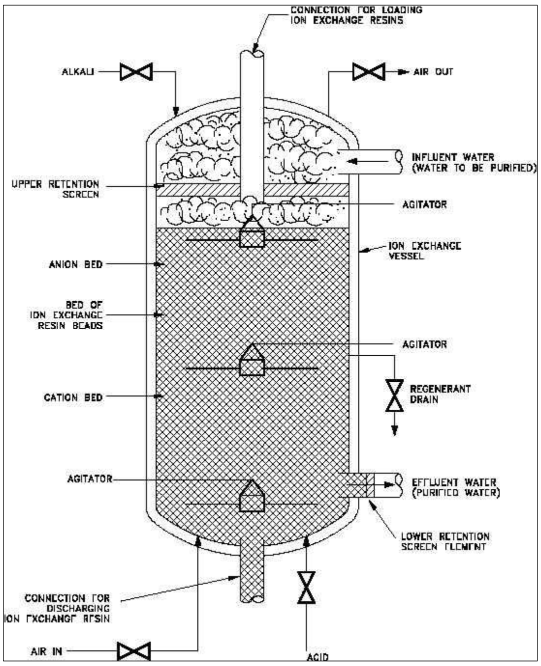
$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$

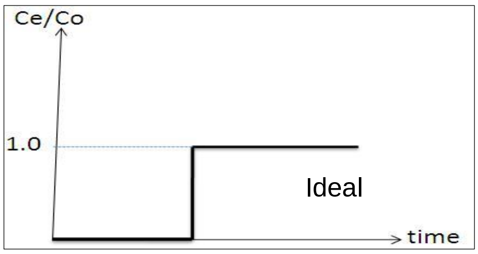
$Mg(HCO_3)_2 + 2\,Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow$

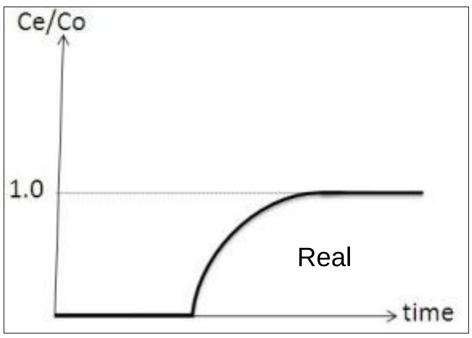
$Mg(SO)_4 + Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 + Mg(OH)_2\downarrow + Na_2SO_4$

- Using basic chemistry, we can figure out the quantities of lime or soda ash to be used in equivalents.
- A way to help us find these quantities is the neutralization box. [will be discussed in Data and Results].

2. Ion exchange: this device is simple exchanging the harmful divalent cations causing hardness like Ca^{+2} and Mg^{+2} with harmless monovalent cations like Na^{+1}.
   - The that ion exchanger works is that its filled with a media called resin that has a charge similar to the charge of our divalent cations [Ca^{+2}, Mg^{+2}], with a high surface area [or what we are interested in which is high specific charge].
   - The resin starts exchanging ions with higher charge, then with higher molecular weight, then with less hydraulic radius. In our case, the resin will start with Ca^{+2} because it has a higher molecular weight.
   - When the exchanger exchanges all the divalent cations, it reaches the saturation level and the concentration of Ca^{+2} in inlet will equal the outlet. At this stage, we will have to regenerate it by add water with very high concentrations of Na^{+}.
   - The main disadvantage of this method is the high cost of operation.







- **Procedure:**
  As in standard methods.

- **Data and results:**

1. Lime soda ash treatment:
   A. Optimum dose:
      I. Lime addition:
         EDTA Concentration = 0.02 molar
         Sample volume = 50 ml

No.	Lime (mg/l)	Lime (ml)	EDTA (ml)	Initial hardness Mg/l as $CaCO_3$	EDTA (ml)	Final hardness Mg/l as $CaCO_3$
1	100	40	17	340	12	240
2	150	60	17	340	11	220
3	200	80	17	340	9	180
4	250	100	17	340	8.5	170
5	300	120	17	340	8	160

Sample of calculation

$$\text{Hardness (mg/l) as } \mathrm{CaCO_3} = \frac{EDTA\ Vol.\times EDTA\ concentration\ \ (molarty)\times 50}{sample\ volume} \times 1000$$

$$= \frac{17\times 0.02\ \times 50}{50} \times 1000 = 340\ \frac{\mathrm{mg}}{\mathrm{l}}\ (\mathrm{mg/l})\text{ as } \mathrm{CaCO_3}$$

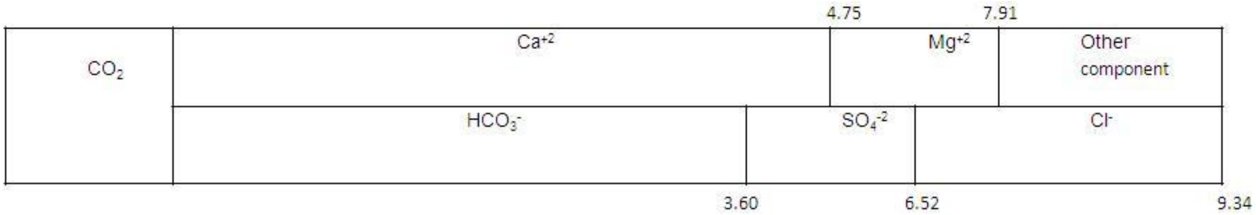
The optimum dose of lime =300 mg/l

II. Soda ash addition:
   Lime dose = 300 mg/l
   EDTA Concentration = 0.02 molar
   Sample volume = 50 ml

No.	Soda ash (mg/l)	Soda ash (ml)	EDTA (ml)	Initial hardness Mg/l as $CaCO_3$	EDTA (ml)	Final hardness Mg/l as $CaCO_3$
1	50	20	17	340	7	140
2	100	40	17	340	5	100
3	150	60	17	340	2	40
4	200	80	17	340	4	80
5	250	100	17	340	3	60

The optimum dose of soda ash =150 mg/l

B. Excess lime treatment:



	Lime meq/l	soda ash meq/l
$Ca(HCO_3)_2$	3.6	0.0
$CaSO_4$	0.0	1.15
$Mg(SO)_4$	1.77	1.77
sum	5.37	2.92

Lime = 5.37 +1.25 = 6.62 meq/l
Lime ($Ca(OH)_2$) = 6.62 meq/l * 37 mg /meq = 244.94 mg/l

Soda ash = 2.92 meq/l
Soda ash(Na_2CO_3)=2.92 meq/l * 53 mg /meq =154.70 mg/l
Concentration of EDTA = 0.2 molar
Sample volume = 50 ml

Soda ash (mg/l)	Lime (mg/l)	EDTA (ml)	Initial hardness Mg/l as $CaCO_3$	EDTA (ml)	Final hardness Mg/l as $CaCO_3$
154.70	244.94	17	340	3	60

C. Ion exchange:
Initial hardness C_o= 390 Mg/l as $CaCO_3$
Q = 3 L/min

Time (min)	C_e (Mg/l as $CaCO_3$)	Time (min)	C_e (Mg/l as $CaCO_3$)	Time (min)	C_e (Mg/l as $CaCO_3$)
0	0	80	28	160	380
10	0	90	40	170	385
20	0	100	70	180	387
30	0	110	100	190	389
40	3	120	152	200	390
50	8	130	220	210	390
60	13	140	330	220	390
70	20	150	360	230	390

1. The volume of water can be treated at C_e=100 mg/l as $CaCO_3$ is:
   C_e=100 mg/l as $CaCO_3$ at 110 min
   V = Q × t =3 L/min × 110 min =330 L

2. What time in required to react this concentration ?
   T = 110 min

3. When you will regeneration resin?
   When $C_e \backslash C_o = 1 \rightarrow Ce = 390\ mg\backslash l$ at 200 minutes.

- **Discussion and conclusion:**

Advantages of hard water	Disadvantages of hard water
Some people prefer the taste.	It is more difficult to form a lather with soap.
Calcium ions in the water are good for children's teeth and bones.	Scum may form in a reaction with soap, wasting the soap.
It helps to reduce heart disease.	Limescale (a hard crust) forms inside kettles. This wastes energy whenever you boil a kettle.
Some brewers prefer using hard water for making beer.	Hot water pipes 'fur up'. Limescale starts to coat the inside of the pipes which can eventually get blocked up.
A coating of limescale inside copper pipes, or especially old lead pipes, stops poisonous salts dissolving into water.	

- Hard water contains calcium ions, $Ca^{2+}(aq)$, or magnesium ions, $Mg^{2+}(aq)$. These ions react with soap, making it difficult to form a lather and producing scum.
- Hard water can be softened by adding washing soda (sodium carbonate) which removes the calcium ions in a precipitation reaction. Alternatively, the hard water can be passed through an ion-exchange resin in a column. Sodium ions replace the calcium ions in the water as it passes through the column.
- Temporary hardness can be removed by boiling the water. The calcium hydrogencarbonate dissolved in the water breaks down when heated and forms limescale.

- <u>Sources of hardness minerals in drinking water</u>: Calcium and magnesium dissolved in water are the two most common minerals that make water "hard." The degree of hardness becomes greater as the calcium and magnesium content increases and is related to the concentration of multivalent cations dissolved in the water.

- <u>Indications of hard water</u>: Clothes laundered in hard water may look dingy and feel harsh and scratchy. Dishes and glasses may be spotted when dry. Hard water may cause a film on glass shower doors, shower walls, bathtubs, sinks, faucets, etc. Hair washed in hard water may feel sticky and look dull. Water flow may be reduced by deposits in pipes.

- <u>Potential Health Effects</u>: Hard water is not a health hazard. In fact, hard drinking water generally contributes a small amount toward total calcium and magnesium human dietary needs, in some instances, where dissolved calcium and magnesium are very high, water could be a major contributor of calcium and magnesium to the diet.

- Interpreting Test Results of hardness:

Classification	mg/l or ppm	grains/gal
Soft	0 - 17.1	0 - 1
Slightly hard	17.1 - 60	1 - 3.5
Moderately hard	60 - 120	3.5 - 7.0
Hard	120 - 180	7.0 - 10.5
Very Hard	180 & over	10.5 & over

- Temporary hardness in water can be easily removed by boiling. On boiling, calcium /magnesium bicarbonate decomposes to give calcium/magnesium carbonate, which is insoluble in water. Therefore, it precipitates out.

- Depending on the pH of the treated water, most waters treated by the ion exchange process, are corrosive waters due to loss of the calcium and magnesium. Blended water or the addition of stabilizing chemicals will correct this.

- Resin problems:
  1. Iron in the ferrous state must not be allowed to enter the ion exchange process, as it will oxidize to the iron oxide state on the resin and become a permanent resident on the resin. If the iron oxide state is achieved prior to entering the ion exchange process, it will be removed from the process water during treatment and is able to be removed from the resin during the normal backwash cycle. Best practice is to remove all iron prior to the ion exchange process.
  2. Modern ion exchange resins are very resilient, with the life expectancy in excess of 15 years, when the process is properly operated. Excessive chlorine residuals will break down the resins, and must therefore not be applied to the resin beds. Surface waters, with accompanying biological growths, higher turbidities, and color values must be treated prior to the ion exchange process in order to prevent these materials coating the resin beads and interfering with the softening process.

- The ion exchange method is the most effective but the most expensive way to remove hardness of water.