SubjectName/Code: ENGINEERING CHEMISTRY (CH1001)

Detailed Syllabus:

Module#	Topics	Hours
Module-1	WaterTreatments:Types of hardness-Units,Alkalinity of water and its significance, Softening methods and Numerical problems based on these methods,Membrane-based processes, Dissolved Oxygen, Problems with Boiler feed water and its Treatments.	9
Module-2	Corrosion Science: Definition and scope of corrosion, Dry and wet corrosion, Direct chemical corrosion, Electro-chemical corrosion and its mechanisms, Types of electro-chemical corrosion (Differential aeration, Galvanic, Concentration cell), Typical Electro-chemicalcorrosionlike Pitting,Soil,Waterline, Factors affecting corrosion,Protection from corrosion.	8
Module-3	InstrumentalTechniques:FundamentalsofSpectroscopy, Principles and applications of molecular spectroscopy such as UV-visible, IR, Elementary idea about XRD, SEM & TEM	8
Module-4	EnergySciences:Typesoffuels,Calorificvalue,Determination of calorific value, Combustion and its calculations, Solid fuel – Coal analysis (Proximate and ultimate analysis), Liquidfuels – Concept of knocking, Anti-knocking, Octane and Cetane Nos, Battery Technology — Fundamentals of primary & secondary cells, Rechargeable batteries – Lead acid storage battery, Lithium ion battery, Fuel cells – Principles, Applications, Solar PV Cells.	9
Module-5	Nanochemistry:Nanomaterials,Classification of nanomaterials, Synthesis and characterization of noble metal nanoparticles (Gold and oxide-based nanoparticles) using Green Synthetic route, Stabilization of nanoparticles using capping agents, Applications of nanomaterials,Carbon based nanomaterials and Their applications, Brief idea on Graphene and Fullerene.	8
	Total	42 Hours

TextBook

EngineeringChemistry,Jain&Jain,DhanpatRaiPublishingCompany Engineering Chemistry,
Wiley-India Editorial Team, Wiley India
FundamentalsofMolecularSpectroscopy,C.N.Banwell,McGraw-Hill Education

ReferenceBook

Nanochemistry-A ChemicalApproachtoNanomaterials,G.A.Ozin&A.CArsenault,RSCPublishing Concepts of Nanochemistry,
J. M. Lehn, L. Cademartiri, Wiley-VCH
Engineering Chemistry, S. S. Dara, 12th Ed
ElementaryOrganicSpectroscopy,Y.R.Sharma,SChand&Co Ltd

OnlineReferenceMaterial(s): Course

Outcome:

CO1	Determinethehardnessofwaterandapplydifferenceprocessestosoftenhardwater
CO2	Utilizetheknowledgeofelectro-chemistryandcorrosionscienceforpreventionofcorrosion
CO3	Applymolecularspectroscopytoanalyzeorganiccompoundsusingspectrophotometer.
CO4	Classifyvariousfuelsbasedoncombustionparametersandunderstandtheworkingprinciplesof various batteries and solar photovoltaic cells.
CO5	Exploresynthesis&characterizationofnanoparticlesthroughgreensynthetic route.

ProgramOutcomesReleventtotheCourse:

PO1	Engineeringknowledge:Applytheknowledgeofmathematics,science,engineeringfundamentals, and an engineering specialization to the solution of complex engineering problems
PO2	Problemanalysis:Identify,formulate,reviewresearchliterature,andanalyzecomplexengineering problems reaching substantiated conclusions using first principles of mathematics, natural sciences, and engineering sciences.
PO3	Design/development of solutions: Design solutions for complex engineering problems and design systemcomponentsorprocessesthatmeetthespecifiedneedswithappropriateconsiderationfor the public health and safety, and the cultural, societal, and environmental considerations.
PO4	Conductinvestigationsofcomplexproblems:Useresearch-basedknowledgeandresearchmethods including design of experiments, analysis and interpretation of data, and synthesis of the information to provide valid conclusions.
PO5	Modern tool usage: Create, select, and apply appropriate techniques, resources, and modern engineeringandITtoolsincludingpredictionandmodelingtocomplexengineeringactivitieswith an understanding of the limitations.
PO6	The engineer and society: Apply reasoning informed by the contextual knowledge to assess societal,health,safety,legalandculturalissuesandtheconsequentresponsibilitiesrelevanttothe professional engineering practice.
PO7	Environmentandsustainability:Understandtheimpactoftheprofessionalengineeringsolutionsin societal and environmental contexts, and demonstrate the knowledge of, and need for sustainable development.
PO8	Ethics:Applyethicalprinciplesandcommittoprofessionalethicsandresponsibilitiesandnormsof the engineering practice.
PO9	Individualandteamwork:Functioneffectivelyasanindividual,andasamemberorleaderin diverse teams, and in multidisciplinary settings.
PO10	Communication: Communicate effectively on complex engineering activities with the engineering communityandwithsocietyatlarge,suchas,beingabletocomprehendandwriteeffectivereports and design documentation, make effective presentations, and give and receive clear instructions.
PO11	Project management and finance: Demonstrate knowledge and understanding of the engineering andmanagementprinciplesandapplythesetoone’sownwork,asamemberandleaderinateam, to manage projects and in multidisciplinary environments.

PO12	Life-longlearning:Recognizetheneedfor,andhavethepreparationandabilitytoengagein independent and life-long learning in the broadest context of technological change.

MappingofCO'stoPO's:(1:Low,2:Medium,3:High)

	PO1	**PO2**	**PO3**	**PO4**	**PO5**	**PO6**	**PO7**	**PO8**	**PO9**
CO1	2	2	1	1	1	2	1	1	
CO2	3	2	1	1	1	2	1		1
CO3	2	2	1	1	1	3	1	1	1
CO4	2	2	1	1	2	2	1	1	1
CO5	2	2		1	1	1	1		

Lecture-1

Water treatment is the process of removing all types of impurities from water, making it suitable for domestic and industrial use.

Impurities in water

Once water has fallen on the earth as rain, it will either start to penetrate the soil, remain on the surface in puddles, or run off into rivers or lakes - depending largely on the type of rock strata found immediately below the earth's surface. Therefore, the main source of impurities is the mineral and organic constituents which make up the upper layers of the earth's crust, and which are dissolved or held in suspension by the water. Surface waters are especially prone to seasonal changes in quality caused mainly by varying levels of organic contaminants. For instance, during the autumn and winter months, dead leaves and decaying plants release large quantities of organic matter into streams, lakes and reservoirs.

Water has been called both 'the matrix of life' and 'the universal solvent'. So in addition to providing a life-support system for a broad range of living organisms, it can dissolve virtually every chemical compound, though not necessarily to a detectable degree. It normally contains < 500 mg/l total dissolved solids TDS - equivalent to a purity of 99.95%. Even so, minute quantities of impurities can have a profound effect on industrial and laboratory processes - hence the need for purification.

The various impurities present in raw waters can be classified as follows:

A. **Dissolved impurities:** It is of three types: (**1**). ***Inorganic salts*** (due to presence of dissolved salts like carbonates, bicarbonates, nitrates, chlorides and sulphates of calcium (Ca), magnesium (Mg), iron (Fe),sodium (Na), etc. (**2**). ***Organic matters*** (due to presence of humic and fulvic Acids) (3) ***Dissolved gases*** **(**includes O_2, CO_2). Dissolved impurities causes corrosion in boilers and imparts hardness to water.

B. **Suspended & Colloidal impurities:** (1) **Suspended Impurities:** *Organic* (includes vegetable & animal matters, industrial & domestic by-products, oil globules, etc.); *Inorganic* (includes clay/silica/sand particles); (3) ***Colloidal*** *(*organic and inorganic)- includes finely divided silica, clay, sand, products from organic wastes, etc. Such impurities impart turbidity, colour and odour to water.

C. **Living Matters:** It is of two types: (1) *Micro-organisms* (include bacteria, fungi, protozoa, and algae); (2) *Macro-organisms* (includes fish, worm, larvae, etc.). Living matters brings health related issues upon consumptions.

Hardness- A water quality parameter of water

Hardness in water is a characteristic by virtue of which it prevents lathering/foaming of soap solution. It is also defined as the soap consuming capacity of water. Higher is the hardness of water larger is the consumption of soap. Hardness is due to presence of dissolved salts of calcium (Ca), magnesium (Mg) and other heavy metals like iron (Fe), manganese (Mn), and aluminum (Al). In other words hardness in water is due to bicarbonate (HCO_3^-), chloride (Cl^-), sulphate (SO_4^{3-}), and nitrate (NO_3^-) of Ca, Mg, Fe, Mn, Al, etc.

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Salts like $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $FeSO_4$, $Al_2(SO_4)_3$, $MnSO_4$, $Mn(HCO_3)_2$, $Fe(HCO_3)_2$, etc. are responsible of hardness of water. **The major contributor towards hardness is Ca and Mg-salts.

N.B.: Chemical constituents like $NaHCO_3$, NaCl, KCl, K_2SO_4, Na_2SO_4, $NaNO_3$, KNO_3, Fe_2O_3, etc. are treated as ***non-hardness constituents***.

Soap consuming tendency of hard water *(Why is hard water consumes more soap?)*

Soaps are sodium (Na) or potassium (K) salt of higher fatty acids (e.g.; Stearic acid $C_{17}C_{35}COOH$, oleic acid $C_{17}C_{33}COOH$, palmitic acid $C_{15}C_{31}COOH$). For example, $C_{17}C_{35}COONa$ (Sodium stearate).

A sample of hard water (let say contains hardness constituent as $CaCl_2$) when treated with soap does not produce enough lather, but on the other hand forms a white scum or precipitate. The precipitation process continues till all the hardness constituents are removed as white scum. After this, soap generates enough foam with water. The chemical reactions involved during this process are as follows:

1. $2C_{17}C_{35}COONa$ (soap) + $CaCl_2$ → $(C_{17}C_{35}COO)_2Ca$ (*Calcium Stearate, White scum*) + 2NaCl
2. Soap + water → Produces enough foam

Hard Water and Soft Water

The water which does not produce lather with soap solution readily, but forms a white curd is called hard water. In fact any cations which produce soft precipitate with soap solution will contribute to hardness. Examples include Ca^{+2}, Mg^{+2}, etc. On the other hand, water which lathers easily on shaking with soap solution is called soft water. Soft water is free from dissolved Ca and Mg-salts. The difference between the two is summarized in the following table.

Sl. No.	**Hard Water**	**Soft Water**
1	Water which does not readily produce lather with soap solution, but forms a white curd, is called "Hard Water".	Water which readily form foam on shaking with soap solution, is called "Soft Water".
2	It contains dissolved Ca, Mg, Fe, Mn-salts.	It does not contain dissolved Ca, Mg, Fe, Mn-salts.
3	Cleansing quality of soap is depressed and a lot of soap is wasted during washing and bathing.	Cleansing quality of soap is not depressed and a little amount of soap is wasted during washing and bathing.
4	B. Pt. of water is elevated.	Water boils at 104 ^{0}C.
5	Hair and skin becomes hard and dull.	Hair and skin becomes soft.
6	It is not a plumbosolvent	**Plumbo-solvency** occurs

***A residual hardness 100-200 ppm as $CaCO_3$ equivalent is needed for drinking purposes.

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***Plumbosolvency*: Plumbosolvency** is the ability of a solvent like water to dissolve lead (Pb latin name-Plumbum). Soft water is a plumbo-solvent. Permissible limit of Pb in water is 0.01 ppm.

Why shouldn't drinking water be too soft?

The reason is that soft water is plumo-solvent and helps in dissolution of Pb as per the following reaction: $\mathbf{2Pb + 2H_2O + O_2 \rightarrow 2Pb(OH)_2}$

N.B: The solubility of Pb in water is diminished in the presence of HCO_3^- (i.e., in hard water)

Also minerals like Calcium is needed *for strong teeth and healthy bones in children.*

Q.2. Which of the following salts are non-hardness constituents?

Na_2SO_4, $NaNO_3$, $Al_2(SO_4)_3$, $MnSO_4$, $Mn(HCO_3)_2$

Ans. Na_2SO_4 and $NaNO_3$

Q. 3. What is plumbo-solvency?

Ans: Plumbosolvency is the ability of a solvent like water to dissolve lead (Pb stands for plumbum in Latin)

$$\mathbf{2Pb + 2H_2O + O_2 \rightarrow 2Pb(OH)_2}$$

Q. 4. Give reason that hard water is not a plumbo-solvent.

Ans. 1. The solubility of Pb (plumbum) in water is diminished in the presence of HCO_3^- , SO_4^{2-} (i.e., in hard water), 2. bicarbonates and sulphates provide a protective layer on the surface of the pipe.

Q. 5. Give reason that hard water consumes a lot of soap.

Ans. A sample of hard water (let say contains hardness constituent as $CaCl_2$) when treated with soap does not produce enough lather, but on the other hand forms a *white scum or precipitate*. The precipitation process continues till all the hardness constituents are removed as white scum. After this, soap generates enough foam with water. The chemical reactions involved during this process are as follows:

3. $2C_{17}C_{35}COONa$ (soap) + $CaCl_2 \rightarrow (C_{17}C_{35}COO)_2Ca$ (*Calcium Stearate, White scum*) + 2NaCl
4. After some time, Soap + water (Free from hardness)→ Produce enough foam

Q. 6. Write the chemical reactions involved when hard water reacts with soap.

Ans. The chemical reactions involved during this process are as follows:

1. $2C_{17}C_{35}COONa$ (soap) + $CaCl_2 \rightarrow (C_{17}C_{35}COO)_2Ca$ (*Calcium Stearate, White scum*) + 2NaCl
2. Soap + water → Produce enough foam

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Disadvantages of Hard Water

A. In domestic use:

1. **Washing:** Causes wastage of lot of soap. The white scum adheres on the fabric giving spots and streaks. If iron and manganese salts are there then may cause staining of cloth.
2. **Bathing:** Cleansing quality of soap is depressed and a lot of it is wasted.
3. **Cooking:** As boiling pint of hard water is high, more fuel and time are required for cooking. Certain foods such as pulses, beans, peas do not cook soft. Tea of coffee prepared has an unpleasant taste and muddy looking extract. Carbonates were found stuck on the inner walls of utensils.
4. **Drinking:** There is a bad effect on our digestion process. Chances of formation of calcium oxalate in the urinary tract are always there.

B. In industrial use

1. ***Textile industries***
   - ✓ Uniform dyeing is not possible if hard water is used
   - ✓ Hard water decreases the solubility of acidic dyes and basic dyes precipitate out
   - ✓ Fe and Mn salts containing water may cause colored spots on fabrics
2. **Sugar Industry**

✓ Hard water results in the formation of deliquescent sugar

✓ Cause difficulty in the crystallization of sugar

3. **Paper Industry**

   Fe and Mn salts affect the brightness and color of the paper

   Hardness increases the ash content of the paper
4. **Laundry:**

   Mn and Fe salts impart grey/reddish shade to the fabric

   Hard water increases soap consumptions
5. ***Boilers in steel industries*:** Hard water leads to corrosion and chocking of boiler.

Advantages and disadvantages of hard water

Advantages	***Disadvantages***
1. Taste of water is better than soft water	*1. It produces white precipitate with soap solution. Thus, the washed clothes look dull.*
2. Dissolved Ca-salts helps in producing strong teeth and healthy bones in children	*2. Causes boiler corrosion. Not used in industries like sugar, textiles, paper, etc.*
3. Not a plumbo-solvent	*3. Increases B. Pt. of water.*

Q. 7. Mention some advantages of hard water. (Refer the above table)

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Q. 8. Mention some disadvantages of hard water. (Refer above)

Q.9. Mention the disadvantages of hard water in sugar industries. [2 marks]

Ans. Hard water results in the formation of deliquescent sugar. It also cause difficulty in the crystallization of sugar

Q.10. **Mention the disadvantages of hard water in paper and textile industries. [3 marks]**

Ans. Paper Industry:

Fe and Mn salts affect the brightness and color of the paper
Hardness increases the ash content of the paper

***Textile industries*:**

- ✓ Uniform dyeing is not possible if hard water is used
- ✓ Hard water decreases the solubility of acidic dyes and basic dyes precipitate out
- ✓ Fe and Mn salts containing water may cause colored spots on fabrics

Types of Hardness

It is of two types: (1) Temporary Hardness and (2) Permanent Hardness

1. *Temporary Hardness:* It is caused by the presence of dissolved carbonates and bicarbonates (HCO_3^-) of Ca and Mg, heavy metals like Al, Mn and carbonates of Fe. The salts responsible are $CaCO_3$, $MgCO_3$, $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, etc. These salts are thermally unstable and undergo thermal decomposition to form insoluble substance as follows;
   a. $Ca(HCO_3)_2 \rightarrow CaCO_3$ (ppt.) + H_2O + CO_2
   b. $Mg(HCO_3)_2 \rightarrow Mg(OH)_2$ (ppt.) + $2CO_2$

So, temporary hardness can be removed by boiling. It is otherwise known as ***carbonate or alkaline hardness*.**

2. *Permanent Hardness:* It is caused by the presence of chloride (Cl^-), nitrates (NO_3^-), sulphates (SO_4^{2-}) of Ca, Mg, Fe, Al, Mn, etc. The salts responsible are $CaCl_2$, $Ca(NO_3)_2$, $CaSO_4$, $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, $Al_2(SO_4)_3$, $FeSO_4$, etc. These salts are thermally stable as present in ionic form in water. So, they can't be remove by heating but removed by softening methods. It is also known as ***non-carbonate or non-alkaline hardness*.**

Total Hardness

All the hardness causing salts contribute towards total hardness. So, total hardness is the sum of temporary and permanent hardness.

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Q. 11. Which of the following salt is a non-hardness constituent?

$MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, $Al_2(SO_4)_3$, $NaHCO_3$

Ans. $NaHCO_3$

Q. 12. Which of the following salts are hardness constituents?

$CaCl_2$, $Ca(NO_3)_2$, K_2SO_4, Na_2SO_4, $NaNO_3$, KNO_3, Fe_2O_3

Ans. $CaCl_2$ and $Ca(NO_3)_2$

Q.13. Which of the following salts are permanent-hardness constituents?

$Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaCl_2$, K_2SO_4 and $FeSO_4$

Ans. $CaCl_2$ and $FeSO_4$

Q.14. Which of the following salts are temporary-hardness constituents?

$Mg(HCO_3)_2$, $Mn(HCO_3)_2$, $NaHCO_3$, $CaCl_2$, K_2SO_4

Ans. $Mg(HCO_3)_2$ and $Mn(HCO_3)_2$

Degree of Hardness (Equivalents of Calcium Carbonate)

How to express hardness of water?

As $CaCO_3$ is almost insoluble in water, it hardly contributes towards hardness of water. But, hardness of water is expressed in terms of equivalent amount of $CaCO_3$ due to following reasons:

A. Ease in calculation as its molecular weight is 100.
B. It is the most insoluble salt that can be precipitated during water treatment.

Equivalent of $CaCO_3$ = (S, strength of hardness substance in mg/L) x [100/ (2 x M/n-factor)]

Where, M = Molar mass of hardness substance.

N.B.: n-factor of all Ca and Mg-salts are 2. For aluminum sulphate, it is 6.

- ✓ All hardness and non-hardness constituents can be expressed as **Equivalent of $CaCO_3$**

Q. 15. Give reason that $CaCO_3$ is used to express hardness of water.

Ans. The hardness of water is expressed in terms of equivalent amount of $CaCO_3$ due to following reasons:

A. Ease in calculation as its molecular weight is 100.
B. It is the most insoluble salt that can be precipitated during water treatment.

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Q. 16. What happens when hard water containing temporary hardness constituents are boiled for some time?

Ans. Temporary hardness constituents like $Ca(HCO_3)_2$ $Mg(HCO_3)_2$ are thermally unstable and undergo thermal decomposition to form insoluble substances like $CaCO_3$ & $Mg(OH)_2$ as follows;

c. $Ca(HCO_3)_2 \rightarrow CaCO_3$ (ppt.) + H_2O + CO_2
d. $Mg(HCO_3)_2 \rightarrow Mg(OH)_2$ (ppt.) + $2CO_2$

Units of hardness and their inter-relations

Hardness can be expressed by the four units.

1. Parts per million (ppm): It is the 1 part of $CaCO_3$ equivalent hardness per 10^6 parts of water.
2. Millligrams per litre (mg/L): It is the no of mg of $CaCO_3$ equivalent hardness present per litre of water.
3. Degree French (^{0}Fr): It is the 1 part of $CaCO_3$ equivalent hardness per 10^5 parts of water.
4. Clarke's degree (^{0}Cl): It is the part of $CaCO_3$ equivalent hardness per 70,000 parts of water.

Relationships between various units of Hardness

5. We know that, 1 ppm = 1 part per 10^6 parts of water => 1 part = 10^6 ppm ----(1)
   1 ^{0}Fr = 1 part per 10^5 parts of water, => 1 part = 10^5 ^{0}Fr -------(2)
   And 1 ^{0}Cl = 1 part per 70, 000 parts of water => 1 part = 70,000 ^{0}Cl –(3)
   From equation (1), (2), and (3), we found that
   1 part = 10^6 ppm = 10^5 ^{0}Fr = 70,000 ^{0}Cl
   Or, 10^6 ppm = 10^5 ^{0}Fr = 70,000 ^{0}Cl ---- (4)
   Now Divide Eq. 4 by 10^6, so that **1 ppm = 0.1 ^{0}Fr = 0.07 ^{0}Cl = 1 mg/L**

Q. 17. Show that 1 ppm = 1 mg/L [1 mark]

Answer: 1 mg/L means 1 mg of $CaCO_3$ eq. hardness in 1L of water

= 1 mg of $CaCO_3$ eq. hardness in 10^6 mg of water *** (for water, 1 L is nearly 1 Kg = 1000 g = 1000,000 mg = 10^6 mg)

=> 1 part of $CaCO_3$ equivalent hardness per 10^6 parts of water = 1 ppm (proved)

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Numerical on Finding Total Hardness

Example-1 Express the following constituents as $CaCO_3$ eq.: (1) 162 mg/L of $Ca(HCO_3)_2$, (2) 111 mg/L of $CaCl_2$, and (3) 117 mg/L NaCl, Given: At mass: Ca = 40, C = 12, O = 16, H = 1, Na = 23, Cl = 35.5

Solution: (1) $Ca(HCO_3)_2$ as $CaCO_3$ eq. = 162 x 100/162 = 100 mg/l, here n-factor = 2

(2) $CaCl_2$ as $CaCO_3$ eq. = 111 x 100/111= 100 mg/l, here n-factor = 2

(3) NaCl as $CaCO_3$ eq. = 117 x 100/2 x 58.5 = 100 mg/l, **here n-factor = 1**

Example-2 A water sample contains 136 mg/L of $CaSO_4$. Calculate the hardness as equivalent amount of $CaCO_3$. (At mass of Ca = 40, S = 32, O = 16)

Solution: Equivalent of $CaCO_3$ = 136 x [100/(2 x 136/2) = 100 ppm

Example-3 How many gram of $MgSO_4$ dissolved per litre gives 200 ppm of hardness as equivalent amount of $CaCO_3$. (At mass: Mg = 24, S = 32, O = 16)

Solution: Equivalent of $CaCO_3$ = (S, strength of hardness substance in mg/L) x [100/ (2 x M/n-factor)]

So, (S, strength of hardness substance in mg/L) = Equivalent of $CaCO_3$/ [100/ (2 x M/n-factor)]

Or S = 200/[100/(120)] = 240 mg/L = 0.24 g/L

Example-4 A sample of water on analysis was found to contain the following impurities:

Impurity	**$Ca(HCO_3)_2$**	**$Mg(HCO_3)_2$**	**$MgSO_4$**	**$CaSO_4$**	**K_2SO_4**
Quantity (mg/L)	**4**	**6**	**8**	**10**	**10**
Mol Wt.	**162**	**146**	**120**	**136**	**134**

Calculate the temporary, permanent, and total hardness of water in ppm, ^{0}Fr and ^{0}Cl.

Solution: *N.B.: K_2SO_4 is a non-hardness constituent.*

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Impurity	Quantity (mg/L)	n-factor	Mol. Wt.	$CaCO_3$ eq. in mg/L
$Ca(HCO_3)_2$	4	2	162	4 x (100/162)= 2.47
$Mg(HCO_3)_2$	6	2	146	6 x (100/146)= 4.11
$MgSO_4$	8	2	120	8 x (100/120)= 8.33
$CaSO_4$	10	2	136	10 x (100/136)= 5.88

(i) **Temporary Hardness (due to bicarbonates of Ca and Mg) =** 2.47 + 4.11 = 6.58 ppm = 6.58 x 0.1 ^{0}Fr = 0.658 ^{0}Fr = 6. 58 x 0.07 ^{0}Cl = 0.46 ^{0}Cl

(ii) **Permanent hardness (due to sulphates of Ca and Mg) =** 5.88 + 8.33 = 14.21 ppm = 1.421 **^{0}Cl** = 0.995 ^{0}Cl

(iii) **Total hardness =** 6.58 + 14.21 = 20.79 ppm = 2.079 ^{0}Fr = 0.9947 ^{0}Cl

Example-5

A sample of water on analysis was found to contain the following impurities:

Impurity	$Ca(HCO_3)_2$	$CaSO_4$	$MgCl_2$	$CaCl_2$	NaCl
Quantity (mg/L)	16.2	27.2	9.5	22.2	10
Mol Wt.	162	136	95	111	58.5

Calculate the temporary, permanent, and total hardness of water in ppm, ^{0}Fr and ^{0}Cl.

Impurity	Quantity (mg/L)	n-factor	Mol. Wt.	$CaCO_3$ eq. in mg/L
$Ca(HCO_3)_2$	16.2	2	162	16.2 x (100/162)= 10
$CaSO_4$	27.2	2	136	27.2 x (100/136)= 20
$MgCl_2$	9.5	2	95	9.5 x (100/95)= 10
$CaCl_2$	22.2	2	111	22.2 x (100/111)= 20

Solution:

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N.B.: NaCl is a non-hardness constituent.

- **(i)** **Temporary Hardness (due to** $Ca(HCO_3)_2$**) = 10 mg/L = 10** ppm = 10 x 0.1 ^{0}Fr = 1.0 ^{0}Fr = 10 x 0.07 ^{0}Cl = 0.7 ^{0}Cl
- **(ii)** **Permanent hardness (due to** $CaSO_4$, $MgCl_2$, $CaCl_2$ **) =** 20 + 10 + 20 = 50 mg/L = 50 ppm = 5.0 ^{0}**F** = 3.5 ^{0}Cl
- **(iii)** **Total hardness =** 10 + 50 = 60 ppm = 6 ^{0}Fr = 4.2 ^{0}Cl

Example-6 Find the Total hardness of water if water containing 100 mg/L of $Ca(HCO_3)_2$, 200 mg/L of $Mg(HCO_3)_2$ and 250 mg/L NaCl is boiled for 15 minute.

Ans. Total Hardness = 0, as Temporary hardness is removed by boiling. NaCl is non-hardness mass.

Example-7 A water sample contains 150 mg/L of $Ca(HCO_3)_2$, 111 mg/L of $CaCl_2$, 12 mg/L of $MgSO_4$, and 250 mg/L of Na_2SO_4. Find the temporary, permanent and total hardness of water after boiling for 10 minute.

Ans. (i) **$Ca(HCO_3)_2$ can be removed by boiling. So, Temp. Hardness = 0**

Na_2SO_4 is a non-hardness mass.

(ii) Here, Permanent hardness is due to presence of dissolved $CaCl_2$ and $MgSO_4$ in water.

So, at first we have to express these hardness constituents as $CaCO_3$ eq.

$CaCl_2$ as $CaCO_3$ eq. = (111 x 100/111) = 100 mg/L; Molar mass of $CaCl_2$ = 111, n-factor = 2

$MgSO_4$ as $CaCO_3$ eq. = (12 x 100/120) = 10 mg/L; Molar mass of $MgSO_4$ = 120, n-factor = 2

So, **Perm. Hardness** = 100 + 10 = 110 mg/l = 110 ppm = 11 ^{0}Fr = 7.7 ^{0}Cl.

(iii)Total hardness = Temp + Perm. = 0 + 110 = 110 mg/l = 110 ppm = 11 ^{0}Fr = 7.7 ^{0}Cl.

Example-8. A water sample contains 150 mg/L of $NaHCO_3$, 111 mg/L of NaCl, 12 mg/L of K_2SO_4, and 250 mg/L of Na_2SO_4. Find the total hardness of water.

Ans. Total hardness of water = 0 (as all are non-hardness constituents.)

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Alkalinity- A water quality parameter

It is a measure of the ability of water to neutralize the acids.

Any substances which can increase the hydroxide ion concentration [OH^-] contribute towards alkalinity of water. Alkalinity is due to presence of ions like CO_3^{2-}, OH^-, HCO_3^- in the water.

N.B.: The possibility of OH^- and HCO_3^- together in water is ruled out. (Why?)

*** Because they combine to form CO_3^{2-} in water as per the following reaction:

$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$ (or $NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O$)

Drawbacks of highly alkaline water

Some of the drawbacks are: 1. it causes alkaline corrosion in boiler known as caustic embrittlement.
2. It may leads to deposition of precipitates in boiler tubes and pipes.
3. Not fit for human consumption for a longer period of time.

Q. Which of the following combination is ruled out and why?

A. OH^- and CO_3^{2-}

B. CO_3^{2-} and HCO_3^-

C. OH^- and HCO_3^-

Ans. **C.** Because they combine to form CO_3^{2-} in water as per the following reaction:

$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$ (or $NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O$)

Dissolved Oxygen (DO): A Water quality parameter

It is the most usual corrosion causing factor in boilers. DO react with the iron (Fe) of boiler in presence of water to form rust (Ferric oxide). Water usually contains 8 mg/L at RT. DO is a temperature dependent parameter.

Chemical reaction:

$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2$ (ferrous form is unstable)

$Fe(OH)_2$ oxidizes in presence of oxygen to form Ferric oxide ($Fe_2O_3 . xH_2O$).

Removal of DO: (1) By heating (Thermal deoxygenation): In this process water is heated in a container (**known as degasifier)** to remove DO.

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(2) Chemical Deoxygenation: By addition of dilute solution of Hydrazine (NH_2-NH_2 or N_2H_4), Sodium sulphite Na_2SO_3 and sodium sulphide Na_2S

1. $O_2 + N_2H_4 \rightarrow N_2 + 2H_2O$
2. $O_2 + 2Na_2SO_3 \rightarrow 2Na_2SO_4$
3. $2O_2 + Na_2S \rightarrow Na_2SO_4$

Q. How to remove DO by adding hydrazine to water?

Ans. $O_2 + N_2H_4 \rightarrow N_2 + 2H_2O$

Specifications for Boiler feed water

Lot of water is used in boilers of steel industries for generation of steam. But, water with specific characteristics is fit for feeding into it.

A boiler feed water should have the following characteristics:

a. Total hardness should be either 0 or less than 2 ppm.
b. Alkalinity should be less than 1 ppm.
c. Should be free from acidic masses
d. Should be free from dissolved gases like oxygen and carbon dioxide

Common problems found in a boiler

The common problems which were arising in boiler due to feeding of hard/alkaline/acidic water are as follows:

A. Formation of soft and hard precipitates known as **sludges ($MgCO_3$, $MgSO_4$) and scales ($MgSiO_3$, $CaSiO_3$, $CaCO_3$)**, respectively
B. Boiler Corrosion

Q. What should be the characteristics of boiler feed water?

Ans. ***A boiler feed water should have the following characteristics:***

a. Total hardness should be either 0 or less than 2 ppm
b. Alkalinity should be less than 1 ppm

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c. Should be free from acidic masses
d. Should be free from dissolved gases like oxygen and carbon dioxide

Boiler Corrosion

It is the decay or loss of boiler body material (usually made of iron) either due to chemical or electrochemical reactions with its environment.

Causes of boiler corrosion:

1. Presence of dissolved O_2 in water: $Fe + O_2 + H_2O \rightarrow Fe_2O_3.xH_2O$ (Rust)
2. Presence of dissolved CO_2 in water: $Fe + 2H^+$ (from H_2CO_3)$\rightarrow Fe^{2+} + H_2$
3. Presence of alkaline masses in water (e.g. NaOH): $Fe + 2NaOH \rightarrow H_2 + Na_2FeO_2$ (sodium Ferrite)
4. Presence of acidic masses in water (e.g. HCl): $Fe + 2HCl \rightarrow FeCl_2 + H_2$
5. Presence hardness causing substance like $MgCl_2$ in water ($MgCl_2 + H_2O \rightarrow Mg(OH)_2$ (ppt.) + 2 HCl)

Disadvantages:

1. Reduces the life of boiler
2. Causes leakages at joints
3. Increases the cost of repair & maintenance

Q. What is boiler corrosion? Mention some of its limitations.

Ans. Boiler corrosion is the decay or loss of boiler body material (usually made of iron) either due to chemical or electrochemical reactions with its environment.

Limitations:

1. Reduces the life of boiler
2. Causes leakages at joints
3. Increases the cost of repair & maintenance

Q. Mention some causes of boiler corrosion.

Ans. Various causes of boiler corrosion are:
1. Presence of dissolved O_2 in water
2. Presence of dissolved CO_2 in water
3. Presence of alkaline masses in water (e.g. NaOH)
4. Presence of acidic masses in water (e.g. HCl)
5. Presence hardness causing substance like $MgCl_2$ in water ($MgCl_2 + H_2O \rightarrow Mg(OH)_2$ (ppt.) + 2 HCl)

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Softening of hard water

Since hard water is unsuitable for domestic as well as industrial use, it is advisable to remove or reduce the amount of hardness causing salts from the water. *The process by which we remove or reduce the hardness of water is termed as "**softening**" of water.*

Water Softening by Lime-Soda Process

Lime (L)-Soda (S) Softening Process

Basic Principle: The basic principle of this process is to convert all the soluble hardness causing constituents into insoluble masses (known as precipitates) by addition of calculated amount of lime **$Ca(OH)_2$** and soda **Na_2CO_3** to the hard water. The precipitates [$CaCO_3$ and $Mg(OH)_2$] are then removed by sedimentation (a settling process) and filtration.

Types of L-S process: Based on the working temperature of the softener, it is of two types.

(1) Cold L-S Process, and (2) Hot L-S Process

Cold L-S Process: In this process calculated amount of chemicals (L & S) are added to the water at room temperature (RT).

But, at RT, the precipitates formed are very fine and do not settle down easily under the force of gravity and can easily pass through the filter too. So, in order to avoid such situation a small amount of **coagulants** like potash alum [$K_2SO_4.Al_2(SO_4)_3.24H_2O$], Aluminium sulfate $Al_2(SO_4)_3$, or sodium aluminate $NaAlO_2$ are added to the water along with L & S. Thus coagulant helps in converting fine particles to coarse particles. This process provides water with a residual hardness of 50-60 ppm.

Hard water + L + S + Coagulant → Precipitates + soften water

1. $CaCl_2$ (hard water) + Na_2CO_3 (soda) → $CaCO_3$ (ppt) + 2 NaCl
2. $MgCl_2$ + $Ca(OH)_2$ (lime)+ Na_2CO_3 (soda) → $Mg(OH)_2$ (ppt) + $CaCO_3$ (ppt) + 2 NaCl

Working process: Hard water and calculated amount of lime, soda and coagulant are fed from the top of the softener fitted with a paddle stirrer at RT (see Figure). Vigorous stirring ensures continuous mixing and softening takes place. The soften water rising up passes through a wood-fibre filter whereby traces of sludge are removed. The precipitates settle down at the bottom by the time the softened water reaches the outlet. Coarse precipitates are settled down and relatively finer one is retained by the wood filter. The precipitates are periodically removed through the sludge outlet.

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Fig. Cold L-S Softener

Limitations of cold L-S process: Some of the limitations are: (1) Residual hardness is high (50- 60 ppm), so not fit for boiler operation; (2) As it operates at RT, softening capacity is low, rate of precipitation is slow; (3) Dissolved gases are not removed; (4) Relatively more chemicals are needed (coagulant is required); (4) Bacteria are not killed; (5) need skilled operator/ supervisor; (5) disposal of huge amount of sludge is a problem

Questions:

Q. Define softening with a suitable example.

Ans. The process by which we remove or reduce the hardness of water is termed as "softening" of water. Example:- Lime-Soda process

Q. What is a coagulant? Give an example.

Ans. Coagulant is a substance which helps in settling of fine particles. Example:-Potash Alum

Q. Define coagulation. Mention a reaction between coagulant and hardness causing mass.

Ans. Coagulation is a process by which finer particles are converted into coarser particles by addition of a coagulant.

$Al_2(SO_4)_3$ coagulant + $3Ca(HCO_3)_2 \rightarrow 2\ Al(OH)_3$ gelatinous ppt. + $3CaSO_4 + 6CO_2$

Q. What is the basic principle of L-S process?

Ans. The basic principle of this process is to convert all the soluble hardness causing constituents into insoluble masses (known as precipitates) by addition of calculated amount of lime $\mathbf{Ca(OH)_2}$ and soda $\mathbf{Na_2CO_3}$ to the hard water. The precipitates [$CaCO_3$ and

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$Mg(OH)_2$] are then removed by sedimentation (a particle settling process) and filtration. This softening process proceeds via precipitation reaction.

Q. **What is the basic principle of L-S process? Describe the cold L-S process with a neat softener diagram.**

Ans. Refer above

Q. Mention the limitations of Cold L-S Process

Ans. *Limitations of cold L-S process:* Some of the limitations are: (1) Residual hardness is high (50- 60 ppm), so not fit for boiler operation; (2) As it operates at RT, softening capacity is low, rate of precipitation is slow; (3) Dissolved gases are not removed; (4) Relatively more chemicals are needed (coagulant is required); (4) Bacteria are not killed; (5) need skilled operator/ supervisor; (5) disposal of huge amount of sludge is a problem

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Hot L-S Process: In this process water is treated with calculated amount of lime and soda at a temperature of 90-100 ^{0}C.

Working process: Raw water, chemicals and steam are thoroughly mixed in a reaction tank maintained at ~100 ^{0}C using steam. The sludge formed after reaction is settled down in a conical *sedimentation vessel*. Then water passed through a ***sand filter*** to obtain clear and soften water with a residual hardness 15-30 ppm.

Fig. Hot L-S process

Advantages of Hot L-S process over cold process:

1. Process is faster, 2. Good softening capacity, 3. No coagulant is required, 4. Relatively less amount of chemicals are needed, 5. Dissolved gases are removed, 6. Pathogenic bacteria are killed, 7. Residual hardness is relatively low

Q. Differentiate between Cold and Hot L-S process.

Sl. No.	***Cold L-S process***	***Hot L-S process***
1	*Performed at RT*	*Performed at ~100 ^{0}C*
2	*Slow process*	*Fast process*
3	*Coagulant is needed*	*Coagulant is not needed*
4	*Filtration is not easy*	*Filtration is easy as viscosity decreases at high temperature*
5	*Residual hardness is 60 ppm*	*Residual hardness is 15-30 ppm*
6	*Dissolved gases are not removed*	*Dissolved gases are removed*
7	*Low softening capacity*	*High softening capacity*
8	*Bacteria are not killed*	*Bacteria are killed*

Q. Mention some advantages of Hot L-S process over cold process.

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Ans: Some of the advantages of hot L-S process are:

1. Process is faster
2. Good softening capacity
3. No coagulant is required
4. Relatively less amount of chemicals are needed
5. Dissolved gases are also removed
6. Pathogenic bacteria are also killed
7. Residual hardness is relatively low

Q. Why is coagulant not required in hot L-S process?

Ans. The hot L-S process is carried out at a temperature of 100-110°C, resulting in the formation of coarse precipitates due to the high reaction rate.

Q. What is the use of sand filter in Hot L-S softener?

Ans. Sand filter is used to remove suspended particles present in the water.

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Chemicals required for various hardness constituents

Key Points:

1. Substances such as NaCl, Na_2SO_4, $NaNO_3$, KCl, K_2SO_4, KNO_3, SiO_2, Fe_2O_3, etc. do not consume any L & S and should therefore be excluded from the calculation of L & S requirements.
2. All substances must be converted into their respective $CaCO_3$ equivalents.
3. Ca-hardness is precipitated as $CaCO_3$, while Mg-hardness is precipitated as $Mg(OH)_2$.

Chemicals requirement for Temporary hardness constituents:

A. $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ -------- needs 1 mole of L (1L)

B. (i) $Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow$ **$Ca(HCO_3)_2$** $+ Mg(OH)_2$ ----- 1L

(ii) **$Ca(HCO_3)_2$** $+ Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ ----- 1L

1L + 1L = 2 L

Or by combining eq. (i) and (ii) we get

$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 + Mg(OH)_2 + 2H_2O$ --- 2L

✓ *1 mole of $Ca(HCO_3)_2$ needs 1 mole of Lime whereas 1 mole of $Mg(HCO_3)_2$ needs 2 moles of Lime.*

Chemicals requirement for Permanent hardness constituents:

A. ***Calcium permanent hardness*** ($CaCl_2$, $Ca(NO_3)_2$, $CaSO_4$)

(i) $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$ ------- needs 1 mole of Soda (1S)

(ii) $Ca(NO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaNO_3$ ----- needs 1 mole of Soda (1S)

(iii) $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$ ----- needs 1 mole of Soda (1S)

✓ *** *All Calcium permanent hardness constituents* [$CaCl_2$, $CaSO_4$, $Ca(NO_3)_2$] *need only 1- mole of Soda (1S)*

B. ***Magnesium permanent hardness*** ($MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$)

(i) $MgCl_2 + Ca(OH)_2 + \rightarrow Mg(OH)_2 + CaCl_2$ ------- needs 1 mole of Lime (1L) *but releasing 1 mole of CaCl2. For its removal we need 1 mole of Soda*

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$ ------- needs 1 mole of Soda (1S)

✓ **So, 1 mole of *Magnesium permanent hardness needs 1 mole of lime and 1 mole of Soda* (1L + 1S).**

***Chemicals requirement for coagulants* ($FeSO_4$, $Al_2(SO_4)_3$):**

(i) $FeSO_4 + Ca(OH)_2 + \rightarrow Fe(OH)_2 + CaSO_4$ ------- needs 1 mole of Lime (1L) *but releasing 1 mole of* $CaSO_4$. *Its removal needed 1 mole of Soda*

$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$ ------- needs 1 mole of Soda (1S)

✓ ***So,*** $FeSO_4$ ***needs 1 mole of lime and 1 mole of Soda* (1L + 1S).**

(ii) $Al_2(SO_4)_3 + 3Ca(OH)_2 + \rightarrow 2Al(OH)_3 + 3CaSO_4$ – 3 moles of Lime (3L)

$3CaSO_4 + 3Na_2CO_3 \rightarrow 3CaCO_3 + 3Na_2SO_4$ ------- needs 3 mole of Soda (3S)

✓ ***So,*** $Al_2(SO_4)_3$ ***needs 3 mole of lime and 3 mole of Soda* (3L + 3S).**

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Q.1 Give reason that 1 mole of *$Ca(HCO_3)_2$ needs 1 mole of Lime whereas 1 mole of $Mg(HCO_3)_2$ needs 2 moles of Lime. (write chemical reactions)*

Ans.

A. $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ -------- needs 1 mole of L (1L)

B. (i) $Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow \mathbf{Ca(HCO_3)_2} + Mg(OH)_2$ ----- 1L

(ii) $\mathbf{Ca(HCO_3)_2} + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ ----- 1L

1L + 1L = 2 L

Q. 2. Give reason that *Calcium permanent hardness constituents need only 1- mole of Soda (1S).*

Ans.

(i) $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\ NaCl$ ------- needs 1 mole of Soda (1S)

(ii) $Ca(NO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\ NaNO_3$ ----- needs 1 mole of Soda (1S)

(iii) $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$ ----- needs 1 mole of Soda (1S)

Q.3. Give reason that 1 mole of *Magnesium permanent hardness needs 1 mole of lime and 1 mole of Soda* (1L + 1S).

Ans. (i) $MgCl_2 + Ca(OH)_2 + \rightarrow Mg(OH)_2 + CaCl_2$ ------- needs 1 mole of Lime (1L) *but releasing 1 mole of $CaCl_2$. For removal of $CaCl_2$ we need 1 mole of Soda as per the following reaction*

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\ NaCl$ ------- needs 1 mole of Soda (1S)

Q.4. Give reason that lime is not consumed by $CaCl_2$ or any calcium-permanent hadness constituents.

Ans. $CaCl_2 + Ca(OH)_2 \rightarrow CaCl_2 + Ca(OH)_2$

See the above reaction, there is no change in reactant and product side. It means there is no reaction between these two constituents.

Solved Numerical

Note:

(A) Lime required for softening of 1L of hard water (mg) = 74/100 (Lime consuming substances as $CaCO_3$ eq.) x Vol. of water x (100/% purity of lime)

(B) Soda required for softening of 1L of hard water (mg) = 106/100 (Soda consuming substances as $CaCO_3$ eq.) x Vol. of water x (100/% purity of soda)

Solved numerical on Lime-soda Process

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Example-1 A sample of water on analysis has been found to contain 100 mg/L of $KHCO_3$ and 200 mg/L of K_2SO_4. Calculate the amount of lime and soda required for softening of 10,000 litres of hard water. (At. mass: K = 39, Ca = 40, H =1, C = 12, O =16, S = 32 g/mol)

Ans. The amount of lime and soda required = 0, as both are non hardness constituents.

Example-2 A sample of water on analysis has been found to contain 100 mg/L of $Mg(HCO_3)_2$ and 200 mg/L of K_2SO_4. Calculate the amount of lime and soda required for softening of 10,000 litres of hard water. (At. mass: Na = 23, Mg= 24, H =1, C = 12, O =16, K=39 g/mol, S = 32 g/mol)

Solution: Na_2SO_4 does not consume chemicals like lime and soda.

N.B: if purity of lime and soda is not mention then take % purity = 100

$Mg(HCO_3)_2$ as $CaCO_3$ eq. = 100 x (100/146) = 68.493 mg/L

$Mg(HCO_3)_2$ require only 2L (**no soda requirement**, that is soda amount = 0)

So, lime required for softening of 10,000 L of hard water = 74/100($Ca(HCO_3)_2$ $CaCO_3$ eq.) x V x (100/% purity of lime)

= (74/100) x **2 x 68.493** x 10,000 L x 100/100 (here purity of lime 100%)

= 1013696.4 mg = 1.013 Kg (Ans.)

Example-3 A sample of water on analysis has been found to contain 150 mg/L of $Ca(HCO_3)_2$ and 100 mg/L of Na_2SO_4. Calculate the amount of lime and soda required for softening of 15,000 litres of hard water after boiling the water for 20 min. (At. mass: Na = 23, Ca = 40, H =1, C = 12, O =16, S = 32 g/mol)

Solution: As boiling removes $Ca(HCO_3)_2$, lime and soda required will be zero.

Example-4 Calculate the amount of lime and soda required for softening of 100 L of hard water having 95 mg/L of $MgCl_2$.

Solution: $MgCl_2$ needs 1L + 1S.

$CaCl_2$ as $CaCO_3$ eq. = 95 x (100/95) = 100 mg/L

- **(A) Lime required = 74/100($MgCl_2$ as $CaCO_3$ eq.) x Vol. of water x (100/% purity of lime) = (74/100) x 100 x 100 x (100/100)= 7400 mg**
- **(B) Soda required = 106/100($MgCl_2$ as as $CaCO_3$ eq.) x Vol. of water x (100/% purity of soda) = (106/100) x 100 x 100 x (100/100)= 10600 mg**

Example-6 Calculate the amount of lime required for softening of 100 L of hard water having 250 mg/L of $CaCl_2$ and 220 mg/L of KCl

Ans. KCl is a non hardness mass.

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$CaCl_2$ do not consume any lime. So, lime required = 0

Example-7 A sample of water on analysis has been found to contain 150 mg/L of $Ca(HCO_3)_2$, 100 mg/L of $Mg(HCO_3)_2$ and 100 mg/L og KCl. Calculate the amount of soda required for softening of 15,000 litres of hard water.

Ans. Soda required = 0

Example-8 A sample of water on analysis has been found to contain 150 mg/L of $Ca(HCO_3)_2$ and 100 mg/L of $CaSO_4$. Calculate the amount of lime and soda required for softening of 15,000 litres of hard water after boiling the water for 20 min. (At. mass: Ca = 40, H =1, C = 12, O =16, S = 32 g/mol)

Solution: Boiling will remove the $Ca(HCO_3)_2$. So only $CaSO_4$ will be remain in the hard water after boiling.

$CaSO_4$ consumes only soda (Mol .mass = 136 g)

$CaSO_4$ as $CaCO_3$ eq. = 100 x (100/136) = 73.529 mg/L

Soda required = 106/100 ($CaSO_4$ as $CaCO_3$ eq.) x V x (100/%purity of soda)

= 106/100 x 73.529 x 15,000 x 100/100 (purity of soda is 100%)

= 1169111.1 mg = 1.169 Kg (take 1 mg = 10^{-6} Kg).

Here, lime required = 0

Example-9 A sample of water on analysis has been found to contain 150 mg/L of $Ca(HCO_3)_2$ and 200 mg/L of $Ca(NO_3)_2$. Calculate the amount of lime required for softening of 15,000 litres of hard water after boiling the water for 20 min. (At. mass: Ca = 40, H =1, C = 12, O =16, N = 14 g/mol)

Solution: Lime required = 0

Example-10 Calculate the amount of Lime and soda needed for the softening of 10 litres of hard water having 146 mg/l of $Mg(HCO_3)_2$.

Solution: We know that $Mg(HCO_3)_2$ consumes 2 moles of lime and no soda.

$Mg(HCO_3)_2$ as $CaCO_3$ eq. = 146 x 100/146 = 100 mg/L or ppm

(i) **Lime reqd.** = 74/100 (2 x $Mg(HCO_3)_2$ as $CaCO_3$ eq.) x Vol. of hard water x (100/% purity)
= (74/100) x 100 mg/L x 10 L x (100/100) = 1480 mg

(ii) **Soda Reqd.** = 0 mg.

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Example-11 **Calculate the amount of Lime and soda needed for the softening of 50,000 litres of hard water having $Mg(HCO_3)_2$ = 144 ppm, $Ca(HCO_3)_2$ = 25 ppm, $MgCl_2$ = 95 ppm, $CaCl_2$ = 111 ppm, Fe_2O_3 = 25 ppm, and Na_2SO_4 = 15 ppm. Also find the cost of chemicals for softening. (Given that cost of lime = Rs.10 per Kg and cost of soda = Rs. 100 per Kg)**

Solution:

As Fe_2O_3 and Na_2SO_4 are non-hardness constituents, they do not consume Lime (L) and Soda (S)

Constituents	Strength (ppm or mg/L)	Mol. Mass	Chemical Need	$CaCO_3$ eq. (mg/L)
$Mg(HCO_3)_2$	144	146	2L	144 x (100/146) =98.63
$Ca(HCO_3)_2$	25	162	1L	25 x (100/162) =15.43
$MgCl_2$	95	95	L + S	95 x (100/95) =100
$CaCl_2$	111	111	S	111 x (100/111) =100

**n-factor = 2 for all the salts

Remember that Lime is reqd. by $Mg(HCO_3)_2$, $Ca(HCO_3)_2$, and $MgCl_2$

(i) **Lime reqd.** = 74/100 [(2 x $Mg(HCO_3)_2$ + $Ca(HCO_3)_2$ + $MgCl_2$); all as $CaCO_3$ eq.] x Vol. of hard water x (100/% purity)
= (74/100) x [2 x 98.63 + 15.43 + 100] mg/L x 50,000 L x (100/100)
= 11569530 mg = 11569530 x 10^{-6} Kg = 11.5695 Kg

Soda is reqd. by only $CaCl_2$ and $MgCl_2$

Cost of lime = 11.5695 x 10 = Rs. 115.695

(ii) **Soda reqd.** = 106/100 [($CaCl_2$ + $MgCl_2$); all as $CaCO_3$ eq.] x Vol. of hard water x (100/% purity)
= (106/100) x [100 + 100] mg/L x 50,000 L x (100/100)
= 10600000 mg = 10600000 x 10^{-6} Kg = 10.6 Kg
Cost of soda = 10.6 x 100 = Rs. 1060
Total cost of chemicals for softening of 50,000L of hard water = 115.695 = 1060 = Rs. 1175.695

Example-12 **20,000 L of hard water to be softens by a chemist using a lime-soda softener. The budget allocated for the said purpose is Rs.500. Do you think the allocated amount is sufficient to get the job done? The sample contains $Mg(HCO_3)_2$ = 73 ppm, $Ca(HCO_3)_2$ = 81 ppm, $MgCl_2$ = 95 ppm, $CaSO_4$ = 68 ppm, and Na_2SO_4 = 30 ppm. The purity of lime is 95% and that of soda is 90%. The costs per 1 Kg of lime and soda are Rs. 100 and Rs. 100, respectively**.

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Solution: As Na_2SO_4 is a non-hardness constituent, it does not consume Lime (L) and Soda (S)

Constituents	Strength (ppm or mg/L)	Mol. Mass	Chemical Need	$CaCO_3$ eq. (mg/L)
$Mg(HCO_3)_2$	73	146	2L	73 x (100/146) =50
$Ca(HCO_3)_2$	81	162	1L	81 x (100/162) =50
$MgCl_2$	95	95	L + S	95 x (100/95) =100
$CaSO_4$	68	136	S	68 x (100/136) =50

Lime is reqd. by $Mg(HCO_3)_2$, $Ca(HCO_3)_2$, and $MgCl_2$

(i) **Lime reqd.** = 74/100 [(2 x $Mg(HCO_3)_2$ + $Ca(HCO_3)_2$ + $MgCl_2$); all as $CaCO_3$ eq.] x Vol. of hard water x (100/% purity)
= (74/100) x [2 x 50 + 50 + 100] mg/L x 20,000 L x (100/95)
= 3894736.842 mg = 3894736.842 x 10^{-6} Kg = 3.894 Kg
(1 mg = 10^{-6} Kg)
Cost of lime = 3.894 x 100 = Rs. 389.4

Soda is reqd. by only $MgCl_2$ and $CaSO_4$

(i) **Soda reqd.** = 106/100 [($CaSO_4$ + $MgCl_2$); all as $CaCO_3$ eq.] x Vol. of hard water x (100/% purity)
= (106/100) x [50 + 100] mg/L x 50,000 L x (100/90)
= 3533333.333 mg = 3533333.333 x 10^{-6} Kg = 3.533 Kg
Cost of soda = 3.533 x 100 = Rs. 353.3

Now, total cost of chemicals = Rs. 389.4 + Rs. 353.3 = **Rs. 742.7**

No, the allocated amount is not sufficient to get the job done.

Manoranjan@Silicon University

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:

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

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

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

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

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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:

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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

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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 x 10^3) x (100/2 x 58.5), for NaCl, n-factor = 1

= (150 x 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.**

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Ion Exchange Resin

Ion-exchange Resins (IER): IER are cross-linked organic co-polymers (e.g., styrene-divinyl benzene or amine-formaldehyde) with a porous structure attached with some functional groups (FGs) like –OH, $-SO_3H$, -COOH, $-NH_2$, etc. responsible for reversibly exchange with ions (e.g., Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}, etc.) present in hard water.

Types of Ion-exchange resins:

Depending on the nature of FG attached to the polymer, they are of two types: (1) Cation exchange resin (CER), and (2) Anion exchange resin (AER)

Cation Exchange Resins (CER): They are mainly styrene-divinyl benzene copolymers containing sulphonic acid ($-SO_3H$) or carboxylic acid (-COOH) FG. The acidic FG having hydrogen ions ($-H^+$) are *exchange with cations* like Ca^{2+}, Mg^{2+} etc. present in the hard water. It means these hardness causing cations are retained by the resin.

Some commercial cation exchange resins are **Amberlite IR-120 and Dowex-50**.

Anion Exchange Resins (AER): They are mainly styrene-divinyl benzene or amine-formaldehyde copolymers containing basic FG like amino or quaternary ammonium or quaternary phosphonium. As such they are of no use. To act as an *anion exchange resin*, it is treated with dil. NaOH solution to convert it to hydroxide form. The OH^- ion of AER is capable of *exchange with anions (Cl^-, NO_3- etc.)* of water.

Some commercial anion exchangers are **Amberlite IR-400 and Dowex-3**.

Softening of hard water using polymeric ion-exchangers

An ion-exchanger consists of two vertical columns: (1) cation exchanger and (2) anion exchanger column.

The hard water is first passed through the cation exchange column so that all cations are removed from it and equivalent amount of H^+-ions are released from the column to water. Let us represent the cation exchange resin as **Res-H^+.** Here the loosly bound H+ ions are capable of exchanging with cations like Ca^{2+} and Mg^{2+}.

$$2Res\text{-}H^+ + Ca^{2+} \rightarrow (Res)_2Ca + 2H^+$$

$$2Res\text{-}^-H^+ + Mg^{2+} \rightarrow (Res)_2Mg + 2H^+$$

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After passing through the first column, the water is passed through anion exchange column to remove all the anions like Cl^-, NO_3^-, SO_4^{2-}, etc. present in the water and an equivalent amount of –OH- ions are released from the column to the water. Let us represent this resin as **Res-OH⁻.**

$$\text{Res-OH}^- + \text{Cl-} \rightarrow \text{Res-Cl} + \text{OH}^-$$

$$\text{Res-OH}^- + \text{NO}_3^- \rightarrow \text{Res-NO}_3 + \text{OH}^-$$

Now the outgoing water is free from all ions so it is ion-free or *deioinized* water. This water also called as *de-mineralized* water. This water is free from any acidic or alkaline masses. Finally the ion-free water is passed through a *de-gasifier* maintained at about 100 ^{0}C to remove dissolved gases like O_2, CO_2, etc.

Regeneration of ion exchange resins

After working for some time, the ion-exchange resins lost their ion-exchange capacity and are said to be exhausted.

The exhausted cation exchange resin column can be regenerated by washing with a solution of dil. HCl or H_2SO_4.

$$(\text{Res})_2\text{Ca} + 2\text{H}^+ \text{ (from HCl)} \rightarrow 2\text{Res-H}^+ + \text{Ca}^{2+}$$

The exhausted anion exchange resin column can be regenerated by washing with a solution of dil NaOH or KOH.

$$\text{Res-Cl} + \text{OH}^- \text{ (from NaOH)} \rightarrow \text{Res-OH}^- + \text{Cl}^-$$

The regenerated resins are then used again for softening.

Fig. Polymeric ion-exchanger

ian@Silicon University

Advantages:

1. This process can be used for softening highly acidic and alkaline waters.
2. Residual hardness lies between 0-2 ppm.
3. De-gasifier removes dissolved gases
4. Water is germ free

Limitations:

1. It is an expensive process
2. Turbid water causes problem
3. Water is not fit for human consumption. (we need minerals like Ca)

Q. 1 What is the use of a de-gasifier in ion-exchange resin softener?

Ans. It is a device used to remove unwanted dissolved gases like O_2, CO_2, etc from the soften water.

Q. 2 Differentiate between soften water and de-mineralized/de-ionised water

Sl. No.	Soften Water	De-mineralized Water
1	its hardness lies between 10- **60 ppm and are not ion free**	Hardness lies between 0-2 ppm but free from ions.
2	May be used for domestic use	Not recommended as such for drinking purpose. Used by many industries.
3	Obtain using L-S or zeolite process	Made by distillation or resin process
4	Not suitable for boiler	Fit for boiler operation

Q 3. Mention some advantages of resin process.

Ans.

1. This process can be used for softening even for highly acidic and alkaline waters.
2. Residual hardness lies between 0-2 ppm. So, fit for boiler operation.
3. De-gasifier removes dissolved gases
4. Water is germ free
5. Water can be used in R& D purpose

Q. 4. Mention some limitations of resin process.

Ans.

1. It is an expensive process
2. Turbid water causes problem

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3. Water is not fit for human consumption. (we need mineral like Ca)

Q.5 How to regenerate an exhausted cation-exchange resin?

Ans. The exhausted cation exchange resin column can be regenerated by passing a solution of dil HCl or H_2SO_4.

$$(Res)_2Ca \text{ (Exhausted resin)} + 2H^+ \text{ (from HCl)} \rightarrow 2Res\text{-}H^+ + Ca^{2+}$$

Q.6 How to regenerate an exhausted anion-exchange resin?

Ans. The exhausted anion exchange resin column can be regenerated by passing a solution of dil NaOH or KOH.

$$Res\text{-}Cl \text{ (Exhausted resin)} + OH^- \text{ (from NaOH)} \rightarrow Res\text{-}OH^- + Cl^-$$

Q7. What is an ion exchange resin? Give an example.

Ans. Ion exchange resin are insoluble, cross-linked organic co-polymers with a porous structure attached with some functional groups (FG) like –OH, $-SO_3H$, -COOH, $-NH_2$, etc. responsible for reversibly exchange with ions (e.g., Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}, etc.) present in hard water.

Example: Styrene-divinyl benzene with $-SO_3H$ group attached to it.

Q8. Differentiate between Zeolite and Resin process.

Ans. Do it yourself (DIY)

Q9. Diffrenetiate between CER and AER.

Ans. DIY

Numerical:

An exhausted CER needs 1,000 L of HCl of strength 100 g/L. One million liters of water was softened by the resin process. Find the hardness of water as $CaCO_3$ eq.

Soln. HCl as $CaCO_3$ Eq. = (100 x 1000 mg/L) x (100/2x36.5) = 136986 mg/L

Now, $S_{HCl} \times V_{HCl} = S_{H2O} \times V_{H2O}$

- ⇨ $136986 \times 1000 = S_{H2O} \times 10^6$
- ⇨ $S_{H2O} = (136986 \times 1000)/ 10^6 = 136.98$ ppm.

Manoranjan@Silicon University